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Department of Imaging and Applied Physics

Development and Characterisation of Cotton and Cotton fabric Reinforced Geopolymer Composites

Thamer Salman Alomayri

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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ABSTRACT

Alternative cement technologies are attracting increasing interest because of their potential to address some of the growing environmental challenges facing the construction industry. New binding materials are believed to be critical for meeting environmental and performance-based requirements in this sector. Fly ash, a waste product of coal-fired power stations, is generated in increasingly huge volumes around the world as global demands for energy increase. Most of it is not effectively re-used, and is disposed to landfills.

One environmentally friendly group of materials that can be produced using fly ash as a source material with low use of energy is geopolymers. These are made from source materials that contain silicon (Si) and aluminium (Al) through a geopolymerisation process that does not emit greenhouse gases. Fly ash-based geopolymer matrix tends to have poor mechanical properties, in particular a brittle nature; however, when reinforced with fibres that are tough and possess good strength and modulus, their mechanical properties can be significantly improved. Carbon, glass and other synthetic fibres have been the most commonly used reinforcements for geopolymers, but these fibres have inherently higher commercial and environmental costs, increasingly salient in a time of global concern over carbon dioxide emissions and climate change.

Natural fibre-reinforced composites are now recognised as a solution for some of the problems arising from synthetic fibres and their composites. Natural fibre reinforced composites are low cost and low density, feature recyclability and renewability, and possess good mechanical properties. Natural fibres provide the benefit of being a non-toxic and renewable material. These properties have seen natural fibre reinforced composites increasingly used in applications in manufacturing, building and construction, and automotive industries.

To date there have been few reported studies concerning the effect of natural fibre on the mechanical properties of geopolymer composites. There appear to be no available reports on some natural fibres such as cotton fibre, with respect to the effects of their

addition to geopolymer composites. Thus, one of the aims of this project was to fabricate high-performance cotton fibre-based geopolymer composites that are carbon neutral and biodegradable.

This investigation was divided into three parts. The first part investigated the effect of short cotton fibres on the properties of geopolymer composites such as, density, porosity, flexural strength and modulus, compressive strength, impact strength, hardness, and fracture toughness. The second part investigated the mechanical and thermal properties of geopolymer composites reinforced with different numbers of woven cotton fabric layers using a self-infiltration-hand lay-up technique. The third part investigated the mechanical and thermal properties of geopolymer composites reinforced with multiple cotton fabric layers using a forced-impregnation (wet out)-hand lay-up technique. The effects of fibre orientation, water absorption and elevated temperature on the mechanical properties of cotton fibre composites were also investigated. X-ray diffraction (XRD), synchrotron radiation diffraction (SRD) and scanning electron microscopy (SEM) were used to examine the microstructures of these composites.

In the first part of the investigation, composites with short cotton fibres were produced and then investigated in terms of density, porosity, flexural strength and modulus, compressive strength, impact strength, hardness, and fracture toughness. Fibre content of 0.5 wt.% was found to be the optimum content and exhibited highest mechanical properties for these composites.

In the second part of the investigation, composites with woven cotton fabric (CF) were fabricated with fibre loadings of 0, 1.4, 2.1, 2.8 and 4.1 wt.% using a self-infiltration-hand lay-up technique. Results indicated that the flexural strength, flexural modulus, facture toughness and impact strength increased at an optimum fibre content of 2.1 wt.%. SEM observations showed a variety of toughening mechanisms such as crack bridging, fibre pullouts, fibre fracture and matrix cracking on the fracture surface of CF/geopolymer composites, which led to good fracture properties for samples reinforced by three woven cotton layers equivalent to 2.1 wt.%.

In contrast, at higher cotton fibre content, beyond 2.1 wt.%, there was a reduction in mechanical properties, because of the higher porosity and the subsequent formation of voids, which in turn reduced the bonding between fibre and matrix. The addition of Ordinary Portland Cement (OPC) was found to be effective in reducing the porosity of these composites and improving fibre–matrix adhesion, thereby enhancing the mechanical properties of the composite due to the formation of calcium silicate hydrate (CSH) gels in geopolymer matrix. The addition of OPC was also found to improve the thermal stability of geopolymer composites

There is a limitation on the number of layers that can be used effectively. The self-infiltration-hand lay-up technique revealed that more than three layers tend to lead to delamination, fibre misalignment and debonding, because of variations in geopolymer binder thickness between fabric layers. A limited amount of the binder is not enough to fill the voids and pores because of the viscosity of the geopolymer binder and its lower penetration. The use of excessive amounts of geopolymer binder could result in low stress transfer capabilities as well as the formation of excessively matrix-rich areas. In addition, variations in binder thickness led to uneven expansion and contraction during curing and the resulting composite experienced internal stresses which could cause cracking and stress failure in use. Alternative processes designed to overcome these problem could ensure a perfect bond between a higher number of fabric layers and a matrix with controllable thickness.

In the third part of the investigation, geopolymer composites made with woven cotton fabric were fabricated with fibre loadings of 0, 3.6, 4.5, 6.2 and 8.3wt.% using a forced-impregnation (wet out)-hand lay-up technique with a roller and brush. It was found that the mechanical properties of cotton fabric-reinforced geopolymer composites, such as flexural strength, flexural modulus, impact strength, hardness, and fracture toughness, are superior to those of a pure geopolymer matrix. Mechanical properties improved by increasing the cotton fibre contents to 3.6, 4.5, 6.2 and 8.3wt.%. The effect of cotton fibre orientation (i.e., horizontal or vertical) showed that when the fabrics are aligned in horizontal orientation with respect to the applied load, higher load and greater resistance to deformation were achieved than in their vertically-aligned counterparts.

The effects of water absorption and high temperature on mechanical properties were also studied. Exposure to water for six months severely reduced the mechanical properties of wet composites as compared to dry composites. Exposure to high temperature was also investigated. Exposure to elevated temperatures of 200, 400, 600, 800 and 1000°C were found to reduce the mechanical strength of the composite. This reduction in mechanical properties was most significant at high temperature, from 800 and 1000°C because of severe fibre degradation and the formation of a large quantity of voids, as confirmed by SEM and optical microscopy.

The motivation for this project was the development of environmentally friendly high-performance geopolymer composites reinforced with natural fibres. In a context where manufacturing entities are increasingly liable for the materials used in their products, this research contributed to the contemporary understanding of natural fibre-reinforced geopolymer composites. This project recommends one pathway that can be followed by fabricating cotton fibre reinforced fly ash-based geopolymer composites. It offers strong indications that the development of fully green composites is achievable.

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STATEMENT OF CONTRIBUTION OF OTHERS

Thamer Alomayri's input into this study and the associated papers include the execution of all the experimental work as well as a dominant contribution to the intellectual input involved in the project. Other scientists made some contributions to the current work, as is almost always the case in the physical sciences. These contributions were significant enough to warrant co- authorship on the resulting journal articles. These are specific below:

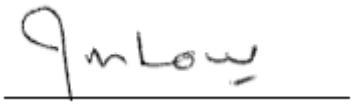
Prof. I.M. Low, provided project supervision and manuscript editing.

Dr F.U.A. Shaikh, provided project supervision and manuscript editing.

Mr Les VICKERS provided interpretation of the thermal analysis results.

Mr Hasan Assaedi provided technical assistance during the preparation and testing of geopolymer composite samples.

Thamer Alomayri



Prof. It-Meng (Jim) Low

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

List of Abbreviations

ASTM	American society for testing and materials
CF	Cotton fibres
EDS	Energy dispersive x-ray spectroscopy
GC	Geopolymer composites
MPa	Mega Pascals
OPC	Ordinary Portland cement
SEM	Scanning Electron Microscopy
SRD	Synchrotron Radiation Diffraction
TGA	Thermogravimetric Analysis
Wt. %	Weight percent
XRD	X-Ray Diffraction
XRF	X-ray fluorescence spectroscopy

1 INTRODUCTION

1.1 Overview of Composite Materials

Composite materials are multiphase materials that consist of at least two distinct components. One of their major attractions is their capacity to optimise the properties of their materials because combining the constituents makes possible interactions that give rise to properties that the constituents on their own cannot achieve. In most cases the primary two constituents are usually distinguishable: one, referred to as the matrix, is generally the dominant material; the second component is typically referred to as the reinforcement.

One of the practical benefits of composites is that there are almost unlimited combinations of matrices and reinforcements. For manufacturers, this means that it is possible to tailor the properties of composites to meet the requirements of specific applications. Typically, manufacturers aim to develop composites that feature improvements in mechanical properties: enhanced strength, stiffness, or toughness, for instance. Other relevant considerations are often the weight of the material, its durability, its thermal stability, and especially its cost. In some settings, the last is increasingly being re-defined to encompass not only private and economic but also public and environmental costs.

Composite materials are commonly classified based on their matrices. Ceramic matrix composites (CMSs), polymer matrix composites (PMCs), and metal matrix composites (MMCs) are arguably the three main structural composites. While all these groups can offer composites with high strength and stiffness, excellent chemical and thermal stability, and relatively low density, one weakness can be material brittleness. The issue is particularly relevant for ceramic matrix composites. Ceramic materials alone have an inherently brittle nature, and this considerably limits their suitability for use in engineering and structural applications.

One way to overcome the brittleness is by adding reinforcement. Fibre is a common reinforcement material because of its capacity to stabilise micro-cracking, the formation of tiny cracks on either side of a main crack front. The incorporation of

short fibre and continuous fibre are the two leading techniques comprising ceramic matrix reinforcement. Of these, continuous fibres are more expensive and more troublesome to mix into matrices; however, their direction of alignment provides superior mechanical properties of the composites. Continuous fibre composites are often used in aviation applications where the benefits of enhanced properties can be fully exploited. In contrast, short fibres are cheaper to develop and easier to produce. Short fibre ceramic composites are well established with regard to applications where lower strength and stiffness are sufficient.

The constituent materials' properties go a long way to influence the properties of the resultant composite materials. Most importantly, the type, amount, distribution and orientation of reinforcement and void content of constituent materials determine the mechanical and other properties of the composite materials. The nature of the interaction between matrix and the reinforcing fibres and load transfer mechanisms at the interface are also important determinants of final composite material properties. To better ensure superior mechanical properties, it is important that a strong bond is formed between the fibres and the matrix. The presence of such bonding enables effective transfer of stress from the dominant matrix to the reinforcing fibres. There are also different techniques to improve the adhesive quality and strength properties of fibre-reinforced composites, such as the addition of minerals and chemical treatment of fibres. The method of processing also influences the properties of composites, because the processing techniques affect the amount and dispersion of fibre within the resultant composite. Thus, researchers and developers are very interested in the role of processing conditions and techniques on performance optimisation.

1.2 Fibre-Reinforced Geopolymer Composites

While ceramic matrix composites have been increasingly studied over the past four decades, their commercial relevance is still small in relation to that of polymer matrix composites and metal matrix composites. One reason for this is the high production cost of ceramic matrix composites, which tend to require materials that are costly and manufacturing temperatures that are extremely high. Thus far, the high

cost of producing ceramic matrix composites has made them undesirable for particular commercial applications. To overcome this issue, there has been renewed interest in identifying novel inorganic, non-metallic materials and techniques that can be used to produce high-strength and cost-effective ceramic matrix composites.

Geopolymers, more formally known as inorganic aluminosilicate polymers, offer an alternative. These materials differ from more common ceramic matrix materials in terms of their favourable density and thermal stability, featuring temperature resistance up to 1000°C. Geopolymers are typically produced using aluminosilicate sources reacting with an alkali activation solution maintained at high pH and near-ambient temperature. Geopolymer binders are generally viscous at the outset. When cured they harden in a manner similar to organic thermosetting resins. The result is a three-dimensional solid material which is generally amorphous and has ceramic-like properties. The reasonable mechanical properties of geopolymers, and low temperature processing, make a unique combination offering considerable potential in the field of cost-effective inorganic composite development (Davidovits, 2002); thus, the use of geopolymers as a replacement for conventional ceramic matrix composites is an important area of interest. Another area of interest is the use of geopolymer technology as a precursor for true ceramic matrix composite fabrication due to the typical transformation of geopolymers into crystalline ceramic phases at higher temperatures.

Davidovits in 1987 started investigating the application of geopolymers as matrix materials (Davidovits, 2002). The rationale for research at the time was that fibres could reinforce geopolymers to form composites for use in moulding patterns and tools for the industry of plastic processing. It has been found that the incorporation of fibres indeed does significantly improve a geopolymer's mechanical properties. Basalt, carbon and glass fibres are the most commonly used, but there are disadvantages in such synthetic fibres (Beckermann, 2007). The first of these is their abrasive character. This means that they increase wear on machinery and are generally dangerous to work with. Another disadvantage is that synthetic fibres, including glass fibres, are troublesome to dispose of legally and with consideration for the environment once their life ends. These fibres, because of their tendency to

result in residues that cause furnace damage, cannot be incinerated. They cannot be recycled as reprocessing operations tend to cause fibre breakages and other associated problems. To date, disposal to landfills is the dominant option for discarding this waste, but this is a costly option when considered on a large scale, given government duties associated with landfill services (Beckermann, 2007)

One response to the disadvantages of synthetic fibres is to re-consider the use of fibres more compatible with the environment. Banana, coir, cotton, flax, hemp, jute, sisal, and wood are examples of natural fibres that meet this description (Sreenivasan et al., 2011). These fibres, unlike many plastics, are biodegradable, meaning that they will not remain on the surface of the earth for thousands of years. Furthermore, natural fibre production uses less energy than carbon or glass fibre production (Venkateshwaran et al., 2011). Natural fibres have lower densities (1.25-1.5 g/cm^3) than the densities of E-glass (2.54 g/cm^3) or carbon fibre (1.8–2.1 g/cm^3); they are also lighter than synthetic fibres (Sgriccia et al., 2008, Anuar and Zuraida, 2011). Another important property of natural fibres is their excellent modulus–weight ratio, which makes them particularly useful for stiffness-critical designs. Natural fibres have been investigated and used in the automobile interior product design industry for some time because of their superior acoustic damping properties. For purposes of noise attenuation, natural fibres are generally superior to carbon or glass (Mallick, 2007). In terms of mechanical properties, natural fibres tend to possess excellent specific modulus, toughness, flexibility, and specific strength properties (Bax and Müssig, 2008, Monteiro et al., 2009). Increasingly it has been noticed that natural fibres tend to be significantly more commercially viable than the majority of synthetic fibres (Dhakal et al., 2007).

Another important benefit of all plant-derived natural fibres is that their initial growth in plant form is dependent on the consumption, not emission of CO_2. This means that these fibres are substantially CO_2 neutral materials. Practically, this means that incineration at their life's end is not considered to release additional carbon dioxide into the atmosphere. In contrast, glass fibres and other synthetic fibres are not attributed CO_2 neutral status, and require that fossil fuels be burned in order for energy to be generated for their production. Recent socio-political

attentions focusing on carbon emissions have meant that the majority of commercial practices rely on the burning of fossil fuels have come under some level of scrutiny. As carbon dioxide emission has been increasingly associated with the greenhouse effect and climate change, social and economic sanctions concerning carbon dioxide emissions are arguably likely to increase before they decrease in the near future.

Natural fibre-reinforced composites feature the benefit of not splintering during fracture. This distinguishes them from most of their glass fibre-reinforced counterparts, and means that they are more suitable for uses where safety is a concern, such as in crash absorption applications. The durability of natural fibres is another advantage. These fibres can generally be recycled and reused with a relatively minimal reduction in strength and stiffness properties. In contrast, synthetic fibres tend to fracture as a result of recycling and further processing, resulting in reduced in fibre length.

Cotton fibre is amongst the most well-known of the natural fibres. It offers excellent absorbency, a natural feel and other properties of comfort. It can be distinguished from most other natural fibres by its cellulose content, which is very high (90–95%) (Andre, 2006). While this fibre has been used in the textile industry for centuries, it has more recently attracted interest as a reinforcement material for composites. Reclaimed cotton fibre is widely used as a cheap to fill composites used as interior parts in the automotive industry (Müssing, 2008). In 2003, it is estimated, 45,000 tonnes of material was used in the German motor vehicle industry for interior products alone (Karus et al. 2005). Cotton fibre, in a similar fashion to other natural fibres, is a lightweight, bio-degradable and eco-friendly material. The advantages of cotton fibres are that they are not as expensive to source and are not as brittle as carbon fibres (Chaudhary & Gohil, 2013). While the weight of cotton fibres is preferable for automobile applications because it reduces the weight of the overall motor vehicle, other advantages are their ability to reduce cabin noise through sound wave attenuation (Bhat et al., 2004). Cotton fibres are also used in commercial applications: they have been used to reinforce gypsum composites producing a high-quality building material. According to Li et al. (2003), the cotton fibre/gypsum

composite features low density, favourable thermal properties, acoustic insulation, and a very high strength-to-weight ratio.

Many studied have been reported recently on the physical, thermal and mechanical performance of cotton fibre-reinforced polymer composites. Hashmi et al. (2007) found that the addition of 27.5% (by Vol.) cotton fibres to an unsaturated polyester resin matrix composite increased the impact strength of the composite, per unit width, from 61 to 971 Nm/s^2; it also increased the flexural strength from 101.8 to 142MPa. The modulus of elasticity at bending was found to have increased from 2.4 to 4.2 GPa. Fervel et al. (2003) carried out studies on polyester composites reinforced with cotton fibres. The team investigated friction and wear of the composite against stainless steel. The result was that as the volume fraction of cotton fibre increased in the composite, the coefficient of friction also increased. A similar result was found with respect to wear: as the volume fraction of cotton fibre increased the rate of wear was found to decrease. This was true to 15 vol.% and after: that is, at greater volume fractions of cotton fibre, the rate of wear was found to be substantially constant. Fervel et al. (2003) also studied the effects of fibre orientation on the cotton fibres/ polyester composites. It was found that after initial variations, and after the friction coefficient had stabilised, the orientation of fibres influenced this coefficient. Hashmi et al. (2006) found that when cotton fibres were added to 33 wt.% to an unsaturated polyester resin matrix, the structural integrity of the composite improved with respect to sliding wear. The team found that the improvement in sliding wear conditions gave a composite with structural integrity twice as good as un-reinforced polyester resins in this regard.

Hendra and Peer Mohamed (2010) investigated the influence cotton fibre addition (10–30 wt.%) on the impact strength, tensile strength, flexural strength and flexural modulus of unsaturated polyester resin matrix composites. They found that each of these properties increased markedly as cotton fibre content increased to 30 wt.%, with tensile strength reported at 65.66 MPa, flexural strength at 180 MPa, flexural modulus at 7.1 GPa and impact strength at 37.5 KJ/m^2. Raftoyiannis et al. (2012) investigated the use of cotton fibre as a reinforcement for composite panels to be used in construction. It was found that the mechanical properties of these cotton fibre

reinforced composites were suitable for the composites to be used in doors and other secondary structural materials. It was also concluded that the structural performance of these cotton fibre composites was satisfactory for building products with low requirements, including wall panels.

Rukmini et al. (2013) studied the effect of cotton fibre addition on the mechanical properties of polypropylene (PP) composites. The team found that the addition of 30 wt.% cotton fibre caused the tensile strength and tensile modulus of the PP composite to increase substantially. While pure PP was found to have a tensile strength of 21.87 MPa and a tensile modulus of 618 MPa, the composite was found to give results of 28.07 and 1867 MPa, respectively. The improvements in flexural strength and flexural modulus were also notable, from 21.7 to 45.3 MPa, and from 813 to 1925 MPa. The team concluded that cotton fibre reinforcement was an effective technique for enhancing the mechanical properties of PP composites.

To date, while there have been a number of investigations into the impact of cotton fibre in polymer matrices, there has been no research into the influence of cotton fibre addition on the mechanical properties of geopolymer composites. Given the context of increasing interest in more environmentally sustainable materials and practices, this present work seeks to address this gap in the prevailing research by exploring the impact of cotton fibre addition on the mechanical properties of geopolymer composites.

1.3 Project Significance

The study focuses on the development of cost effective, eco-friendly material design with respect to cotton fibre reinforced geopolymer composites. When reinforced with natural fibres, it has been found, polymeric composites become lightweight, inexpensive, impact-resistant materials suitable in numerous applications. For example, growing environmental awareness and pressure to ensure sustainability in the construction industry has led to efforts to look for alternative fibres to reinforce cementitious materials.

The abundance of natural fibres has attracted investigators of cementitious composites. Reproducible, carbon neutral and environmentally friendly productions are further benefits that distinguish natural fibres from their synthetic counterparts such as glass and carbon fibres and conventional steel. Natural fibres tend to have additional advantages such as low density and high specific strength, which are relevant to their use as reinforcing fibres for cementitious materials. To date, the addition of bamboo, banana, coconut, cotton stalk, hemp, jute and sisal fibres to cementitious composites has been studied with promising results. Yet there is limited research into the effects of natural fibre addition to geopolymer composites, although the structural performance of these composites is of particular importance to industry. The specific addition of cotton fibre to geopolymer composites appears not to have been reported at all in the literature to date; so an attempt here is made to study the performance of cotton fibre reinforced geopolymer composites.

There appears to be very limited information with respect to the effects of elevated temperature, fibre orientation, water absorption and other environmental and processing conditions on the quality of natural fibre-reinforced geopolymer composites. This information is vital for the informed use of these composites in structural applications; and this project aims to increase the understanding of the effects of varying the quantity of cotton fibre on the properties of geopolymer composites. The effects of altering environmental conditions such as water immersion and high temperature on the mechanical properties of natural fibre-reinforced geopolymer composite are also investigated.

It is anticipated that the findings of this project will be useful to material scientists and corporations with interest in the development of geopolymer technology. It is also anticipated that the conclusions reported herein will aid in the development and use of environmentally friendly composites. Immediate practical applications for cotton fibre-reinforced geopolymer composites arguably includes slabs or shingles for siding, certain types of roofing, and certain interior products in the construction industry. Natural fibres such as cotton can be used as insulator to keep the house cool during summer by preventing heat from coming in from outside. It is expected that

cotton fibre-reinforced geopolymer composites will also have applications in pipes and cooling towers.

1.4 Project Objectives

The main aim of this research was to better understand the cotton fibre-reinforced geopolymer composites, and in particular, to better understand the best practice design to ensure maximum cost effectiveness and optimum performance of the composites. The specific objectives of this project were as follows:

- to gain a better understanding of the mechanical properties of geopolymer composites reinforced with cotton fibres.
- to determine the optimum fibre content to obtain the desired physical and mechanical properties of short cotton fibre-reinforced geopolymer composites.
- to study the effect of cotton fabric (CF) on the mechanical and thermal properties of geopolymer composites.
- to study the mechanical and thermal properties of ambient-cured fly ash-based geopolymer matrices and CF reinforced geopolymer composites containing different quantities of Ordinary Portland Cement (OPC).
- to investigate the effect of fibre orientation on the mechanical properties of woven cotton fabric-reinforced geopolymer composites.
- to investigate the effect of elevated temperature (200–1000°C) drying shrinkage and the mechanical properties of cotton fabric-reinforced geopolymer composites.
- to examine the effect of water absorption on the mechanical properties of cotton fibre-reinforced geopolymer composites.

1.5 Research Plan

To address the objectives of the research project, the following investigation tasks were conducted:

- fabrication of geopolymer composites by reinforcing geopolymer with short cotton fibres
- fabrication of geopolymer composites by reinforcing geopolymer with woven cotton fabric using self-infiltration-hand lay-up technique
- fabrication of OPC/geopolymer composites by reinforcing geopolymer with cotton fabric and different content of OPC
- fabrication of multiple cotton fabric layers-reinforced geopolymer composite using forced- impregnation (wet out)-hand lay-up
- characterisation of raw materials and composites using X-ray diffraction (XRD) and synchrotron radiation diffraction (SRD)
- investigation of the influence of cotton fabric layers on the physical, mechanical and thermal properties of geopolymer composites
- determination of the effect of moisture absorption on the mechanical properties of geopolymer composites
- determination of the effect of high temperature on the mechanical properties of geopolymer composites
- observation of fracture surfaces, failure mechanisms and crack path features by scanning electron microscopy (SEM).

2 LITERATURE REVIEW

2.1 Composites

2.1.1 Overview

Composite material preparation and investigation represents an increasingly important area of contemporary materials science, and the application of composite materials is evident in the majority of the most advanced technologies and industries. The notion of a composite material is neither new nor complicated. There are several materials of natural and artificial source that are effectively composites (Kelly et al., 1994). Broadly, a composite is any material that is made up of at least two dissimilar constituents; beyond this, definitions widely vary depending on the field of application, and definition given above is a very flexible one enabling almost any material or substance to be deemed a composite (Mallick, 2007). For the purposes of this study, positioned within the greater field of materials engineering, composites will be defined as materials that: (i) consist of at least two chemically and physically distinct phases, (ii) are artificially bonded together and (iii) produce a structural material with enhanced properties that cannot be obtained with either of these phases taken separately (Mallick, 2007). The two fundamental phases, in practice, are a matrix, which can be thought of as a continuous phase, and an embedded phase, also referred to as the reinforcement or dispersed phase, which can take the form of particles or fibres, amongst other phases. The area of matrix and embedded phase that makes contact is the interface (Mallick, 2007).

2.1.2 Classification of composites based on matrix material

Classification of composites in the first instance is based on the matrix material used: Polymers, ceramics, and metals are the three primary types. The composites that result from these base materials are referred to as polymer-matrix composites, ceramic-matrix composites, and metal-matrix composites. For each class of these main classes of composite, there is an extremely wide range of materials that can be used in the fabrication of particular composites with unique properties. Some of these areas will be discussed in more detail following.

2.1.2.1 Polymer-matrix composites (PMC)

Polymers are the most commonly used materials for the matrix of composites. Generally polymer matrices by themselves have low strength and stiffness. For this reason, when they are reinforced with fibres, it is the properties of the fibres that tend to influence the strength and stiffness of the overall composite most significantly (Mallick, 2007; Pandey, 2004).

Polymers can be divided into those that are thermosets, those that harden because of a curing process concerning polymeric chain cross-linking; and those which are thermoplastics, those which melt at a certain temperature but then harden when cooled to room temperature (Mallick, 2007; Pandey, 2004). Thermosets and thermoplastics are both used in the composite industry; however, the former, in particular thermosetting resins, dominate polymer matrix composite production (Mallick, 2007; Pandey, 2004). Thermosets, as mentioned, are distinguished by the reaction of curing that underpins their creation. As this reaction occurs, cross-linking of polymeric chains hardens and forms the thermoset polymer (Mallick, 2007; Pandey, 2004). One very commonly used thermoset polymer matrix is epoxy. Unsaturated polyester and phenolics are other thermosets that are commonly used, but unlike thermoplastics, they rely on a particular curing process and cross-linking. Temperature alone, for the most part, determines the state of thermoplastics (Mallick, 2007; Pandey, 2004). Common thermoplastics include polyethylene, polycarbonate, polyether ether ketone, and nylon.

2.1.2.2 Ceramic-matrix composites (CMC)

Ceramics generally possess favourable hardness, strength, stiffness, chemical resistance, and low density. These desirable properties coupled with the material's excellent temperature stability underpin their general usefulness (Bansal and Boccaccini, 2012). Notwithstanding, a major weakness of ceramics is their inherent brittleness (Bansal and Boccaccini, 2012). This, together with their propensity for catastrophic failure, means that their use in structural applications can be limited. To overcome this inherent shortcoming, fibres can be used to reinforce ceramic

matrices, but must be incorporated with care in order to make sure the two components interact as favourably as possible (Bansal and Boccaccini, 2012).

Ceramics can be divided into oxide and non-oxide ceramics (Mark et al., 2005). The latter category, the non-oxide ceramics, are difficult to make by the melt or powder fusion techniques that are common fabrication methods for oxide ceramics. Non-oxide ceramics include silicon carbide, silicon nitride, aluminium nitrides and boron nitride, and are the highest melting materials. In contrast, oxide ceramics, such as silicate structures, are relatively low melting (Mark et al., 2005).

2.1.2.3 Metal-matrix composites (MMC)

Metal-matrix composites, like ceramics-matrix composites, also possess favourable properties. They typically possess superior strength, elastic modulus, thermal resistance and fatigue resistance over unreinforced metallic alloys (Guden and Hall, 1998). As in general composite science, the concept of metal-matrix composites is underpinned by the combination of at least two materials, typically the metal-matrix and the reinforcement. The properties of the final composite depend on those of the matrix and reinforcement, and on the quality of their interface (Pandey, 2004). While there has been interest in a broad range of matrix materials for the manufacture of metal matrix composites, the predominant focus recently has been on aluminium and titanium alloys, because these materials can significantly improve thrust-weight ratio for space and aerospace automotive engines (Pandey, 2004).

One of the limitations of aluminium alloys is that they tend to have maximum usage temperatures which are low, generally below 400°C.In order to achieve thermal performance suitable for aerospace applications, beyond 400°C, researchers have turned to the investigation of high temperature alloys (Pandey, 2004). Titanium alloys have attracted interest as they have temperature and strength capabilities which are typically superior to those of aluminium alloys, making them very attractive from a metal matrix composite perspective (Pandey, 2004). However, processing titanium alloys is not without its difficulties. To make sure that the quality of the material is maintained and free from processing damage, a cumbersome processing procedure is required. The specialised care and attention that are

mandated by this process to date mean that there are typically high production costs (Pandey, 2004).

2.1.3 Classification based on reinforcement type

Particulate, laminate, and fibrous composites are the three typical types of reinforcement, as shown in Figure 2.1. As the names suggest, particulate composites are reinforced by particles, laminate composites by laminates and fibrous composites by fibres.

2.1.3.1 Particulate composites

A composite will be a particulate reinforced composite when a particle is added to a matrix and that added particle has dimensions that are equiaxed: that is, approximately equal in all directions. Particles are used as reinforcements for a number of reasons including reducing shrinkage, improving performance at high temperatures, increasing wear resistance, and reducing friction (Akovali, 2001). Particles are also added for load-sharing purposes within the matrix; however, they are not as common in this regard as fibres. This means that particle reinforcement will not necessarily strengthen a material, although it may improve its stiffness (Akovali, 2001).

Particles tend not to have any directional preferences. Their usual purpose in reinforcement is either to enhance composite properties or to lower the overall cost of materials of an isotropic nature. Particles used in reinforcement typically have order unity length/diameter ratios and dimensions ranging from the nano-scale to several millimetres (Akovali, 2001; Matthews and Rawlings, 1994). Particles used for the reinforcement of composites can be cubic, platelet-like, spherical, or any other irregular or regular geometric shape (Matthews and Rawlings, 1994). As mentioned, particulate reinforcements are equiaxed. In nature they have strong reinforcing capabilities. Two particle reinforced composite sub-classes are large particle reinforced composites and dispersion-strengthened composites. Composites reinforced by large particles are usually harder and stiffer than the matrix and tend to restrain movement of the matrix (Akovali, 2001, Matthews and Rawlings, 1994).

2.1.3.2 Laminate composites

Laminate composites are layered composites in which the matrix holds layers of embedded material. These composites typically feature alternative arrangements of layers, which are conducive to achieving the best possible bonding between reinforcement and matrix bonding (Valodkar, 2012). Depending on the application of the resultant composite, laminates can feature fibre reinforcement which is either bi-directional or uni-directional in orientation (Valodkar, 2012). Laminates can be further distinguished by whether they are angle-ply, cross-ply, symmetric or uni-directional (Valodkar, 2012) It is also possible to fabricate what is known as a hybrid laminate, one based on different constituent materials or two or more different reinforcing patterns of the same material (Valodkar, 2012). Most laminate composites that are produced for commercial applications use synthetic reinforcement as opposed to natural fibre reinforcement because of the former's capacity to provide good thermal and mechanical behaviour (Valodkar, 2012).

2.1.3.3 Fibre reinforced composites

Fibrous composites, perhaps better known as fibre reinforced composites, are highly popular in industrial and commercial applications because of their favourable strength and stiffness (Agarwal and Broutman, 2006). Fibres are well-known for their load carrying capabilities and fibre reinforced composites exhibit excellent structural performance. Typically they are made up of a high strength, high elastic modulus fibre which is bonded to a matrix (Agarwal and Broutman, 2006). The fibre and matrix, while retaining their respective chemical and physical identities, form a materials partnership allowing enhanced new properties that are not attainable by the fibre or matrix separately.

The fibre dispersed in the matrix may be continuous or discontinuous, as shown in Figures 2.1c and d. Continuous or long fibre composites are made when a dispersed phase in the form of continuous fibres is used to reinforce a given matrix; discontinuous or short fibre composites have short or staple fibres embedded in the matrix. In continuous fibre reinforcement the applied load can be effectively transferred from the matrix to the fibres, whereas in discontinuous (or short) fibre

reinforcement, effective load transfer from the fibre to the matrix occurs when the length of fibres is neither too long to allow individual fibres to entangle with each other nor too short for the fibres to lose their fibrous nature (Singh, 2013). Composites in which the short fibres are well dispersed in the matrix have excellent mechanical properties compared to composites with poor dispersion of short fibres. The distinction between continuous and discontinuous fibres, or long and short, on end performance of the composites is clear: as the behaviour of short fibre composites is dominated by the end effects, they are generally not good agents of reinforcement; the shorter the fibre, the less stress it can bear (Singh, 2013). Thus discontinuous fibre composites are by definition shorter and provide less strength than composites prepared with continuous fibres (Singh, 2013).

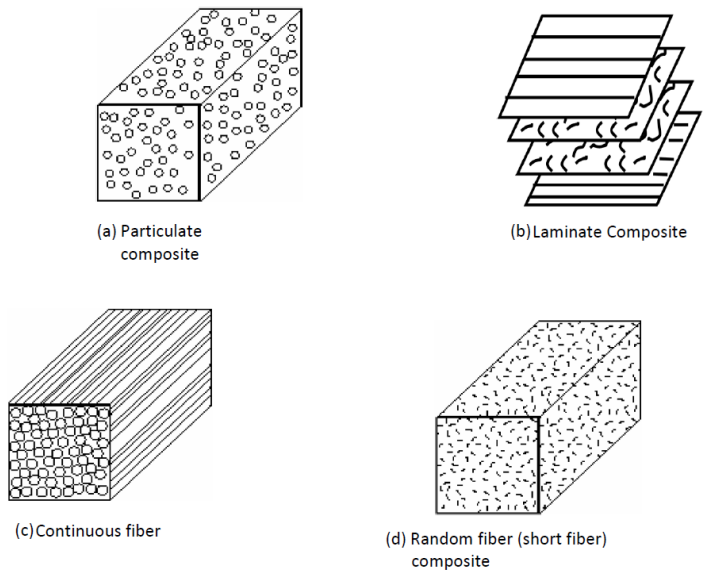


Figure 2.1: Schematic diagram of different types of composite (Singh, 2013).

2.1.4 Hybrid fibre composites

Hybrid composites are those in which two or more types of fibre with different mechanical properties have been incorporated into a single matrix material. Hybrid fibre composites are developed primarily to enhance composite properties and reduce cost. Intraply, interply, intimately mixed, and sandwich types are sub-classes of hybrid composites (Mallick, 2007; Thomas and Pothan, 2009). The manner in which the materials are incorporated determines to which sub-class a particular hybrid composite belongs.

‘Intraply’ refers to those composites in which two or more materials are arranged in rows, in either a random or regular manner. ‘Interply’ hybrid composites are those in which the constituent materials are regularly stacked. ‘Intimately mixed’ are heavily mixed composites so that no over-concentration of either type is present in the composite material. In ‘sandwich hybrids’, as the name suggests, one material is sandwiched between two layers of another (Mallick, 2007; Thomas and Pothan, 2009).

2.1.5 Textile composites

Textile composites are another important class of composites. One of the most commonly prepared textile composite classes is that prepared from woven fabrics, and woven fabric reinforcements are the most common used form of textile structural reinforcement (Thomas and Pothan, 2009). These provide a number of strength, cost, and mechanical property-related advantages over non-woven reinforcements. Furthermore, their manufacture is cost-effective as the process uses the material’s near-net shape formed by interlacing warp and weft. One of the unique advantages of woven fabric is its ability to be able to overcome lateral cohesion problems that are encountered in the preparation of reinforcing elements (Anandjiwala, 2007; Thomas and Pothan, 2009). Twisted yarns have been reported to increase the lateral cohesion of the filaments as well as to improve ease of handling. By twisting the yarns any micro damage within the yarn can be localised, leading to a possible decrease in the failure strength of the yarn (Anandjiwala, 2007).

Woven fabrics are attractive as reinforcements because of their conformability, viability, and integrity. For example, an interesting favourable characteristic of woven fabrics is their drapeability, their ability to permit the formation of complex shapes. The viability of woven fabrics arises from their reduced manufacturing costs, and a favourable production quality is that they have easy handling requirements (Gao et al., 1999; Thomas and Pothan, 2009). For example, instead of using two non-woven piles, a single two-dimensional biaxial fabric can be used. With respect to integrity, woven fabric reinforcements exhibit superior impact damage resistance (Gao et al., 1999). Moreover, woven fibre composites typically have superior toughness, strength and stiffness to nonwoven fibre composites (Gao et al., 1999;

Thomas and Pothan, 2009). They offer higher impact resistance, more balanced properties, and lower fabrication costs particularly for components with complex shapes, when compared with unwoven unidirectional composites (Gao et al., 1999; Thomas and Pothan, 2009). Figure 2.2 shows the different types of woven fibre reinforcement that are commercially available.

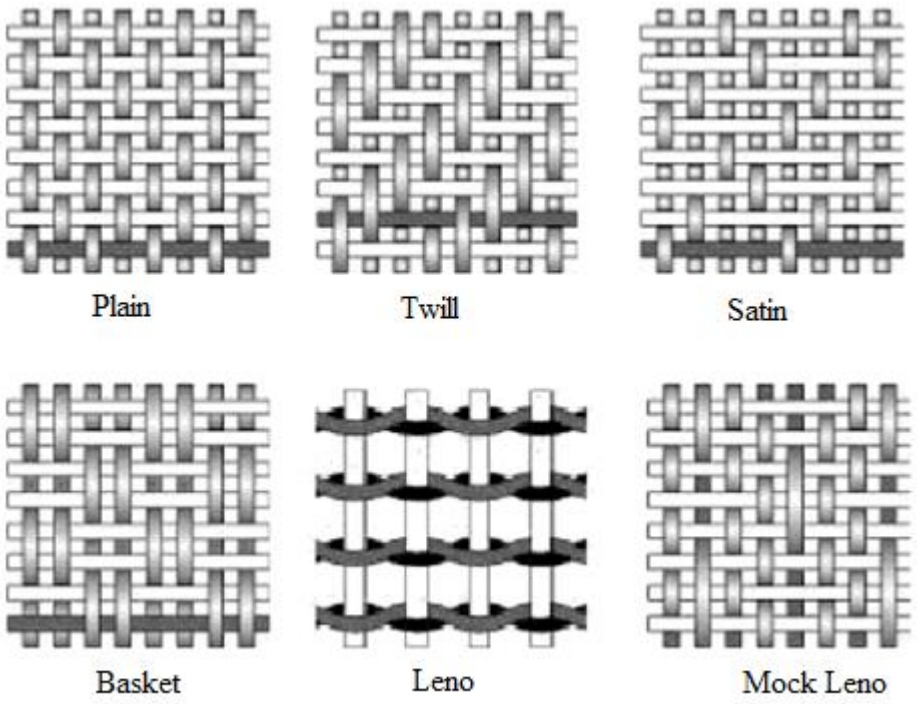


Figure 2.2: Some typical woven styles used as reinforcements in making compositesm (Thomas and Pothan, 2009).

2.1.6 Factors controlling performance of fibre reinforced composites

The mechanical properties of fibre reinforced composites are influences significantly by fibre orientation, volume fraction and dispersion, and by fibre/matrix adhesion.

2.1.6.1 Fibre orientation

Fibre orientation angle is a critical determinant of mechanical properties (White and De 1996) because the orientation of each fibre in relation to the loading axis determines the quality of stress transfer between the matrix and the fibre (White and De 1996). Well-oriented fibres in composites are likely to improve mechanical

performance. For this reason control of the fibre orientation during fabrication is considered one of the most important factors affecting the mechanical properties of fibre reinforced composites (Kardos, 1985).

The ultimate mechanical properties of composites are dependent on the orientation of each individual fibre with respect to the loading axis (Aldousiri et al., 2013). Maximum reinforcement is possible when the fibres lie horizontal to the applied load. In contrast, loading the fibres vertically so they have a vertical orientation in relation to the applied load increases the probability of early detachment and decomposition of the composite (Aldousiri et al., 2013) because the bonding area is weakened as the load transfers to shear force along the fibre/matrix interface (Aldousiri et al., 2013). When the fibres are orientated horizontally to the applied load they contribute equally to the load bearing capacity (Aldousiri et al., 2013).

2.1.6.2 Fibre volume fraction

Fibre volume fraction is an important factor that significantly influences the mechanical properties of fibre reinforced composite materials. The 'Rules of Mixtures' is a model that can be used to predict tensile strength and other composite properties based on fibre content, as shown in Figure 2.3, which involves extrapolation of matrix and fibre strength to fibre volume fractions of 0 and 1 (Taib, 1998). The most typical pattern is that as a lower fibre volume fraction is used, the resultant composite exhibits a lower tensile strength: in other words, the lower the fibre content, the lower the tensile strength. This is believed to be caused by two separate phenomena. Firstly, there is a general dilution of the matrix. Secondly, and perhaps more importantly, the fibres tend to have high stress concentrations at the end because of flaws along the fibre ends that leads to the breaking of the bond between fibre and matrix (Bibo and Hogg, 1996; Bonnia et al., 2010). Where there is high fibre concentration, there is more capacity for stress to be distributed evenly. Moreover, at higher fibre concentrations there is more potential for the matrix to be sufficiently restrained. At this point, the dilution effect, which weakens the composites when a low fibre volume fraction is added, is outweighed by the reinforcing effect of the high fibre volume fraction (Bibo and Hogg, 1996; Bonnia et al., 2010). However, increasing fibre volume fraction does not lead to enhanced

properties indefinitely, and an optimum point of concentration will be met. This occurs when the maximum strength of the composite is reached. Once optimum concentration is met, increasing fibre content is likely to lead to decreases in strength, as beyond this concentration there is believed to be insufficient matrix material to bond with the fibres, and thus the composite overall lacks interfacial adhesion (Bibo and Hogg, 1996; Bonnia et al., 2010).

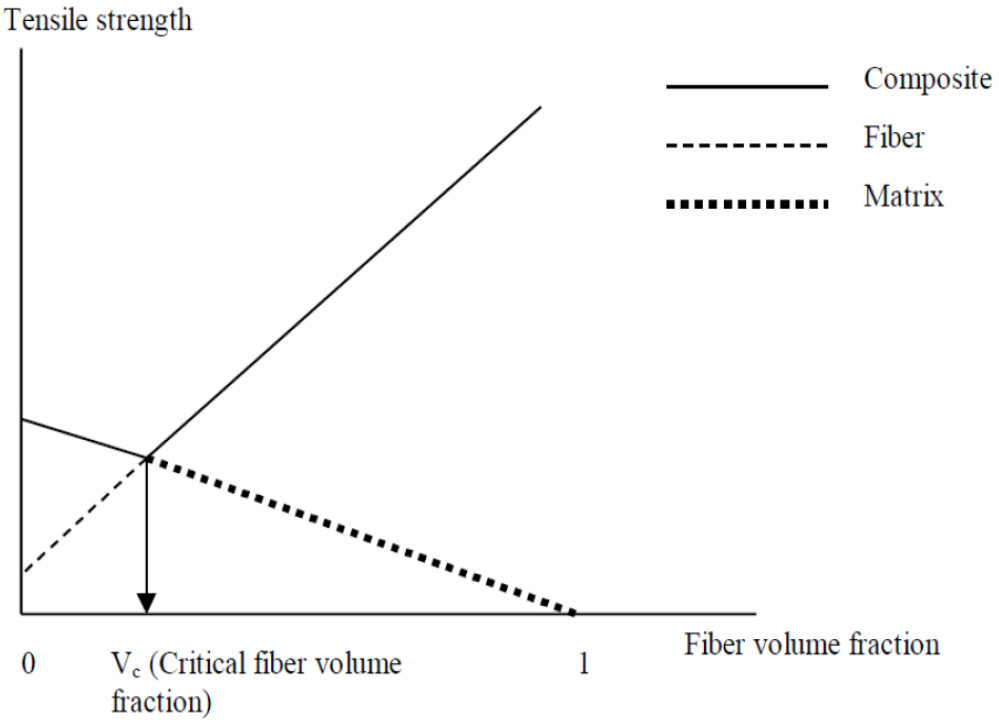


Figure 2.3: Typical relationship between tensile strength and fibre volume fraction for short fibre-reinforced composites (Taib, 1998).

2.1.6.3 Fibre dispersion

Fibre dispersion, the extent to which fibres are evenly distributed within the matrix, is believed to be a dominant factor underpinning high-performing fibre reinforced composite materials. Good fibre dispersion does not refer to even distribution alone, but also to the condition where each fibre is separated from another and is thus surrounded by matrix material (Bachtiar et al. 2008). The absence of agglomerations or clumps of any description is a sign of good dispersion.

Poor fibre dispersion results in a mixture which is inhomogeneous, featuring fibre-rich areas and resin-rich areas (Taib, 1998). The problem is that clumps of fibre-rich areas are highly susceptible to micro-cracking, and resin-rich areas tend to suffer from inherent weakness. Where microcracking occurs, the composites will suffer from inescapable inferior mechanical performance. To avoid this situation and ensure maximum performance and strength, composite developers make sure fibre dispersion is homogeneous (Taib, 1998).

Fibre length and fibre–fibre interaction, such as strong hydrogen bonding between fibres, are two factors that influence fibre dispersion (Ebnesajjad, 2013). The same two factors also account for some fibres, particularly cellulose fibres, agglomerating and forming clumps during the mixing process. In order to achieve satisfactory fibre dispersion, developers need to consider the length of the fibres that will be used in a composite's preparation. If the lengths are too great the fibres are likely to tangle and compromise dispersion quality (Ebnesajjad, 2013); if too little, the effectiveness of reinforcement they offer in the first place will come into question. About 0.4mm is a suitable length for favourable dispersion of polyester, rayon, and nylon fibres, according to Derringer (1971).

A number of techniques to enhance fibre dispersion have been recommended in the literature. Chemical treatment of fibre surfaces is a leading approach. This type of modification can involve the pre-treatment of fibre with acetylation. Stearic acid can also, or alternatively, be used as an independent dispersing agent. Increasing the mixing time can also improve the dispersion of fibres (Ebnesajjad, 2013).

2.1.6.4 Fibre/matrix adhesion

Fibre/matrix adhesion is another fundamental pre-requisite of high-performing composite materials. Good adhesion quality is particularly important for short fibre composites (Ebnesajjad, 2013). Poor fibre/matrix adhesion in hydrophobic thermoplastics, coupled with poor fibre dispersion, leads to poor wetting composites with particularly poor mechanical properties. As loads are applied to the composites, it is important that they are transferred from the matrix to the fibres; this enables composites to have both useful strength and toughness. Thus not only does the

fibre/matrix interface need to be adhesive, but it needs to have suitable interaction. Problems with fibre/matrix adhesion quality can be overcome by a number of means. For example, the interfacial bonding of thermoplastic matrix and fibre interfaces can be improved through chemical grafts, fibre pre-treatments, polymer coating materials, and the use of coupling agents (Ebnesajjad, 2013). These improve fibre-matrix adhesion as well as fibre dispersion.

Given the factors that affect the properties of fibre-reinforced composites, it is important that developers pay attention to processing conditions and aids, and in particular to length of fibre and treatment options so that the highest performing composites can be manufactured (Ebnesajjad, 2013).

2.1.6.5 Presence of voids

The presence of voids is caused in some instances when air or volatiles of other description become trapped within the material. They exist in the cured composites as microvoids, and often compromise the composite's mechanical properties considerably. These microvoids are in two classes: those which form along individual fibres, and those which form in resin-rich regions and between fibre layers during processing.

The most common cause of void formation is the inability of the matrix to displace air from fibre surfaces as they pass through the resin impregnator. The angles of contact between fibre and matrix, the resin's viscosity, and the rate of transport of reinforcements into the matrix are the most important factors influencing the presence of trapped air during the production of composites (Thomas and Pothan, 2009). When voids exceed 20% by volume, the resultant material will typically have lower fatigue resistance, greater susceptibility to water diffusion and greater scatter (variation) of mechanical properties than the same material with a lower proportion of trapped air (Thomas and Pothan, 2009). It should also be noted that the production of voids is also possible due to the actions of volatiles produced during thermosetting and thermoplastic polymers curing cycles (Thomas and Pothan, 2009).

2.1.7 Fabrication of composites

Composite fabrication is primarily a task of ensuring that fibres that are added to a matrix are suitably incorporated into, surrounded by and wetted by the matrix. For thermosetting polymers, the most typically applied techniques are described below.

2.1.7.1 Hand lay-up

Hand lay-up is the oldest, most straightforward and most often used method for the fabrication of reinforced products. Hand lay-up typically relies on the use of a plastic, metal, or wood mould, surface or cavity, or a combination of these, as a base. For convenience this part of the method will be referred to as the mould. This mould is treated with a release agent to make sure that no components adhere to it. Once it has been selected and treated, the reinforcements, i.e. the fibres, are cut and laid into the mould (Mallick, 2007; Thomas and Pothan, 2009). The fibre type, quantity and orientation are important considerations for the developer: as mentioned, these choices will dramatically affect the performance of the end product.

Following this step, the resin is added. A squeegee, brush, or roller is often used to facilitate the impregnation of the fibres with the resin.

2.1.7.2 Spray-up

Spray-up is a similar to the hand lay-up process, developed to provide a more efficient and cost-effective method of fabricating reinforced products. The distinguishing feature of this method is the use of a specialised spray gun to apply the resin and reinforcements in the mould, with a greater consistency and speed than manual techniques.

While the spray gun makes it difficult to produce an accurate thickness of sample and fibre volume fraction, the techniques does result in less void content. The upshot is that spray-up is a technique that is highly dependent on the operator, and thus typically is not appropriate for the development of components that are reliant on dimensional accuracy (Mallick, 2007).

2.1.7.3 Pultrusion

Pultrusion can be considered the answer to the weaknesses of earlier techniques. It is a process of continuous manufacturing which is capable of fabricating long, straight fibre-reinforced composites which exhibit a consistent cross-section (Mallick, 2007; Thomas and Pothan, 2009). Machinery draws fibres from a creel stand and gradually brings them together, pulling them into a bath of resin, where fibre/matrix incorporation occurs. A pre-former is used to remove excess resin, and the incorporated fibres are transferred to a hot die setting which cures and solidifies the composites. The composites then enter a pulling system which, using continuous force, moves the composite forward. It is then cut to the required size (Mallick, 2007; Thomas and Pothan, 2009).

2.1.7.4 Filament winding

Filament winding is the technique used to manufacture surfaces of revolution such as cylinders, pipes, spheres and tubes, and is used for the production of large pipe and chemical storage tank works for the chemical industry. Filament winding produces a composite structure in which continuous reinforcements are impregnated with resins during winding, and towed on a rotating mandrel. When the winding process is completed, the composite is placed in an oven to cure. This gives a product with good mechanical properties and structural integrity. Once the composite has cured, the mandrel is removed (Mallick, 2007; Thomas and Pothan, 2009).

2.1.7.5 Bag moulding process

Bag moulding was developed because of the need for a more versatile method of composite manufacture (Thomas and Pothan, 2009; Mallick, 2007). Its distinguishing feature is that once the lamina have been laid in the mould and the resin spread or coated, a flexible diaphragm or bag is used to cover the composite. Then heat and pressure are applied for curing. The pressure bag, the vacuum bag, and the autoclave are the three basic moulding methods. The pressure bag method has the shortcoming of high cost, because it combines expensive tooling and curing and is only useful for a specific shape. The vacuum bag and autoclave are more commonly

used as they offer inexpensive tooling and curing and greater production versatility (Thomas and Pothan, 2009; Mallick, 2007).

2.1.7.6 Resin transfer moulding

Resin transfer moulding is a promising novel technique, and may able to take over much of the work of laminated fabrication. It involves cutting and shaping a dry reinforcement material into a 'preform', a preformed piece, which is later positioned into a prepared mould cavity. To reduce air entrapment, resin is injected at the lowest point and fills the mould upward to several holes located at the highest points of the mould. These holes allow entrapped air to escape. When resin starts to leak into the resin trap, the tube is clamped to minimize loss (Mallick, 2007; Thomas and Pothan, 2009).

Resin transfer moulding often does not require a high injection pressure, and as it typically takes place in a mould which is closed, styrene evolution is minimised. For simple and smaller components injection time is typically a few minutes; complex or large components with high fibre content can requires hours for injection to be complete. When resin starts to flow from the vent areas, the flow is stopped and curing can begin (Mallick, 2007; Thomas and Pothan, 2009).

Resin transfer moulding relies on relatively low temperatures and pressures, and has the advantage of relatively modest start-up requirements. Figure 2.4 provides a schematic representation of the technique.

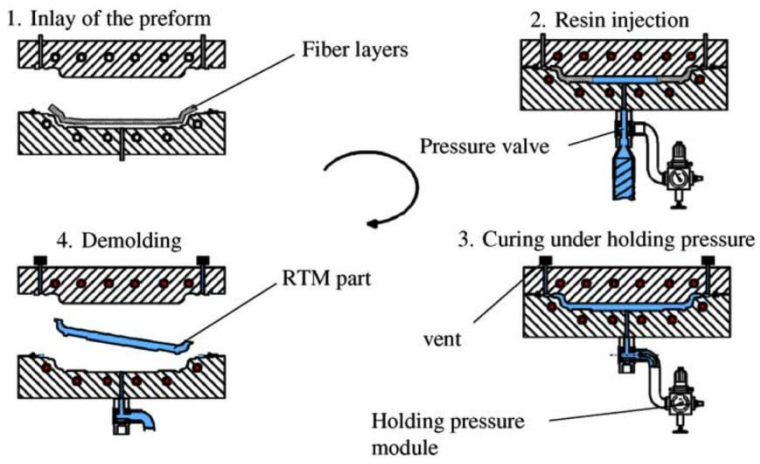


Figure 2.4: The resin transfer moulding (RTM) process (Schmachtenberg et al., 2005).

2.1.8 Toughening mechanisms in composite materials

The behaviour of ceramic under loading has been the focus of intense investigation (Awaji et al., 2002; Ohji et al., 1998; Steinbrech, 1992; Wachtman et al., 2009). The study of the toughening behaviours of fibre-reinforced ceramic composites has been a part of this investigation (Belitskus, 1993; Low, 2006; Saruhan, 2003; Suemasu et al., 2001).Researchers have confirmed that fibre-reinforced ceramic composites exhibit microcracks, fibre/matrix interface crack deflection, crack-bridging, and crack plane fibre pull-out (Belitskus, 1993; Low, 2006; Saruhan, 2003; Suemasu et al., 2001). These four behaviours are often reported or referred to as the four toughening hall-marks (Belitskus, 1993; Low, 2006; Saruhan, 2003; Suemasu et al., 2001).

The following section discusses the relationships between fibre addition and the mechanisms of microcracking, crack deflection, crack bridging and fibre pull-out and how these relationships lead to increases in fracture toughness in fibre reinforced composites.

2.1.8.1 Microcracking

Microcracking can be used as a mean of toughening mechanism. It is important that microcracking occurs only in response to stress that is created in close proximity to

crack tips and that it is restricted to small well-dispersed sites to avoid microcrack linkage (Warren, 1991). Cracks that form during processing will not be as valuable in terms of providing a toughening mechanism. The formation of a zone of microcracks ahead of the crack contributes to toughening by creating a zone of lower elastic modulus and absorbing strain release energy (Warren, 1991). The nature and morphology of microcracking is dependent on the fibre and matrix type. Fibres with higher moduli tend to result in composites with more tortuous and wider microcracks (Timmerman et al., 2002).

Lin et al. (2010) investigated the effects of micro crack propagation and distribution on fracture behaviour in short carbon fibre reinforced geopolymer matrix composites. They found that micro cracks initiate in the geopolymer matrix of a sample when the bending stress is greater than the strength of the matrix. When a higher load is applied, the micro crack propagates and encounters the reinforced fibres, whose high mechanical strength tends to maintain integrity of the composite. This means that the proliferation of micro cracks will be retarded, causing accumulation of internal stress between the matrix and the reinforced fibres. When accumulation of internal stress is high enough, other new micro cracks will occur on the surface of the sample, indicating that the stress distribution in the matrix has been better changed due to the enhancement effect of the reinforced fibres. Figure 2.5 (a-e) shows a series of environmental scanning electron microscope (ESEM) images of crack initiation and propagation process on the side of the beam of a short carbon fibre reinforced geopolymer matrix composite.

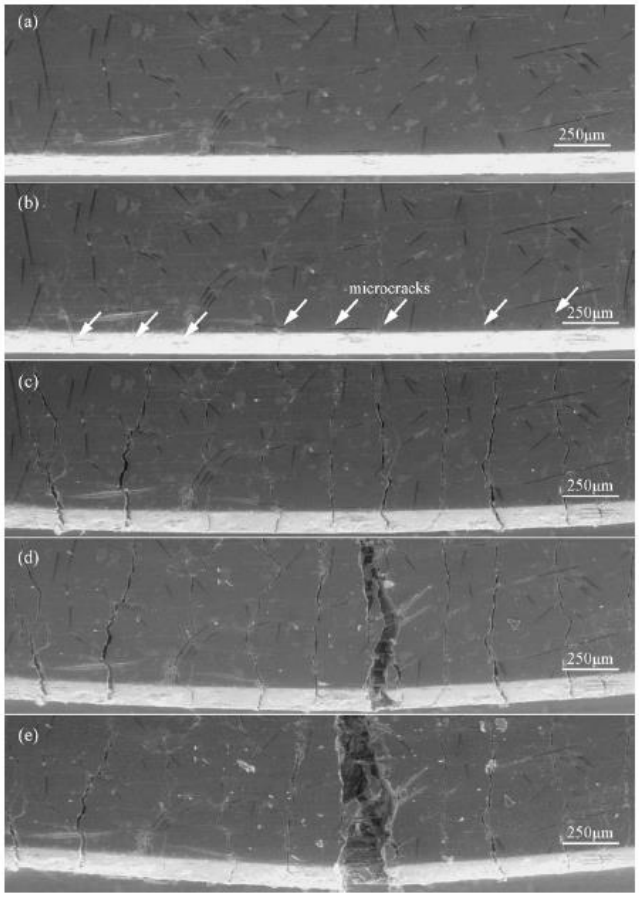


Figure 2.5: Series of ESEM images (a)–(e) of crack initiation and propagation on the side of a beam sample of the C_f/geopolymer composite, corresponding to positions a–e of the load/displacement curve in Figure 2.6 (Lin et al., 2010).

The typical load/displacement curve for C_f/geopolymer composites is given in Figure 2.6. It can be seen that during the bending test, composites with a low volume percentage of carbon fibres (3.5 vol.%) display significant deformation and obvious non-catastrophic fracture behaviour. As the bending load increases, the composites exhibit elastic deformation and obvious displacement in initial stages (stages I and II). Beyond the elastic limit, the applied load yields plastic deformation until the ultimate load is reached; then the load gradually decreases with the increasing displacement, producing a long tail (stage III) (Lin et al., 2010).

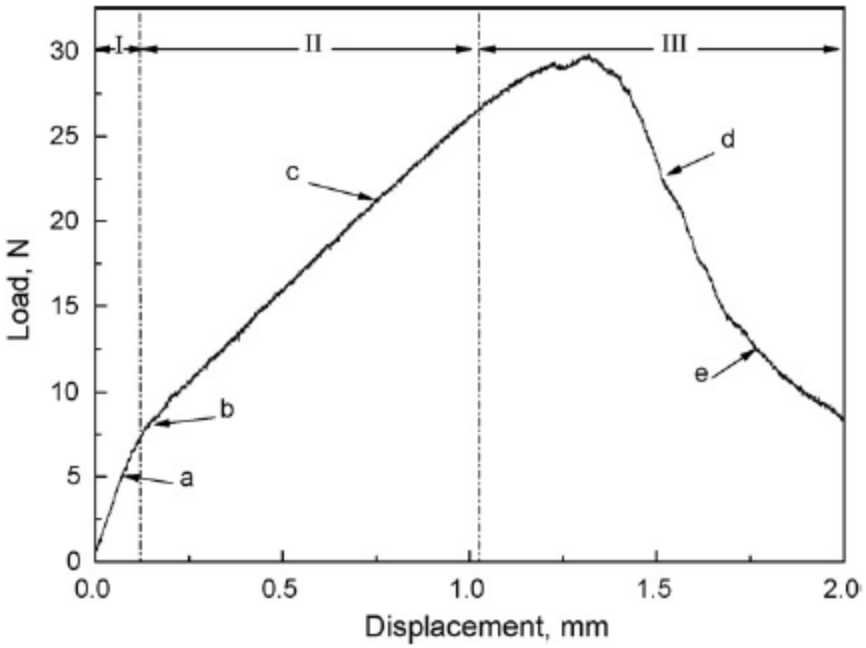


Figure 2.6: Load/displacement curve for C_f/geopolymer composites (Lin et al., 2010).

2.1.8.2 Crack deflection by fibres

Another toughening mechanism for fibre reinforced composites is the deflection of matrix cracks at the interface of fibre and matrix, essential to achieve toughness in brittle composites. From a toughness perspective, compared to brittle cracking through fibres, crack deflection is a more desirable mode of failure. In ceramic-matrix composites, crack deflection at the fibre/matrix interface is an initial mechanism underpinning enhanced toughness (Ahn et al., 1998).

When loading is increased in the fibre direction, micro cracking grows until it reaches the fibre/matrix interface. At this point it may either deflect along the interface or penetrate the fibre. Figure 2.7 shows a moving crack's penetration or deflection through a fibre/matrix interface (Berti, 2012). Where interfaces are weak enough that the matrix crack is deflected along the interface, fibres remain intact, maintaining the composite's toughness. Where the interface is too strong, matrix cracks will penetrate into fibres and cause the composite to become brittle in a manner similar to a monolithic ceramic (Ahn, 1997). The propagation behaviour of a

crack at the interface between the fibres and matrix in ceramic matrix composites is therefore critical to toughening. Many researchers have recently investigated the conditions required to obtain an interfacial debond crack from a main matrix crack in terms of energy release rates (Martínez and Gupta, 1994; Ming et al., 1994). The findings hold that matrix crack deflection at fibre/matrix interfaces is presumed when the energy required to proliferate the interfacial debond crack is less than the amount of energy required to grow the crack across the interface.

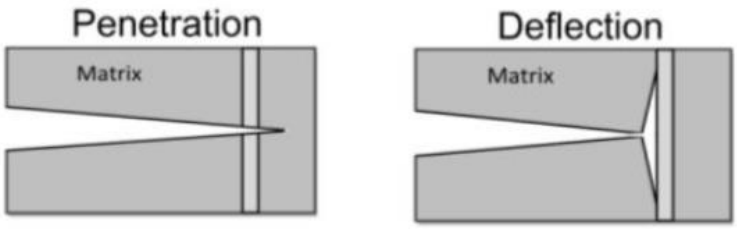


Figure 2.7: penetration or deflection of a moving crack through a fibre/matrix interface (Berti, 2012).

Crack growth rate in composites is often reported as lower than that found in unreinforced matrix specimens. The presence of fibres bridging the matrix crack reduces crack growth rate. As matrix cracks reach fibres, they are deflected at the interface between fibre and matrix. Further opening of the crack surface is restrained by frictional sliding, which also reduces crack-tip stress. During loading, energy is further dissipated through interfacial friction (Cook et al., 1964; Martínez and Gupta, 1994; Ming et al., 1994).

Local crack tip stresses can aid crack deflection, as can differences of fracture work along alternative crack paths (Gupta et al., 1992). When probing the crack-tip stress field, the local stress criterion for crack deflection requires de-cohesion stress for tensile or for shear separation along the interface to be reached before cohesive strength is reached at the crack tip (Gupta et al., 1992). In contrast, complementary fracture work criteria require that when cracks are about to grow the fracture work should be less alongside the interface than ahead into fibre for virtual extensions of a crack ahead in its plane or along the interface (Gupta et al., 1992).

2.1.8.3 Crack bridging by fibres

Crack bridging is another mechanism for toughening plain and fibre reinforced concrete, whisker-reinforced ceramic and metal matrix composites, glassy polymers, and matrices reinforced with ductile secondary phases (Ballarini and Muju, 1993). The role of fibre, in this mechanism, is to bridge the crack tip and slow crack growth. As fibres can act as springs keeping two crack surfaces shut, bridging mechanisms and crack arresting can lead to high energy absorption and toughness (Ballarini and Muju, 1993).

The structural features of a material will largely determine the effectiveness of fibre bridging, governing whether a matrix crack will be bridged and the extent of fibre strength. Strong fibres tend to cause fully bridged cracks, which can grow in the matrix while the fibres remain intact. As shown in Figure 2.8, this noncatastrophic or ductile mode of failure causes large strains, as loading beyond first matrix crack causes multiple matrix cracking. In such cases ultimate strength is governed by bundle strength (Ballarini and Muju, 1993). In contrast, weak fibres lead to matrix cracks which are bridged in small regions behind crack tips as propagation occurs. Ultimately this leads to specimens being broken in two as partially bridged cracks propagate and break sequentially (Ballarini and Muju, 1993).

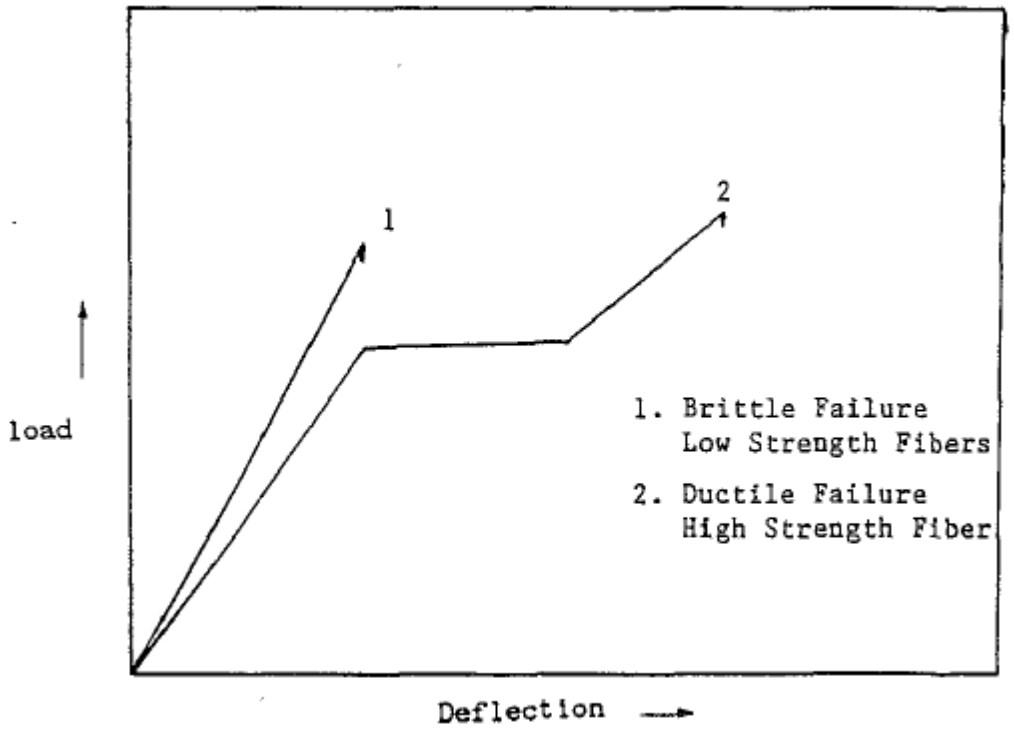


Figure 2.8: Possible failure modes of brittle matrix composites (Ballarini and Muju, 1993).

Mobasher et al. (2006) reported on the contribution of reinforcing fabric in terms of crack arresting and bridging (see Figure 2.9). They noted that crack arresting and bridging mechanisms tend to improve energy absorption and mechanical performance in the case of glass-fabric reinforced cement composites.

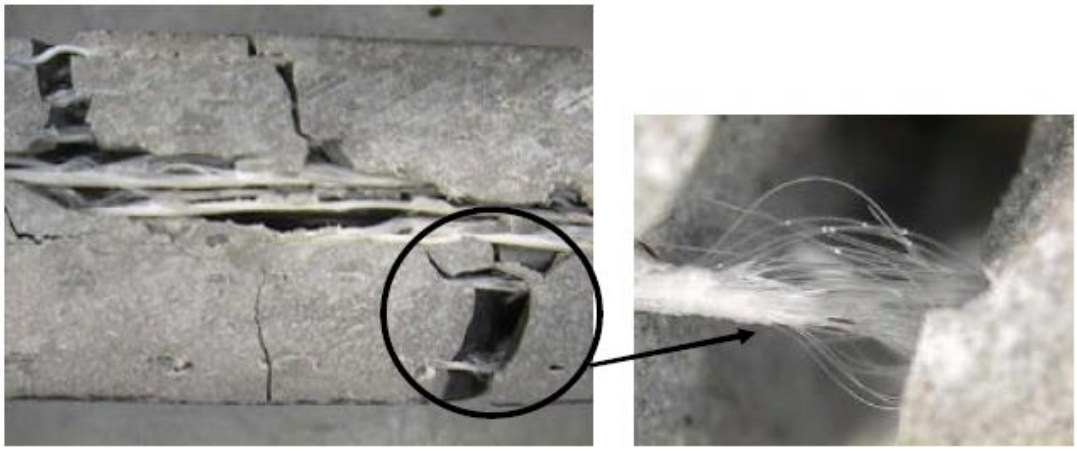


Figure 2.9: Failure of the fabric and distributed cracking at the end of testing in glass-fabric reinforced cement composite (Mobasher et al., 2006).

Elbadry et al. (2012) found crack bridging to be the dominant cause of increased mechanical properties in the case of unsaturated polyester matrix composites reinforced with natural jute fabric. The SEM micrographs of fracture surfaces show fibre bridging under load of bending at a fibre weight of 36%. This is shown in Figure 2.10.

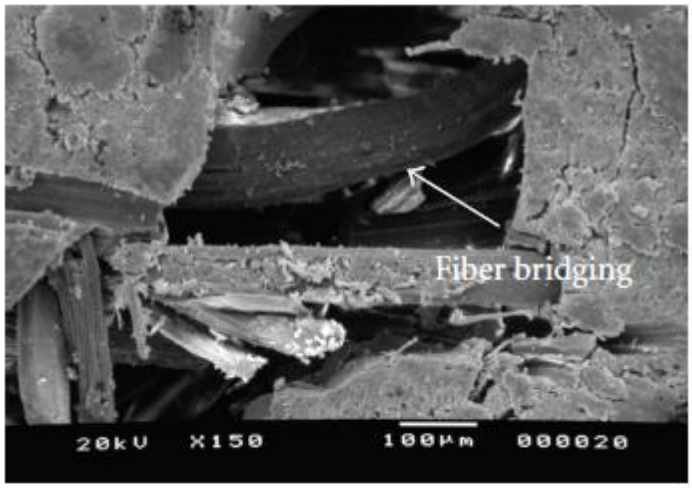


Figure 2.10: SEM micrographs of selected fracture surface of the composite with 36 wt% of jute fibre (Elbadry et al., 2012).

Dias and Thaumaturgo (2005) found that the addition of 1.0% basalt fibres led to marked improvement in fracture toughness of the geopolymer composites. They also reported that the fibre bridging mechanism allowed by the basalt fibres caused a greater absorption of fracture energy. The following Figure 2.11 shows this bridging action.

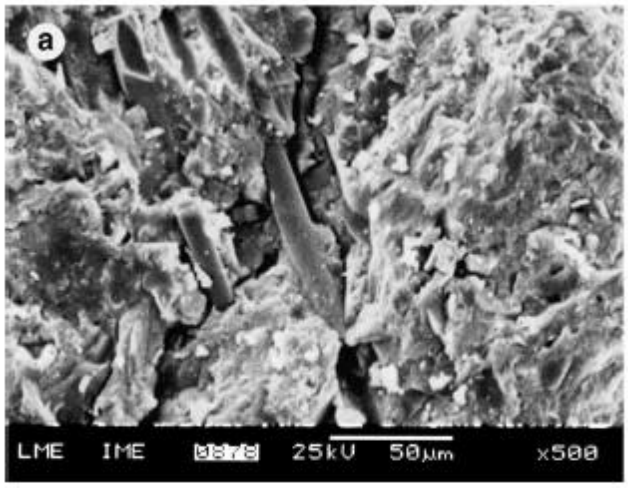


Figure 2.11: Toughening mechanism in a geopolymer composite with 1.0% basalt fibres (Dias and Thaumaturgo, 2005).

2.1.8.4 Fibre pull-outs

Fibre pull-out is another toughening mechanism in fibre-reinforced composites. Fibre pull-out is significant in providing toughness in composites. As cracking occurs, fibres can be either fractured or pulled out of composite. This phenomenon depends upon the strength of the bond with the matrix (Low, 2014); where there are very strong fibre/matrix interface characteristics, fibres often rupture instead of being pulled out. Depending on the properties of the matrix, rupture tends to limit the composite's energy absorption capacity. In contrast, where there are weak interfacial bond, fibres tend to slip out of the matrix instead of rupturing with absorbing a higher amount of energy (Low, 2014).

Fibre pull-out occurs when a crack is near the end of the fibre. If the crack is not near the end of the fibre, the fibre will fracture instead. This causes the energy absorbed

by fibre pull-out to be higher than the energy absorbed by fibre rupture. Fibre rupture and fibre pull-out of the matrix are shown in Figure 2.12.

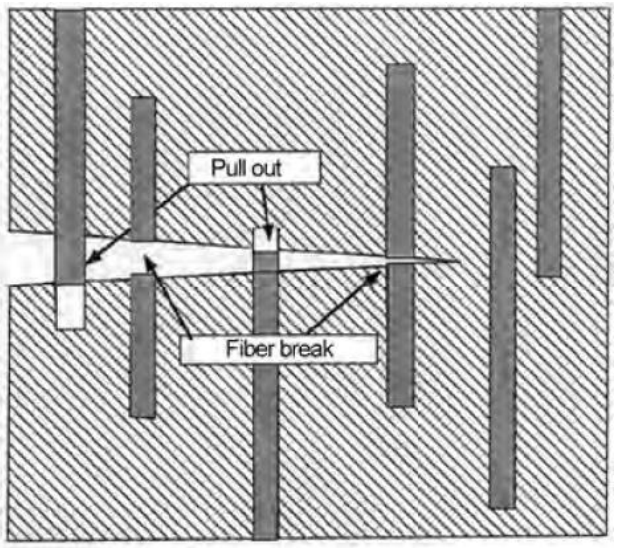


Figure 2.12: Sketch showing some fibres fracturing at a crack and others pulling out (Hosford, 2005).

The increase in energy absorption is dependent on fibre type, length, and the extent to which content is pulled out during loading. Typically, short fibre pull-out length makes little contribution to fracture toughness (Daniel, 1994). Given the shallow decrease in fibre stress with distance from the matrix crack, large pull-out lengths cause fractures at fibre flaws further from the crack, as shown in Figure 2.13 (Daniel, 1994). More energy is required to create large fibre pull-out lengths and is characteristic of good fibre reinforced ceramic matrix composites (Daniel, 1994; Stocchi, et al. 2007).

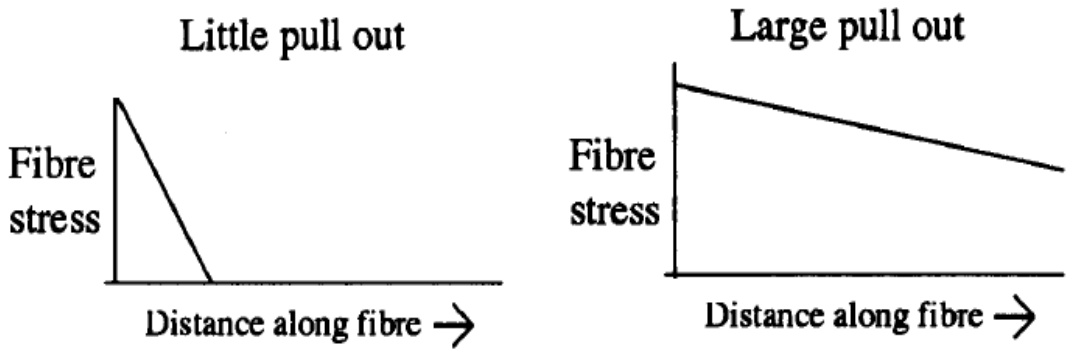


Figure 2.13: Probable fibre failure site depending on the effect of pull-out length (Daniel, 1994).

Lin et al. (2009) investigated the pull-out effect on geopolymer composites reinforced with carbon fibres and found that the addition of 3.5% volume carbon fibres led to a significant enhancement of strength and toughness. They attributed the enhanced toughness to fibre-pull. Figure 2.14 shows the density of fibre pull-out on the fracture surface of 3.5% carbon fibre composites. Also relevant is the length of pull-out, observable in Figure 2.14, which the authors believed prevented catastrophic fracture of these composites. However, it was reported that this length decreased significantly from 600 to 100 μm with the increase of carbon fibre volume fraction from 3.5 to 7.5%. It is believed that higher shear stresses at fibre/fibre intersections and increased cohesion strength of fibre/matrix interfaces causes fibres to favour rupture as opposed to pulling-out, as shown in Figure 2.14.

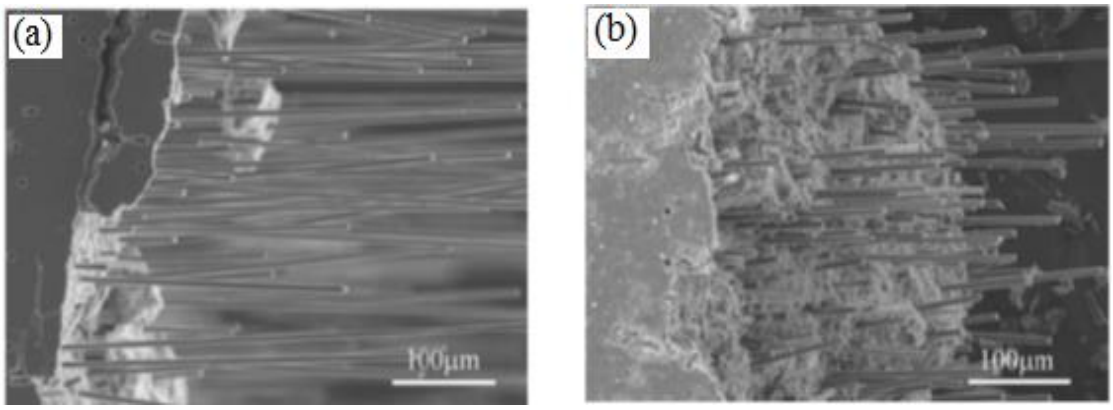


Figure 2.14: Scanning electron micrographs of the fracture surface of (a) 3.5 vol% and (b) 7.5 vol% carbon fibre/geopolymer composites (Lin et al., 2009).

2.2 Fibres

Fibres are typically categorised as synthetic if man-made, and natural if naturally occurring (Mishra and Yagci, 2008).

2.2.1 Synthetic fibres

Synthetic fibres are manufactured from the basic chemical units formed by chemical synthesis (Mishra and Yagci, 2008). An extremely large group, they are used primarily to reinforce composites and feature varying elastic moduli and strengths depending on their manufacture. Table 2.1 provides values of elastic moduli and strengths for a set of commercially available fibres.

Table 2.1: Typical Synthetic Fibre Properties (Bentur and Mindess, 2007).

Fibre Type	Diameter [mm]	Tensile Strength [MPa]	Elastic Modulus [MPa]	Ultimate Elongation [%]
Acrylic	0.020-0.350	200-1,000	14,000-19,000	10-50
Carbon	0.008-0.019	500-4,000	30,000-480,000	0.5-2.4
Kevlar	0.010-0.012	2,300-3,500	63,000-120,000	2-4.5
Nylon	0.023-0.400	750-1,000	4,100-5,200	16-20
Polyester	0.010-0.200	230-1,200	10,000-18,000	10-50
Polyethylene	0.025-1.000	80-600	5,000	3-100
Polyolefin	0.150-0.640	275	2,700	15
Polypropylene				
-Monofilament	0.100-0.200	450-500	3,500-5,000	15-25
-Fibrillated	0.300-1.000	550-760	3,500-9,000	8
PVA	0.014-0.650	800-1,500	29,000-36,000	5.7
Steel	0.100-1.000	500-2600	210,000	0.5-3.5
Concrete	-	3-7	10,000-45,000	0.02

Problems exist with synthetic fibres, of which poor elastic modulus is dominant. The reinforcing potential of fibres is significantly reduced when their elastic modulus is lower than the matrices they are intended to strengthen, although it has been found that improved toughness, strain capacity, impact resistance and crack control are achievable notwithstanding the lower elastic modulus of some fibres (Halvaei et al., 2012; Pereira et al., 2012; Zheng and Feldman, 1995). Alumina-, boron-, glass-, carbon-, aramid- and silicon-based fibres are amongst the most common; of these, glass, carbon and aramid synthetic fibres will be discussed in detail later. Table 2.2 presents the mechanical properties of three types of fibres (Ali, 2012).

Table 2.2: Properties of common fibre types used in civil engineering (Ali, 2012).

Type of fiber		Density (g/cm^3)	Tensile strength (MPa)	Modulus of elasticity (GPa)	Elongation at rupture (%)	Maximum temperature of use (^oC)
Glass:	C-glass	2.6	3310	69	4.8	
	D-glass	2.1	2410	52	4.6	770
	E-glass	2.5	3400	75	4.8	550
	R-glass	2.5	4400	80	5.5	650
	S-glass	2.5	4800	84	5.4	650
Carbon:	SM	1.70	3700	250	1.2	2500
	IM	1.80	4800	250	1.4	
	HS	1.90	3000	500	0.5	2000
	UHM	2.10	2400	800	0.2	
Aramid:	Kevlar 29 HR	1.44	3620	83	4	400
	Kevlar 49 HR	1.44	3620	131	2.8	425
	Kevlar 149 UR	1.47	3470	186	2	

HR: high resistance. UR: Ultrahigh resistance. SM: Standard modulus. IM: Intermediate modulus. HS: High strength. UHM: Ultra-high modulus.

2.2.1.1 Glass fibres

Figure 2.15: Glass fibre (Singh, 2011).

Glass fibre is the synthetic fibre most commonly used for the purposes of composite reinforcement because of their high strength, temperature resistance and chemical resistance (Goud and Rao, 2012; Kuriger et al., 2002; Sathish et al., 2012). Glass fibres consist of silicon oxide with the addition of small quantities of other oxides (Sathish et al., 2012). AR-glass (alkali-resistant glass), C-glass (chemical glass), E-glass (electrical glass), and S-glass (structural glass), are the more common types of glass fibre. E-glass is the most commonly used due to its useful strength properties and affordability. S-glass is another interesting glass fibre because of its superior

tensile strength, having originally been developed by defence forces for use in aircraft components and casings for missiles (Balaguru et al., 2009). However, it is expensive to produce (Balaguru et al., 2009).

When applications require chemical stability, as in corrosive settings, C-glass is useful. C-glass is able to resist corrosion, particularly in relation to acids, to a greater extent than other glass fibres. It is often used in laminate surface coatings in chemical pipes and tanks. While used to provide chemical stability in corrosive environments, AR-glass is preferred to provide stability in alkaline environments. AR-glass was developed specifically for applications involving concrete and cement substrates (Balaguru et al., 2009; Hollaway and Head, 2001; Mishra and Yagci, 2008).

2.2.1.2 Carbon fibres

Figure 2.16: Carbon fibres (Singh, 2011).

Compared with glass fibres, carbon fibres offer lower density, greater specific strength and modulus, but much more expensive to produce (Kuriger et al., 2002). Carbon fibres are made from three types of precursors: rayon, polyacrylonitrile (PAN) and petroleum pitch. Fibres made from polyacrylonitrile (PAN) and petroleum pitch are cheaper than those made from rayon (Balaguru et al., 2009; Kuriger et al., 2002), while those made from petroleum pitch and rayon have a lower tensile strength than those made from polyacrylonitrile (PAN) (Balaguru et al., 2009; Kuriger et al., 2002). Carbon fibres are produced in four different grades: standard,

intermediate, high, and ultra-high (Balaguru et al., 2009; Hollaway and Head, 2001; Mishra and Yagci, 2008). They have gained popularity in the industry because of their chemical inertness, resistance to moisture absorption, and resistance to acidic and alkaline environments (Chen et al., 2007), qualities that increasingly see them sought for inclusion in applications where lightness and strength are necessary.

Despite their many useful properties, the galvanically inert nature and the cost of carbon fibres are two significant practical drawbacks to their wider exploitation. In addition, as cathodic reaction can lead to the degradation of carbon (graphite)/polymer composites (Tucker, 1991), carbon fibres are not appropriate for applications that require contact with metal or immersion in salt water.

2.2.1.3 Aramid fibres

Figure 2.17: Aramid fibres (Singh, 2011).

Aramid fibres, which are organic polymers, are well recognised under their commercial name, Kevlar, introduced by DuPont in 1972: Kevlar 49, 29, and 149 are the commercially available types (Balaguru et al., 2009). The first of these, Kevlar 49, has been designed for reinforcing composites, and offers a high modulus and tensile strength. Kevlar 29 has a comparable tensile strength but with a reduced modulus, while Kevlar 149 has a very high modulus (Balaguru et al., 2009; Hollaway and Head; 2001; Mishra, 2008). Aircraft wheel parts, body armour, engine

cowlings, high-pressure casings for rockets, marine cordage, oxygen bottles, propeller blades and tyre cords are some typical applications (Balaguru et al., 2009).

One of the weaknesses of aramid fibres is their poor resistance to moisture (Verpoest and Springer, 1988). The absorption of water leads to swelling in the material, creating stress and the consequent degradation of the fibres (Cervenka et al., 1998). Exposure to aqueous hydrochloric acid and sodium hydroxide, particularly in environments of increased temperature or stress, has been found to cause severe hydrolysis of at least Kevlar 49 (Karbhari et al., 2003).

2.2.2 Natural fibres

Natural fibres, which are of more interest of this study, are those that occur in nature. They can be typically classified into three categories, depending on their origin: animal, mineral and vegetable/plant. Figure 2.18 shows the classification of natural fibres (Ho et al., 2012), and details are provided in the following subsections.

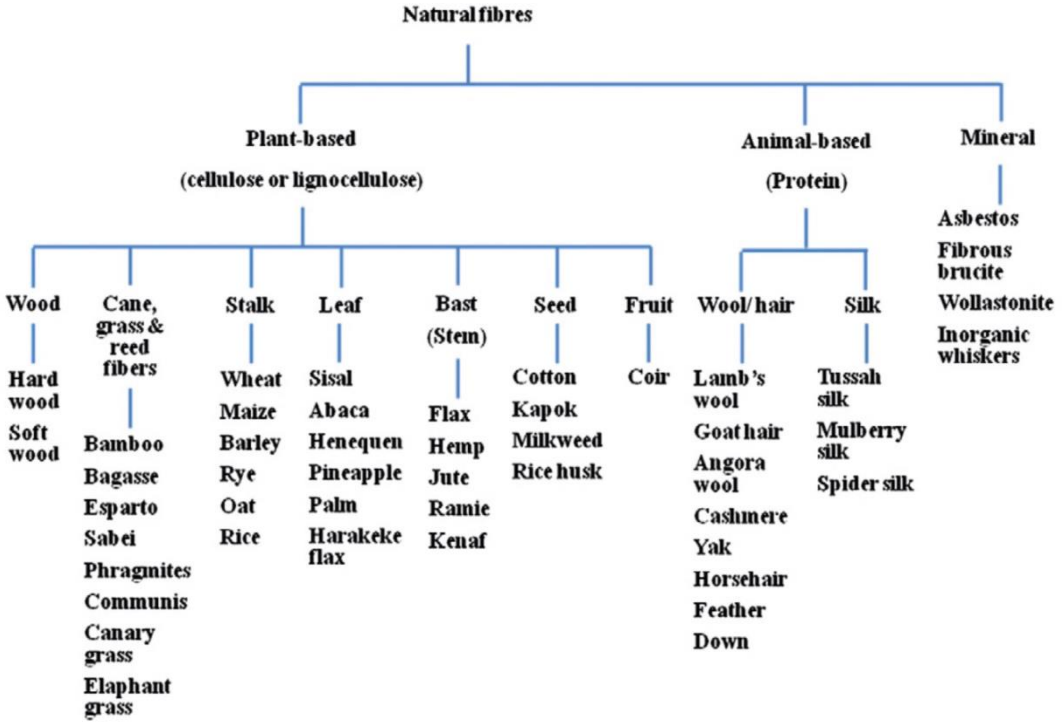


Figure 2.18: Classification of natural fibres (Ho et al., 2012).

2.2.2.1 Animal based fibres

Animal based fibres are produced from animals have been used for centuries e.g. wool from sheep, silk from silk worms, feathers from chickens and webs from spiders are ancient and well known examples (Ho et al., 2012). Contemporary applications for animal fibres include orthopaedics and bioengineering (Cheung et al., 2009). The strengths of these fibres tend to be related to their extensive hydrogen bonding, hydrophobic nature, and protein constitution, which offer environmental stability (Cheung et al., 2009).

2.2.2.2 Mineral fibres

These fibres are often preferred because of their affordability, desirable strength properties, particularly tensile strength, resistance to chemical, electrical, fire, and heat damage, and sound insulation qualities (Saxena et al., 2011). Such properties make mineral fibres useful in applications related to construction and machinery (Riedel and Nickel, 2005). Asbestos is a well-known natural mineral that occurs in the environment as fibre bundles (Saxena et al., 2011). In recent years its use has been banned in a number of applications due its link with lung cancer and other fatal respiratory diseases (Fubini and Fenoglio, 2007; Liddell and Miller, 1991).

2.2.2.3 Plant fibres

Plant fibres can be defined as those obtained from different parts of plants. Banana, coconut, flax, jute, cotton, hemp, sisal, ramie, cereal, fruit, seed, and wood fibres are commonly used examples of this category (John and Thomas, 2008). Plant fibres perform an important role in nature, strengthening the plants from which they originate: this quality is exploited when natural fibres are used to reinforce composites or to make products such as bags, carpets, and ropes (Saxena et al., 2011).

Research interest in natural plant fibres has been bolstered in recent decades by the recognition of adverse environmental effects caused by carbon dioxide emissions and the acceptance of the finite nature of fossil fuels (Riedel and Nickel, 2005). Natural plant fibres, unlike finite resources, are arguably renewable resources (Riedel and

Nickel, 2005). While there is still a substantial amount of work to be done regarding commercial applications of natural plant fibres, the construction industry offers an example of plant fibre-technology being used for further sustainable development (Müssig, 2010).

Mechanical properties such as favourable breaking length qualities make some natural plant fibres particularly useful for reinforcement applications (Riedel and Nickel, 2005). Reinforced polymers are a leading example of reinforcement products in which plant fibres are used (Riedel and Nickel, 2005). In 2000, for instance, the motor vehicle industry in Europe combined plants fibres, particularly flax, with polyurethane, polyester, and polypropylene to produce over 70% of its interior automobile components, including doors, headrests, and sunroof shields (Xanthos, 2005; Suddell and Evans, 2003).

2.2.3 Plant fibre structure

The generic internal structure of plant fibres consists of hollow cellulose fibrils held together by a matrix of lignin and hemicellulose (John and Thomas, 2008). The cell wall in natural fibres is not a homogenous membrane: each fibril exhibits a complex layered structure with a thin primary wall that encircles a three-layered secondary wall (Figure 2.19) (Rong et al., 2001). The thickest middle layer of the secondary wall is the most important in determining the mechanical properties of each fibre. This layer consists of a series of cellular microfibrils that are wound helically around the fibrils; the angle between the microfibrils and the fibre axis is termed the microfibrillar angle. These microfibrils generally contain between 30 and 100 molecules of cellulose and have a 10 to 30 nm diameter in extended chain formations; these provide the mechanical strength of the fibre (John and Thomas, 2008).

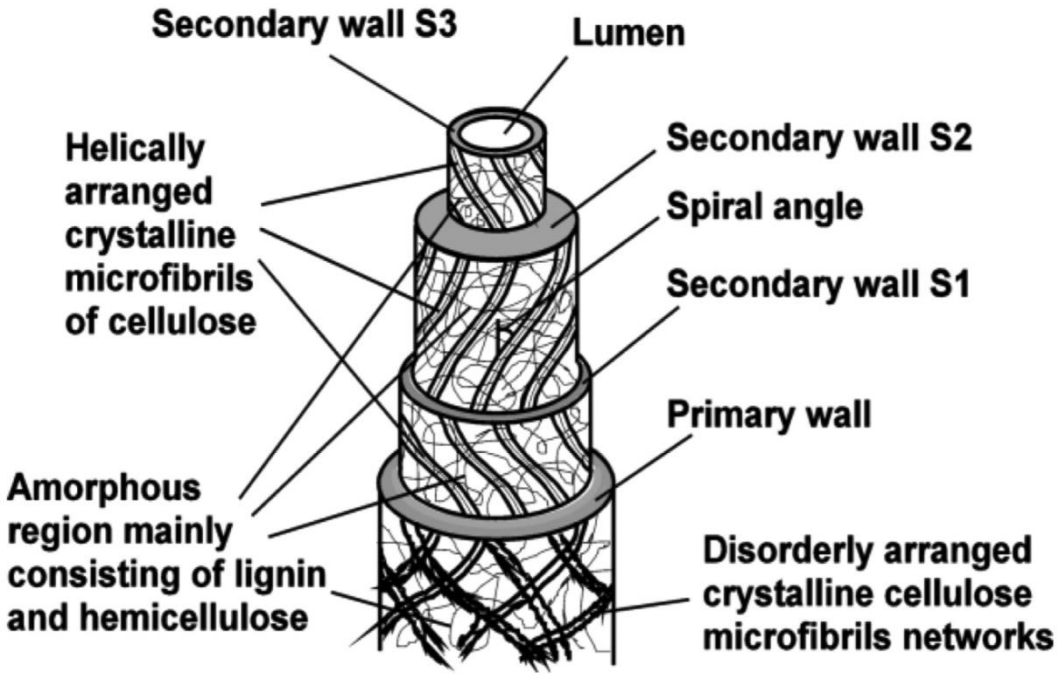


Figure 2.19: Structural constitution of a natural vegetable fibre cell (Rong et al., 2001).

2.2.4 Plant fibre chemical composition

The properties of each type of natural plant fibre vary greatly depending on their chemical composition. Table 2.3, which shows the chemical composition of plant fibres, reveals that cellulose, hemicellulose, lignin and pectin are the main components of the natural plant cell wall. These elements are discussed in the next sub-section.

Table 2.3: Chemical composition of plant fibres (Mohanty et al., 2005).

Fiber	Cell ulose (wt%)	Hemice lluloses (wt%)	Lignin (wt%)	Pectin (wt%)	Moi sture Content (wt%)	Waxes (wt%)	Micro fibrillar Angle (deg)
Flax	71	18.6–20.6	2.2	2.3	8–12	1.7	5–10
Hemp	70–74	17.9–22.4	3.7–5.7	0.9	6.2–12	0.8	2–6.2
Jute	61–71.5	13.6–20.4	12–13	0.2	12.5–13.7	0.5	8
Kenaf	45–57	21.5	8–13	3–5			
Ramie	68.6–	13.1–16.7	0.6–0.7	1.9	7.5–17	0.3	7.5
Nettle	86				11–17		
Sisal	66–78	10–14	10–14	10	10–22	2	10–22
Henequen	77.6	4–8	13.1				
PALF	70–82		5–12.7		11.8		14
Banana	63–64	10	5		10–12		
Abaca	56–63		12–13	1	5–10		
Oil palm EFB	65		19				42
Oil palm mesocarp	60		11				46
Cotton	85–90	5.7		0–1	7.85–8.5	0.6	
Coir	32–43	0.15–0.25	40–45	3–4	8		30–49
Cereal straw	38–45	15–31	12–20	8			

2.2.4.1 Cellulose

Cellulose forms the dominant part of most plant fibres. For example, the dry weight of wood consists of about 45% cellulose (Pérez et al., 2002). Cellulose is a linear polymer of D-anhydroglucose (C_6H11O_5) with 1,4-β-D glycosidic bonds linking the repeating glucose units at carbon atoms at the first and fourth positions (Figure 2.20) (John and Thomas 2008; Mohanty et al., 2005). Three hydroxyl groups are present in each repeating unit, and these and the associated hydrogen bonding facilitate the crystalline packing arrangement and consequently the cellulose's physical properties (John and Thomas 2008, Mohanty et al., 2005).

Molecules of cellulose have a degree of polymerisation (DP) of roughly 10,000 D-glucose units, which determines the size of the cellulose molecules. Although cellulose features excellent strong-alkali resistance and is also resistant to oxidising agents to some extent, acidic environments can result in the hydrolysis of cellulose, creating water-soluble sugars (John and Thomas 2008; Ramos, 2003).

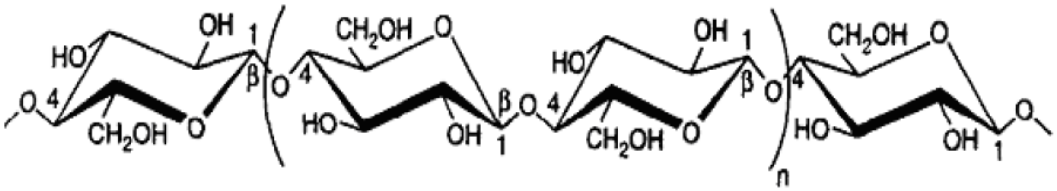


Figure 2.20: The structure of cellulose (Sjostrom, 1993).

2.2.4.2 Hemicelluloses

Hemicelluloses consist of several separate units of sugar, distinguishing them from cellulose, which contains solely 1,4-β-D-glucopyranose units (Bjerre and Schmidt, 1997). Hemicellulose contains D-galactopyranose, D-glucopyranose, D-xylopyranose, D-mannopyranose, L- arabinofuranosic and D-glucopyranosyluronic acid, with minor quantities of other sugars (Jusoh, 2008), as shown in Figure 2.21. Hemicelluloses exhibit considerable chain branching, which is another distinguishing aspect of this constituent: in contrast, cellulose is a strictly linear polymer. In addition, hemicellulose has a much lower DP, often one hundred times lower, than cellulose (John and Thomas 2008).

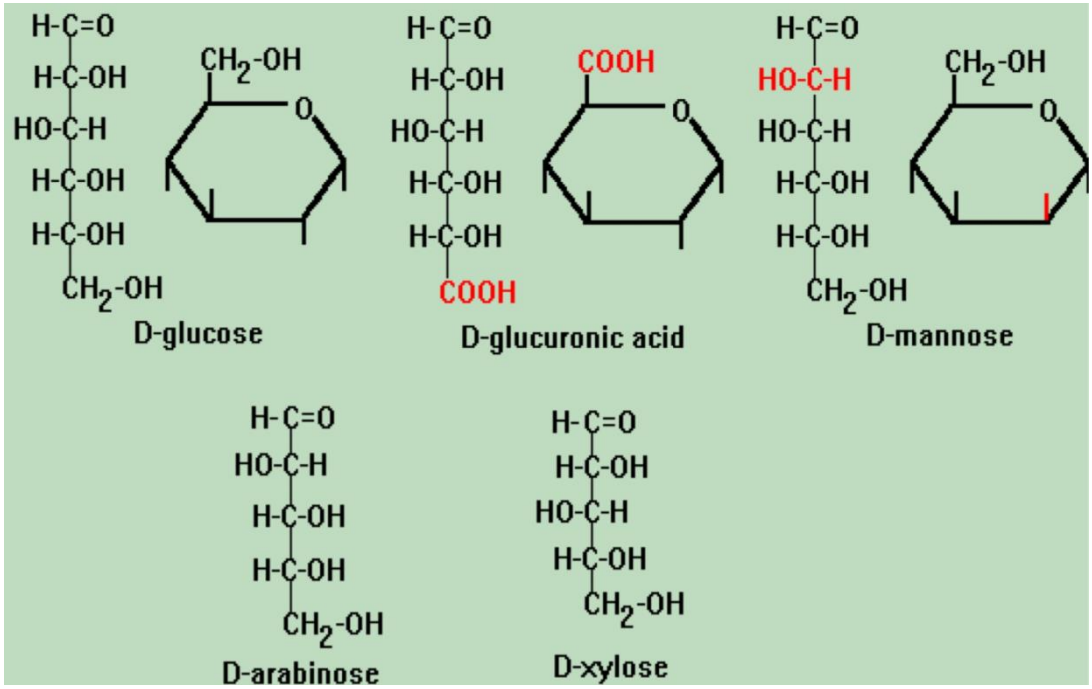


Figure 2.21: Monomers of hemicellulose (Jusoh, 2008).

Covalent bonds are formed between hemicelluloses and lignin through the attachment of p-coumaric residues and ferulic acid (Bjerre and Schmidt, 1997; Sun et al., 2012). This linking ability plays a critical role in the maintenance of fibre bundle strength, and degradation of the hemicelluloses leads to fibre disintegration within the cellulose microfibrils, weakening the fibre properties (Morvan et al., 1990).

Hemicelluloses, due to the attachment of acid residues, are hydrophilic. As this increases their propensity to absorb moisture and consequently to be exposed to microbiological threats that may cause fibre degradation (Kukle et al., 2011), poor resistance to water can be an issue. Hemicelluloses also exhibit lower resistance to heat than cellulose, with thermal degradation starting between 150 and 180°C; cellulose begins to degrade at 200 to 230 °C (Kukle et al., 2011).

2.2.4.3 Lignin

Lignin is a complex chemical compound that can be derived from wood and is an integral part of plants' cell walls. The word lignin is derived from the Latin for wood, *lignum* (Thomas and Pothan, 2009). Lignin is the second most important component in natural fibres after cellulose (Thomas and Pothan, 2009). Lignin can be considered

as the glue that holds the natural structure of the plant cell walls together, providing rigidity and protecting the cellulose from chemical and physical damage. In addition, lignin plays a crucial part in conducting water along the plant stem and makes the plant cell wall waterproof, in contrast to the cell wall's polysaccharides which are hydrophilic and thus permeable to water (Credou and Thomas, 2014; Demirbas, 2010). The lignin prevents water from entering the vascular tissue of the plant, leading to the development of cells for the efficient transport of water and nutrients (Credou and Thomas, 2014; Demirbas, 2010). A third role played by lignin is as a barrier against microorganisms, protecting the plant cells from microbial degradation (Demirbas, 2010). Chemicals can be used to dissolve lignin and separate the fibres. Lignin photochemically degrades when exposed to ultraviolet light (Hao and Alan, 2013).

2.2.4.4 Pectin

Pectin consists of a complex set of polysaccharides. It is found in citrus fruits particularly and in bast fibres, as well as other non-wood matter in plants. Poly-α-(1-4)-D-galacturonic acid residues, which are homopolymeric and partially methylated, are the main constituents of pectin (Hao and Alan, 2013; Thygesen, 2006). The substance is known commercially as a gelling agent and is used as a health supplement, with properties similar to dietary fibre (Hao and Alan, 2013; Thygesen, 2006). However, alternating sections of α-(1-2)-L-rhamnosyl-α-(1-4)-D-galacturonosyl make non-gelling areas containing branch-points with predominantly neutral side-chains consisting of D-galactose (rhamnogalacturonan-I) and Larabinose. Because of pectin's carboxylic acid groups it is highly hydrophilic, one reason why it is highly susceptible to degradation through defibration with fungi (Hao and Alan, 2013; Thygesen, 2006). Another vulnerability is that at elevated temperatures pectin can be hydrolysed (Hao and Alan, 2013, Thakur, 2014).

2.2.5 Plant fibre properties

2.2.5.1 Mechanical properties

Natural fibres do not have mechanical properties which are as favourable overall as synthetics such as glass and carbon fibres (Goud and Rao, 2012), but do possess

some advantages in terms of mechanical properties. For example, natural fibres have lower densities than synthetic fibres generally, with many almost 30–50% less dense than their synthetic counterparts (Beckwith, 2008). Moreover, the reinforcing potential of natural fibres tends to be more favourable that comparable synthetic fibres. The dominant advantage of natural fibres other than these mechanical properties is their affordability (Beckwith, 2008); thus, while synthetic fibres have superior strength properties, natural fibres are gaining acceptance for their adequate tensile strength, stiffness, good mechanical performance, availability and load bearing capacity (Hodzic and Shanks, 2014). A good combination of these properties and their eco-friendliness make natural fibres popular contemporary choices for use in the furniture, automotive and construction fields. Table 2.4 shows the mechanical properties of commonly used natural fibres and industrial fibres.

Table 2.4: Mechanical properties of commonly used natural fibres and industrial fibres (Hodzic and Shanks, 2014).

Fibre	Density (g/cm^3)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)
Natural fibre				
Cotton	1.5–1.6	7.0–8.0	287–597	5.5–12.6
Jute	1.3	1.5–1.8	393–773	26.5
Flax	1.5	2.7–3.2	500–1500	27.6
Hemp	1.47	2.0–4.0	690	70
Ramie	–	3.6–3.8	400–938	61.4–128
Sisal	1.5	2.0–2.5	511–635	9.4–22
Coir	1.2	30	175	04-June
Soft wood kraft	1.5	4.4		
Kenaf	1.45	1.6	930	53
Pineapple		2.4	170–1627	60–82
Banna		3	529–914	27–32
Industrial fibres				
E-glass	2.5	0.5	2000–3500	70
S-glass	2.5	2.8	4570	86
Aramid	1.4	3.3–3.7	3000–3150	63–67
Carbon	1.4	1.4–1.8	4000	230–240

2.2.5.2 Thermal properties

Natural fibres generally do not have thermal properties that compare favourably with those of synthetic fibres. Low thermal stability and degradation temperatures for natural fibres are considered two dominant obstacles to their commercial exploitation (Araújo et al., 2008; Shebani et al., 2008). For example, in order to be used in thermoplastics, fibres need to be able to withstand processing temperatures which are often over 200°C: but many natural fibres degrade at around 200°C (Araújo et al., 2008). Natural fibres tend to follow a two-step degradation process. First the

glycosidic cellulose linkages are broken in a process known as hemicelluloses thermal depolymerisation, and then α-cellulose is decomposed (Albano et al., 1999; Manikandan et al., 2001). This process causes discoloration, release of volatile chemicals, toxins, and odours, and causes a dramatic deterioration of the mechanical properties of the fibre (Mallick, 2007).

The cellulose, hemicelluloses and lignin each has characteristic properties with respect to thermal degradation, based on polymer composition. Lignin, specifically the low molecular weight protolignin, degrades first and at a slower rate than the other constituents (Marcovich et al., 2001), as shown in Figure 2.22 (b). The thermogravimetric analysis (TGA) indicates that lignin begins to degrade at around 180°C; the rate of degradation is always lower than that of cellulose, as shown in Figure 2.22: it can be observed that the weight loss in the cellulose sample is negligible below 300°C, but above that is rapid (see Figure 2.22 (a)). At about 400°C only residual char is found (Marcovich et al., 2001).

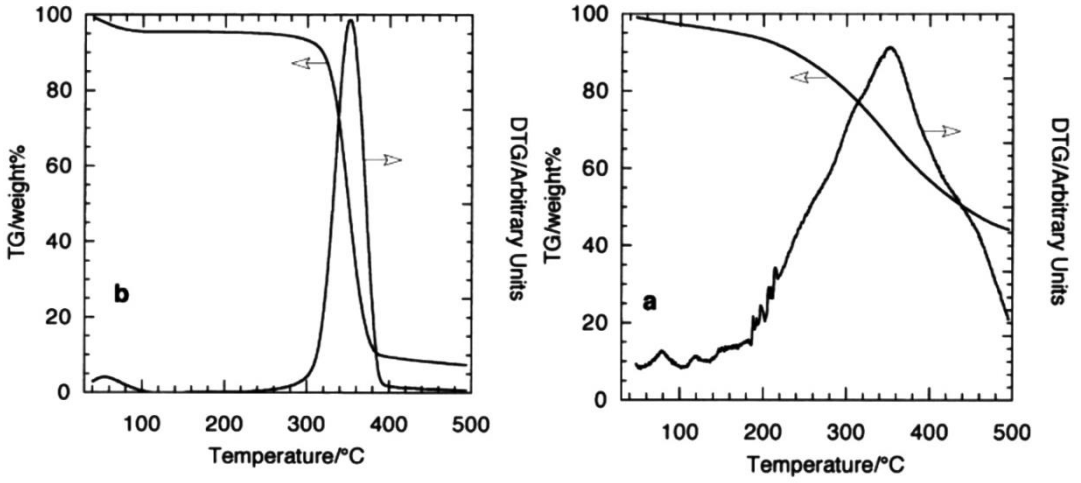


Figure 2.22: TG (percentage of weight) and DTG (derivative) vs. temperature curves: (a) Cellulose, (b) Lignin. (Marcovich et al., 2001).

Manfredi et al. (2006) studied the thermal degradation pattern of flax, jute, and sisal (Figures 2.23 and 2.24), finding that in sisal, lignin decomposes at 215 °C, hemicelluloses at 290°C, and α-cellulose at 340°C. In jute there is no discernable difference between the decomposition temperatures of lignin and hemicellulose. Flax was found to resist thermal degradation to a greater extent than sisal or jute.

Manfredi et al. (2006) attribute this to the lower lignin content of flax. While a reduction in lignin content results in improved thermal stability for flax, the fibre has the lowest resistance to oxidation.

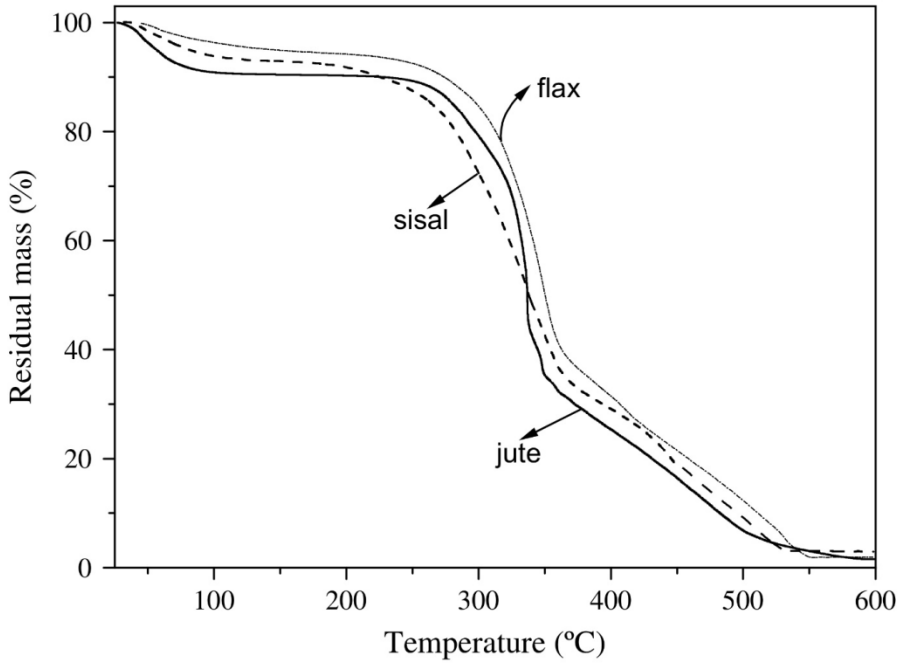


Figure 2.23: Temperature versus residual mass for flax, sisal, and jute (Manfredi et al., 2006).

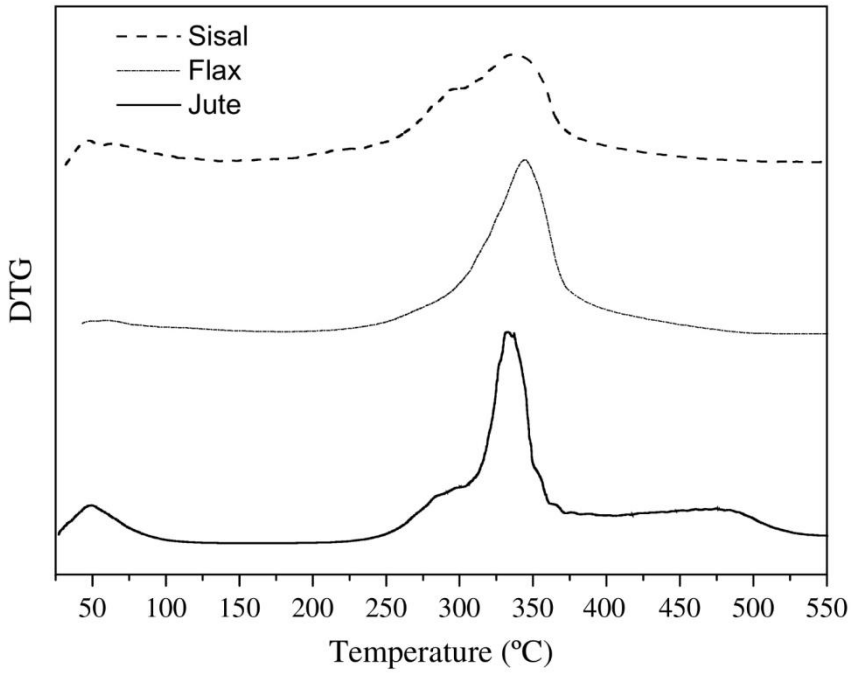


Figure 2.24: The derivative of the residual mass percentage (DTG) for the three natural fibres studied, flax, sisal, and jute (Manfredi et al., 2006).

2.2.5.3 Moisture properties

Natural fibres are hygroscopic, meaning that they attract or absorb moisture from the air, depending on environmental conditions (Célino et al., 2014; Patel et al., 2013). Since amorphous cellulose and hemicellulose contain hydroxyl groups that are easily accessible and give the overall fibre a hydrophilic character, these constituents are responsible for the high moisture absorption of natural fibres, which occurs as molecules of water readily form hydrogen bonds with the cell wall's hydroxyl groups; this leads to fibre swelling, which is the build-up of moisture within the cell wall (Célino et al., 2014; Patel et al., 2013). The schematic representation is given in Figure 2.25.

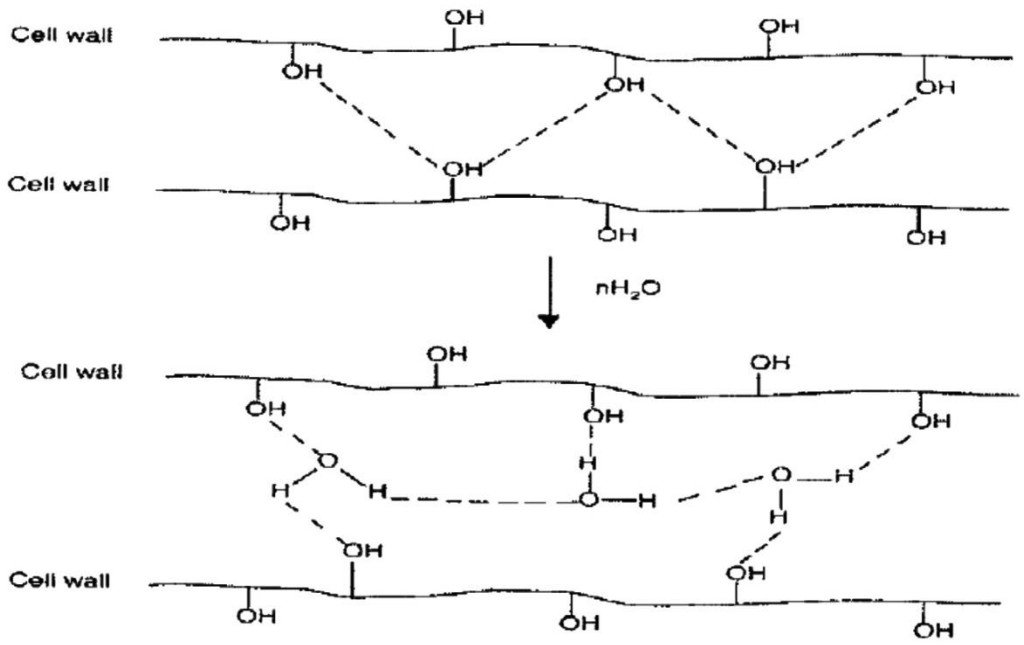


Figure 2.25: Schematic representation of water absorption cellulosic fibres (Mwaikambo and Ansell, 2002).

Water absorption also affects the mechanical properties of natural fibres, and can lead to a significant reduction in their mechanical properties, as shown in Table 2.5.

Table 2.5: The moisture absorption influence on the mechanical properties of plant fibres (Célino et al., 2014).

Kind of fiber	Hygroscopic conditions	Young's modulus evolution	Failure strength evolution	Elongation at break evolution
Flax and nettle	30, 40, 50, 60, and 70%	Decreases	Not significative effect	
Flax and sisal			Maximum for RH = 70%	
Flax	30, 66, 93%		Increases and stabilizes at RH = 66%	
Hemp	10, 25, 50, et 80%	increases	Maximum for 50 < HR < 70%	
Jute, flax, sisal, hemp, coir, agave	65, 90% et immersion	Increases until a threshold, then decreases (depend on the fiber)	Not significative effects	increases

2.3 Geopolymers

Geopolymers are a type of binder reported as having superior sustainability properties (Duxson et al., 2007a; Ng et al., 2012; Zhang et al., 2014). They are semi-crystalline aluminosilicate binder materials produced through a reaction of sources of aluminosilicates in an aqueous alkaline medium (Bakharev, 2005a; Wallah and Rangan, 2006). Davidovits in 1978 first introduced the term 'geopolymer' to describe this new type of binder materials produced at moderately low temperatures (Bakharev, 2005a; Wallah and Rangan, 2006). Interest was originally motivated by a desire to find new inorganic polymer materials that were non-combustible, non-flammable, and heat resistant, to replace common organic plastics (Davidovits, 2002); the outcome was the patenting of alkali-activated aluminosilicate binders, today called geopolymers (Davidovits, 2002). As the field of geopolymer has expanded, the term has come to refer to a wide range of similar aluminosilicate binders, typically synthesised by mixing fly ash or other aluminosilicate sources with alkaline activation solutions such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate or potassium silicate (Davidovits, 2008). Geopolymers are sometimes referred to in the literature as alkali-activated cement, geocement, alkali-bonded ceramic, inorganic polymer concrete, zeocement, hydroceramic, zeoceramic and low-temperature aluminosilicate glass (Fernández-Jiménez et al., 2008; Mallicoat et al., 2008; Pacheco-Torgal et al., 2013; Palomo and Palacios, 2003; Rahier et al., 1996; Sofi et al., 2007). Alkali-activated aluminosilicate materials can be considered an appropriate descriptive name for geopolymers. The defining feature of geopolymers is the formation of a three-dimensional, aluminosilicate gel framework which is largely amorphous, and which consists predominantly of tetrahedral AlO_4- and SiO_4 units (Davidovits, 1991; Fu et al., 2012).

2.3.1 Advantages of geopolymers

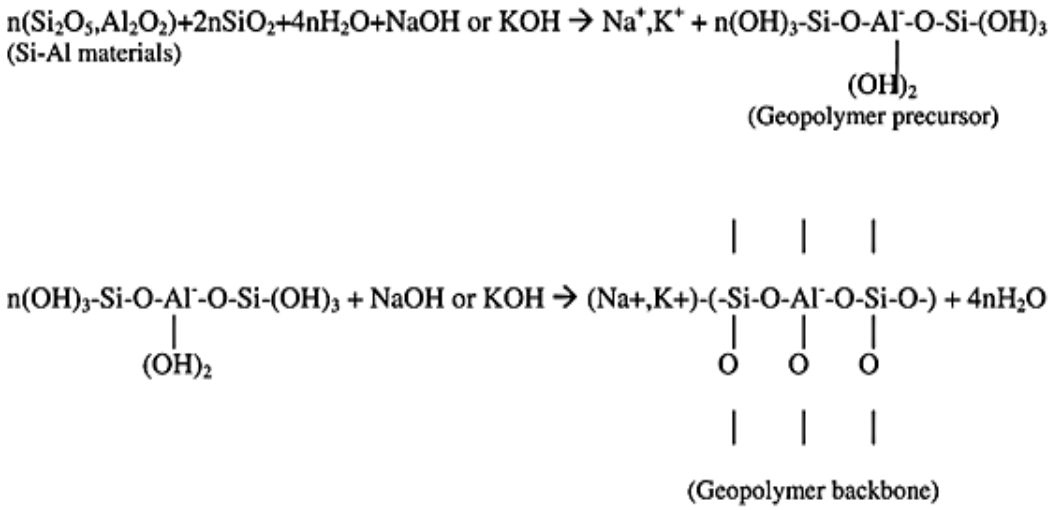
Geopolymer research and development is predominantly focused on the development of cost-efficient construction materials and in particular an alternative production process for cement. One of the primary advantages of geopolymers for use in cement

production is their lower calcination temperature, which may be as low as 600°C, and is one reason the process is responsible for producing a lower quantity of CO_2 compared to OPC (Fu et al., 2012; McLellan et al., 2011; Zhang et al., 2007). Another advantage is that geopolymers use industrial wastes as source materials that can be activated by an alkaline activator to act as binder. This reduces environmental pollution and the use of natural resources (Anuar et al., 2011). High compressive strength, greater resistance to fire and low shrinkage at high temperature are other benefits offered by the geopolymers used as construction materials (Duxson et al., 2007b; Temuujin et al., 2011).

2.3.2 Geopolymer reaction model

Geopolymers are inorganic. While they are similar in chemical composition to zeolitic materials in nature, geopolymers have an amorphous as opposed to a crystalline microstructure (Palomo et al., 1999; Xu and Van Deventer, 2000). As Davidovitis hypothesised in 1978, aluminium (Al) and silicon (Si) would react, i.e. polymerise, with an alkaline liquid in a geological source material to produce geopolymer binders (Davidovits, 2008).

Geopolymerisation involves a substantially chemical reaction between aluminosilicate solid materials and alkaline solution in highly alkaline conditions. This reaction occurs at temperatures not exceeding 100^{o}C and at atmospheric pressure. The result is the formation of amorphous to semi-crystalline polymeric structures which consist of Si–O–Si and Si–O– Al bonds (Dimas et al., 2009). This is described in the equation below (Davidovits, 1994; van Jaarsveld et al., 1997), which describes the reaction to form a sodium or potassium poly(sialate-siloxo) geopolymer.



Other geopolymeric networks can be formed depending on the Si:Al ratio. Figure 2.26 represents several fundamental poly(sialates) as proposed by Davidovits (2008).

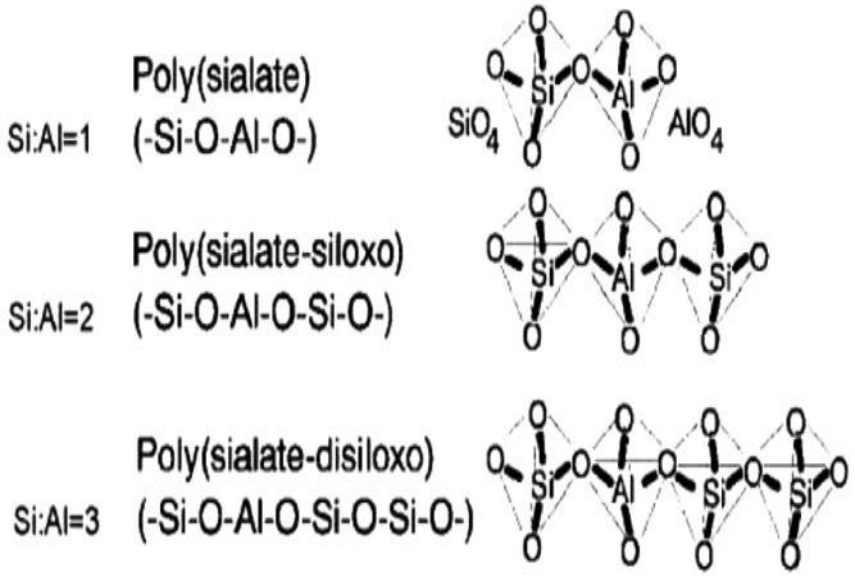


Figure 2.26: Chemical structure of polysialates (Davidovits, 2008).

Transforming a solid aluminosilicate source into a desirable geopolymer can be thought of as consisting of five key processes. First, highly alkaline ions are used to dissolve the solid aluminosilicate source into silicate and aluminate species. Second, these two species are mixed to form an aluminosilicate solution. Third, a high pH is used to form a highly concentrated aluminosilicate solution, and this instigates a

gelling or gelation process which produces a geopolymer gel. The fourth step is known as gel network reorganisation and involves development of the microstructure and pores of the geopolymer. Finally, the three-dimensional geopolymer is produced (Duxson et al., 2007b). These reaction mechanisms are shown in Figure 2.27.

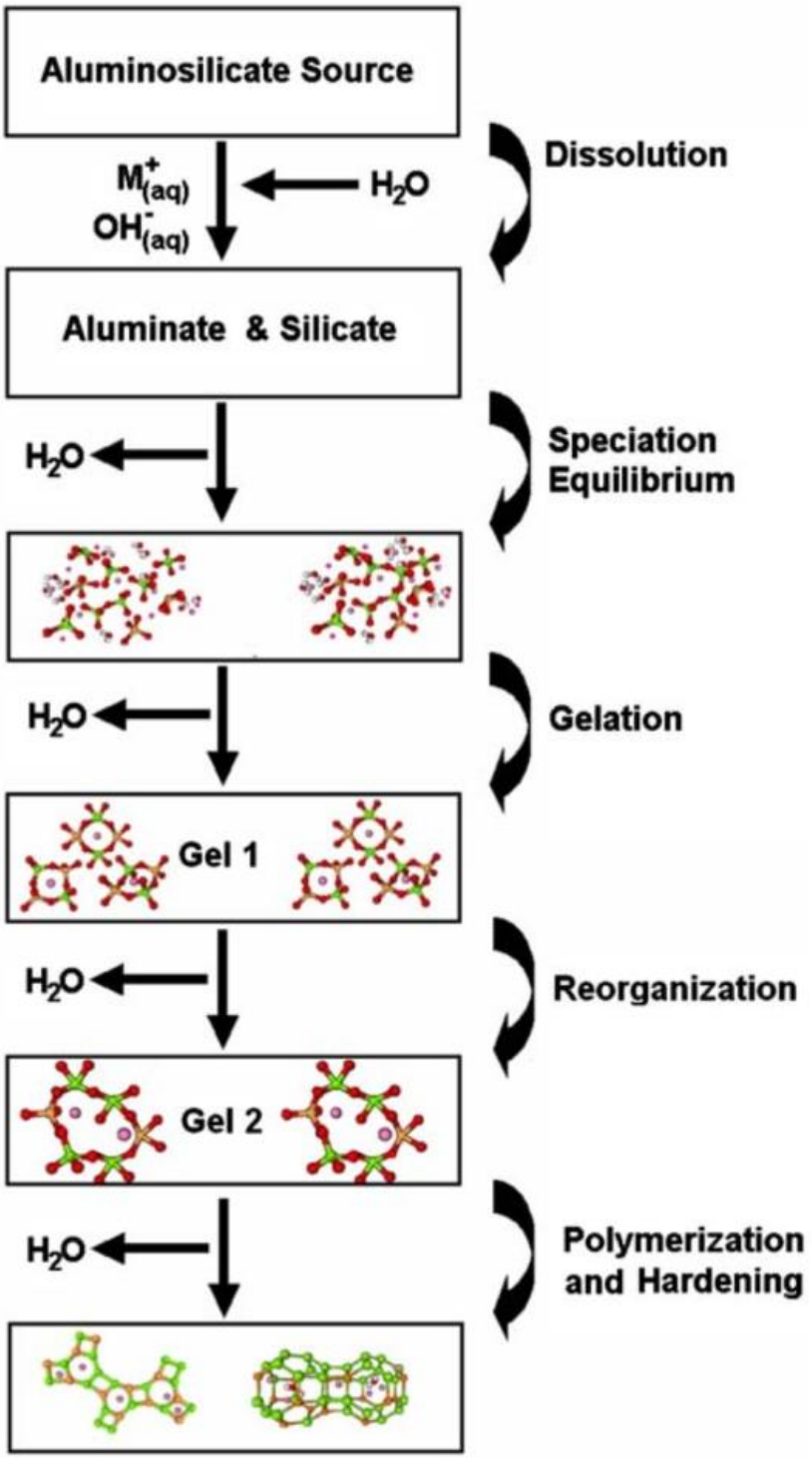


Figure 2.27: Conceptual for geopolymerisation (Duxson et al., 2007b).

2.3.3 Factors Affecting Geopolymerisation

Three factors affect the quality of geopolymerisation (Khale and Chaudhary, 2007). Aluminosilicate mineralogy and composition is the first category. As part of this, the quantity of amorphous Al_2O_3 and SiO_2 is a relevant sub-factor, as is the dissolution rate for Al_2O_3 and SiO_2. Concerning aluminosilicate mineralogy, the raw material's physical properties and extent of impurities are relevant sub-factors (Khale and Chaudhary, 2007). Activating solution composition and concentration is the second factor category. The silicate concentration, that is, the SiO_2/M_2O ratio, is a relevant sub-factor, as are the alkali metal cation type and the alkali solution concentration, namely, the H_2O/M_2O ratio, where M represents K and Na. The water content (water/binder ratio) is another relevant sub-factor (Khale and Chaudhary, 2007). Curing conditions are the third factor category. The humidity, duration of curing, and temperature are relevant sub-factors (Khale and Chaudhary, 2007).

2.3.4 Geopolymer matrix synthesis

2.3.4.1 Alkaline liquids

The choice of alkaline liquid to prepare geopolymer is important. Sodium hydroxide (NaOH) with sodium silicate (Na_2SiO_3), and potassium hydroxide (KOH) with potassium silicate (K_2SiO_3) are common liquids used (Bhosale and Shinde, 2012; Shankar and Khadiraniakar, 2013; Khadiraniakar and Shankar, 2014), although a single alkali activator has been used in some studies (Palomo, 1999). The efficiency of an activator is based on its type, dosage, ambient temperature and ratio of water to source material (Kupaei et al., 2013; Sajedi and Razak, 2010).

Sodium hydroxides are the most common activator used for their affordability, availability, and low viscosity (Kupaei et al., 2013). The hydroxyl ion is essential to start geopolymerisation and to enhance the dissolution of aluminate and silicate networks in the source materials and thus develop the geopolymer network (Kupaei et al., 2013). A high concentration of sodium hydroxide increases the strength of the material: for instance, Hardjito and Rangan (2005) report that increasing the concentration of sodium hydroxide improves the compressive strength of fly ash-based geopolymer concrete.

Sodium silicate (Na_2SiO_3) can be sourced as a powder or a liquid (Olivia, 2011). At high concentrations its viscosity influences the workability of the mixture, and it is useful in increasing the strength of the geopolymer by encouraging binding, giving a denser product (Olivia, 2011). The ratio of sodium hydroxide and sodium silicate must be accurate in order to produce a geopolymer paste with strong bonds, because too much sodium silicate will result in excessive porosity (Olivia, 2011).

2.3.4.2 Source materials

As mentioned, source materials for geopolymers should be alumina silicate-based and contain abundant aluminium (Al) and silicon (Si). Minerals in nature and industrial waste products can contain these elements in amorphous form. Table 2.6 provides a list of aluminosilicate sources that are commonly used and some details of their typical compositions.

Table 2.6: Common aluminosilicate sources for geopolymer synthesis (Rickard, 2012).

Source	Typical Composition	
	Reactive Aluminosilicates	Secondary Phases
Metakaolin	$SiO_2 + Al_2O_3 = 80 – 99$ % Si:Al = 1	Kaolin, rutile, quartz, muscovite
Fly ash (class C)	$SiO_2 + Al_2O_3 = 30 – 50$ % Si:Al = 1-10	CaO usually ≥ 10 % Iron oxides, quartz, mullite, unburnt coal (< 6%)
Fly ash (class F)	$SiO_2 + Al_2O_3 = 30 – 70$ % Si:Al = 1-10	CaO usually < 10 % Iron oxides, quartz, mullite, unburnt coal (< 6 %)
Volcanic ash	$SiO_2 + Al_2O_3 = 50 – 90$ % Si:Al = 5-15	Iron oxides, quartz, feldspar, trace heavy metals
Rice husk ash	$SiO_2 = 85 – 95$ % Si:Al >> 10	Quartz, cristobalite, unburnt rice husks
Blast furnace slag	$SiO_2 + Al_2O_3 = 5 – 20$ % Si:Al = 1-10	CaO = 30 – 50 %, periclase, quartz, calico-olivine, mayenite, calcite, mullite

Fly ash is probably the most widely used aluminosilicate source (Bouzoubaâ et al., 1999), and geopolymer concretes based on fly ash have excellent properties for

engineering. Furthermore fly ash is readily available, as it is a by-product of coal-fired power stations (Ilyushechkin et al., 2012).

2.3.5 Fly Ash

Fly ash is formed as part of the coal combustion process. The abundance of coal has led to its use as one of the most common energy production methods; however, it has been criticised for its production of large quantities of waste by-products, including bottom ash and fly ash (Ilyushechkin et al., 2012). There has been intense interest in reducing the release of fly ash into the atmosphere, and in some places regulations control the storage of fly ash (Ilyushechkin et al., 2012). For this and general practical reasons, techniques using fly ash are of great interest to governments (Ilyushechkin et al., 2012). Fortunately, fly ash has been demonstrated to be a highly useful aluminosilicate source for the preparation of geopolymers. It offers significant performance, environmental, and cost advantages over Ordinary Portland cement (Al Bakri et al., 2011), and is a substantial source of aluminosilicate for geopolymer-based cement production (Bouzoubaâ et al., 1999).

Fly ash is formed when coal passes through an incinerator at temperatures of 1400°C or more (Kutchko and Kim, 2006). This great heat causes impurities in the inorganic minerals in the coal to react with oxygen, becoming fluid or volatile (Kutchko and Kim, 2006); the residual unburnt material tends to condense as particle coatings, forming spherical amorphous particles or crystalline solids during cooling (Kutchko and Kim, 2006). Typically, these processes are organised so that cleaning systems ultimately receive the flue gas and particles suspended within: the end product collected in this cleaning system is essentially fly ash (Goodwin, 1993; Malhotra and Mehta, 1996). Residue not suspended within the flue gas coagulates and falls, and is thereby referred to bottom ash (Goodwin, 1993; Malhotra and Mehta, 1996).

2.3.5.1 Fly ash classification

Fly ash is categorised into class F, class C, and class N based on the criteria provided by the ASTM C618-08a Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete (2008) (ASTM C618-08a). The

classification is determined by the composition of the fly ash. Class F and C fly ashes are often differentiated based on maximum calcium oxide content. Although this is not specified as a criterion for all classes, a sub-note in ASTM C618-08a states that class C fly ash contains at least 10 wt.% total calcium content. In contrast, class F fly ash has a lower total calcium content, typically between 2 and 6 wt.% (Manz, 1999).

The typical contents of class C fly ash include free CaO, anhydrite ($CaSO_4$), tricalcium aluminate ($3CaO.Al_2O_3$), calcium aluminosulphate ($4CaO.3Al_2O_3.SO_4$), periclase (MgO), alkali sulphates and quartz (SiO_2) (Malhotra and Mehta, 1996). Other than quartz and periclase, most of the typical minerals contained within class C fly ashes react pozzolanically with water. Class F fly ash, along with its lower calcium content, commonly contains magnetite (Fe_3O_4), hematite (Fe_2O_3), mullite ($3Al_2O_3.2SiO_2$), sillimanite ($Al_2O_3.SiO_2$) quartz (SiO_2) and other the crystalline minerals (Malhotra and Mehta, 1996).

Class F and class C fly ash have different production sources. Bituminous or anthracite coal combustion produces the low calcium class F. In contrast, the combustion of sub-bituminous or lignite produces high calcium content class C (Malhotra and Mehta, 1996). Class F and class C both have pozzolanic properties, reacting with water and calcium hydroxide at room temperature to form cementitious compounds. In contrast, class N fly ash requires calcination in order to induce satisfactory properties (Malhotra and Mehta, 1996). Table 2.7 lists the physical and compositional requirements set out by the standard for classes of fly ash.

Table 2.7: Chemical and physical requirements for fly ash classification according the ASTM C618-08a.

Requirement	Class		
	N	F	C
$SiO_2 + Al_2O_3 + Fe_2O_3$, minimum wt.%	70	70	50
Sulphur trioxide (SO_3), maximum, wt.%	4.0	5.0	5.0
Moisture content, maximum, wt.%	3.0	3.0	3.0
Loss on ignition, maximum, wt.%	10.0	6.0	6.0
Amount passing 45 μm sieve, minimum wt.%	66	66	66

2.4 Properties of geopolymers

2.4.1 Compressive strength

Compressive strength refers to the capacity of a material to withstand forces that tend to reduce its size (Hardjito and Rangan, 2005). For binding materials, compressive strength is an important physical property, dictating the maximum load the material can bear and consequently the range of applications for which it capable of being used (Hardjito and Rangan, 2005). Compressive strength tends to be a critical consideration for construction applications, but is less relevant for applications requiring superior thermal resistance (Hardjito and Rangan, 2005).

For concrete, measurements of compressive strength serve as the dominant characterisation method with respect to mechanical properties. Studies concerned with geopolymers and their mechanical properties are often limited to investigations of compressive strength (Rickard, 2012). While this narrow approach is cost-effective and conceptually straightforward, and is arguably sufficient in the case of geopolymer concretes, for more sophisticated applications of geopolymers more detailed engineering property characterisations may need to be determined. This may be particularly important for geopolymer-based structural composite materials (Rickard, 2012).

Compositional ratios, porosity, cracking, and other morphological features, conditions of curing and aluminosilicate source material reactivity have been found to affect the compressive strength of geopolymer materials (Cai et al., 2013; Rickard, 2012). The addition of fibre reinforcements also affects compressive strength (Ghazali et al., 2013).

The compositional ratios of silicon to aluminium (Si:Al), and sodium or potassium to aluminium (Na [or K]:Al) affect geopolymer compressive strength. Figure 2.28 shows how variations of compositional ratios for metakaolin geopolymers affect their compressive strength. If there is insufficient alkaline activator, a portion of the aluminosilicate source material will not be geoploymerised. Too much activator is

also undesirable because the proportion of activator not used in the reaction remains in the system, leading to a weakening of the material structure (Rowles and O'Connor, 2003). While insufficient and excessive activator are both undesirable, there is no consensus about the optimum ratio of alkaline activator to aluminium (Na or K:Al). This is most likely underpinned by the wide range of techniques of synthesis and conditions of curing used from study to study (Rowles and O'Connor, 2003).

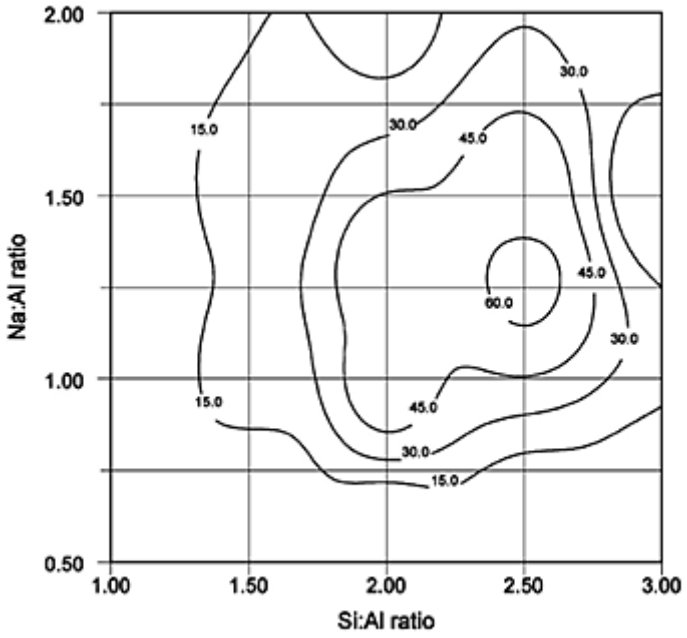


Figure 2.28: The compressive strength (MPa) of metkaolin geopolymer as a function of total Si:Al and Na:Al ratios (Rowles and O'Connor, 2003).

Insufficient silicon affects geopolymer compression strength (Rowles and O'Connor, 2003). This is expressed by the principle of aluminium avoidance or Lowenstein's rule, where Al – O – Al bonding is unfavourable and the preferred bonding is Si – O – Al. In order to have satisfactory structural integrity, geopolymers should be synthesised to contain more silicon than aluminium (Si:Al > 1) (Lowenstein et al., 1954; Rowles and O'Connor, 2003). In one study by Subaer (2005), the ratio Si:Al of 1.5 with Na:Al = 0.6 was used to synthesis sodium alkali-activated metakaolin geopolymers; the resultant compressive strength was 86 MPa**.** In another study, the ratio of Si:A = 2.50 and Na:Al = 1.29 was used to produce sodium hydroxide- and

sodium silicate-activated metakaolin geopolymers; the compression strength is found to be 64MPa (Rowles and O'Connor, 2003). The different compressive strengths for these three studies are believed to be caused by factors outside the results for compositional ratio, such as porosity, cracking and other morphological features, conditions of curing, and aluminosilicate source material reactivity (Skvara et al., 2005).

Curing conditions include the temperature and length of time of curing amongst other sub-factors. The degree of thermal energy used is important. For example, geopolymers cured at room temperature will gain strength more slowly than those cured at elevated temperatures (Bakharev, 2006); faster strength is associated with elevated curing temperatures: the longer the amount of time used for curing, the greater the compressive strength. Increasing the curing time increases the likelihood of geopolymerisation within the geopolymer, and subsequently results in higher compressive strength (Rangan, 2007). The same study proposed that a room temperature pre-curing period of 24 hours followed by another 24 hour period at 60°C is an efficient curing regime. It was reported that higher temperatures for curing, or longer curing times, did not produce geopolymers that were significantly stronger (Rickard, 2012). The precise nature and reactivity of the source materials determines the optimum curing conditions (Rickard, 2012).

2.4.2 Hardness

Hardness is the ability of a material to resist plastic deformation, usually by penetration (Zhou, 2013). One technique to study hardness of geopolymers is Vickers indentation testing (Lecomte et al., 2003); results of such testing are referred to as the Vickers hardness of a material. Lecomte et al. (2003) studied the hardness of geopolymers using Vickers indentation with 5 kg loads, recording results for hardness values of potassium-based geopolymers as high as 200 MPa. The team finds that the hardness values using Vickers indentation testing for potassium-based geopolymers does not change significantly in response to different Si/Al ratios or different precursor type uses, namely potassium (K) or sodium (Na) (Lecomte et al., 2003).

In contrast to these findings, Lizcano (2011) finds that Vickers hardness increases as Si/Al ratios increase for sodium-activated and potassium-activated geopolymers. Lizcano (2011) also finds that potassium-based geopolymers have a marginally higher hardness than sodium-based samples. An important finding concerns the precise increase in Vickers hardness with the Si/Al ratio: until Si/Al = 2 Vickers hardness increases, but beyond Si/Al=2 microstructural issues occur and Vickers hardness decreases, as shown in Figure 2.29. Notwithstanding these decreases, Vickers hardness results in Lizcano's (2011) study are over the 200MPa published in Lecomte et al.'s (2003) study. Similarly, Kim (2010) reports that hardness increases as Si/Al ratio increases, up to Si/Al of 3 or 4 and then decreases with further increases in the Si/Al ratio, as shown in Figure 2.30. Kim's results are close to those published by Lizcano (2011).

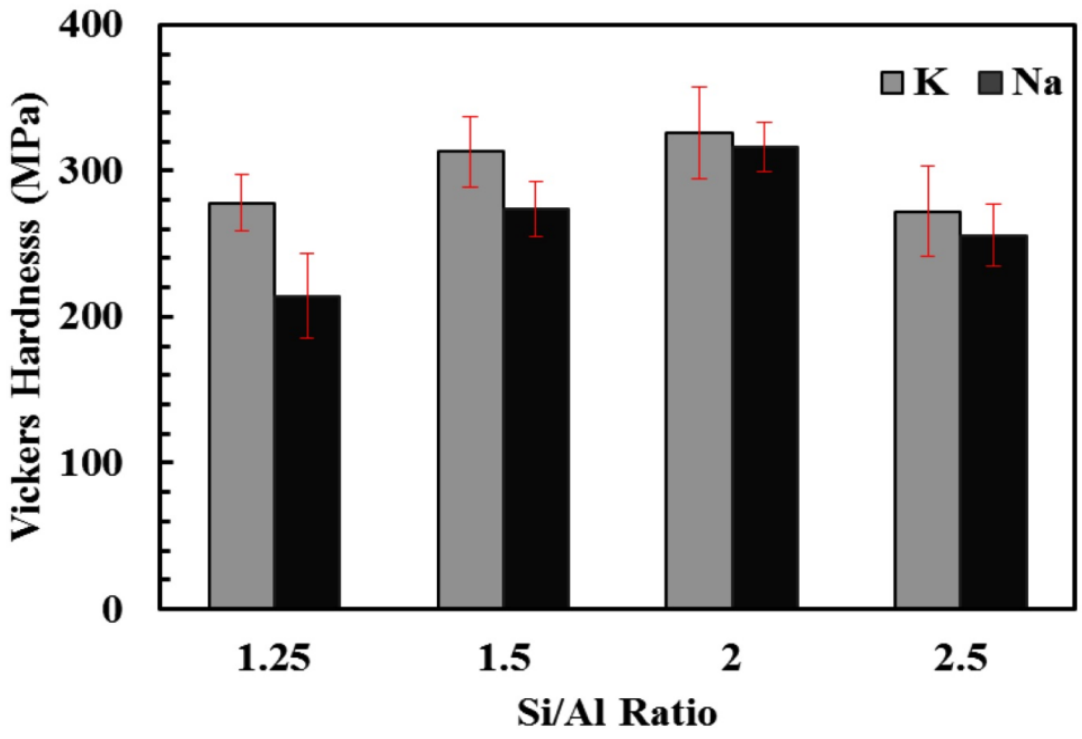


Figure 2.29: The average Vickers hardness values of K- and Na-based geopolymer. Error bars above columns represent standard deviation (Lizcano, 2011).

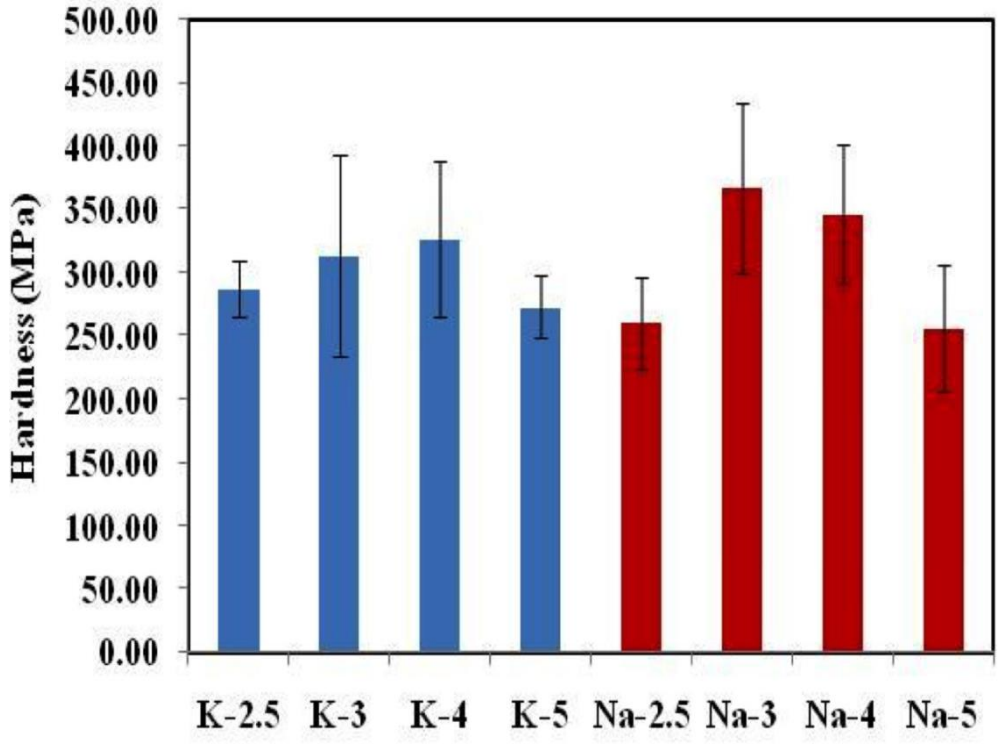


Figure 2.30: The hardness values of geopolymer (Kim, 2010).

Another technique to measure hardness is Avery Rockwell testing, and the value identified from this testing is known as Rockwell hardness (Chen-Tan, 2010). In order to investigate the Rockwell hardness of a series of geopolymer paste samples made from beneficiated Collie fly ash, Chen-Tan (2010) used an Avery Rockwell hardness tester with H Rockwell hardness scale.

Beneficiation refers to the process of locating, sourcing, sieving, milling and magnetically separating fly ash, which results in several subsets of the original

material (Chen-Tan, 2010). The researcher reported a significant difference in the Rockwell hardness of the subsets of Collie fly ash geopolymers. For example, the team observed a 20% difference in Rockwell hardness between non-magnetic sieved fly ash (NM-SFA) and sieved fly ash (SFA) (Chen-Tan, 2010). Other differences were reported in relation to the Rockwell hardness of milled-sieved fly ash (MFA) and non-magnetic milled-sieved fly ash (NM-MFA) (Chen-Tan, 2010); these are shown in Table 2.8.

Table 2.8: Rockwell hardness of different geopolymers (Chen-Tan, 2010).

Feedstock	Rockwell Hardness (HRH)
UFA	79 ± 4
NM-UFA	85 ± 3
SFA	86 ± 4
NM-SFA	88 ± 4
MFA	72 ± 3
NM-MFA	70 ± 3

Chen-Tan (2010) finds milled fly ash-based geopolymers have a lower Rockwell hardness than sieved geopolymers, and concludes that this is related to their microstructures, which are distinctly different. He finds milled-fly ash-based geopolymers contain a larger proportion of geopolymer gel, resulting in less resistance to deformation than the sieved fly ash samples with large secondary phases.

2.4.3 Fracture toughness

Fracture toughness (K_{IC}) is the ability of a material to resist unstable crack growth (Zhou, 2013). Despite fracture toughness being an important physical property, there is surprisingly little in publication on this property of geopolymers. Latella et al. (2008) studied the fracture toughness of metakaolin-based geopolymers with molar ratios of Si/Al = 2 ratio and Na/Al = 1 using various precursors: (a)-SAGP - sodium aluminate ($NaAlO_2$), Ludox (SiO_2) and metakaolin (MK); (b)-FSGP -NaOH, fumed silica and MK; (c)-LGP: Ludox, NaOH and MK; and (d)- SGP - sodium silicate and MK (see Figure 2.31). The team used three-point bending to determine fracture toughness of notched geopolymer. They finds that fracture toughness starts at 0.25 $MPa \cdot m^{1/2}$ and increases to 0.56 $MPa \cdot m^{1/2}$ in response to increases in the density of the geopolymers. They conclude that porosity, unreacted phases, and impurities are important determinants of fracture toughness.

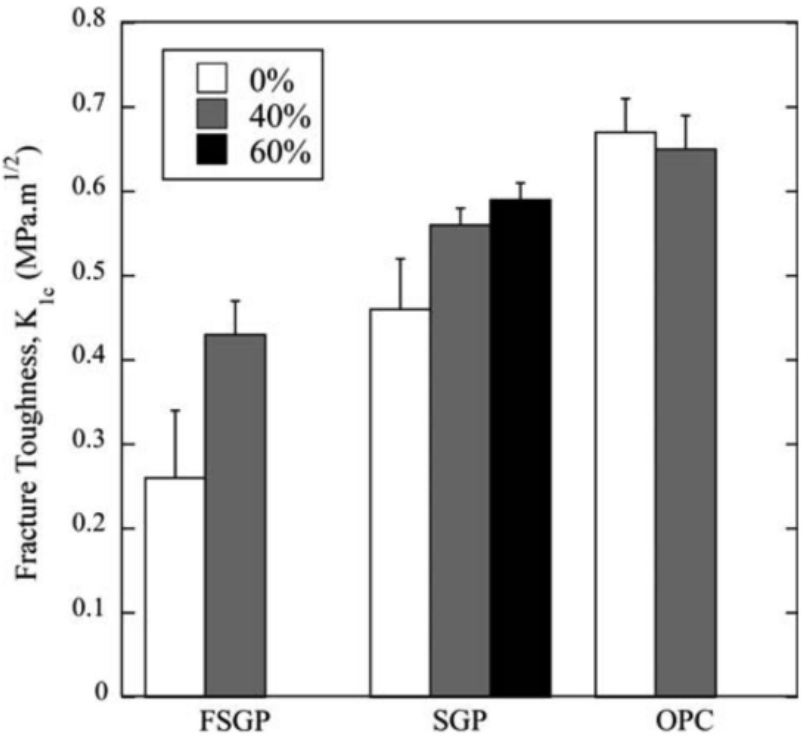


Figure 2.31: Fracture toughness of FSGP, SGP and OPC with no sand and different levels of sand additions. Errors bars are standard deviations (Latella et al., 2008).

Lizcano (2011) studied the effect of Si:Al ratios and sodium and potassium activators on the fracture toughness of metakaolin-based geopolymers with findings consistent with those of Latella et al. (2008), but also notes that as the Si:Al ratio increases so does fracture toughness as shown in Figure 2.32.

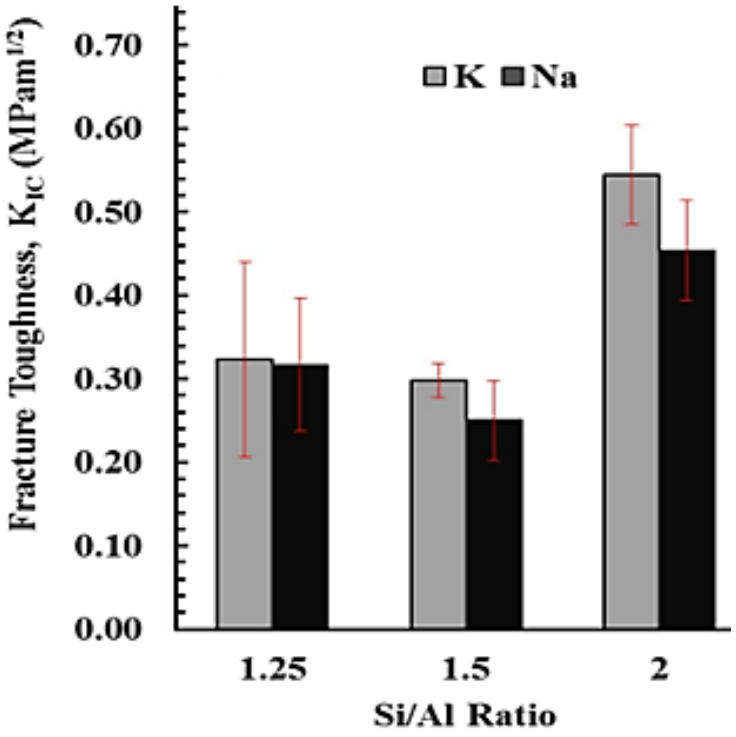


Figure 2.32: Average fracture toughness values for K- and Na-based geopolymer with different Si/Al ratios (Lizcano, 2011).

2.4.4 Chemical resistance

Geopolymers have excellent resistance to acidic environments. This is an important advantage they hold over conventional OPC: for instance, their ability to withstand corrosive environments has led to their use in sewerage pipes (Gourley, 2005). Typically bacteria proliferate within sewerage pipes and cause highly corrosive sulphuric acid to accumulate. Pipes built from conventional OPC without acid resistance tend to have a 50-year lifetime; in contrast, it is anticipated that geopolymers, which resistance to all organic solvents and acidic conditions, will last up to 150 years (Gourley, 2005).

The resistance to acidic environments was investigated by Bakharev (2005b), who prepared cylindrical samples of fly ash-based geopolymer and immersed them in solutions of 5% acetic and sulphuric acid. Samples of Ordinary Portland cement (OPC) and OPC with 20% fly ash replacement were also prepared and immersed. After five months, it was found that there was very limited change in the geopolymer samples, while the OPC samples had undergone severe deterioration. The change in strength was measured after six months of immersion, and reveals that the geopolymer samples have lost 38.3% of their strength while the OPC samples have lost 91% and the OPC samples containing 20% fly ash have lost 84%. Bakharev (2005b) concludes that geopolymer materials are superior at resisting acidic conditions.

Wallah et al. (2005) investigated fly ash-based geopolymers' resistance to sulphuric acid and sulphate attack, finding that the fly ash-based geopolymer samples demonstrate excellent resistance to deterioration on being immersed in 0.5% and 1 wt.% sulphuric acid for 12 weeks. However, when immersed for the same length of time in the more concentrated 2 wt.%, the sulphuric acid is found to reduce the compressive strength of the samples. Fly ash-based geopolymer samples immersed in concentrated 5 wt.% sodium sulphate show excellent resistance.

Wallah and Rangan (2006) studied fly ash-based geopolymer concrete acid resistance using various mortar and concrete samples and solutions of sulphuric acid. The team compared geopolymer samples that had been immersed in sulphuric acid for one year with samples that had been left in the laboratory at ambient conditions. The findings are that the geopolymer samples that had been immersed in sulphuric acid have surface erosion; the greater the concentration of acid, the greater the extent of damage.

Thokchom et al. (2009) conducted studies using 10 wt% sulphuric acids and 10 wt% nitric acid. The researchers find that after fly ash-based geopolymer mortars have been immersed in acid for 24 weeks they lose 2 wt% weight and feature minor erosion of surfaces. An important finding of this set of tests is that geopolymers remain generally resistant to even extremely highly acidic environments. However, while the authors claim that the samples are highly resistant, they also note,

significantly, that some of the samples lose 70% of their strength, from an initial strength of 100MPa to 30MPa.

Song et al. (2005) also studied the effect of 10 wt.% sulphuric acid on fly ash-based geopolymers over an eight-week period. The researchers used a class F fly ash; and the final geopolymer concrete, after 24 hours curing, was found to have a compressive strength between 53 MPa and 62 MPa. They then immersed the samples in 10 wt.% sulphuric acid and tested their durability after 1, 4, and 8 weeks. Using the ASTM C267 test, they find that even after 8 weeks the samples exhibit only a 3% weight loss; they still possess a substantial load capacity and are still structurally intact.

2.4.5 Permeability

Miloud (2005) defines the permeability of concrete as the rate at which water or aggressive agents (such as chlorides ions and sulphates) can penetrate. Permeability is an important consideration for concrete because the penetration of water or an aggressive solution may cause deterioration. Low permeability maintains structural integrity and makes the concrete strong and durable for a long time. There is competing evidence about whether geopolymer-based cement or Ordinary Portland cement (OPC) offers more favourable permeability.

Zhang et al. (2010) investigated the permeability of metakaolin-based geopolymer concrete with the addition of 10 wt.% granulated blast furnace slag (GBFS) and different ratios of liquid/solid. They find that permeability increases with an increasing liquid/solid ratio, but is lower than that of OPC. They also find that the addition of GBFS, i.e. greater than 10 wt.%, could be beneficial in reducing geopolymer permeability. They suggest that the slag had a packing influence on the structure of geopolymer.

Others have compared the permeability of geopolymer and OPC concretes. For example, Sagoe-Crentsil et al. (2011) investigated the gas and high pressure water permeability of both under ambient conditions and steam curing conditions. The two are comparable in their gas permeability, that of geopolymer concrete being 6.19

$x10^{-17}$ m^2 and that of OPC concrete 6.32 $x10^{-17}$ m^2. With respect to high pressure water permeability, geopolymer concrete is found to return a much higher result, 1.52 $x10^{-10}$ m/s, compared with OPC concrete's 1.73 $x10^{-11}$ m/s.

Olivia et al. (2008) studied the permeability of geopolymer concrete and other properties of water penetrability such as sorptivity, permeable void volume and water absorption. The research team mixed low-calcium fly ash with a combination of sodium hydroxide and sodium silicate as an alkaline activator to produce a geopolymer. The geopolymer samples demonstrate low sorptivity, low permeable void volume and reduced water absorption, leading the researchers to conclude that the determinants of favourably low water penetrability are the well-graded aggregate and low water/binder ratio.

Olivia and Nikraz (2011a) later evaluated fly ash-based geopolymer permeability and durability in seawater settings. Interestingly, they find that in comparison with OPC concrete, certain paste formulations of fly ash-based geopolymer lead to faster corrosion of embedded steel and greater chloride penetration, although superior performance is observed with some geopolymer concrete formulations. They conclude that the extent of corrosion is determined by the geopolymer paste characteristics.

Olivia and Nikraz (2011b) studied permeability, water absorption properties and strength of fly ash-based geopolymer in seawater settings. The pair determines that a 'low' classification can be given to geopolymers that exhibit water absorption not exceeding 5 wt%. They note that decreasing the water to solids ratio, increasing the alkaline to fly ash ratio, and increasing the aggregate to solids ratio all reduce water absorption. They conclude that the fly ash geopolymer has an 'average' void content varying from 8.2% to 13%. From this they argue that fly ash-based geopolymer concretes have the potential to be manufactured to existing standards of commercial concrete performance.

2.5 Applications of Geopolymers

While discussion of geopolymer application thus far has concentrated on the construction industry and overwhelmingly on its use as a concrete, there are a variety of other roles for this material, including use in the aerospace, civil engineering, non-ferrous foundries, motor vehicle and plastic industries (Davidovits, 1999). The potential for application is categorised by Davidovits, who matches application type to the Si:Al ratio. The results are shown in Figure 2.33.

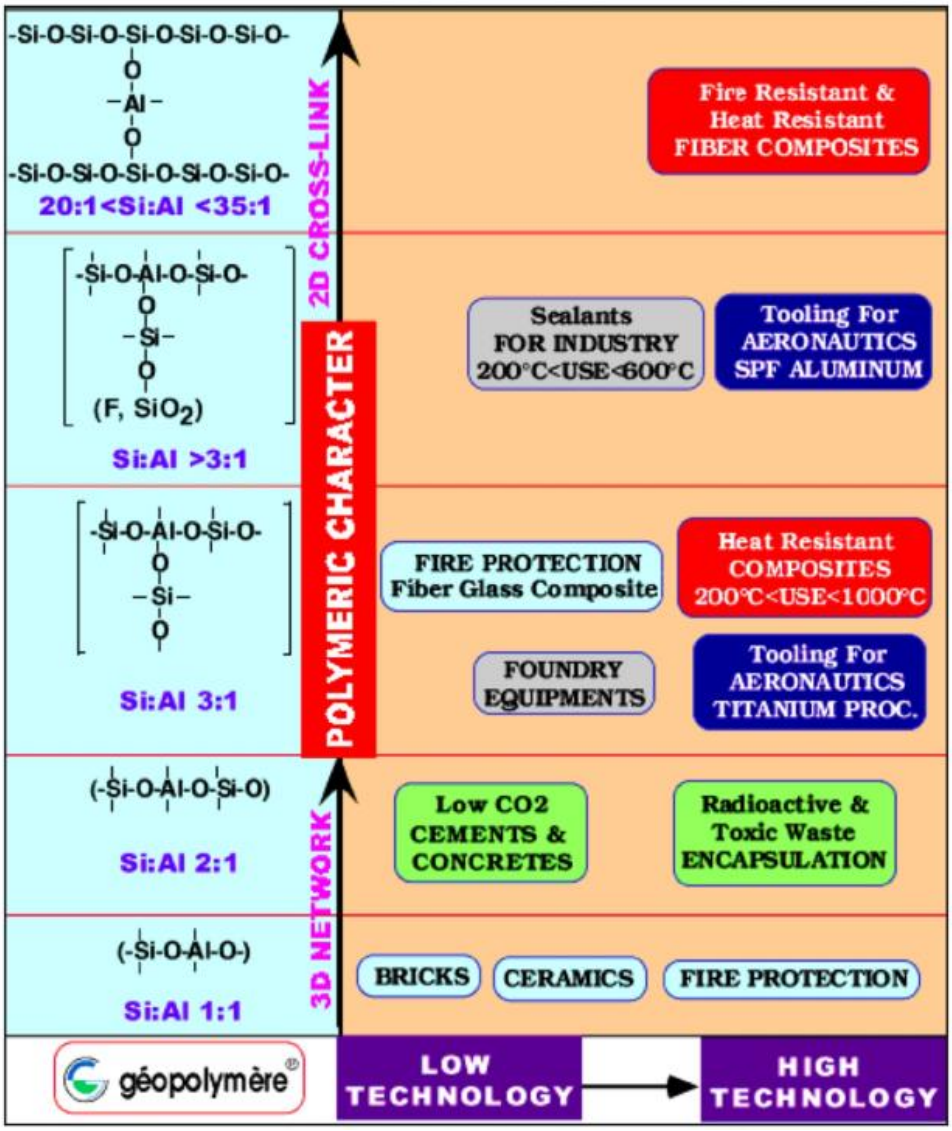


Figure 2.33: Geopolymer types involved in successful applications (Davidovits, 1999).

An interesting sustainable development application of geopolymer materials is in the management of toxic and hazardous waste, because geopolymer materials have properties similar to zeolitic materials, which are known for their capacity to absorb toxic and hazardous waste types (Davidovits, 2002).

Balaguru et al. (1997) investigated the use of geopolymers for the purposes of fastening carbon fabric to the surface of reinforced concrete beams. They find that geopolymer offers excellent adhesion of the carbon fabric's inter-laminar to the reinforced concrete surface. They report that the geopolymer is chemically compatible with the reinforced concrete, that it does not undergo UV radiation degradation, and that it is fire resistant.

In Australia to date there has been broad application of geopolymer technology, with notable developments in building products such as chemically-resistant wall panels and fire-resistant construction materials; further afield, geopolymer technology has been applied in railway sleepers, masonry units, protective coatings, high-performing fibre-reinforced laminates, repairs materials and sewer pipeline products (Gourley, 2003; Gourley and Jahnson, 2005).

2.6 Properties of geopolymer composites

As mentioned, geopolymers are effectively ceramics that are capable of being cured and hardened at near-ambient temperature with typical strength and temperature resistance (Low, 2014). Other desirable attributes of geopolymers are their low shrinkage, relatively high strength properties and elastic modulus. However, like other ceramic-type materials, geopolymers exhibit brittle failure. Fibre reinforcement is a preferred technique for overcoming this, and as a technique for developing high-performing polymer-matrix composites involves embedding fibres within support matrices to enhance certain properties (Low, 2014).

Although Davidovits's (2008) original interest in geopolymers was in the fabrication of moulding tools and patterns for the plastics processing industry, since this time there have been a number of investigations aimed at better understanding the nature, properties, and potential applications of geopolymer composites. Primarily these

studies have used inorganic reinforcements such as glass and carbon fibres (Lin et al., 2008; Vijai et al., 2012). After several years in which the use of synthetic fibres has dominated, however, natural fibres are now replacing them in various applications (Abdul Khalil et al., 2012). Geopolymer composites with natural fibres can become products that are inexpensive, light-weight, impact resistant, corrosion resistant, and have high specific strength and modulus.

Overall the incorporation of fibre reinforcement enhances the mechanical properties of geopolymer matrices, with its primary objective to overcome the inherently brittle nature of geopolymers and prevent catastrophic failure (Low, 2014). As fibre content is increased, this reinforcement component gradually asserts control over the set of composite mechanical properties. The following section presents current knowledge of the engineering properties of fibre-reinforced geopolymer composites. While it has previously been shown, in section 2.11, that geopolymer matrices (without fibres) exhibit diverse properties, the following section will present a variety of properties that geopolymer composites demonstrate.

2.6.1 Compressive strength

The compressive strength of geopolymer concrete is generally higher than that of OPC concrete (Rangan, 2007). However, the range of controversial results thus far suggests that such a clear pattern does not exist in relation to the compressive strength of fibre-reinforced geopolymer composites (Shaikh, 2013). For example, Bernal et al. (2010) report that the compressive strength of steel fibre-reinforced slag-based geopolymer composite containing 40 kg/m^3 steel fibres is reduced by 25% at day 7 and 23% at day 28, compared with an unreinforced geopolymer composite. Bernal et al. (2010) find that increasing the content of steel fibre from 40 kg/m^3 to 120 kg/m^3 does not lead to an increase in the compressive strength of slag-based geopolymer composites. A different outcome is found in the investigation of the compressive strength of fibre-reinforced concrete composites: while there is a reduction in compressive strength of approximately 25% after adding fibre reinforcement to geopolymer composites, there is no comparable compressive strength reduction when adding fibre reinforcement, 40Kg/m^3 of steel fibre, to concrete composites (Bernal et al., 2010). Moreover, while increasing the content of

steel fibre from 40 kg/m^3 to 120 kg/m^3 does not lead to an increase in the compressive strength of slag-based geopolymer composites, in concrete composites increasing the steel-fibre content from 40 kg/m^3 to 120 kg/m^3 leads to a large reduction in compressive strength, of 20% at day 7 and 15% at day 28 (Bernal et al., 2010).

Puertas et al. (2003) investigated the compressive strength of polypropylene fibre-reinforced geopolymer composites using fly ash, slag and slag/fly ash with polypropylene fibre at 0 %, 0.5% and 1% by mortar volume. The compressive strength was determined at day 2 or day 28. Unlike the findings in Bernal et al.'s (2010) study, Puertas et al. (2003) do not find a reduction in compressive strength with the addition of polypropylene fibre. They find that adding 0.5% and 1% polypropylene fibre to slag-based geopolymer composite has no significant impact on compressive strength at day 2 or day 28. In contrast, increasing polypropylene-fibre in fly ash-based geopolymer composite increases its compressive strength at day 2, while unusually at day 28 the strength has decreased. In both slag- and fly ash-based geopolymer composites increasing polypropylene-fibre content from 0.5 to 1.0% gives a slight increase in the compressive strength of the composites at days 2 and 28.

A similar study by Zhang et al. (2009) compared the compressive strength of fibre-reinforced geopolymer composite with non-reinforced composite, using fly ash and calcined kaolin to prepare geopolymers. The researchers report that after a polypropylene-fibre addition to 0.5 wt.% the compressive strength increased by 67.8% at day 1 and 19.5% at day 3. However, when polypropylene is added at a greater proportion than 0.5 wt.% the rate of increasing compressive strength decreases.

Al Bakri et al. (2013) studied measurements of compressive strength for fly ash-based geopolymer composites reinforced with wood fibres. The preparation involved activation of fly ash powder using sodium silicate/sodium hydroxide at a 2.5 ratio. Short-wood fibres were introduced into the composites at percentages ranging from 10 wt% to 50 wt%. The results suggest that increasing wood fibre content decreases the compressive strength of geopolymer composites at 7 and 14 days. This is

believed to be due to the wood-fibre acting as a filler within the matrix: in other words, the reduction is believed to be due to the increased surface area of the filler materials that bonds with the geopolymer matrix and the respective decrease in the geopolymer surface area itself.

2.6.2 Flexural strength

Dealing with the high risk of brittle failure in cements is the primary aim of fibre introduction (Shaikh, 2013). Geopolymer composites demonstrate increased flexural strength when reinforced with fibres, in a manner similar to cement-based fibre composites (Shaikh, 2013). Bernal et al. (2010) studied the flexural strength of steel fibre-reinforced geopolymer composites at days 7, 14 and 28. An increase was observed at each stage, and as the curing time increased, an increase in flexural strength of the composites was reported. At day 28, it was found to have increased from 6.4 to 8.86 Mpa. Bernal et al. (2010) conclude that the increase in strength is attributable to an improvement in post-cracking behaviour after the addition of the steel fibres.

Zhang et al. (2009) investigated the flexural strength of polypropylene fibre-reinforced geopolymer composites, finding significant improvement on day 1 and day 3. The addition of 0.25, 0.50 and 0.75 wt.% fibres was found to increase the flexural strength of the composites. These results contrast with the earlier results of Puertas et al. (2003) in which the addition of polypropylene fibres was found not to improve the flexural strength of the composites at 2 and 28 days, The inferior performance observed in Puertas et al.'s investigation could be attributed to the poor workability due to the addition of polypropylene fibres into geopolymer matrix (Shaikh, 2013).

Natali et al. (2011) investigated the flexural behaviour of metakaolin/slag-based geopolymer composites with polyvinyl alcohol (PVA), high tenacity (HT) carbon, E-glass, and polyvinyl chloride (PVC). The researchers find improvement in flexural strength with the addition of polyvinyl alcohol (PVA), high tenacity (HT) carbon, E-glass, and polyvinyl chloride (PVC), concluding that each of fibre type, on addition to the system, leads to a favourable bridging effect. The addition 1 wt.% of fibre to

the geopolymer matrix increased flexural strength by between 30% to 70%, depending on fibre type. Natali et al. (2011) find that polyvinyl chloride (PVC) and carbon fibre reinforcement result in the greatest improvement in post-crack behaviour. They also find that these reinforcements give the composite the greatest ductility once the first crack load has been reached. This is shown in Figure 2.34.

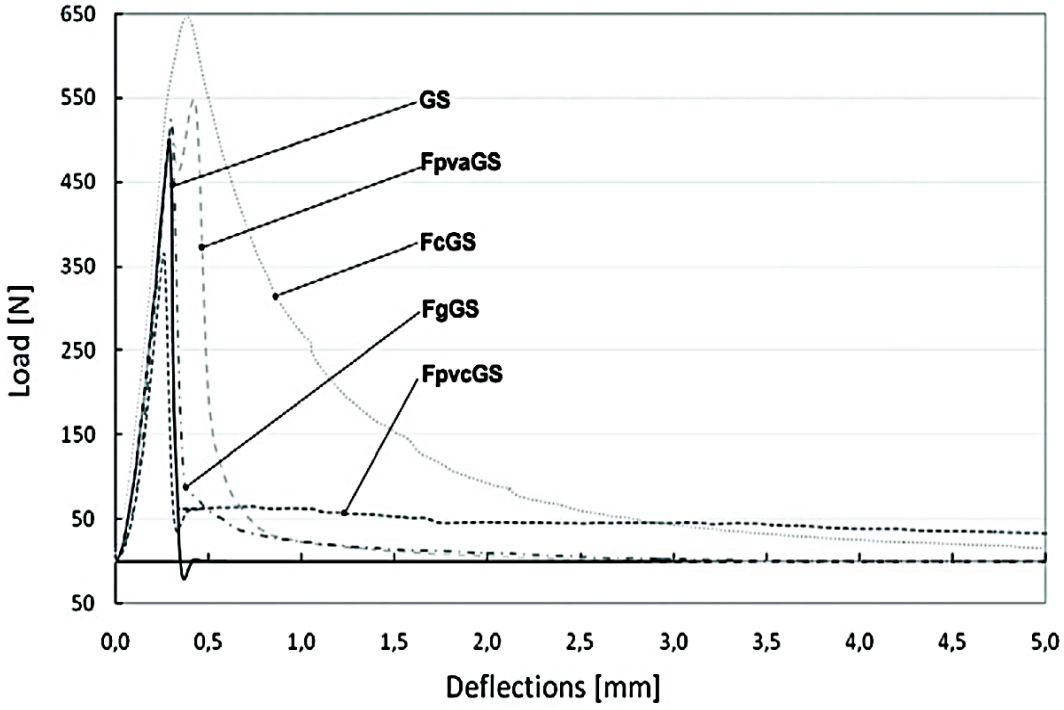


Figure 2.34: Load-deflection curves for all geopolymer samples (Natali et al., 2011).

Note: GS: reference sample, FcGS: Carbon fibre-reinforced sample, FgGS: Glass fibre-reinforced sample, FpvaGS: PVA fibre-reinforced sample, FpvcGS: PVC fibre-reinforced sample.

Lin et al. (2009) also investigated the flexural behaviour of metakaolin-based geopolymers composites, adding short carbon fibre reinforcement to a metakaolin-based geopolymer matrix. The team used a solution of potassium silicate to activate the metakaolin powder, and composites with different volume fractions of short carbon fibre of 3.5, 4.5, 6 and 7.5 % were prepared. They report that as the carbon-fibre volume fraction increases from 3.5% to 4.5%, an increase in the flexural strength of the composites is noted. As part of this, at carbon-fibre volume fraction

4.5%, an increase from 16.8 MPa for the geopolymer matrix alone, to 96·6 MPa for the carbon-fibre geopolymer composite, is seen. Notwithstanding this significant improvement, at fibre volume fraction of 6 and 7.5%, the effect of strengthening is reduced. This result is shown in figure 2.35. Lin et al. (2009) believe that this reduction is possibly due to fibre damage, with high shear stress formation at the fibre/matrix interface under higher forming pressure.

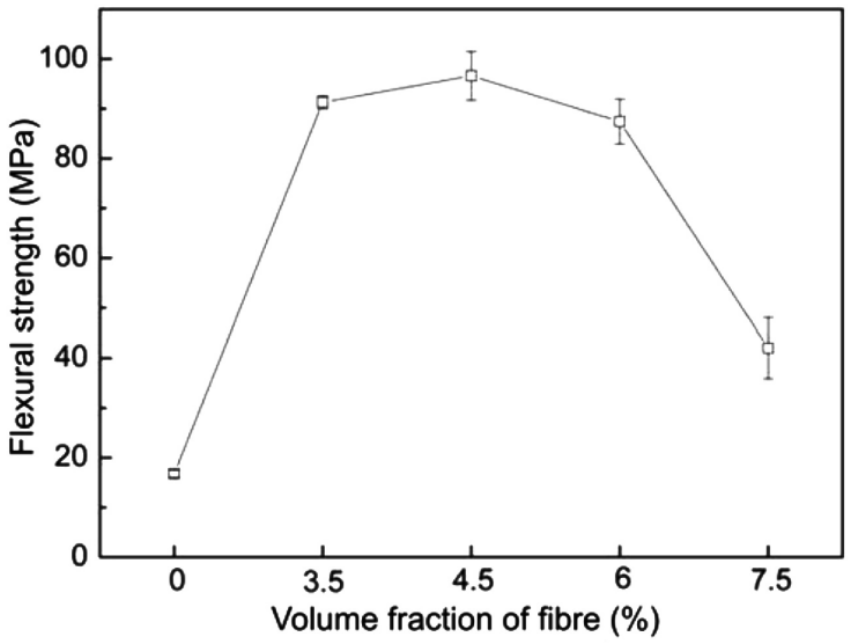


Figure 2.35: Variation of flexural strength of C_f/geopolymer composites as a function of volume fraction of short carbon fibre (Lin et al., 2009).

Chen et al. (2014) studied the flexural behaviour of fly ash-based geopolymer composites after the addition of fibres of sweet sorghum. The researchers find that this property rose as the fibre content increased, to a maximum of 2 wt%. When fibre exceeds 2%, a reduction in flexural strength is noted. The authors conclude that 2 wt% of sweet sorghum fibre is the optimum, effectively allowing a greater tensile load to be carried throughout the composite and thus delaying micro-crack growth and increasing overall flexural strength. Beyond the optimum content there is poor workability, and a non-uniform dispersion of fibres which leads to the entrapment of air bubbles. These flaws tend to cause concentrations of stress and ultimately lead to

a reduction of flexural strength in the composites. Figure 2.36, shows the influence of sweet sorghum fibre content on the flexural strength of geopolymer composites.

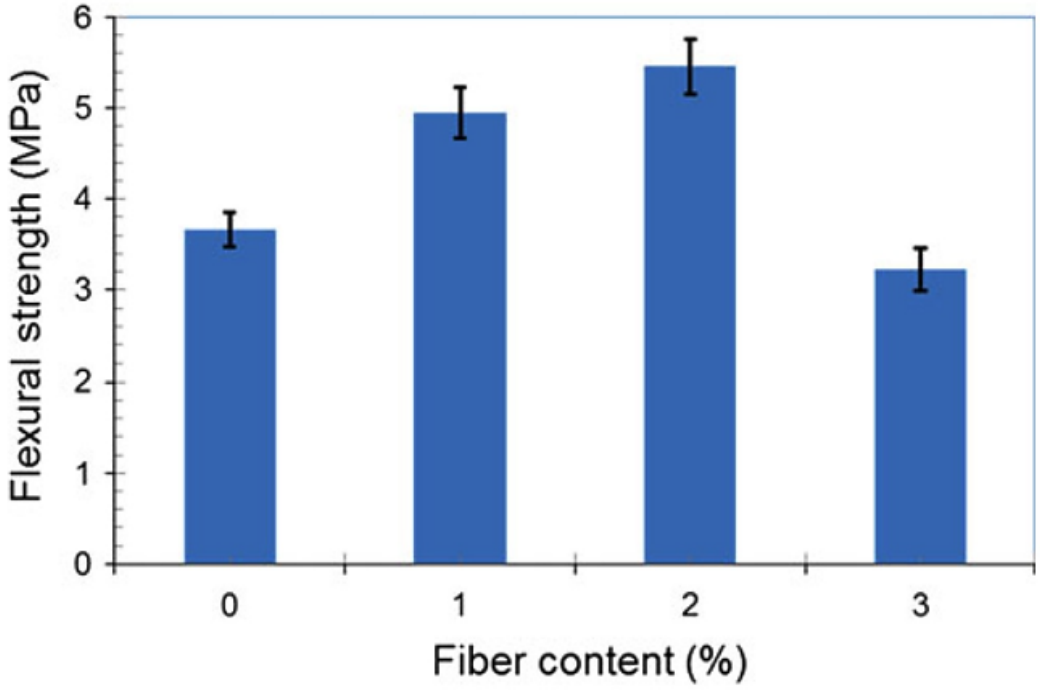


Figure 2.36: Effect of fibre content on flexural strength of geopolymer paste (Chen et al., 2014).

Alzeer and MacKenzie (2012) investigated the effect of adding unidirectional natural protein-based fibres (carpet fibres and merino wool) on the flexural strength of metakaolin-based geopolymer composites. The surface of the wool fibre was subjected to chemical treatment in order to enhance its reinforcing properties and alkali resistance. The researchers find that while unreinforced matrices exhibit brittle failure, the addition of chemically-treated wool fibres leads to a 40% increase in flexural strength and a significant improvement in the failure characteristics.

In another study, Alzeer and MacKenzie (2013) investigated the flexural behaviours of metakaolin-based geopolymer composites after the addition of 4 to 10% content of unidirectional natural flax fibres. The authors report that the composites exhibit greatly improved flexural strength after reinforcement, from 6 MPa prior to reinforcement to approximately 70 MPa after the addition of 10% fibre. Figure 2.37

shows typical stress-strain curves for the unreinforced geopolymer matrix and the flax-geopolymer composites.

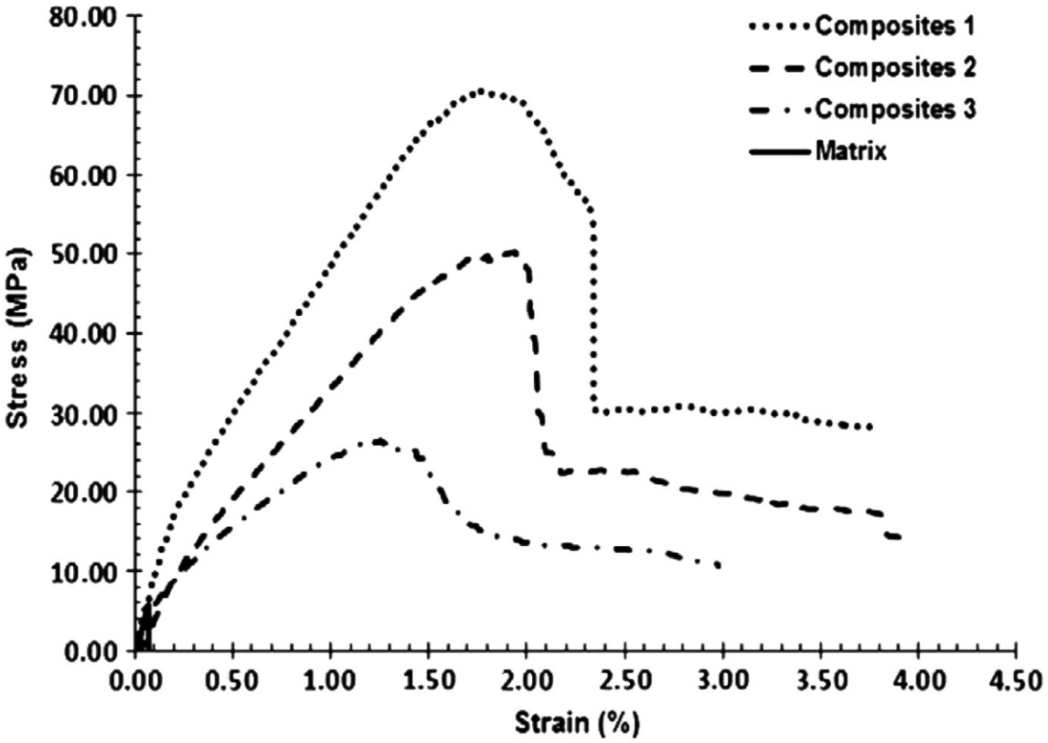


Figure 2.37: Typical stress-strain curves for geopolymer matrix and the flax-geopolymer composites containing various fibre contents (Alzeer and MacKenzie, 2013).

Note: composites 1, 2 and 3 contain 10,7and 4wt.% of flax fibres, respectively.

2.6.3 Impact strength

Despite the relatively high number of studies of the compressive strength and flexural behaviour of fibre-reinforced geopolymer composites, there have been few results to date concerning the impact strength of this class of material. One of the exceptions is Zhang et al.'s (2006) study of the effect of the addition of polyvinyl alcohol fibres (PVA) and fly ash to metakaolin-based geopolymer composites, manufactured using the extrusion technique.

An interesting part of Zhang et al.'s (2006) study is the effect of increasing the polyvinyl alcohol fibre volume fraction on the impact strength of the metakaolin-based geopolymer composites. The highest impact strength is found in the non-

reinforced geopolymer mortar at 450N. This material, however, has a small internal displacement result at 0.84mm. Related to this, beyond peak load it is unable to exhibit loading resistance, resulting in a sharp drop in its impact curve. In practical terms this means that non-reinforced geopolymer mortar is susceptible to immediate brittle failure once peak load has been exceeded. However, a property transformation of brittleness to ductility occurs after polyvinyl alcohol fibres are added to 2% by volume. The impact behaviour beyond peak load is found to exhibit strain-hardening behaviour and gives a response of ductility. Zhang et al. (2006) find that the peak load is 429.6N and a displacement result of approximately 2.5mm. After peak load is exceeded the bearing capacity drops gradually until reaching 7.5 mm. The impact behaviour of metakaolin-based geopolymer composites is shown in figure 2.38.

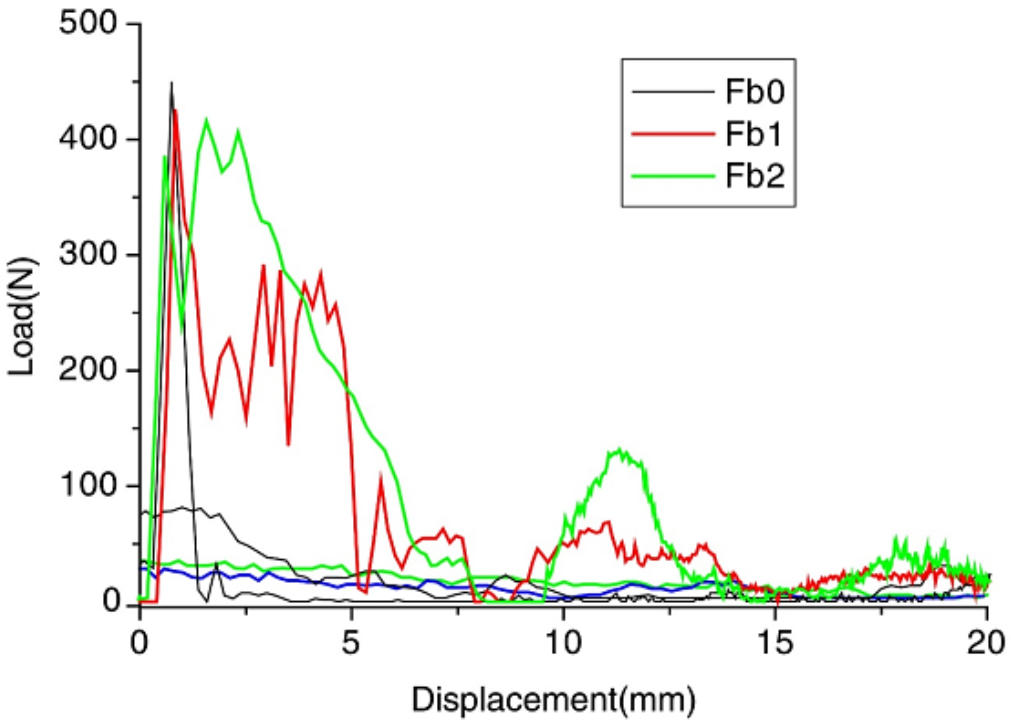


Figure 2.38: Impact curves of geopolymer extruded with different volume fraction of fibre in normally curing condition (Zhang et al., 2006).

Note: Fb0 indicates 0% PVA fibres, while Fb1 and Fb2 indicate 1% and 2% PVA fibre, respectively.

Zhang et al. (2006) show that after the addition of 10 wt.% fly ash the absorbed energy, originally 1833 mJ, rises to 2108 mJ. Stiffness and impact strength are also enhanced. However, at greater concentrations, such as those above 30%, there is a reduction in impact resistance, and at 50 wt.% this reduction becomes dramatic. Zhang et al. (2006) find that as the percentages of fly ash are increased at this point, there is an increase in the rates of reduction. Compared with composites without fly ash, the geopolymer composite with 50% fly ash has a toughness, stiffness, and impact strength that are 28.7%, 39.1%, and 37.4% lower respectively.

Li and Xu (2009) also investigated impact behaviour, energy absorption capacity and deformation of geopolymer concretes reinforced by basalt fibres using a Hopkinson pressure bar system with a 100 mm diameter for testing. The results suggest that basalt fibre-reinforced geopolymer concretes demonstrate a strong strain rate of dependency: this means that as the strain rate increases so does the quality of the impact properties. Reinforcement with basalt fibre significantly enhances the energy absorption and deformation capacities of the concrete. The optimal basalt fibre loading in terms of maximising energy absorption is 0.3% volume fraction.

Edvaldo et al. (2013) studied the impact properties of geopolymer composites with natural fibres. The team added 3% volume fraction pineapple leaf fibre (PALF) and sisal fibre to metakaolin-based geopolymer composites, and prepared samples with 60 x 10 x 10 mm dimensions. They find that using PALF and sisal fibres as reinforcements lead to a considerable improvement in impact behaviour. The impact strength of the composites with PALF was lower than that of those with sisal fibre; however, the PALF results should not be overlooked because they demonstrate an undeniable gain compared with the geopolymer matrix without fibre. This indicates that it is possible to propose a composite with natural fibres that combines good mechanical properties. Figure 2.39 shows the impact performance of these composites.

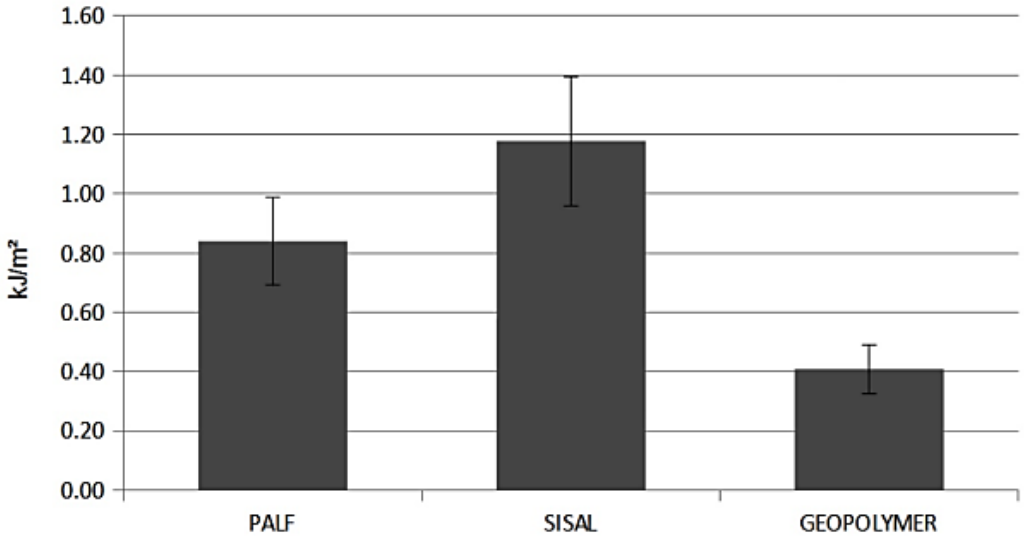


Figure 2.39: Impact test results (Edvaldo et al., 2013).

Edvaldo et al. (2013) captured visual evidence of the impact strength of their PALF and sisal fibre metakaolin-based composites, presented in Figure 2.40.

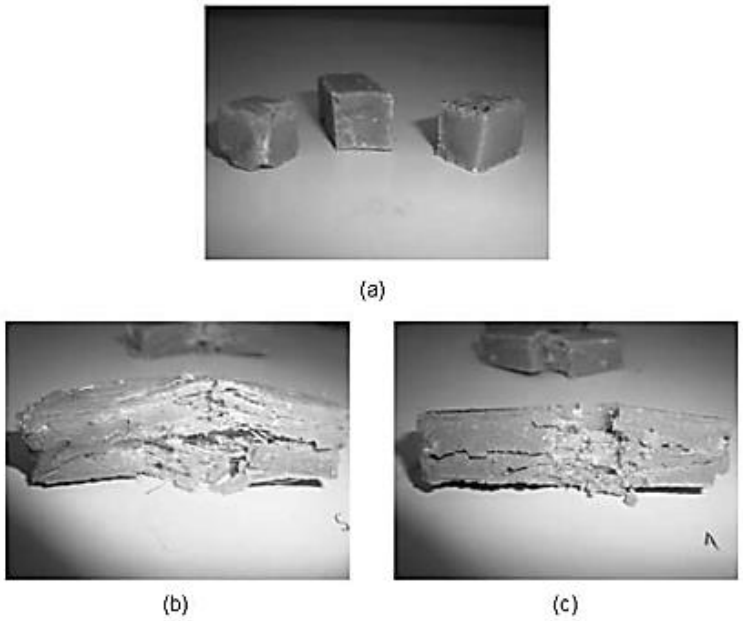


Figure 2.40: Impact test samples: (a) geopolymer, (b) Sisal and (c) PALF (Edvaldo et al., 2013).

2.6.4 Fracture toughness

The toughness of a material is its ability to absorb energy and deform without fracture (Low, 2014). In materials science, the term is used to quantify the resistance of a given material to the formation and propagation of cracks (Low, 2014). In composite materials, the addition of fibres provides an important control against cracking, made possible by the bridging action of the fibres which enables a brittle matrix to improve in fracture toughness because they mitigate the forces related to micro and macro cracking (Low, 2014).

There have been few publications concerning the fracture performance of geopolymer composites to date. One exception to this dearth is Dias and Thaumaturgo's (2005) study of the fracture performance of basalt fibre-reinforced geopolymer concretes. Dias and Thaumaturgo (2005) added basalt fibre to volumes of 0.5% and 1.0% in metakaolin-based geopolymer concrete, finding a 14% increase in fracture toughness on the addition on 0.5% basalt fibres and a 111% increase on the addition of 1% basalt fibres. They conclude that basalt fibres efficiently strengthen and toughen geopolymer concrete to a greater extent than they do normal concretes, and that this is due to the favourable bond between the geopolymer matrix and the fibres.

Lin et al. (2008) also investigated the fracture behaviour of short carbon fibre-reinforced metakoalin geopolymer matrix composites. The team find that the maximum work of fracture values of the geopolymer composites reinforced with 7-mm short carbon fibres increases from 54.2 to 6435.3 J/m^2 (118.3 times increase). Even after three-point bending testing, Lin et al. (2008) find that a 7-mm short carbon fibre-reinforced geopolymer composite sample will not break completely, although they undergo significant deformation which indicates that the composites reinforced by carbon fibres absorb much energy to avoid catastrophic fracture behaviour, as shown in Figure 2.41 (b). In contrast, the non-reinforced geopolymer matrix shows a typical brittle failure mode, shown in Figure 2.41 (a).

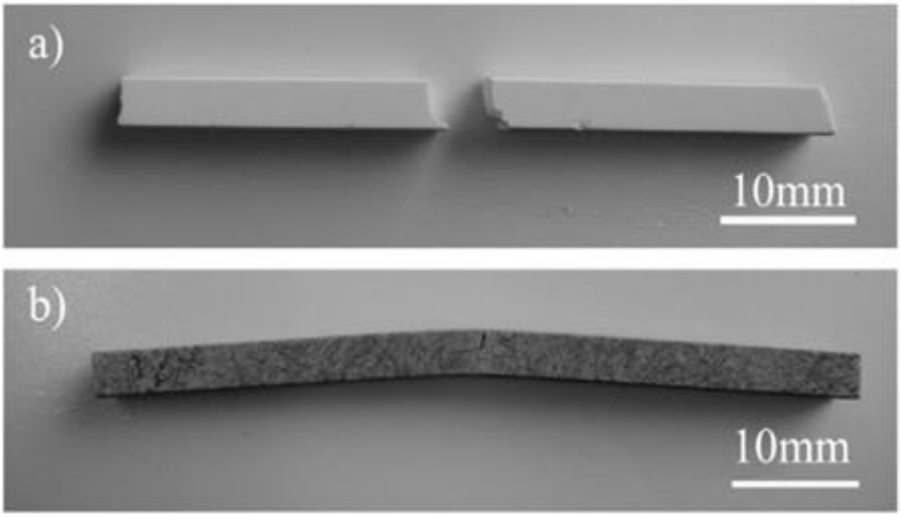


Figure 2.41: Images of bar specimens of (a) geopolymer matrix and (b) C_f/geopolymer composites after a three-point bending test (Lin et al., 2008).

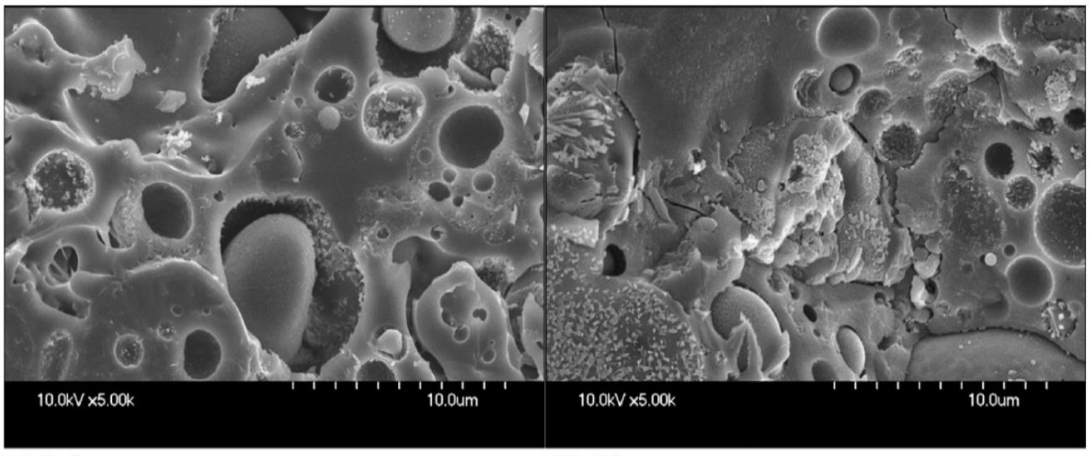
Silva and Thaumaturgo (2003) concur that fibre-reinforced geopolymer composites have superior fracture toughness to conventional cement. They investigated the effect of reinforcing geopolymer mortar with wollastonite micro fibres and report that geopolymer mortar with wollastonite micro fibres has higher fracture toughness than its cement-based counterpart. It is believed that the high quality bond between the matrix and the fibre leads to greater reinforcing efficiency in the geopolymer composite.

2.7 Properties of geopolymers and composites exposed to elevated temperatures

Kong et al. (2007) investigated the effect of elevated temperature on the performance of geopolymers made with fly ash and metakaolin. Potassium hydroxide and sodium silicate solutions were used to synthesise both types. The samples were left at room temperature for 24 hours and then cured for the same length of time at 80°C. To investigate the effect of elevated temperature, the samples were exposed to increasing heat, from room temperature to 800°C, at an incremental rate of 4.4 °C minutes. The samples were left in the furnace to cool once the desired temperature was reached. The research team measured the compressive strengths of the samples prior to and after heating; they also subjected the geopolymers to scanning electron

microscopy, Mercury Intrusion Porosimetry (MIP) and thermo-gravimetric analysis (TGA) at the age of three days. The sample of metakaolin-based geopolymer composite was found to have lost 34% of its strength after heating to 800°C. Interestingly, after the same exposure to temperature the fly ash-based geopolymer was found to increase 6% in strength. Scanning electron microscopy reveals that fly ash-based geopolymers possess small pores under conditions of heating, as shown in Figure 2.42. These small pores permit moisture to escape on heating and this prevents greater matrix damage. The metakaolin-based geopolymers do not possess the same distribution of pores, as shown in Figure 2.43: in other words, the lack of small pores is believed to underpin the metakaolin-based geopolymer sample's matrix damage and reduction in strength. Mercury Intrusion Porosimetry (MIP) results confirm that the metakaolin geopolymer has a lower proportion of micro-pores than fly ash geopolymer. The increased strength of 6% observed in the fly ash-based geopolymers is attributed to the sintering of unreacted fly ash particles.

Results of the TGA indicate that fly ash and metakaolin geopolymer composites undergo reductions of mass with increasing temperature (Kong et al., 2007). The fly ash samples are reduced by 11% on average whereas the metakaolin samples reduce by 30% on average; that is, the weight loss of the fly ash samples is less than that of the metakaolin samples. Kong et al. (2007) attribute the weight loss to the loss of evaporable water.



(a) Before exposure **(b) After temperature exposure**

Figure 2.42: Photographs of fly ash geopolymer (a) before and (b) after temperature exposure (Kong et al., 2007).

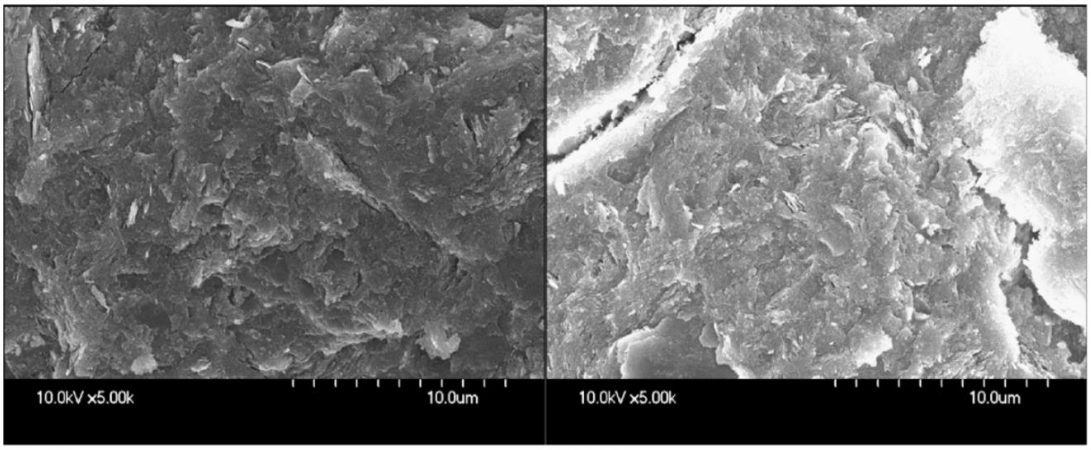


Figure 2.43: Photographs of metakaolin geopolymer (a) before and (b) after temperature exposure (Kong et al., 2007).

Skvára et al. (2005) also investigated the temperature resistance of geopolymers made with fly ash. The alkaline activator concentration was between 4 and 10% sodium oxide in relation to the binder mass, and the water/solid ratio of the pastes and mortars ranged from 0.27 to 0.35. They exposed the samples to temperatures of between 250 and 1,100°C at increments of 5°C per minute, and the samples were left at the maximum temperatures for two hours. They find that fly ash-based geopolymer composite samples lose 40% of their strength after exposure to high temperatures. The minimal values of residual compressive strength occur between 600 and 700°C; this is attributed to the solidifying melt. Nevertheless, the fly ash-based geopolymer sample is found to have a higher residual strength than Portland cement after the heat treatment.

Kong and Sanjayan (2010) investigated the temperature resistance of fly ash geopolymer concrete, using potassium hydroxide and sodium silicate solutions to synthesise the geopolymer samples. Aggregate type, aggregate sizing, sample sizing and superplasticiser type were investigated. Kong and Sanjayan (2010) conclude that the geopolymer sample size is relevant to its strength at elevated temperatures because thermal cracking is induced by differences in temperature at the surface and

at the core. Such large-scale incompatibility of thermal conditions is believed to be an underpinning factor concerning sample size effects. Kong and Sanjayan (2010) also find that the size of the aggregate is important in determining the performance of geopolymer concretes under elevated temperatures. When aggregates are smaller, for example less than 10 mm, they promote spalling and extensive cracking. In contrast, aggregates more than 10 mm large are more likely to be stable at elevated temperatures.

Conventional superplasticisers are commonly used to improve the workability of fresh concrete (Kong and Sanjayan, 2010). However, when superplasticiser is added to fly ash-based geopolymer concrete it causes a clear reduction in strength and the concrete exhibits poor performance at elevated temperatures, so that superplasticiser is contraindicated where elevated temperature performance is required. The interface between the matrix and its aggregate components is believed to underpin this loss of strength because they are incompatible in terms of thermal expansion. This theory has been demonstrated in studies of geopolymer concretes made with different aggregates holding distinctly different characteristics of thermal expansion.

Bernal et al. (2011) prepared geopolymers with SiO_2/Al_2O_3 molar ratios and different degrees of granulated blast furnace slag (GBFS) substituting for metakaolin (MK). The team investigated the effect of exposing these geopolymers to temperatures between room temperature and 1000°C, increasing the temperature 200°C at a time and leaving them to cool to room temperature inside the furnace, to avoid thermal shock and potential cracking. Compressive strength tests and thermogravimetric analysis (TGA) were conducted before and after exposure to temperature. The team concludes that the inclusion of GBFS improves the overall performance of materials prepared with MK when exposed to high temperature and gives a much higher residual compressive strength.

Bernal et al. (2012) later investigated the effect of elevated temperature on metakaolin-based geopolymers reinforced with refractory aluminosilicate particles and fibres, measuring the compressive and flexural strength of these materials at temperatures between 600°C and 1000°C. They find that adding refractory aluminosilicate particles and fibres leads to improvement in compressive and flexural

strength after exposure to heat, compared with samples without these reinforcements; there is also reduced shrinkage. This is attributed to cracking control in these specimens, as the incorporation of particles and fibres enhances their volumetric stability after exposure to high temperatures.

He et al. (2010a) also investigated the thermal resistance behaviour geopolymer composites reinforced with unidirectional carbon fibres prepared by ultrasonic-assisted slurry infiltration. Part of the preparation included heating the system to 1100°C. In order to deal with cracks and pores formed during the heat treatment process, the team impregnated the system with Sol-SiO_2. The team referred to the composites prior to the impregnation as HC, and after as ImHC. They find that as the temperature increases from 700°C to 900°C, both HC and ImHC show anomalous gains in strength: higher than the corresponding strength results at ambient conditions, with HC 19.8% higher and ImHC 16.8% higher. Interestingly, ImHC at 1100 ^{o}C shows superior high-temperature properties because of the Sol-SiO_2 sealing effect, which improves fibre integrity. Figure 2.44 shows the flexural strength of geopolymer composites at high temperature.

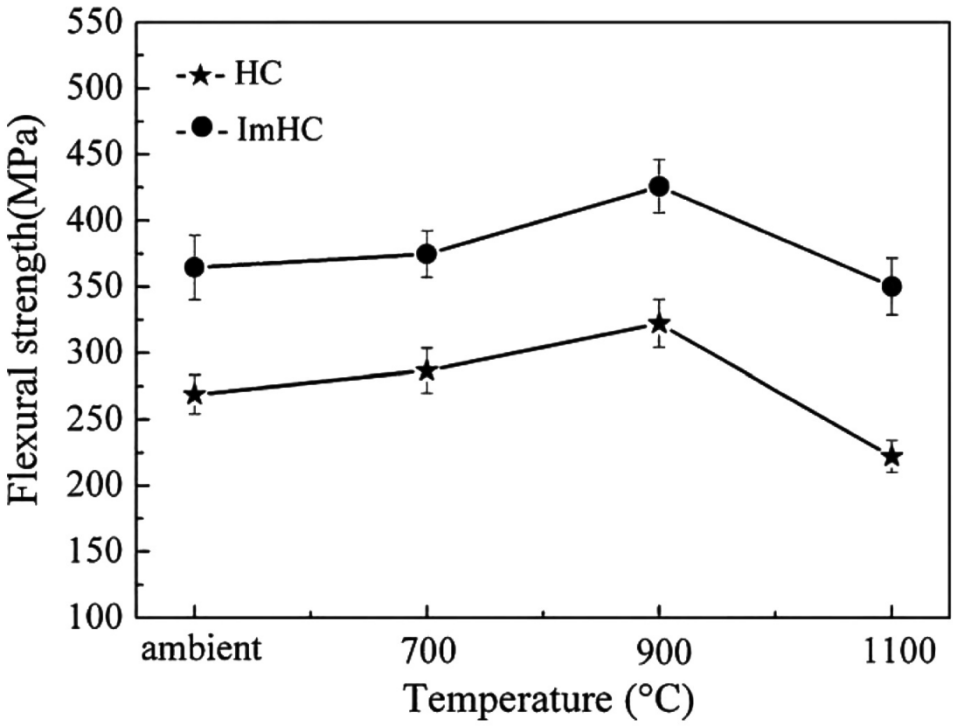


Figure 2.44: Flexural strength vs. temperature of HC and ImHC composites (He et al., 2010a).

He et al. (2010a) find that all composites (HC and ImHC) exhibit non-catastrophic fracture behaviour, which can be seen in the typical stress–displacement curves of the composites at room and elevated temperatures (Figure 2.45a and b).

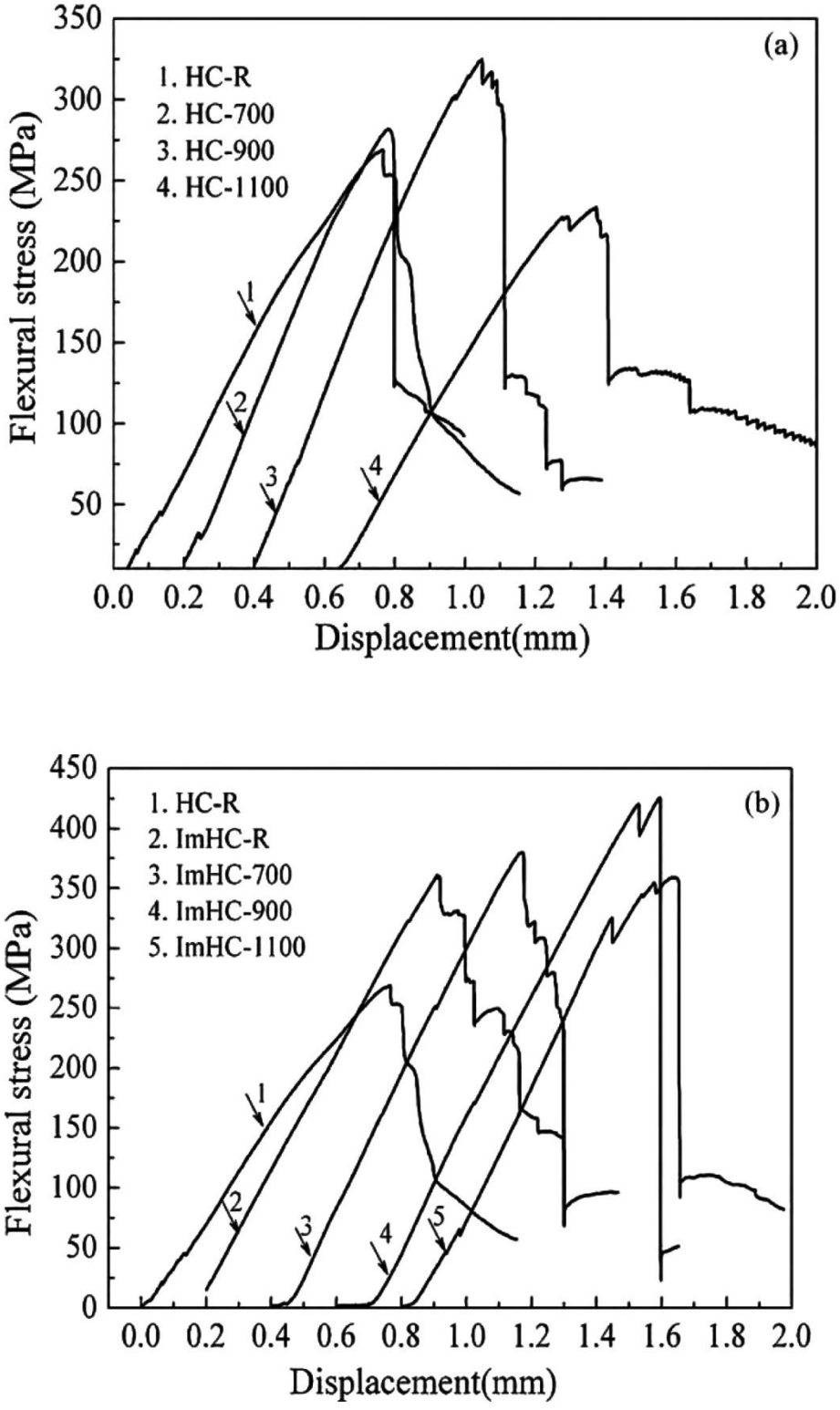


Figure 2.45: Typical load–displacement curves corresponding to their flexural strength tests at different temperatures: (a) HC and (b) ImHC (He et al., 2010a).

In another study, He et al. (2011b) studied the effect of exposure to high temperature on metakaolin geopolymer that contained 25% (by volume) of short carbon fibres. The study involved heating the geopolymers to various temperatures up to 1400°C and maintaining heat at particular temperatures for 90 minutes in an argon atmosphere. Interestingly, the researchers find that heating to 1000°C results in a reduction in flexural strength and modulus from the original values of 133 MPa and 36.5 Gpa to 95.6 MPa and 30.4 GPa, but that heating to 1100°C leads to the highest flexural strength (234 MPa) and modulus (64 GPa): at this high temperature the greatest fracture results are found. The samples lose flexural performance once treatment reaches 1400°C. Figure 2.46 presents the mechanical properties of geopolymer composites after heat treatment at different temperatures.

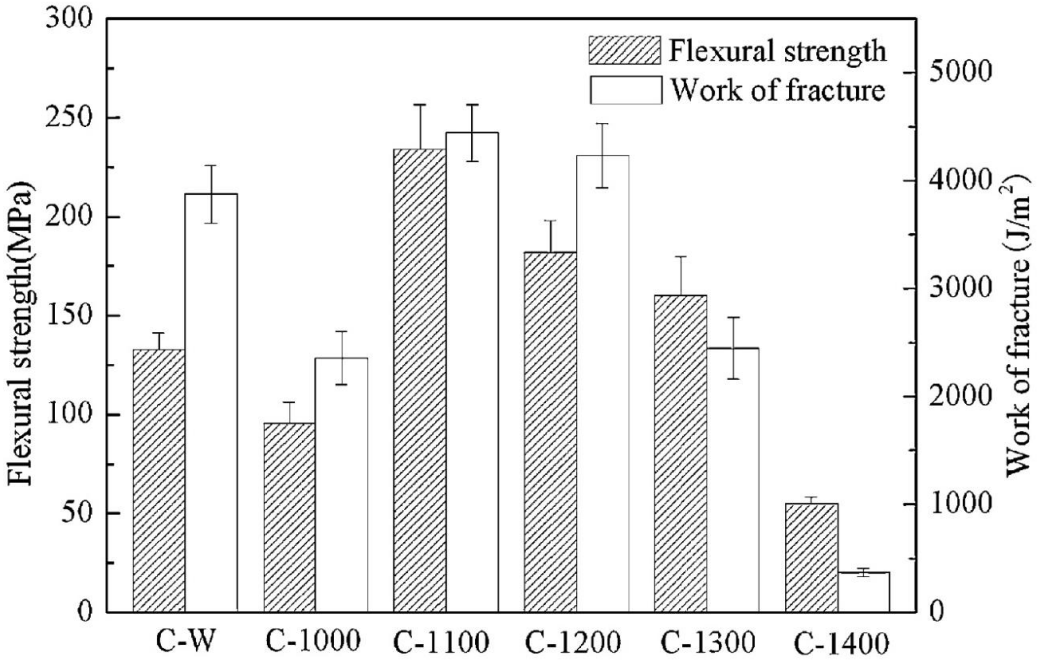


Figure 2.46: Variations of flexural strength and work of fracture of carbon fibre/geopolymer composites without and after heat treatment at different temperatures (He et al., 2010b).

Interestingly, the samples that were heated up to 1300°C did not undergo catastrophic failure and exhibited elastic region and non-linear region, although catastrophic fracture behaviour was observed above 1300°C, as shown in Figure 2.47.

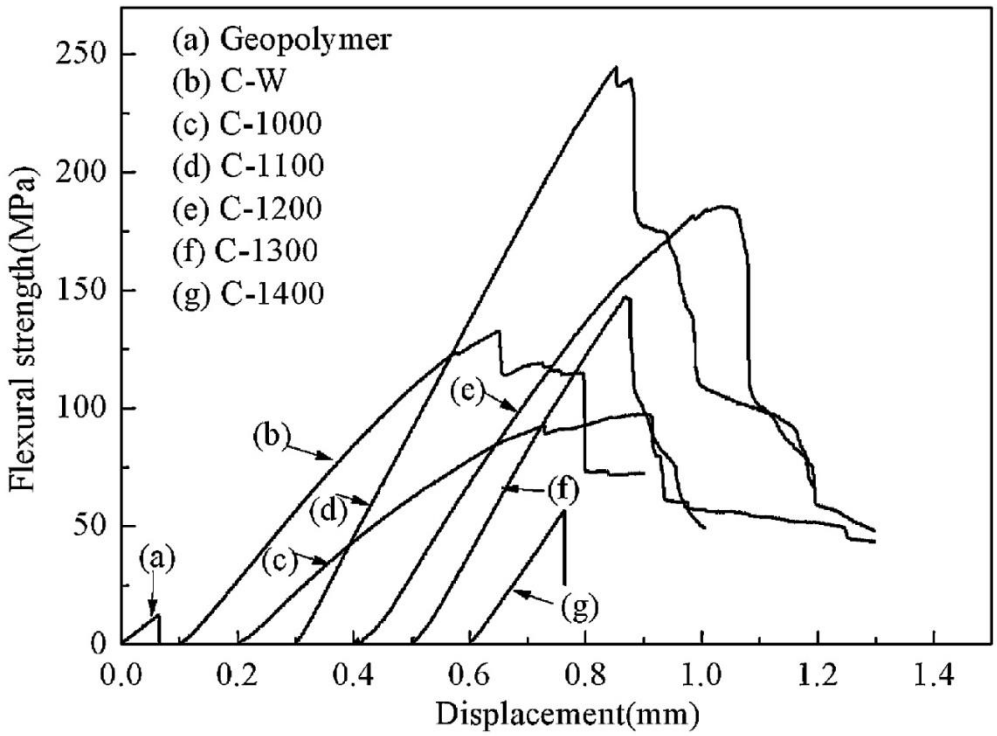


Figure 2.47: Typical load-displacement curves of geopolymer and carbon fibre/geopolymer composites without and after heat treatment (He et al., 2010b).

Figure 2.48 (a–f) provides the morphology of fracture surfaces of the composites at different temperatures. Figure 2.48 (a–e) shows pull-out length is greater for composites heated up to 1300°C. This fibre pull-out mechanism underpins enhanced fibre/matrix bond strength and favourable strength and toughness (He et al., 2010b). In contrast, temperatures exceeding 1300°C result in shorter pull-out lengths, as shown in Figure 2.48 (f). This observation serves as evidence of increased fibre/matrix bond strength affecting other properties, in this case leading to lower toughness and strength (He et al., 2010b).

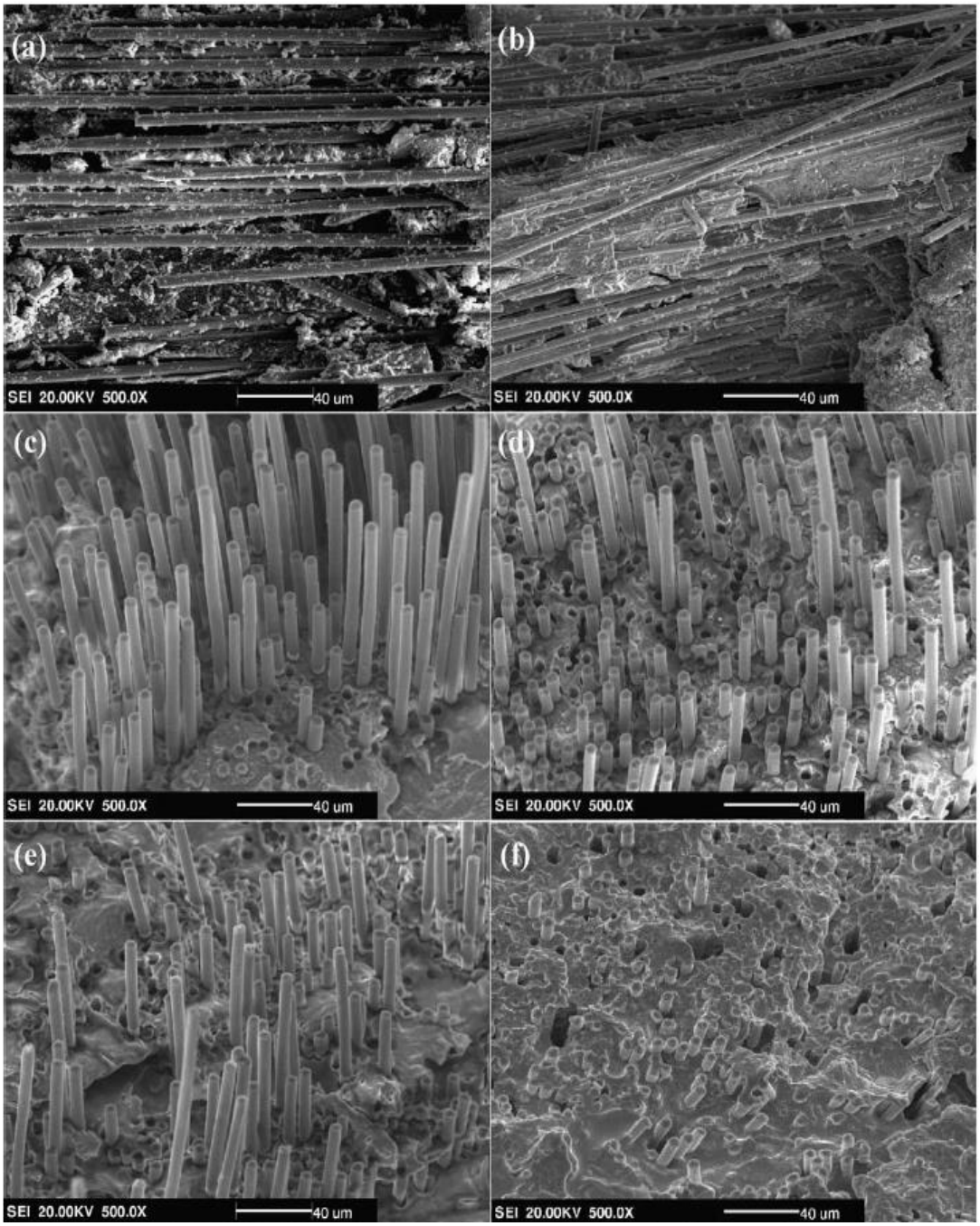


Figure 2.48: Typical microstructure of fracture surface of carbon fibre/geopolymer composites without and after heat treatment at (a) C-W; (b) C-1000; (c) C-1100; (d) C-1200; (e) C- 1300 and (f) C-1400 (He et al., 2010b).

Kuenzel et al. (2013) studied the mechanical properties and microstructure of metakaolin-derived geopolymer mortars containing 50 wt% of silica sand, after exposure to temperatures from 200°C to 1200°C. The team prepared samples using coarse, medium and fine grades of silica sand. Samples were cured for 77 days at

22°C. Kuenzel et al. (2013) report after treating those with temperatures up to 800°C, compressive strength, hardness, and geopolymer microstructure are not greatly affected. In contrast, flexural strength is found to decrease when the temperature reaches 750°C. From 850 °C to 1000°C, the researchers find that the compressive, Vickers hardness and flexural strengths tend to increase because the total porosity decreases as a result of sintering and sample densification. They also report that the size of the sand particles affects the properties of the geopolymers. Fine grade sand leads to more favourable compressive strength results than coarse or medium grades, as the crack width in the geopolymer phase decreases and the cracks tend to heal during sintering if the filler particle size is below 100 µm. However, above 100µ m, the cracks are too large to heal. Figure 2.49 present the compressive strength of geopolymers containing different particles size of sand at different temperatures.

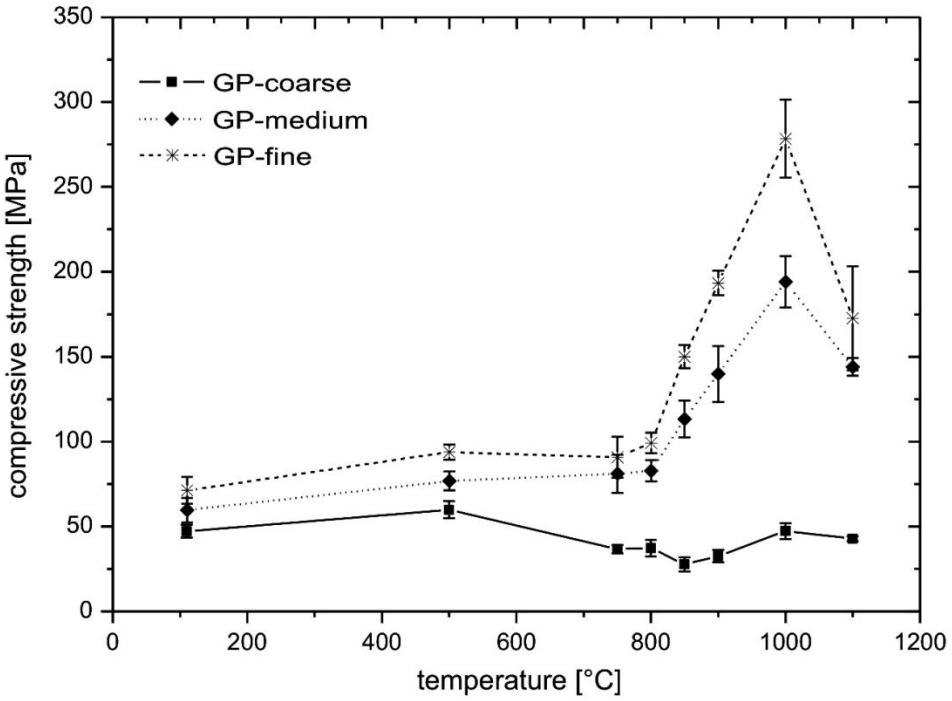


Figure 2.49: Compressive strength of geopolymer/sand mortar samples as a function of the heat treatment temperature (Kuenzel et al., 2013).

3 PUBLICATIONS FORMING PART OF THIS THESIS

3.1 Characterisation of Cotton Fibre-reinforced Geopolymer Composites

ALOMAYRI, **T**., SHAIKH, F. U. A. and LOW, I. M. 2013. Characterisation of cotton fibre-reinforced geopolymer composites. *Composites Part B: Engineering*, 50, 1-6.

Composites: Part B 50 (2013) 1–6

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Characterisation of cotton fibre-reinforced geopolymer composites

T. Alomayri [a], F.U.A. Shaikh [b], I.M. Low [a,*]

[a] Department of Imaging & Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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ABSTRACT

This paper describes the physical, mechanical and fracture behaviour of fly-ash based geopolymer reinforced with cotton fibres (0.3–1.0 wt%). Results show that the appropriate addition of cotton fibres can improve the mechanical properties of geopolymer composites. In particular, the flexural strength and the fracture toughness increase at an optimum fibre content of 0.5 wt%. However, as the fibre content increases, the density of geopolymer composites decreases due to an increase in porosity and tendency of fibre agglomeration.

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1. Introduction

Geopolymers are aluminosilicate inorganic polymers which are formed from polymerisation of aluminosilicates with alkaline solutions. Geopolymers have several desirable attributes which include good mechanical properties and durability [1]. In addition, they are environmentally friendly, being derived from natural materials and because they can be prepared at room temperature they do not emit high levels of carbon dioxide that is associated with the preparation of Portland cement [2,3].

Cements have been reinforced with natural fibres for many years, particularly in developing countries that have used local materials such as bamboo, sisal, jute and coir with some success [4–6]. These natural materials are not only cheap, but their low density and favourable mechanical properties make them attractive alternatives to the synthetic fibre composites used in more industrialised countries [7,8]. Such naturally-occurring materials have environmental advantages since they are both renewable and non-toxic [9,10].

It is well established that the choice of fibres used to reinforce concrete can affect its mechanical properties, as do decisions about how to disperse them in the matrix. The type of fibres, its form, surface properties and matrix properties, all need to be considered [11]. For instance, Rahman et al. [12] found that bamboo fibres can improve the flexural strength of concrete, and Lin et al. [13] also observed a similar improvement in wood-fibre reinforced concrete. Similarly, the use of hemp fibres has been found to improve the fracture toughness of natural fibre-reinforced concrete (NFRC) [14]. Hitherto, no report exists on the use of cotton fibres as reinforcement for geopolymers. The use of cotton fibres has several advantages which include low cost, renewability, and low weight when compared to synthetic fibres.

This paper presents the microstructures, physical and mechanical properties of cotton fibre reinforced geopolymer composites. The motivation of this work was to investigate the feasibility of using renewable cotton fibres to impart improvements in mechanical and fracture properties for geopolymers. Cotton fibre-reinforced geopolymer composites with different fibre contents (0, 0.3, 0.5, 0.7 and 1 wt%) were fabricated and their mechanical properties such as flexural strength, flexural modulus and fracture toughness were evaluated. Synchrotron radiation diffraction (SRD) and scanning electron microscopy (SEM) were used to characterise the phase composition, microstructure, fibre dispersion and failure mechanisms of cotton fibre reinforced geopolymer composites.

2. Experimental investigation

2.1. Materials

Low calcium fly-ash (ASTM class F), collected from the Collie power station in Western Australia, was used as the source material to prepare the geopolymer composites. The chemical composition and the microstructure of fly ash are shown in Table 1 and in Fig. 7f. Alkali resistant cotton fibres with an average length of 10 mm, average diameter of 0.2 mm and density of 1.54 g/cm^3 were used to reinforce the geopolymer matrix. The alkaline

* Corresponding author. Tel.: +61 8 92667544; fax: +61 8 92662377.
E-mail address: j.low@curtin.edu.au (I.M. Low).

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Table 1
Chemical compositions of fly-ash.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
50%	28.25%	13.5%	1.78%	0.89%	0.38%	0.32%	0.46%	1.64%

Table 2
Formulations of mixtures for the fabrication of geopolymer composites.

Sample	Fly ash (g)	NaOH solution (g)	Na_2SiO_3 solution (g)	Added water (g)	Fibre content (wt%)
1	409	41	102	0	0
2	409	41	102	0	0.3
3	409	41	102	0	0.5
4	409	41	102	53	0.7
5	409	41	102	95	1

activator for geopolymerisation was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes with 98% purity were used to prepare the solution. The chemical composition of sodium silicate used was Na_2O 14.7%, SiO_2 29.4% and water 55.9% by mass. An 8 M concentration of sodium hydroxide solution was prepared, and combined with the sodium silicate solution 1 day before mixing.

2.2. Preparation of geopolymer composites

Five samples of geopolymer composites reinforced with 0, 0.3, 0.5, 0.7 and 1 wt% cotton fibre were prepared. Additional water was added to improve the workability and dispersion of cotton fibres in the composite. The formulations of mixtures for the fabrication of geopolymer composites are shown in Table 2.

The geopolymer composites were prepared with an alkaline solution to fly-ash ratio of 0.35. The ratio of sodium silicate to sodium hydroxide solution was fixed at 2.5. The fibres were added slowly to the dry fly ash in a Hobart mixer at low speed until the mix become homogeneous, at which time the alkaline solution was added. This was mixed for 10 min on low speed and another 10 min on high speed. The walls of the mixing container were scraped down to ensure consistency of mix. This procedure was followed for all four test specimens. Each mix was cast in 25 rectangular silicon moulds of 80 mm × 20 mm × 10 mm and placed on a vibration table for 5 min. The specimens were covered with a plastic film and cured at 105 °C for three hours, then rested for 24 h before de-moulding. They were then dried under ambient conditions for 28 days.

2.3. Characterisation

The values of density and porosity were determined to ascertain the quality of geopolymer composite samples. The thickness, width, length and weight were measured in order to determine the density. The calculation of bulk density (D_b) was carried out by using the following equation:

$$D_b = \frac{M}{V} \tag{1}$$

where D_b = bulk density, M = mass of the test specimen, and V = volume of the test specimen.

The value of apparent porosity (D_a) was determined using the Archimedes principle in accordance with the ASTM Standard (C-20) [15] and tap water was used as the immersion water. The apparent porosity (D_a) was calculated using the following equation:

$$D_a = \left(\frac{m_1}{m_2 - m_3}\right)D \tag{2}$$

where m_1, m_2 and m_3 are the mass of the sample weighted in the balance, the mass of the sample hanging on the balance arm in the air and the mass of the sample hanging on the balance arm immersed in water respectively, and D is the density of water at room temperature.

The phase compositions of fly-ash, cotton fibres, geopolymer and composite samples were characterised using synchrotron radiation diffraction (SRD). The collection of SRD data was conducted using the Powder Diffraction beamline at the Australian Synchrotron in Melbourne. The diffraction pattern of each sample was collected using an incident angle of 30° and wavelength of 0.11267 nm or photon energy of 11.0 keV.

The microstructures and the fracture surfaces of fly ash were examined using a Zeiss EVO-40 (Carl-Zeiss, Germany) scanning electron microscope (SEM). Fracture surfaces of geopolymer samples with dimensions of 10 mm × 7 mm × 5 mm were placed in a vacuum desiccator for 2 days to allow complete out-gassing before being mounted on an aluminium stub and coated with a thin layer of platinum prior to examination.

2.4. Mechanical properties

Three-point bend tests were conducted to determine the flexural strength, flexural modulus and fracture toughness of geopolymer composites. Five specimens, measuring 80 mm × 20 mm × 10 mm, were used in each test using a LLOYD Material Testing Machine. The support span was 40 mm with a loading rate of 1.0 mm/min. The flexural strength was calculated using the following equation:

$$\sigma_F = \frac{3}{2}\frac{p_m S}{WD^2} \tag{3}$$

where P_m is the maximum load at crack extension, S is the span of the sample, D is the specimen thickness and W is the specimen width. The flexural modulus was computed using the initial slope of the load–displacement curve, $\Delta P/\Delta X$, using the following formula:

$$E_F \frac{S^3}{4WD^3}\left(\frac{\Delta P}{\Delta X}\right) \tag{4}$$

A crack with a length to width (a/W) ratio of 0.4 was introduced into the specimen using a 0.4 mm diamond blade to evaluate fracture toughness. The fracture toughness (K_{IC}) was calculated as follows [16]:

$$K_{IC} = \frac{p_m S}{WD^{2/3}} f\left(\frac{a}{W}\right) \tag{5a}$$

where p_m is the maximum load at crack extension, S is the span of the sample, D is the specimen thickness, W is the specimen width, a is the crack length and $f(a/W)$ is the polynomial geometrical correction factor given by [16]:

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}\left[1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)\right]}{2(1 + 2a/W)(1 - a/W)^{2/3}} \tag{5b}$$

3. Results and discussion

3.1. Synchrotron radiation diffraction

The synchrotron radiation diffraction (SRD) patterns of commercial fly ash, cotton fibres and of prepared geopolymer reinforced with 0.3, 0.5, 0.7 and 1.0 wt% of cotton fibres are shown in Fig. 1. The crystalline phases present were indexed using Powder Diffraction Files (PDFs) from the Inorganic Crystal Structure Database (ICSD). The diffraction pattern of cotton fibres shows typical characteristic peaks, indicating the presence of cellulose. Fly ash displays peaks caused by the presence of quartz and mullite as well as other crystalline phases. These crystalline phases are not involved in the geopolymerisation reaction, but the amorphous phase generated by coal combustion is actively involved in geopolymerisation reactions. The amorphous phase is crucial for geopolymerisation reactions [17] which lead to the formation of a geopolymer [17,18].

Comparing the SRD spectra of the original fly ash with those of the hardened geopolymeric composites, Fig. 1 indicates that the crystalline phases (quartz, mullite, etc.) originally existed in the fly ash have apparently not been altered by the activation reactions; hence they do not participate in the geopolymerisation reaction. The diffraction patterns of geopolymer composites reinforced with 0, 0.3, 0.5, 0.7 and 1 wt% cotton fibres all showed the sharp peaks of the crystalline phases from fly ash, thus confirming that these phases are neither reactive nor involved in geopolymerisation, but are simply present as inactive fillers in the geopolymer network.

3.2. Density and porosity of geopolymer composites

The density and porosity values of the geopolymer composites after 28 days of curing at ambient temperature are presented in Figs. 2 and 3, respectively. Fig. 2 shows that density decreases as the weight percent of cotton fibre increases. The geopolymer composite reinforced with 1.0 wt% of cotton fibre has the lowest density of 1.8 g/cm^3 whereas the control sample displays the highest value of ~2.0 g/cm^3. These results are in agreement with those obtained by other investigators [19,20]. For instance, the study on bagasse fibre-reinforced cement composite reported that the density values decreased with increase of fibre content [19]. Similarly, in another study by Abdullah et al. [20] on coconut fibre reinforced cement, they reported that density values of cement composites decreased with increasing fibre content.

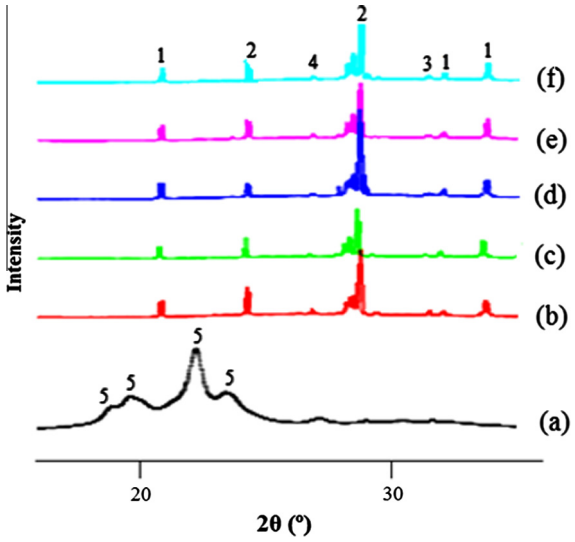

Fig. 1. Synchrotron radiation diffraction patterns of (a) cotton fibres (CF), (b) fly-ash, and geopolymer composite with (c) 0.3 wt% CF, (d) 0.5 wt% CF, (e) 0.7 wt% CF, and (f) 1.0 wt% CF. [Legend: 1 = mullite (PDF 15–776), 2 = quartz (PDF 33–1161), 3 = maghemite (PDF 25–1402), 4 = hematite (PDF 13–534), 5 = cellulose (PDF 00-060-1502)].

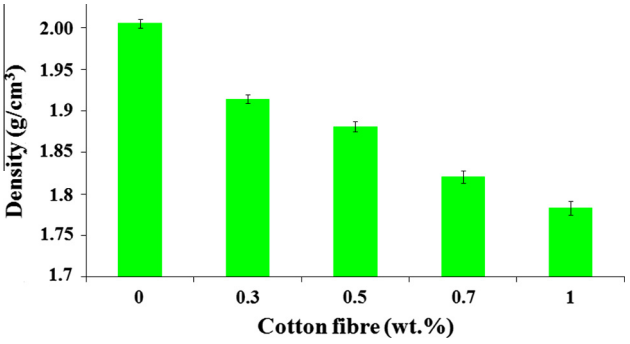

Fig. 2. Density of geopolymer composites as a function of fibre content.

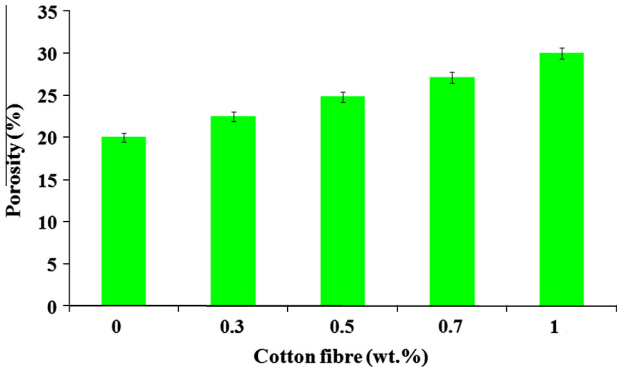

Fig. 3. Porosity of geopolymer composites as a function of fibre content.

The value of porosity increases with increases in the weight percent of cotton fibres as shown in Fig. 3. The lowest value of porosity (20%) is found in the control sample that contained no cotton fibres whereas the composite containing the highest amount of cotton fibre has the highest porosity of 30%.

The effect of the initial water content on density and porosity has perhaps the most important implications in this study. In order to reduce the viscosity of the geopolymer composites with 0.7 and 1.0 wt% of cotton fibres, a high water/fly ash ratio was required, and this caused an increase of porosity in the resulting composites. The addition of extra water results in larger amounts of "free" water that is trapped in inter-granular space or large pores after geopolymerisation and evaporates during curing and extended ageing, leaves large quantities of inter-granular pores in the microstructure [21,22].

The increase in porosity with increasing cotton fibre content may also be explained by the fact of water absorbed by the fibres. It is possible that fibres tend to clump together during mixing, entrapping water-filled spaces that subsequently turn into voids. Thus increased fibre content may enhance the potential for fibre clumping which is undesirable for achieving a uniform microstructure [23].

3.3. Mechanical properties

3.3.1. Flexural strength and modulus

The effects of fibre content on the flexural strength and flexural modulus of cotton fibre-reinforced geopolymer composites are shown in Figs. 4 and 5, respectively. In Fig. 4, experimental results

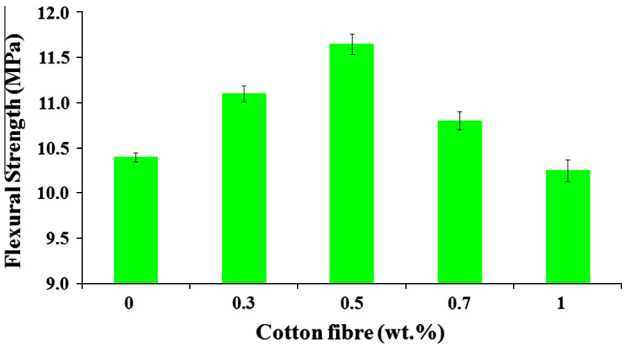

Fig. 4. Flexural strength of geopolymer composites as a function of fibre content.

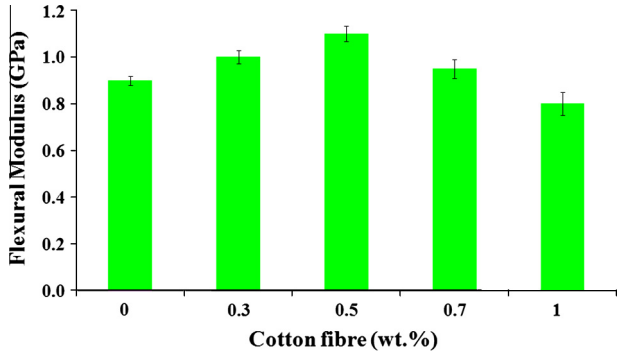

Fig. 5. Flexural modulus of geopolymer composites as a function of fibre content.

indicate that the flexural strength of composites increases initially with increasing cotton fibre content of up to 0.5 wt%, and then decreases thereafter. The enhancement in flexural strength may be ascribed to the good dispersion of cotton fibres throughout the matrix which helps to increase the interaction or adhesion at the matrix/cotton fibre interface. Hence, this permits the optimum operation of stress-transfer from the matrix to the cotton fibres, thus resulting in the improvement of strength properties. However, the flexural strength of composites decreases when fibre content increases to more than 0.5 wt% (see Fig. 7d–e) where a high content of cotton fibres inhibits the non-homogeneity within the matrix such that agglomerations are formed which degrade the interfacial adhesion between the fibre and the matrix. In addition, these agglomerations may act as stress concentrators to cause reductions in flexural strength [24].

It was observed that increasing the content of cotton fibre caused discernible increase in matrix viscosity, which in turn allowed residual air bubbles to be introduced either through mixing or by being trapped in the geopolymer during pouring into the mould. These conditions may be implicated in sample failure at relatively low stress. A lower loading of cotton fibres offers less potential for microvoid formation and more uniform dispersion; both contribute to strength improvement.

The flexural strength of the neat geopolymer paste increased from 10.4 to 11.7 MPa after the addition of 0.5 wt% cotton fibres. However, adding more cotton fibres (0.7 and 1.0 wt%) led to a reduction in strength.

The flexural modulus of geopolymer composites are shown in Fig. 5, and indicate similar trends to flexural strength values. The addition of 0.5 wt% cotton fibres in the geopolymer matrix increases the flexural modulus over plain geopolymer, but this trend reverses, reducing to 0.95 and 0.80 GPa, with the addition of 0.7 and 1.0 wt% cotton fibres. Two reasons may account for this observation: (1) increased viscosity, voids, and poor dispersion due to high cotton fibre content; and (2) presence of high proportion of other constituents (e.g. quartz and mullite) which act as inactive fillers and thus leads to insufficient geopolymer binders. The presence of quartz in a source material is particularly undesirable when designing geopolymers because it can cause microcracking, which reduces the strength of the material. This problem becomes more significant as the particle size of the quartz increases [18]. The presence of small amount of cotton fibres in the geopolymer matrix serves to counteract this, thereby increasing the flexural strength and flexural modulus of the geopolymer composites over plain geopolymer. The optimum content of cotton fibres in geopolymer composites is 0.5 wt%.

3.3.2. Fracture toughness

The effect of cotton fibre content on the facture toughness of geopolymer composites is presented in Fig. 6. Cotton fibres play a significant role in enhancing the facture toughness of the matrices through several energy-absorbing functions such as fibre rupture, fibre/matrix interface debonding, fibre pull-out and fibre-bridging which slow crack propagation and therefore increase fracture energy [25–29]. The fracture toughness of geopolymer reinforced with 0.5 wt% cotton fibres increases by 1.12 MPa $m^{1/2}$ over neat geopolymer. This significant enhancement in facture toughness is due to fibre pull-out, fibre fracture and fibre-bridging, as clearly shown in the SEM images of Fig. 7b–e.

Some short fibres, such as poly vinyl alcohol (PVA) and basalt, have previously been employed to improve the mechanical performance of geopolymers because they provide some control of cracking and increase the fracture toughness of a brittle matrix by their bridging action during both micro and macro-cracking. It has been reported that short PVA fibres with an optimum volume fraction of 1.0% ameliorated the brittle properties of ash-based geopolymer [30]. Similarly, Dias and Thaumaturgo [31] investigated fracture toughness of geopolymeric concretes reinforced with basalt fibres and found that geopolymeric concretes with 0.5–1.0 wt% basalt fibres showed higher fracture toughness than Portland cement concretes. In another study, Li et al. [32] reported that the addition of basalt fibres with an optimum volume fraction of 0.3% significantly improved deformation and energy absorption capacities of geopolymeric concrete.

However, the fracture toughness decreased with increasing fibre content due to the poor dispersion of cotton fibres in the slurry. The dispersion of cotton fibre in the geopolymer matrix has a considerable influence on the properties of the fresh mix, in particular on workability. The addition of 0.7 and 1.0 wt% cotton fibres resulted in a reduction in the consistency of the matrix. This had to be compensated for by an increase in the water content of the

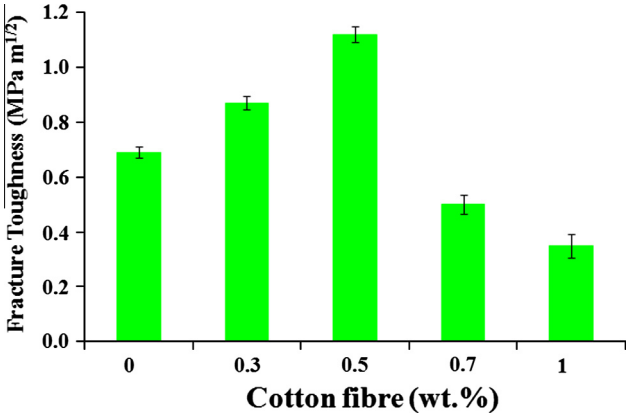

Fig. 6. Fracture toughness of geopolymer composites as a function of fibre content.

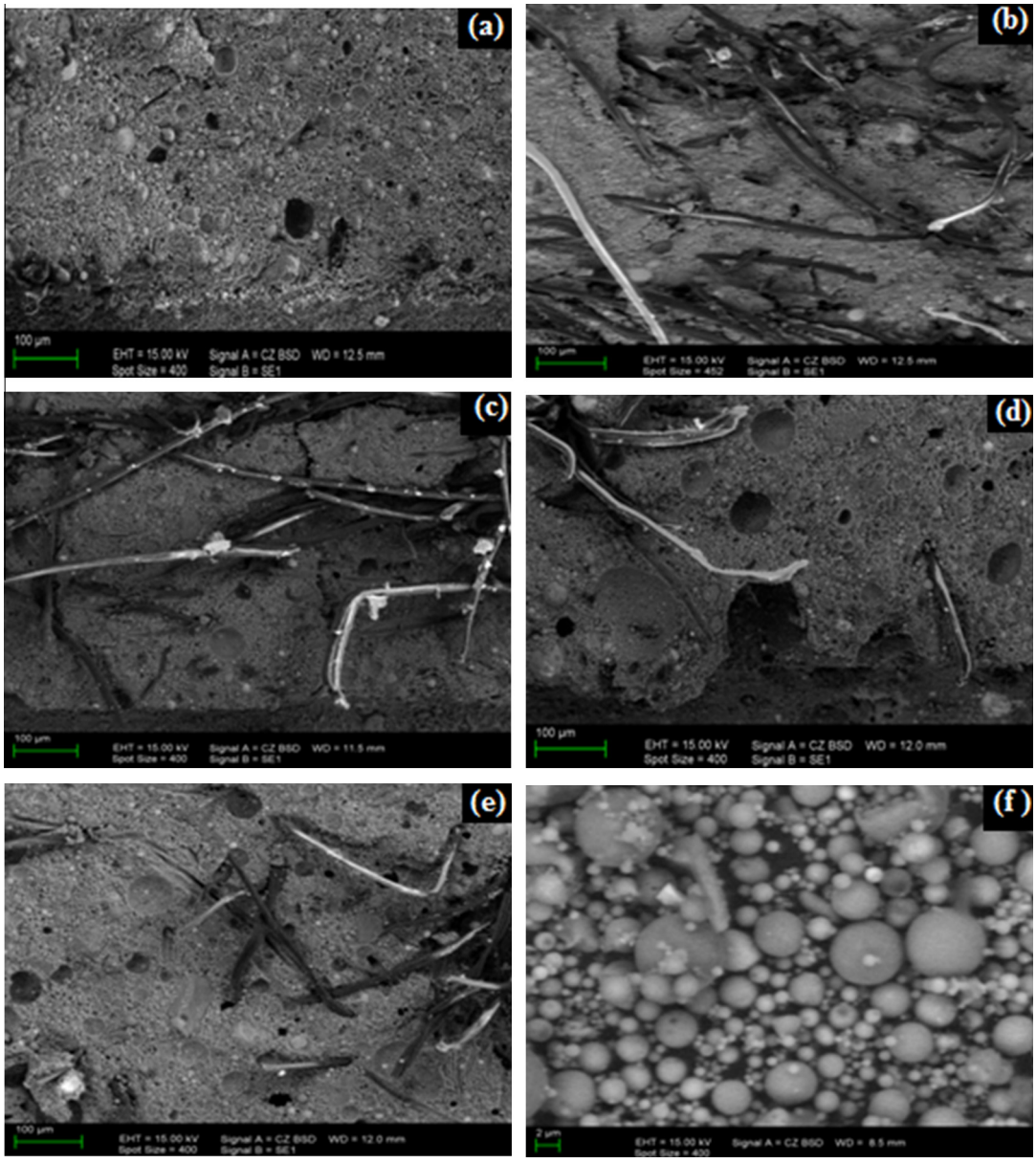

Fig. 7. SEM images showing the fracture surfaces of geopolymer composites reinforced with varying content of cotton fibres (a) 0, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 1.0 wt%. The microstructure of as-received fly-ash is shown in (f).

mix. Increasing water content to overcome such a problem may lead to other adverse effects, such as an increase in porosity and microcracking. These limitations usually lead to the reduction in bonding at the fibre–matrix interface, which results in lower stress transferred from the matrix to the fibres.

In short, optimum enhancements in mechanical and fracture properties of geopolymer composites could be achieved at 0.5 wt% cotton fibres. Possible applications for these cotton fibre-reinforced geopolymer composites may include slabs or shingles for siding, certain types of roofing and some interior uses in the construction industry. They may also be used for other applications such as pipes and cooling towers.

4. Conclusions

This study indicates that cotton fibres can be used as reinforcement in the development of geopolymer composites. Increasing the content of cotton fibres (up to 0.5 wt%) increases the flexural strength, flexural modulus and fracture toughness of the composites. However, further increase in cotton fibre content beyond 0.5 wt% caused a reduction in the mechanical properties due to poor workability which led to formation of voids and fibre agglomerations. The density of geopolymer composites decreases with an increase in fibre content. SEM results show an increase in energy dissipation events for composites with lower fibre content when compared to their higher fibre content counterparts. Composites containing lower fibre contents show better fibre matrix interfacial bonding than those with higher fibre contents.

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3.2 Synthesis and Characterization of Mechanical Properties in Cotton Fiber-reinforced Geopolymer Composites

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Synthesis and characterization of mechanical properties in cotton fiber-reinforced geopolymer composites

T. Alomayri, I.M. Low *

Department of Imaging & Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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ABSTRACT

Geopolymers are inorganic aluminosilicate materials that possess relatively good mechanical properties and desirable thermal stability but they exhibit failure behavior similar to brittle solids. This limitation may be remedied by fiber reinforcement to improve their strength and toughness. This paper describes the synthesis of cotton fiber-reinforced geopolymer composites and the characterization of their mechanical properties. The effects of cotton fiber content (0–1.0 wt.%) and fiber dispersion on the mechanical characteristics of geopolymer composites have been investigated in terms of hardness, impact strength and compressive strength. A fiber content of 0.5 wt.% was observed for achieving optimum mechanical properties in these composites.

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1. Introduction

Inorganic aluminosilicate Portland cements are used in many building and construction applications because of their good mechanical performance. However, the emission of greenhouse gases associated with their manufacture is a serious problem. In recent years, a new class of environment-friendly and sustainable inorganic aluminosilicate polymers (also known as geopolymers) have emerged as an alternative to cements. These inorganic compounds can be cured and hardened at near-ambient temperatures to form materials that are effectively low-temperature ceramics with the typical temperature resistance and strength of ceramics [1,2]. However, despite their many desirable attributes such as relatively high strength, elastic modulus and low shrinkage, geopolymers suffer from brittle failure like most ceramics. This limitation may be readily overcome through fiber reinforcement as in high performance polymer-matrix composites. As in thermosetting polymers, the low synthesis temperatures of geopolymers renders them particularly suitable as matrices for a range of fibers including organic fibers, with setting times and mechanical properties comparable to Portland cement [3]. Hitherto, the most common fiber reinforcement used in geopolymer composites is based on carbon, basalt and glass fibers, but other inorganic fibers such as silicon carbide, alumina, mullite or boron can be utilized [4–6]. Maximum flexural strengths of >500 MPa have been reported by several authors for unidirectional carbon fiber-reinforced geopolymer composites [4,7] and desirable non-brittle fracture was observed when short carbon fibers were used [8].

Current concerns over the environment and climate change have also given rise to an increasing interest in replacing the synthetic fibers currently used in geopolymer composites or other brittle matrices with natural plant fibers. Plant fibers cost less, have low density and display good mechanical properties when compared with industrial fibers [9–11]. Investigations on natural fibers such as bamboo, sisal, jute and cellulose have revealed desirable effects on the mechanical and physical properties of brittle organic and inorganic matrices. For instance, the mechanical and fracture properties of epoxy resin have been significantly improved as a result of cellulose fiber reinforcement [12–14]. Similarly, Rahman et al. [15] found that bamboo fibers are effective in improving the flexural strength of concrete, and Lin et al. [16] observed a similar desirable effect in wood fiber-reinforced concrete. In another study, Li et al. [17] found that hemp fibers enhanced the toughness of concrete. Wool fibers have also been successfully used in reinforcing geopolymer composites with concomitant improvements in mechanical and fracture properties [18]. However, the use of cotton fibers as reinforcement for geopolymers has not been investigated. The use of cotton fibers has several advantages, which

* Corresponding author. Tel.: +61 8 9266 4759; fax: +61 8 9266 2377.
E-mail addresses: j.low@curtin.edu.au, low246@gmail.com (I.M. Low).

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include low cost, renewable, and low weight when compared with synthetic fibers.

In this paper, we have synthesized geopolymer composites reinforced with short cotton fibers and characterized their mechanical properties in terms of hardness, compressive strength and impact strength. The effect of fiber contents (0.3, 0.5, 0.7 and 1 wt.%) and their dispersion on mechanical properties were investigated. Scanning electron microscopy (SEM) was used to examine the microstructures of fly-ash and the resultant composites.

2. Experimental procedure

2.1. Materials

Low calcium fly-ash (ASTM class F) [19] collected from the Collie power station in Western Australia was used as the source material to prepare the geopolymer composites. The chemical compositions of fly-ash are given in Table 1. Alkali resistant cotton fibers with an average length of 10 mm, average diameter of 0.2 mm, density of 1.54 g/cm^3, tensile strength of 400 MPa, and Young's modulus of 4.8 GPa were used to reinforce the geopolymer composites. The alkaline activator for geopolymerization was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes with 98% purity were used to prepare the solution. The chemical composition of sodium silicate is Na_2O 14.7%, SiO_2 29.4% and water 55.9% by mass.

2.2. Sample preparation

To prepare the geopolymer composites, an alkaline solution to fly-ash ratio of 0.35 was used and the ratio of sodium silicate solution to sodium hydroxide solution was fixed at 2.5. Four samples of geopolymer composites reinforced with 0.3, 0.5, 0.7 and 1 wt.% cotton fibers were prepared. Additional water was added to improve the workability and dispersion of cotton fibers in the composites.

An 8 M concentration of sodium hydroxide solution was prepared and it was combined with the sodium silicate solution 1 day before mixing. The fibers were added slowly to the dry fly-ash in a Hobart mixer at a low speed until the mix became homogeneous at which time the alkaline solution was added. This was mixed for 10 min on low speed and for another 10 min on high speed. The walls of the mixing container were scraped down to ensure consistency of the mix. This procedure was followed for all the four test specimens. The mix was cast in 25 rectangular silicon molds of 80 mm × 20 mm × 10 mm and placed on a vibration table for 5 min. The specimens were covered with a plastic film and cured at 105 °C for 3 h, then rested for 24 h before demolding. They were then dried under ambient conditions for 28 days.

2.3. Synchrotron radiation diffraction (SRD)

The Powder Diffraction beamline at the Australian Synchrotron was used to collect the diffraction patterns of fly-ash, cotton fibers and the geopolymer composites. The diffraction pattern of each sample was collected using an incident angle of 3° and wavelength of 0.11267 nm or photon energy of 11.0 keV over the 2θ range of 10°–40°.

Table 1
Chemical composition of fly-ash.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
50%	28.25%	13.5%	1.78%	0.89%	0.38%	0.32%	0.46%	1.64%

LOI: Loss on Ignition.

2.4. Scanning electron microscopy (SEM)

A Zeiss Evo 40XVP scanning electron microscope was used to examine the microstructures of fly-ash and geopolymer composites. The specimens were mounted on aluminum stubs using carbon tape, and then coated with a thin layer of platinum to prevent charging before the observation.

2.5. Rockwell hardness

The hardness of geopolymer composites was measured using an Avery Rockwell hardness tester at hardness scale *H*. Before measurement, the surfaces of test samples were polished using a Struers Pedamat polisher finishing with 10-μm grade diamond paste.

2.6. Compressive strength

The measurement of compressive strength testing was conducted using the methodology of ASTM C39 for concrete specimens. Cylindrical samples with a 2:1 height to diameter ratio were cut with a precision diamond blade such that the ends were perpendicular to the sides. A minimum of five samples were tested. Following demolding, the samples were air dried for 1 day before the compressive test. An EZ50 (Lloyd Instruments Ltd., West Sussex, UK) was used to apply a constant stress rate of 0.25 MPa/s, after a 50 N preload, until failure.

The compressive strength (C) of a sample was calculated using the following formula:

$$C = \frac{P}{A} \tag{2}$$

where P is total load on the sample at failure and A is calculated area of the bearing surface of the specimen.

2.7. Impact strength

Rectangular bars with dimensions 80 mm × 20 mm × 10 mm were prepared for Zwick Charpy impact testing to evaluate the impact strength of geopolymer composites. A pendulum hammer with 1.0 J was used during the test to break the samples. Unnotched samples were used to compute the impact strength (σ_i) using the following formula:

$$\sigma_i = \frac{E}{A} \tag{1}$$

where E is the impact energy to break a sample with a ligament of area A.

3. Results and discussion

3.1. Synchrotron radiation diffraction

The synchrotron radiation diffraction (SRD) patterns of commercial fly-ash, cotton fibers and prepared geopolymer reinforced with 0.3, 0.5, 0.7 and 1.0 wt.% of cotton fibers are shown in Fig. 1. The diffraction pattern of cotton fibers shows typical characteristic peaks, indicating the presence of cellulose. Fly-ash displays peaks due to the presence of quartz and mullite as well as other crystalline phases. These crystalline phases are not involved in the geopolymerization reaction, but the amorphous phase generated by coal combustion is actively involved in geopolymerization reactions [20]. Rickard et al. [21] have recently shown that amorphous aluminosilicates in fly-ash are reactive during the formation of a geopolymer.

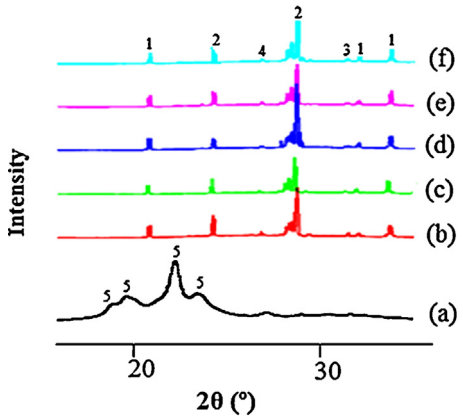

Fig. 1. Synchrotron radiation diffraction patterns of (a) cotton fibers (CF), (b) fly-ash, and geopolymer composite with (c) 0.3 wt.% CF, (d) 0.5 wt.% CF, (e) 0.7 wt.% CF, and (f) 1.0 wt.% CF. [Legend: 1 = mullite, 2 = quartz, 3 = maghemite, 4 = hematite, 5 = cellulose].

Comparing the SRD spectra of the original fly-ash with those of the hardened geopolymeric materials (see Fig. 2) indicates that the crystalline phases (quartz, mullite, etc.) originally existing in the fly-ash have apparently not been altered by the activation reactions; hence they do not participate in the geopolymerization reaction. The diffraction patterns of geopolymer reinforced with 0, 0.3, 0.5, 0.7 and 1 wt.% cotton fibers showed the sharp peaks of the crystalline phases from fly-ash, thus confirming that these phases are neither reactive nor involved in geopolymerization but are simply present as inactive fillers in the geopolymer network.

3.2. SEM observation

The SEM micrographs of fly-ash and geopolymer composites loaded with fiber content of 0.5 wt.% are shown in Figs. 2 and 3. Fig. 2 shows the microstructure of the original fly-ash before being activated with the alkaline activator. As seen in the figure, the fly-ash consists of spherical particles of different sizes. Some particles may contain smaller particles in their interior [22]. The surface texture of fly-ash particles appears to be smooth [23]. The surface of the fly-ash includes the existence of some quartz particles or some vitreous unshaped fragments [24].

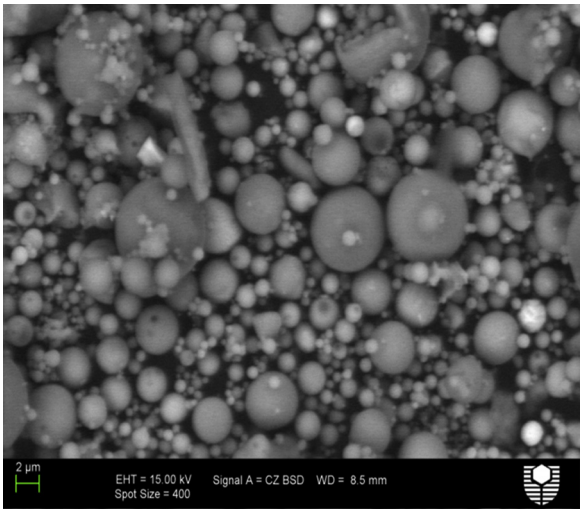

Fig. 2. SEM micrograph showing the typical microstructure of as-received fly-ash. SEM, Scanning electron microscopy.

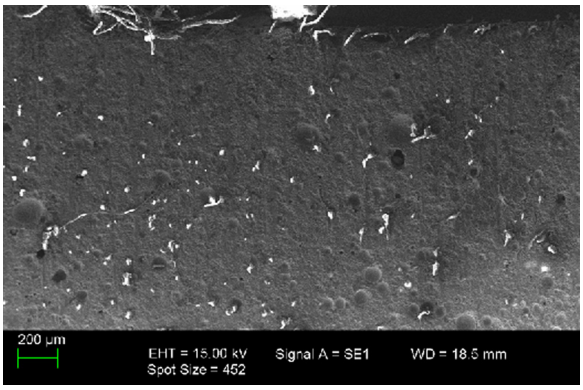

Fig. 3. SEM micrograph showing the typical microstructure of geopolymer composite reinforced with 0.5 wt.% cotton fibers. SEM, Scanning electron microscopy.

Fig. 3 shows that at 0.5 wt.% cotton fiber, the fibers are distributed homogeneously within the matrix. The uniformity of cotton fiber distribution in the matrix plays crucial roles in governing the properties of the composites. To gain advantageous properties, the following factor should be considered during fabrication of cotton fiber-reinforced geopolymer composites.

3.3. Hardness of geopolymer composites

The effect of cotton fiber content on the hardness of the cotton fiber-reinforced geopolymer composites is presented in Fig. 4. The hardness of geopolymer reinforced with 0.5 wt.% cotton fiber increased from 70 to 93 Rockwell hardness H (HRH) relative to the neat geopolymer. This significant enhancement in hardness is due to distribution of the test load on the fibers, which decreased the penetration of the test ball to the surface of the composite material and consequently raising the hardness of this material [25].

However, the hardness decreased with increasing fiber content due to the poor dispersion of cotton fibers in the slurry. The addition of 0.7 and 1.0 wt.% cotton fibers resulted in a reduction in the consistency of the matrix as well as low wettability between the fibers and the paste, and the fibers could be separated from the paste easily. This had to be compensated for by an increase in the water content of the mix. Increasing water content to overcome such a problem may lead to low hardness. The research conducted by Kunal [26] revealed that higher water content results in samples with low hardness. Because a higher than normal water content was needed for the samples to be flexible, the strength of the samples was reduced.

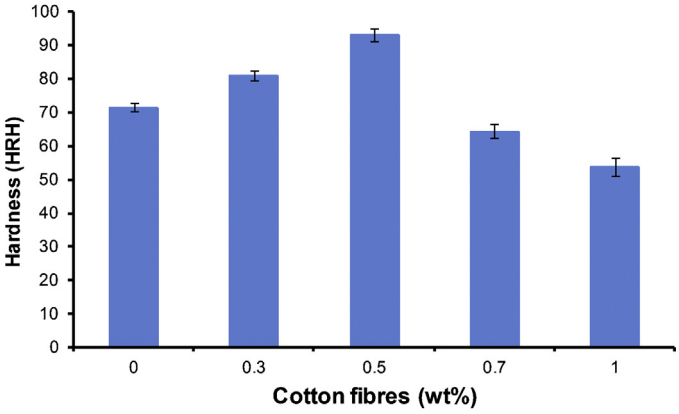

Fig. 4. Hardness of geopolymer composites as a function of fiber content.

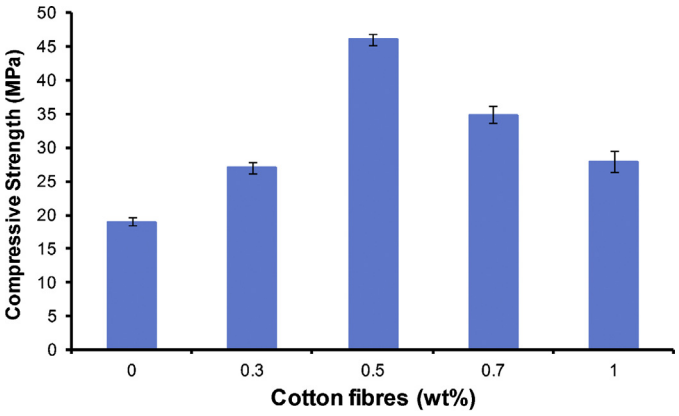

Fig. 5. Compressive strength of geopolymer composites as a function of fiber content.

Similarly, this decrease has been reported by other researchers when dealing with natural fiber based composites. Anup [27] reported that with increasing flax fiber content, the hardness value of high-density polyethylene/flax fiber composites and polypropylene/flax fiber composites decreased. Khairaih and Khairul [28] also reported decreasing hardness values with increasing fiber content when they worked on polyurethane and empty fruit bunch blend composites. They concluded that the decrease was due to the inability of the matrix to encapsulate the fiber strands.

3.4. Compressive strength of geopolymer composites

The 28-day average values of compressive strength of the composites are given in Fig. 5 and their corresponding stress/strain curves are shown in Fig. 6. It can be seen that geopolymer composite with 0.5% cotton fibers had the highest compressive strength. This is attributed to the possibility that the higher loads transferred from the matrix to the fibers, thus resulting in a higher load carried by the fibers. Another reason for such favorable behavior could be good dispersion of cotton fibers throughout the matrix that increases the bonding strength between the fiber and the matrix. From the stress–strain curves in Fig. 6, it is interesting to note that geopolymer composites displayed some non-linearity during fracture whereas a linear fracture behavior was observed for geopolymer. This implies the feasibility of using cotton fibers to mitigate the brittle failure in geopolymers.

However, the geopolymer composites cast with cotton fiber in the amount of about 0.7 and 1% fiber content by weight yielded a weak compressive strength. The reason for the reduction in compressive strength instead of an improvement with the addition of cotton fibers may be attributed to a greater probability of these fibers balling together and leaving voids in the matrix [29].

Other reasons for this weakness may be that the cotton fibers had absorbed too much water, denying the geopolymer around the fibers enough water for geopolymerization, which in turn decreased the bonding strength between the fiber and the matrix.

Similar results were reported by Li et al. [17], who investigated the compressive properties of hemp fiber-reinforced concrete. They found that compressive strength improves slightly when the fiber content by weight is lower than 0.6%, and continuously decreases when the fiber content is greater than this value.

In the present study, the compressive strength of the neat geopolymer paste increased from 19.1 to 46.0 MPa after the addition of 0.5 wt.% cotton fibers. However, adding more cotton fibers (0.7 and 1.0 wt %) led to a reduction in compressive strength.

3.5. Impact strength of geopolymer composites

The impact strength of fiber-reinforced polymer is governed by the matrix fiber interfacial bonding, and the properties of the matrix and the fibers. When the composites undergo a sudden force, the impact energy is dissipated by the combination of fiber pull out, fiber fracture and matrix deformation [30].

The effects of fiber content on the impact strength of cotton fiber-reinforced geopolymer composites are plotted in Fig. 7. It can be seen that the impact strength of the composites increases with an increase in cotton content of up to 0.5 wt.%, and then it decreases thereafter. The enhancement in impact strength may be ascribed to the good dispersion of cotton fibers throughout the matrix, which helps to increase the interaction or adhesion at the matrix/cotton fiber interface. In addition, the increases in impact strength as fiber content increases are due to the increase in fiber pull out and fiber breakage [31]. Hence, this permits the optimum operation of stress-transfer from the matrix to the cotton fibers, thus resulting in an improvement of strength properties.

However, the impact strength of composites decreases when fiber content increases to >0.5 wt.%. This reduction in impact strength at higher content of cotton fiber was due to the formation of fiber agglomerates and voids as a result of increased system viscosity due to the presence of the cotton fiber, which in turn reduced the fiber matrix adhesion.

The impact strength of the neat geopolymer paste increased from 1.9 to 4.5 kJ/m^2 after the addition of 0.5 wt.% cotton fibers. However, adding more cotton fibers (0.7 and 1.0 wt %) led to a reduction in strength.

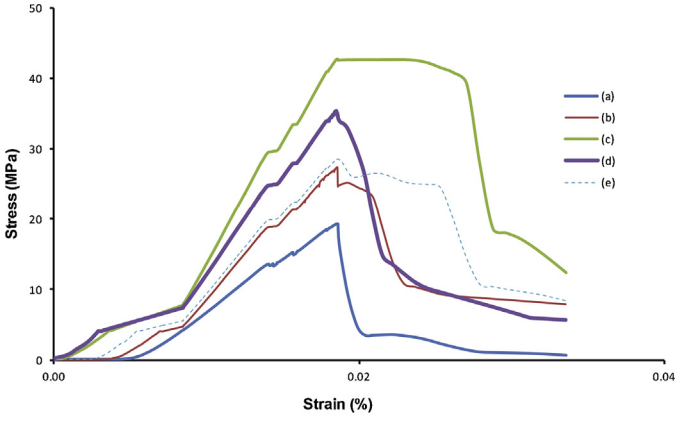

Fig. 6. Typical stress–strain curves of geopolymer composites with various cotton fiber contents (a) 0 wt.%, (b) 0.3 wt.%, (c) 0.5 wt.%, (d) 0.7 wt.%, and (e) 1.0 wt.%.

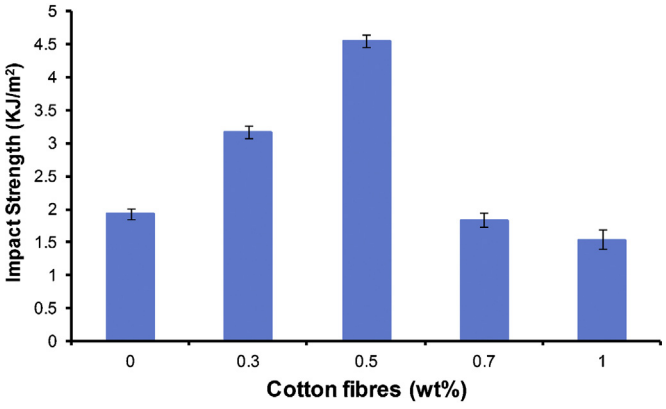

Fig. 7. Impact strength of geopolymer composites as a function of fiber content.

4. Conclusions

Geopolymer composites reinforced with cotton fibers have been fabricated and characterized. Optimum enhancements in hardness, compressive strength and impact resistance were achieved for composites containing up to 0.5 wt.% cotton fibers. However, further increase in cotton fiber content beyond 0.5 wt.% led to fiber agglomerations with a concomitant reduction in mechanical properties by virtue of increased viscosity, voids formation and poor dispersion of fibers within the matrix.

Conflict of interest statement

The authors declare that there are no conflicts of interest.

Acknowledgements

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3.3 Thermal and Mechanical Properties of Cotton Fabric-reinforced Geopolymer Composites

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Thermal and mechanical properties of cotton fabric-reinforced geopolymer composites

T. Alomayri · F. U. A. Shaikh · I. M. Low

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Abstract As natural fibres, cotton fabrics (CF) offer good opportunities as reinforcement material for geopolymer composites as they have good intrinsic mechanical properties. This article presents thermal and mechanical properties of CF-reinforced geopolymer composites containing up to 4.1 wt% CF. Thermo-gravimetric analysis was conducted to characterise their thermal performance and their mechanical properties, such as flexural strength, fracture toughness, flexural modulus and impact strength were evaluated. Results show that the enhancement of mechanical properties was achieved at an optimum fibre content of 2.1 wt%. Results of thermal analysis show that fly-ash based geopolymer can prevent the degradation of cotton fabric at elevated temperatures.

Introduction

The use of fibres as reinforcement in cement is essential in order to improve its physical and mechanical properties. In particular, the use of short fibres as reinforcement of cementitious compounds offers physical and mechanical advantages. However, their use can be limited due to fibre damage, agglomeration of fibres and the generation of voids, which compromise the quality of the composite [1–3].

Recently, the utilization of continuous fibres, instead of short fibres, for reinforcement has shown promise in various applications, and researchers have focused their attention on continuous fibre-reinforced cement composites, with very promising results [4–9]. However, few of these published studies considered the use of continuous fibres or fabrics to reinforce geopolymers.

Geopolymers are a new class of environmentally-friendly and sustainable inorganic aluminosilicate polymers that have emerged as an alternative to cements. These inorganic compounds are effectively low-temperature ceramics, with typical temperature resistance and strength of ceramics [10, 11]. However, despite their many desirable attributes, such as relatively high strength, elastic modulus and low shrinkage, geopolymers suffer from brittle failure. This limitation may be readily overcome with fibre reinforcement, as in polymer–matrix composites [12, 13, 18]. Hitherto, the use of carbon, basalt and glass fibres are most common for geopolymer composites [14–16]. However, a little study has been reported on the use of natural fibres. Natural fibres have special advantages when compared to their synthetic counterparts, where the former represents an environmentally friendly alternative, with lower density, lower cost, non-toxicity, ease of processing, renewability and recyclability [17, 18]. In addition, the use of natural fibres in geopolymer composites has the potential to produce materials with higher specific strength and specific modulus, due to their lower density.

Upto date, no reference has been made to the use of cotton fabric as reinforcement in geopolymer matrix. This article reports the use of cotton fabric to reinforce the geopolymer matrix, and considers the viability of developing a green composite material, using geopolymer as the

T. Alomayri · I. M. Low (✉)
Department of Imaging and Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
e-mail: j.low@curtin.edu.au

T. Alomayri
Department of Physics, Umm Al-Qura University, Mecca 21955, Saudi Arabia

F. U. A. Shaikh
Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

matrix and cotton fabric as the reinforcement. The cotton fabric reinforced geopolymer composites were subjected to bending and impact tests, in order to determine their flexural strength, flexural modulus, fracture toughness and impact strength. Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to investigate their thermal behaviour, micro-structure and failure mechanisms. Results suggest that this is a promising area of investigation, adding significantly to the body of literature on natural and green alternatives to concrete.

Experimental procedure

Materials

Cotton fabric (CF) of 30 cm × 7.5 cm was used as reinforcement for the fabrication of geopolymer composites. Low calcium fly-ash (ASTM class F), collected from the Collie power station in Western Australia, was used as the source material of the geopolymer matrix. The chemical composition of fly-ash is shown in Table 1. Alkali resistant cotton fibres with an average diameter of 0.2 mm, density of 1.54 g/cm^3, tensile strength of 400 MPa and Young's modulus of 4.8 GPa were used to reinforce the geopolymer composites. The alkaline activator for geopolymerization was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes with 98 % purity were used to prepare the solution. The chemical composition of sodium silicate is 14.7 % Na_2O, 29.4 % SiO_2 and 55.9 % water by mass.

Sample preparation

To cast the composite samples, five wooden moulds with open tops were prepared, and greased to avoid the samples sticking during de-moulding. The fabric was pre-dried for 60 min at 70 °C. An 8-molar concentration of sodium hydroxide solution was prepared and combined with the sodium silicate solution 1 day before mixing. The fly ash and alkaline solution were mixed in a Hobart mixer at a low speed for 10 min, and for another 10 min at high speed. A thin layer of geopolymer paste was spread in the wooden mould, and the first layer of CF was carefully laid on that layer. The fabric was then covered by another layer of geopolymer paste, and the process repeated for desired number of CF layers. Each specimen contained a different number of CF layers (see Table 3). For each specimen the final layer was geopolymer paste, and the alkaline solution to fly ash ratio was kept 0.35, whereas, the ratio of sodium silicate solution to sodium hydroxide solution was kept 2.5. The formulation of matrix for the fabrication of geopolymer composites are shown in Table 2. The specimens were covered with plastic film and cured at 105 °C for 3 h in the oven, then rested for 24 h before de-moulding. They were then dried under ambient conditions for 28 days.

To investigate the effect of fibre content on the physical and mechanical properties of cotton fabric-reinforced geopolymer composites (CFG), samples with different geopolymer binder and CF reinforcement percentages were fabricated, as shown in Table 3.

Density and porosity

Density and porosity tests were performed to determine the quality of each geopolymer composite sample. The values of bulk density (D) and apparent porosity (P_s) were determined in accordance with the ASTM Standard (C-20) [19]. After 28 days of drying, five samples from each composite were oven-dried at a temperature of 105 °C for 24 h and weighed; these weights were determined as the dry weight, W_d. The samples were then immersed in water for 24 h and weighed while still in water; the resulting weight is denoted as W_w. The density of water was assumed as 1.0 g/cm^3. Finally, the saturated sample was weighed in air and denoted as W_a. The bulk density (D) and apparent porosity (P_s) were calculated using the following equations:

$$D = \frac{W_d}{W_a - W_w} \tag{1a}$$

$$P_s = \frac{W_a - W_d}{W_a - W_w} \times 100 \tag{1b}$$

Thermogravimetric analysis (TGA)

The thermal behavior of the composites was determined by taking 10 mg solid samples, and using a thermogravimetric analyzer (TGA) from 50 to 800 °C at a heating rate of 10 °C/min under atmospheric condition.

Flexural strength and flexural modulus

Rectangular bars with a length of 40 mm were cut from the fully cured samples and subjected to three-point bend tests,

Table 1 Chemical composition of fly-ash

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
50 %	28.25 %	13.5 %	1.78 %	0.89 %	0.38 %	0.32 %	0.46 %	1.64 %

Table 2 Formulation of matrix for the fabrication of geopolymer composites

Sample	Fly ash (wt %)	NaOH solution (wt %)	Na_2SiO_3 solution (wt %)
CFG0	74.1	7.4	18.5
CFG2	74.1	7.4	18.5
CFG3	74.1	7.4	18.5
CFG4	74.1	7.4	18.5
CFG6	74.1	7.4	18.5

Table 3 Formulations of samples

Sample	Fabric layers	Fabric mass (g)	Fibre content (wt %)
CFG0	0	0	0
CFG2	2	11.4	1.4
CFG3	3	17.2	2.1
CFG4	4	22.8	2.8
CFG6	6	34.2	4.1

to evaluate their flexural strength and flexural modulus. A LLOYD Material Testing Machine (50 kN capacity) with a displacement rate of 1.0 mm/min was used to perform the tests. Five specimens of each composition were tested. The flexural strength (σ_F) was determined using the following equation:

$$\sigma_F = \frac{3}{2}\frac{P_m S}{BW^2} \tag{2}$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width and W is the specimen thickness (depth).

Values of the flexural modulus E_F were computed using the initial slope of the load–displacement curve, $\Delta P/\Delta X$, using the following formula:

$$E_F = \frac{S^3}{4BW^3}\left(\frac{\Delta P}{\Delta X}\right) \tag{3}$$

Impact strength

A Zwick Charpy impact tester with a 1.0 J pendulum hammer was used to determine the impact strength. Five bars of 40 mm long were used. The impact strength (σ_i) was calculated using the following equation [18]:

$$\sigma_i = \frac{E}{A} \tag{4}$$

where E is the impact energy required to break a sample with a ligament of area A.

Fracture toughness

Rectangular bars of 80 mm long and cross-sectional dimension of 20 × 20 mm were used in fracture toughness measurements. A crack with a length to thickness (depth) (a/W) ratio of 0.4 was introduced into the specimen using a 0.4 mm diamond blade, to evaluate the fracture toughness. The fracture toughness K_{IC} was calculated using the equation proposed by Low et al. [18]:

$$K_{IC} = \frac{P_m S}{BW^{3/2}} f\left(\frac{a}{W}\right) \tag{5a}$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width, W is the specimen thickness (depth), a is the crack length and $f(a/W)$ is the polynomial geometrical correction factor given by [18]:

$$f(a/W) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \tag{5b}$$

Microstructure examination

Scanning electron microscopy (SEM) imaging was carried out using a Tescan Lyra machine. The SEM investigation was carried out in detail on the fractured surfaces of the CFGs. Specimens were coated with a thin layer of gold before observation by SEM in order to avoid charging.

Results and discussion

Density and porosity

Measured density and porosity of all composites are shown in Table 4. As the cotton fibre weight increased, the geopolymer composite density decreased. However, an increase in the fibre weight of composites caused a gradual increase in porosity. This increase may be the result of voids becoming trapped beneath the CF sheets during casting, creating higher porosity, and thus leading to poor adhesion between the fibre and matrix. These values closely agree with earlier experimental results by the authors [3].

Thermal properties

Thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability of the composites. The thermograms of pure geopolymer, geopolymer composite and

Table 4 Density and porosity values of CFGs

Sample	Fibre content (wt %)	Density (g/cm^3)	Porosity (%)
CFG0	0	2.02 ± 0.03	21.1
CFG2	1.4	1.84 ± 0.02	24.8
CFG3	2.1	1.76 ± 0.02	26.2
CFG4	2.8	1.68 ± 0.03	29.6
CFG6	4.1	1.59 ± 0.05	32.6

cotton fibre are shown in Fig. 1. The thermogram of geopolymer binder shows weight loss from 50 to 300 °C, due to the dehydration of physically adsorbed water. Above 300 °C, the weight loss is attributed to the dehydroxylation of the chemically bound water. However, the geopolymer composite shows a weight loss up to about 250 °C; this is due to the evaporation of moisture. Two further small weight losses from 250 to 800 °C in the composite may be attributed to the decomposition of the cotton fibres.

Geopolymer composite had lower water content and a better thermal stability than the pure geopolymer. Compared to the weight loss of 5.3 % for pure geopolymer, the weight loss of geopolymer composite was only 4 % at 250 °C.

In contrast, the TGA of pure cotton fibre reveals substantial weight loss in three stages. In the first stage, from 50 to 250 °C, the weight loss is due to moisture loss. Cotton fibres are hydrophilic in nature, so one can expect some water content to be retained by the cotton fibres. In the second stage, from 250 to 370 °C, the cotton fibre displays a great weight loss, which is attributed to the degradation of cellulose, as expected from the literature [20]. In the third stage, in the temperature range of 370–800 °C, the fibre continues to decompose slowly with 10 % of the weight retained. It can be seen that geopolymer composite reduces the weight loss from 87 to 12 % compared with neat cotton fibre. Therefore, the geopolymer is acting to protect cellulose from the effect of thermal degradation, possibly acting as barrier to reduce the ingress of air and the resultant oxidative degradation. Thermal degradation resistance of cotton fibre can be improved by the use of geopolymer paste.

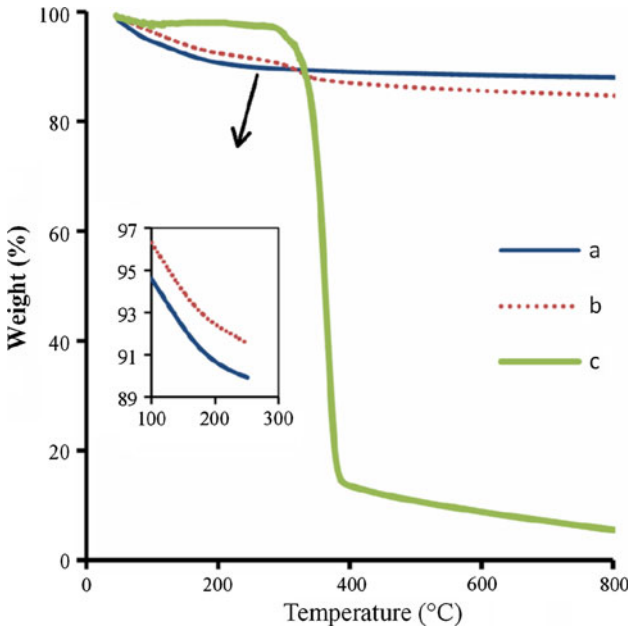

Fig. 1 TGA curves of: (*a*) pure geopolymer, (*b*) geopolymer composite and (*c*) cotton fibre

Flexural strength and flexural modulus

The effect of fibre content on the flexural strength of CFGs is shown in Fig. 2, and its corresponding stress/strain curve is shown in Fig. 3. It is observed that the flexural strength of geopolymer composites increases with increase in cotton fabric contents up to 2.1 wt%, and after that the strength of the composites decreases. This study finds that 2.1 wt% of cotton fibre provides the highest flexural strength. The highest value of flexural strength, exhibited by 2.1 wt% fibre content, may be explained by the orientation of the fibres within the matrix. At this stage, fibres achieve the maximum level of orientation within the matrix. This is because when the load is applied, the stress is uniformly distributed among the fibres [21]. As a result, the flexural strength of the composites achieves its maximum value.

Increasing the amount of cotton fibres to 2.8 and 4.1 wt% reduces the flexural strength. This reduction might be caused by misalignment of the cotton fabric, which is due to the hand lay-up procedure. This imperfection affects the mechanical properties of the composites because the misalignment can lead to the inability of the fibre to support stress transferred from the geopolymer matrix and poor interfacial bonding between the fibre and the matrix [8]. Therefore, the strength of geopolymer composites

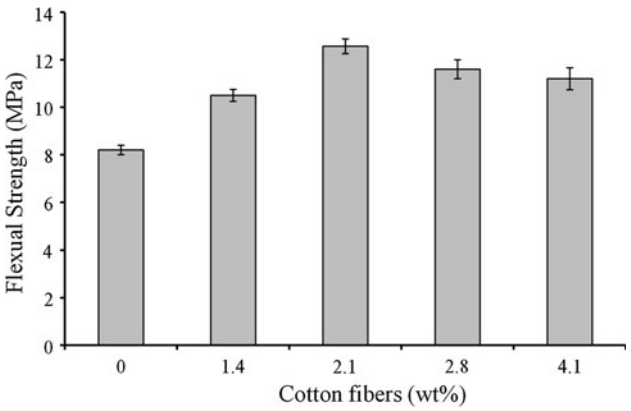

Fig. 2 Flexural strength of geopolymer composites as a function of fibre content

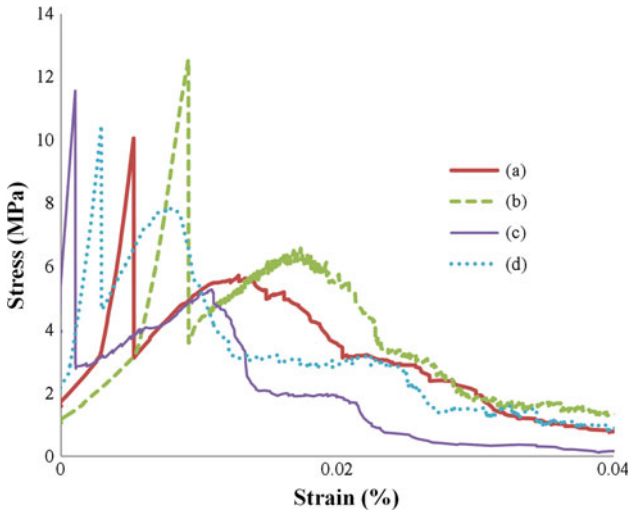

Fig. 3 Typical stress–strain curves of geopolymer composites with various cotton fibre content (*a*) 1.4 wt%, (*b*) 2.1 wt%, (*c*) 2.8 wt% and (*d*) 4.1 wt%

decreased with the increase in the cotton fabric content beyond 2.1 wt%.

The same reasons can explain a similar trend observed with the flexural modulus (see Fig. 4). This reduction in modulus could additionally be attributed to the fact that the cotton fibres are hydrophilic in nature, and tend to absorb moisture from ambient air, which in turn, causes swelling of the fibre, forming voids and micro cracks at the fibre–matrix interface, resulting in a reduction of mechanical properties [22].

Impact strength

The impact strength of fibre-reinforced polymer is governed by the fibre–matrix interfacial bonding, and the properties of both the matrix and the fibres. When the composites undergo a sudden force, the impact energy is dissipated by the combination of fibre pull-out, fibre fracture and matrix deformation [23]. The experimental results presented in Fig. 5 indicate that the impact strength of the composites initially increases as cotton fibre content increases to 2.1 wt%, then decreases thereafter. The enhancement in impact strength may be ascribed to good fibre–matrix adhesion, which improves the ability of these composites to absorb impact energy. However, as fibre loading increases, the impact strength significantly decreases. This reduction in impact strength at higher fibre loading is due to their higher porosity and the subsequent formation of voids, which in turn reduced the bond between the fibre and the matrix.

Fracture toughness

In general, natural fibre–polymer composites display crack deflection, de-bonding between fibre and matrix, pull-out effect and a fibre-bridging mechanism, all of which contribute to fracture toughness [13]. In terms of the matrix alone, plastic deformation provides toughness using an energy dissipation mechanism [24, 25], which is hindered by the addition of fibres. Nonetheless, overall the materials are tougher due to the toughness mechanisms provided by natural fibres.

It can be seen that higher values of fracture toughness are obtained at lower cotton fibre content (2.1 wt%), as shown in Fig. 6. This enhancement in fracture toughness at 2.1 wt% cotton fibre is due to the embedding of cotton fibre in the geopolymer matrix (see Fig. 7b), which results in better adhesion between fibres and the geopolymer paste because the spaces between fibres in the cotton fabric are filled by the geopolymer paste, and improve the energy absorption capacity of composites [26].

In contrast, at higher cotton fibre content, there is a reduction in fracture toughness. This is thought to be due to

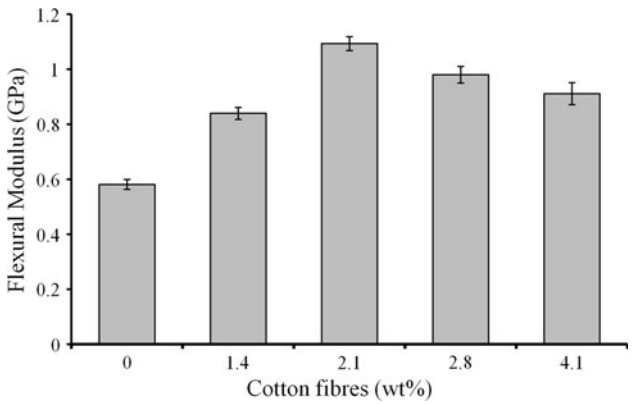

Fig. 4 Flexural modulus of geopolymer composites as a function of fibre content

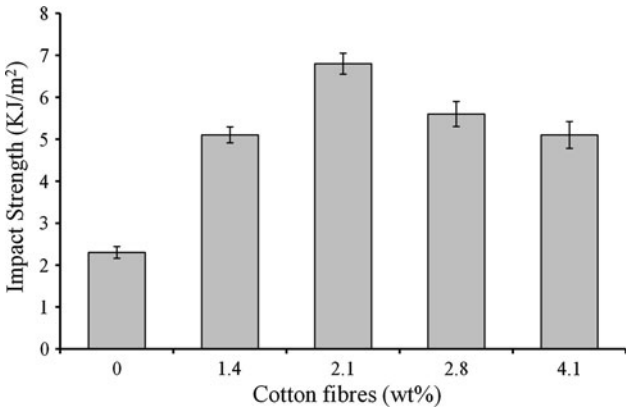

Fig. 5 Impact strength of geopolymer composites as a function of fibre content

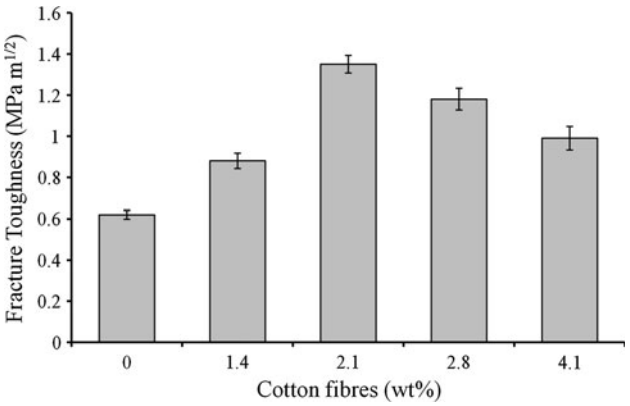

Fig. 6 Fracture toughness of geopolymer composites as a function of fibre content

the variation in the amount of geopolymer binder that penetrates the openings in the fabric. The penetration of geopolymer binder into the fabric may be maximized when a sufficient amount of the binder holds the fabric together, and gives better adhesion between the fabric and matrix. As the quantity of fabric grows, the amount of binder diminishes, and less is available to penetrate through the fabric openings. As a result, the limited amount of binder penetrating the space of the fabric is not sufficient to improve the bonding between the fabric and the matrix. This limitation leads to a reduction in bonding: fibre pull-out occurs readily and composites exhibit poor toughness results. Therefore, achieving optimal fibre–matrix adhesion is paramount. The results of this study reveal a suitable

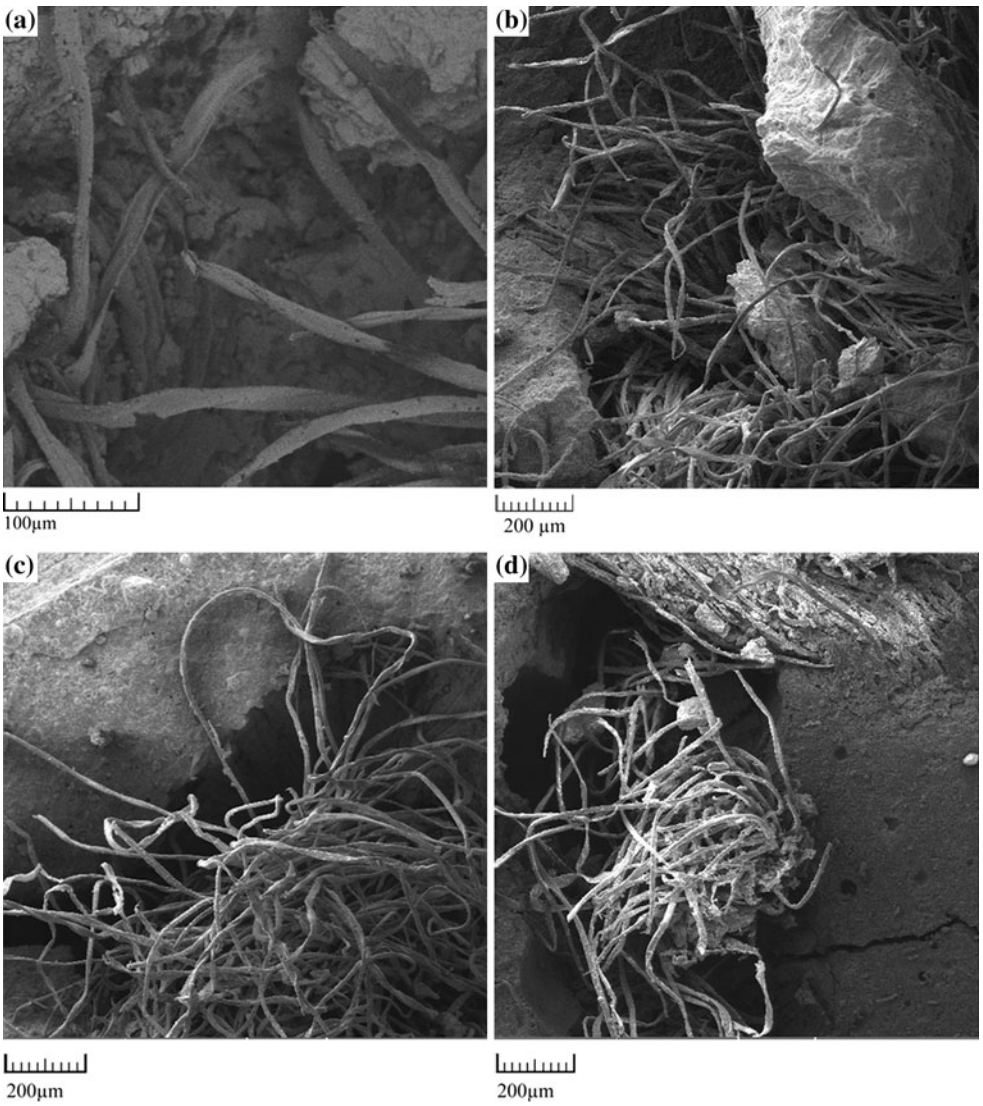

Fig. 7 SEM images of the fracture surface for geopolymer composites reinforced with varying content of cotton fibres: **a** 1.4 wt%, **b** 2.1 wt%, **c** 2.8 wt% and **d** 4.1 wt%

cotton fibre content that leads to improved fibre–matrix adhesion, with satisfactory fracture toughness and strength.

Microstructure of geopolymer composites

The microstructural analyses of fracture surfaces are shown in Fig. 7. It can be observed that the composites with 1.4 and 2.1 wt% cotton fibre show better penetration of the matrix between the fabric openings (see Fig. 7a, b). This leads to enhancement in the interfacial bonding between the fibre and matrix. However, Fig. 7c, d clearly indicates that fibre pull-out is quite high, and the bonding between cotton fibre and matrix is very poor. A large gap is evident in the matrix near the cotton fibres. In addition, microcracks can be seen in the fracture surfaces of geopolymer composites with 4.1 wt% cotton fibre, which confirms that fibre–matrix de-bonding has occurred, and thus strength has been reduced. This is clear evidence that the fibre matrix interfacial adhesion is better for CFGs with 1.4 and 2.1 wt% than for those with 2.8 and 4.1 wt%. The data presented above for the mechanical properties of geopolymer composites is also supported by the SEM observations.

Conclusions

Increasing the cotton fibre content in geopolymer matrix has increased the mechanical properties of composites. Results show that the flexural strength, fracture toughness, flexural modulus and impact strength all increased at an optimum fibre content of 2.1 wt%. However, increases in cotton fibre content beyond 2.1 wt% caused a reduction in the mechanical properties due to poor fibre–matrix interfacial bonding. The density of geopolymer composites decreased with an increase in fibre content. Geopolymer composites loaded with up to 2.1 wt% cotton fibres showed better fibre–matrix interfacial bonding than those loaded with fibre beyond this value. The fly-ash based geopolymer matrix also protected the degradation of cotton fabrics at high temperatures.

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3.4 Mechanical and Thermal Properties of Ambient Cured Cotton Fabric-Reinforced Fly Ash-Based Geopolymer Composites

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Mechanical and thermal properties of ambient cured cotton fabric-reinforced fly ash-based geopolymer composites

T. Alomayri[a,b], F.U.A. Shaikh[c], I.M. Low[a,*]

[a]Department of Imaging & Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b]Department of Physics, Umm Al-Qura University, Makkah 21955, Saudi Arabia
[c]Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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Abstract

This paper presents the mechanical and thermal properties of cotton fabric (CF)-reinforced fly ash-based geopolymer composites cured under ambient condition. Setting and hardening of above composite at ambient temperature are achieved by partial replacement of small amount of fly ash with Ordinary Portland cement (OPC). The effects of different quantities of OPC on flexural strength, fracture toughness, impact strength and thermal stability of above composite are evaluated, and the microstructural characterisation of each composite and its matrix is also conducted. Results show that the mechanical properties of the composites are improved with the addition of OPC; however, SEM images of fracture surfaces reveal that OPC hinders toughening mechanisms by limiting the prevalence of fibre pull out and fibre debonding. At high temperatures, the thermal stability of the geopolymer composites increases with the presence of either OPC or CF layers.
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Keywords: C. Mechanical properties; C. Thermal properties; Fracture toughness; Geopolymer composites

1. Introduction

Ordinary Portland cement (OPC) is a commonly used binder in concrete and other cement based construction materials. It is well known that the production of OPC results in environmental problems and releases a notable amount of greenhouse gases [1], and concrete researchers have been investigating for alternative binders. One of these is geopolymer, a class of inorganic polymer formed by reaction between an alkaline solution (e.g., sodium hydroxide and sodium silicate) and an aluminosilicate source (e.g., metakaolin, fly ash, slag, etc.). Currently, fly ash-based geopolymer concrete is proving to be a sustainable alternative for cement concrete owing to its excellent engineering properties [2–4], and geopolymer technology is attracting increasing attention because it offers viable economical alternative to organic polymers and inorganic cements in diverse applications, such as fire-proof and refractory adhesives [5,6]. The interest is also due to their exceptionally high thermal and chemical stability, excellent mechanical strength, adhesive behaviour and long-term durability. Geopolymers are environmentally friendly materials whose manufacture creates less CO_2 emission than that of Portland cement [7]. These features make geopolymers a promising material for utilisation, and for the development and application of new materials.

In recent years, utilisation of high performance geopolymer for structural applications has attracted keen interest by researchers and structural engineers. A number of studies [8–11] have been reported in the literature concerning the use of mineral additives to enhance the mechanical properties and to reduce the material cost of geopolymers. These may include slag, calcium and waste gypsum. The use of mineral additives could increase the slump of the concrete mixture without increasing its cost. Moreover, the incorporation of mineral additives also eliminates the need for viscosity-enhancing chemical admixtures. Portland cement (OPC) is a mixture of several silicate and aluminate minerals. The strength development of Portland cement involves the formation of C-S-H,

*Corresponding author. Tel.: +61 8 92667544; fax: +61 8 92662377.
E-mail address: j.low@curtin.edu.au (I.M. Low).

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which is believed to give strength to the binder. The formation of the calcium silicate hydrate (C-S-H) phase with the geopolymeric gel has been demonstrated to improve the mechanical properties of the final product [12,13]. Therefore, Portland cement is a good choice to increase the mechanical properties of geopolymer as it forms C-S-H within the geopolymeric binder, as well as being readily available at very reasonable cost. The addition of OPC not only improves the mechanical and durability properties of geopolymers but also the elevated temperature curing of most geopolymers specially the fly ash based geopolymers can be avoided due to high calcium oxide content in OPC.

Cement based binders have been reinforced with natural fibres for many years, particularly in developing countries which used local materials such as bamboo, sisal, jute and coir with some success [14–19]. These natural materials are not only cheap, but their low density and favourable mechanical properties make them attractive alternatives to the synthetic fibre composites. Other natural fibres employed to reinforce geopolymer composites include wood, wool and cotton [20–23]. Such naturally-occurring materials have environmental advantages since they are both renewable and non-toxic [24–27]. However, their certain drawback is the incompatibility between natural fibres and polymer matrices.

The strength of fibre–matrix adhesion is an essential factor that influences the mechanical performance of polymer composites [28]. The role of the matrix in a fibre-reinforced polymer composite is to transfer the load to the fibres through shear stresses at the interface. A strong bond between the polymeric matrix and the fibres is required in this process [29–31], and various physical and chemical methods have been proposed to improve compatibility between the natural fibres and the polymer matrix [32–35]. In general, the properties of composites depend on the nature of matrix, fibre, interfacial bonding, and quality of adhesion [36,37]. The use of OPC could be another possible method to improve the fibre–geopolymer matrix interface, thereby increasing the composite strength.

In this study, the effect of OPC and its content on the mechanical performance of fly-ash based cotton fabric reinforced geopolymer composites have been studied. X-ray diffraction analysis and scanning electron microscopy were used to characterise their phase composition, microstructure and failure mechanisms. Thermogravimetric analysis (TGA) was also used to investigate their thermal stability.

2. Experimental procedures

2.1. Materials

Cotton fabric (CF) of 30 cm × 7.5 cm was used as a reinforcing material for the fabrication of geopolymer composites. Low calcium fly-ash (ASTM class F), collected from the Collie power station in Western Australia, was used as the source material of geopolymer matrix, which in this study consisted of fly ash and Ordinary Portland cement. The chemical compositions of fly-ash and Ordinary Portland cement are shown in Table 1. The alkaline activator for geopolymerisation was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes with 98% purity were used to prepare the sodium hydroxide solution. The chemical composition of sodium silicate solution was 14.7% Na_2O, 29.4% SiO_2 and 55.9% water by weight.

2.2. Sample preparation

2.2.1. Geopolymer matrix

Wooden moulds with open tops were prepared and greased to avoid the samples sticking during demoulding. An 8-molar concentration of sodium hydroxide solution was used and added to the sodium silicate solution one day prior to mixing.

The geopolymer matrices were prepared by mixing fly ash and alkaline solutions with three different contents of OPC (i.e., 5, 8 and 10 wt%), using a Hobart mixer. The final mixture was poured into wooden moulds and covered with plastic film and allowed to cure for 24 h at ambient temperature before de-moulding. Subsequently, the mixtures were left for 28 days at room temperature. Pure geopolymer (GP) samples without OPC addition was also made, as a control.

2.2.2. CF-reinforced geopolymer composites

In the preparation of CF reinforced geopolymer composites the fabric was initially pre-dried for 60 min at 70 °C in an oven. A thin layer of geopolymer matrix was spread into the wooden mould and the first layer of CF was carefully laid upon it and fully impregnated (wet out) with geopolymer paste with a roller before placing the next layer. This process was repeated for the desired number of cotton fibre layers. In each specimen, the final layer was geopolymer matrix. The alkaline solution to fly-ash ratio was kept at 0.35, while the ratio of sodium silicate solution to sodium hydroxide solution was fixed at 2.5. After casting, each sample was pressed with a 20 kg load for 5 h, after which the specimens were covered with plastic film and allowed to cure for 24 h at ambient condition before de-moulding. All specimens were then kept in ambient condition for 28 days.

The same process was used to prepare the composites without the addition of OPC. The amount of CF in the final products was approximately 17.2 wt% (three layers). All the samples made are summarised in Table 2.

Table 1
Chemical composition of fly-ash (FA) and Ordinary Portland cement (OPC).

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO (wt%)	SO_3	Na_2O	K_2O	LOI
FA	50	28.25	13.5	1.78	0.89	0.38	0.32	0.46	1.64
OPC	21.10	5.24	3.10	64.39	1.10	2.52	0.23	0.57	1.22

Table 2
Compositions of synthesised geopolymer matrix and CF-reinforced geopolymer composites.

OPC/geopolymer	OPC content (wt%)	CF-reinforced geopolymer composite	OPC content (wt%)
Pure geopolymer (GP)	0	GP/CF	0
GP/OPC5	5	GP/CF/OPC5	5
GP/OPC8	8	GP/CF/OPC8	8
GP/OPC10	10	GP/CF/OPC10	10

2.3. X-ray diffraction

An x-ray diffraction pattern was collected on a D8 Advance diffractometer (Bruker AXS, Germany) using a Cu Kα source. The data was accumulated using a nominal 2θ step size of 0.01°, a count time of 0.5 s per step and a 2θ range of 10–70°.

2.4. Density and porosity

Both density and porosity tests were performed to determine the quality of each geopolymer composite sample. The values of bulk density (D) and apparent porosity (P_s) were determined in accordance with the ASTM Standard (C-20) and calculated using the following equations [38]:

$$D = \frac{W_d}{W_a - W_w} \tag{1a}$$

$$P_s = \frac{W_a - W_d}{W_a - W_w} \times 100 \tag{1b}$$

where W_d = weight of the dried sample, W_w = weight of the sample saturated with and suspended in water, and W_a = weight of the sample saturated in air.

2.5. Flexural strength

Rectangular bars with a length of 40 mm were cut from the fully cured samples and subjected to three-point bend tests to evaluate their flexural strength. A LLOYD Material Testing Machine (50 kN capacity) with a displacement rate of 1.0 mm/min was employed to perform the tests. In total, five specimens of each composition were tested. The flexural strength (σ_F) was determined using the following equation:

$$\sigma_F = \frac{3}{2}\frac{P_m S}{B W^2} \tag{2}$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width and W is the specimen thickness or depth.

2.6. Impact strength

A Zwick Charpy impact tester with a 1.0 J pendulum hammer was employed to determine the impact strength. In all, five bars of 40 mm long were used. The impact strength (σ_i) was calculated using the following equation

$$\sigma_i = E/A \tag{3}$$

where E is the impact energy required to break a sample with a ligament of area A.

2.7. Fracture toughness

Rectangular bars 80 mm in length with a cross-sectional dimension of 20×20 mm^2 were used in fracture toughness measurements. Subsequently, a crack with a length to thickness (depth) (a/W) ratio of 0.4 was introduced into each specimen by means of a 0.4 mm diamond blade, to estimate the fracture toughness (K_{IC}), calculated using the equation proposed by Low et al. [39]:

$$K_{IC} = \frac{p_m S}{B W^{3/2}} f\left(\frac{a}{W}\right) \tag{4a}$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width, W is the specimen thickness (depth), a is the crack length and $f(a/W)$ is the polynomial geometrical correction factor given by the equation below [39]:

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \tag{4b}$$

2.8. Microstructure examination

Scanning electron microscopy was carried out using a Tescan Lyra SEM machine. The SEM investigation was performed in detail on the fractured surfaces of the composites. In order to avoid charging, the specimens were coated with a thin layer of gold before observation.

2.9. Thermogravimetric analysis (TGA)

A Mettler Toledo thermogravimetric analyser (TGA) was used to study the thermal stability of the composites. Samples with 10 mg were placed in an alumina crucible and tests were carried out in nitrogen atmosphere with a heating rate of 10 °C/min from 50 to 800 °C.

3. Results and discussion

3.1. XRD analysis

Figs. 1 and 2 show the XRD analysis results for the Portland cement and fly ash powders and geopolymer composites containing 0 wt% and 10 wt% OPC. It can be seen from

Fig. 1 that the XRD pattern of the OPC powder represents many important phases in this study: portlandite [$Ca(OH)_2$] (PDF 00-044-1481), dicalcium silicate [C_2S] (PDF 00-033-0302), tricalcium silicate [C_3S] (00-049-0442), Ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$] (PDF 000411451), Gypsum [$Ca(SO_4)(H_2O)_2$] (PDF 040154421), Quartz [SiO_2](PDF 000461045) and Calcite [$CaCO_3$](PDF 000050586). The fly ash powder is mainly consisting of mullite (PDF 015-0776) and quartz (PDF 005-0490) as well as other crystalline phases as shown in Fig. 2a. These phases are not involved in the geopolymer reaction except the amorphous phase generated by coal combustion. The amorphous phase is crucial for the geopolymer reaction [40,41]. Comparing the XRD of the original fly ash with that of the hardened geopolymeric composites (0 wt% OPC), Fig. 2a and b indicates that the crystalline phases (quartz, mullite, etc.) originally existed in the fly ash have apparently not been altered by the activation reactions; hence, they did not participate in the geopolymer reaction.

However, there is a new phase (calcium silicate hydrate [C-S-H](PDF 014-0035) formed as a result of the hydration reaction in the presence of OPC (see Fig. 2c); this observed C-S-H phase has also been reported by other researchers [12,13]. Buchwald et al. [42] observed the formation of C-S-H

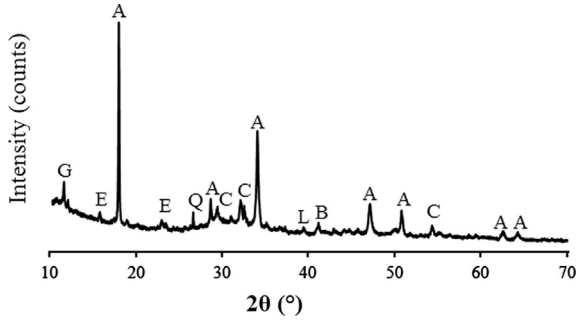

Fig. 1. XRD pattern of Ordinary Portland cement powder [Legend: A=Ca$(OH)_2$, B=C_2S, C=C_3S, E=Ettringite, G=Gypsum, Q=Quartz, L=Calcite].

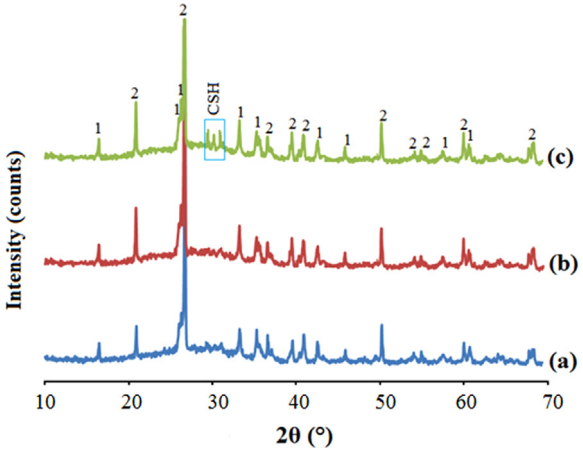

Fig. 2. XRD patterns of (a) fly ash and geopolymer specimens prepared with (b) 0 wt% OPC and (c) 10 wt% OPC [Legend: 1=mullite, 2=quartz, CSH=calcium silicate hydrate].

gel in the slag-metakolin based geopolymeric system. Ahmari et al. [43] reported a comparable observation when they prepared geopolymer specimens with different proportions of ground waste concrete (GWC) powder. Their observations ascertained that the inclusion of GWC powder improved the strength of geopolymer binding because of the formation of C-S-H gel in the geopolymer system.

3.2. Density and porosity

The density and porosity of geopolymer matrices and CF-reinforced geopolymer composites are shown in Tables 3 and 4, respectively. The density of geopolymer matrices varied from 1.85 to 2.21 g/cm^3 (see Table 3) and the density of CF-reinforced geopolymer composites varied between 1.78 and 1.91 g/cm^3 (see Table 4). The porosity of geopolymer matrices ranged from 23.8 to 18.6%, whereas the porosity of geopolymer composites varied from 26.6 to 21.7% (see Table 4). It can be seen that, the porosities of geopolymer matrices and composites are reduced due to the addition of OPC. This indicates that OPC has a pore-filling effect in geopolymer paste composites with or without CF. This reduced porosity level can be attributed to the increased matrix density as a result of decalcification of the C-S-H gels, which fill the pore structure of the geopolymer paste and yield a more consolidated microstructure, as reported by Bernal et al. [44]. Pressing the top surface of the samples also contributes to a reduction in porosity by expelling trapped air from inside the sample and forcing cement into the voids and pore spaces. These factors may have resulted in the reduction in porosity and an increase in density.

3.3. Mechanical properties

3.3.1. Flexural strength

The flexural strength of the geopolymer matrix and CF-reinforced geopolymer composites containing different wt% of OPC is shown in Fig. 3. In general, the incorporation of OPC into the geopolymer matrix led to an enhancement of flexural strength as shown in the figure. The addition of 10 wt% OPC resulted in the highest flexural strength of all the geopolymer samples and the flexural strength increased with increase in OPC contents. The flexural strength of the geopolymer matrix containing 10 wt% OPC was increased by 15% compared to pure geopolymer matrix. This improvement can be attributed to two mechanisms. First is the filling effect, where the OPC particles fill the voids or pores in the geopolymer paste and make the microstructure of the matrix denser than that of the geopolymer paste without OPC. The second mechanism is the pozzolanic reaction, in which the OPC with fly ash produces C-S-H gel in the geopolymeric system, and reduce porosity, thereby enhancing the mechanical properties [10,13]. X-ray diffraction analysis reveals formation of calcium silicate hydrate (C-S-H) phase that also contributes to increased flexural strength in the samples with added OPC. The SEM–EDS provides evidence of the formation of C-S-H within the geopolymeric gels as shown in Fig. 4.

Table 3
Densities and porosities of geopolymer matrices.

Sample	OPC content (wt%)	Density (g/cm^3)	Porosity (%)
GP	0	1.85 ± 0.03	23.8
GP/OPC5	5	1.96 ± 0.02	21.7
GP/OPC8	8	2.18 ± 0.05	19.2
GP/OPC10	10	2.21 ± 0.03	18.6

Table 4
Densities and porosities of CF-reinforced geopolymer composites.

Sample	OPC content (wt%)	Density (g/cm^3)	Porosity (%)
GP/CF	0	1.78 ± 0.02	26.6
GP/CF/OPC5	5	1.84 ± 0.04	24.5
GP/CF/OPC8	8	1.89 ± 0.02	22.5
GP/CF/OPC10	10	1.91 ± 0.03	21.7

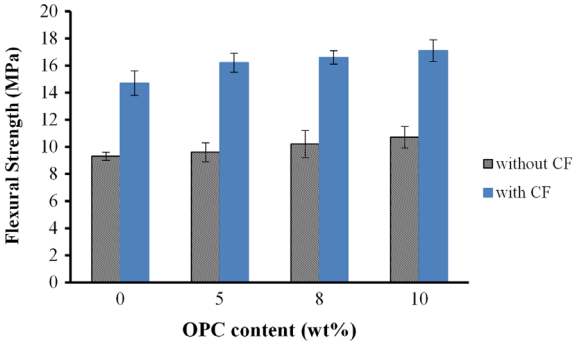

Fig. 3. Flexural strength as a function of OPC content for geopolymers with and without CF.

The higher flexural strength of samples with added OPC compared to those without is a result of the increased reactive amorphous phase of the mixture, resulting from the blending of fly ash with OPC. Fig. 5 shows micrographs of geopolymers without OPC and 10 wt% OPC, cured at ambient temperature. The micrographs show that the addition of OPC forms more homogeneous and refined microstructure (see Fig. 5b) than without OPC content (see Fig. 5a), where unreacted fly ash particles can be seen. Increasing the OPC content created a more compact and finer microstructure, indicating that OPC is acting as a seeding or precipitating element. Previous studies [45,46] have found that the C-S-H gel has a positive impact on the mechanical strength of geopolymeric binders. The current findings are in agreement with these studies.

The flexural strengths of CF-reinforced geopolymer composites are also shown in Fig. 3. It can be seen that the presence of CF significantly improved the flexural strength for all samples. Additionally, the flexural strength of neat geopolymer increased from 9.3 to 14.7 MPa after the addition of CF. This enhancement in flexural properties is clearly the contribution of the cotton fabrics in the composites. The inclusion of OPC in the CF-reinforced geopolymer composite also improved the flexural strength; the flexural strengths of composites containing 5, 8 and 10 wt% OPC were 16.2, 16.6 and 17.1 MPa,

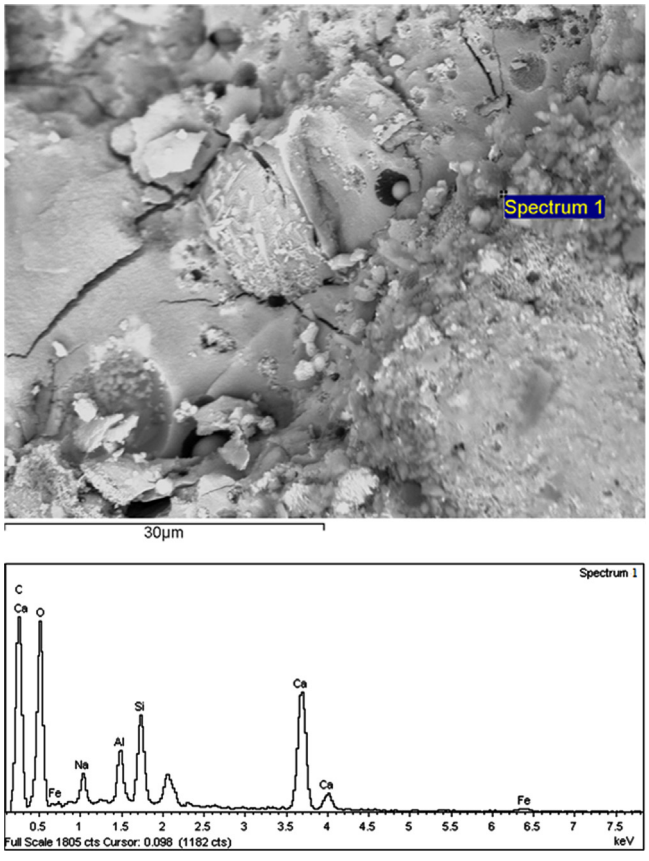

Fig. 4. SEM micrograph and EDS of the fracture surface region of geopolymer composite containing 10 wt% OPC.

respectively. The increase in flexural strength of geopolymer composites after the addition of OPC can be attributed to the enhancement in the interfacial adhesion between the fibre and the matrix as can be seen in Fig. 5c. Good interfacial bonding results in enhanced composites strength properties, since stress can be effectively transferred between the fibre and the matrix. This indicates that the addition of OPC is useful in improving the flexural strength of fly ash based geopolymer composites.

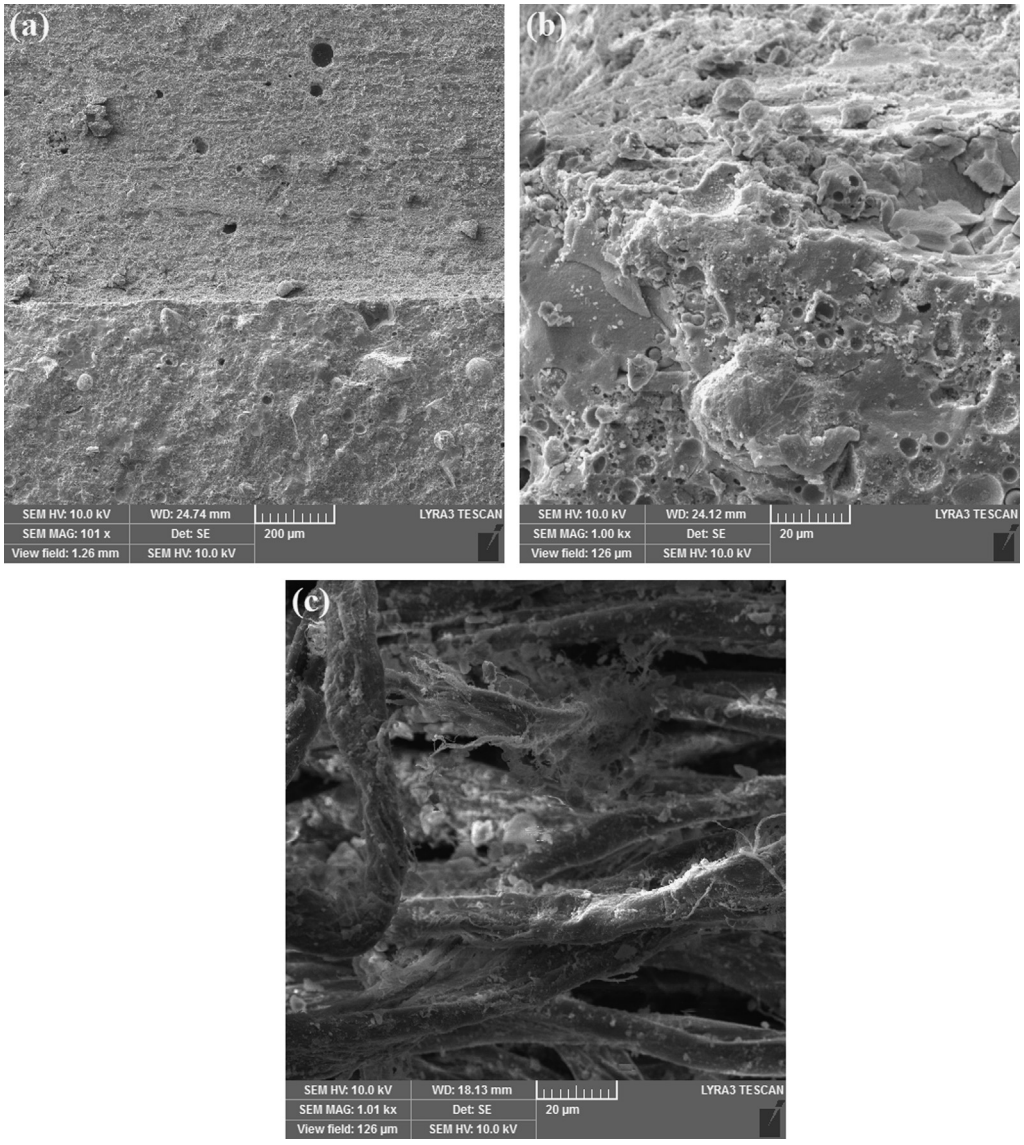

Fig. 5. SEM micrographs showing the microstructures of geopolymer with (a) 0 wt% OPC, and (b) and (c) 10 wt% OPC.

3.3.2. *Impact strength*

The impact strength of geopolymer matrix containing different OPC contents is shown in Fig. 6. The impact strength of the geopolymer matrix containing OPC is higher than that of pure geopolymer. Moreover, the enhancement in the impact strength of geopolymer matrix containing different OPC contents is similar to that of flexural strength. As indicated in Fig. 6, the addition of OPC enhanced the impact strength, with maximum improvement reaching 3.2 KJ/m^2 about 60% at 10 wt% OPC compared to that without OPC.

The impact strength of geopolymer increases with an increase in OPC content. The impact strength of neat geopolymer increased from 1.9 kJ/m^2 to 2.5 kJ/m^2, 2.9 kJ/m^2 and 3.2 kJ/m^2 with the addition of 5 wt%, 8 wt% and 10 wt% of OPC, respectively. This enhancement in impact strength of the geopolymer matrix with increasing OPC content could be attributed to the higher toughness (discussed in the next section) and the ability to absorb energy by forming tortuous pathways for crack propagation which enhance the impact strength [23]. These results confirm that the addition of OPC to a geopolymer system improves the mechanical properties of the matrix; they also suggest that an increase in OPC content is very useful in terms of improving the impact strength of a geopolymer matrix.

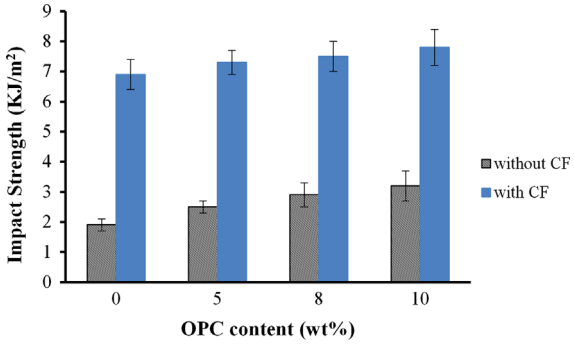

Fig. 6. Impact strength as a function of OPC content for geopolymers with and without CF.

The impact strength of CF-reinforced geopolymer composites is also illustrated in Fig. 6. The cotton fibres significantly improved the impact strength of all composites, a function of their superior capacity to absorb impact energy than that of un-reinforced geopolymer. The addition of 5, 8 and 10 wt% OPC to CF-reinforced geopolymer was also found to improve the impact strength of the composites from 6.9 kJ/m^2 to 7.3 kJ/m^2, 7.5 kJ/m^2 and 7.8 kJ/m^2, respectively. This enhancement in impact strength is due to a good penetration of CSH into the cotton fabric, which strongly holds the filaments of the fabric together and leads to enhancement in the interfacial bonding between fabric and matrix as can be seen in Fig. 7. Fibre–matrix adhesion, as mentioned earlier, is an important factor for composite action in any fibre reinforced composite. In fibre-reinforced composites, the matrix transfers load to the fibres through shear stress due to bonding action. The effective transfer of load requires a strong bond between the matrix and the fibres [36]. The presence of OPC in this study plays an important role in improving the adhesion between fibre and matrix, thereby enhancing the mechanical properties of the composite.

3.3.3. Fracture toughness

The influence of OPC content on the fracture toughness of the geopolymer matrix and CF-reinforced geopolymer composites is shown in Fig. 8. Among different OPC contents, the fracture toughness of geopolymer matrix and composite containing 5 wt% OPC was highest than others. It can also be seen that the fracture toughness of CF reinforced composites is much higher than the geopolymer matrix with and without OPC. The reason for such a difference is the ability of cotton fibres to bridge the cracks, which results in increased energy dissipation from crack-deflection at the fibre–matrix interface, fibre-debonding, fibre-bridging, fibre pull-out and fibre-fracture [47–51]. Previous studies have documented this improvement in fracture toughness in cement composites reinforced with natural fibres [52].

However, fracture toughness decreased when the OPC content increased beyond 5 wt%. It has already been considered that the OPC addition results in desirable strength properties as a result of the improvement in fibre–matrix adhesion; but this also makes the composites brittle, as indicated by the lower fracture toughness results for all the samples. The addition of OPC causes fibre–matrix adhesion to be high, but hinders the energy absorption mechanisms provided by fibre pull out and fibre de-bonding.

The fracture surfaces of composites are shown in Fig. 9, which reveal an extensive occurrence of fibre pull-outs. These micrographs also reveal useful information about the fibre surfaces and interfacial debonding. It is worth noting that the pull-out happened in geopolymer composites with 5 wt% OPC (Fig. 9a) than fibre rupturing in composites with 10 wt% OPC (Fig. 9b). This supports the notion that the interfacial adhesion is stronger in composites with 10 wt% OPC than in those with 5 wt% OPC. In the presence of weak interfacial adhesion, cracks tend to propagate through the fibre–matrix interfaces and result in greater fibre pull-out lengths. In contrast, when fibre–matrix adhesion is strong fibres rupture than pull-out. Interestingly, as the loading of OPC increased from 5 to 10 wt%, the lengths of fibre pull-outs reduced. For example, in the composites with 10 wt% OPC, almost no fibre pulled out rather ruptured. These observations are the result of strong adhesion between the fibres and the matrix.

3.3.4. Thermal stability

The thermal stability of the samples was determined using thermogravimetric analysis (TGA). In this test, thermal stability was studied in terms of weight loss as a function of temperature under atmospheric conditions. The thermograms (TGA) of the geopolymer matrix and CF-reinforced geopolymer composite are shown in Figs. 10 and 11, respectively.

In general, the thermogram of pure geopolymer shows weight loss from 50 to 300 °C, because of the dehydration of physically adsorbed water. Above 300 °C, the loss is attributed to the de-hydroxylation of the chemically bound water. The weight loss of neat geopolymer decreased as a

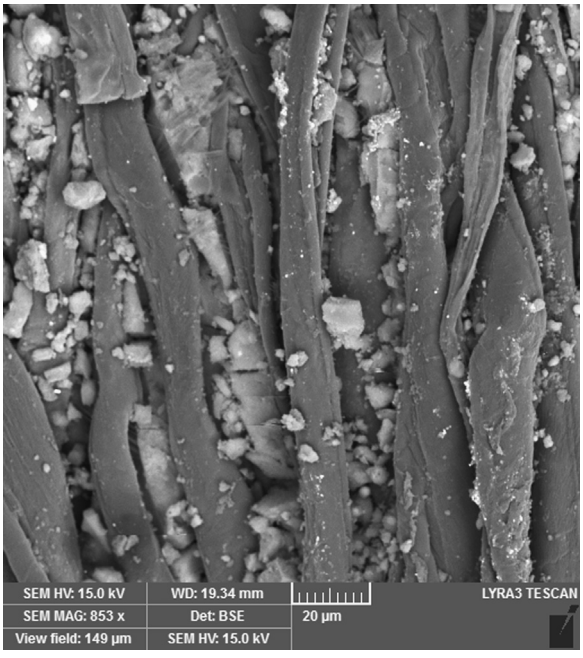

Fig. 7. SEM observation of CF-reinforced geopolymer composite containing 10 wt% OPC.

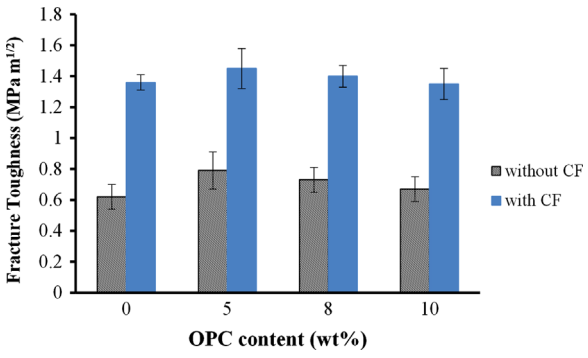

Fig. 8. Fracture toughness as a function of OPC content for geopolymers with and without CF.

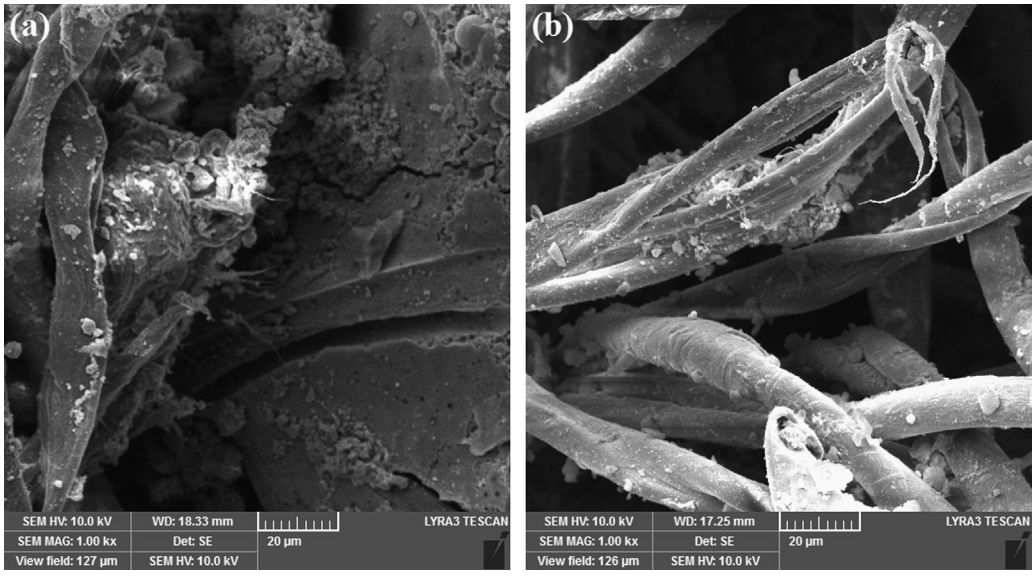

Fig. 9. SEM images showing the fracture surfaces of CF-reinforced geopolymer composite containing (a) 5 wt% OPC and (b) 10 wt% OPC.

result of the presence of OPC (see Fig. 10). The presence of 5, 8 and 10 wt% OPC decreased the weight loss of geopolymer from 11.16% to 10.2%, 9.11% and 9.06%, respectively, revealing that the addition of OPC decreased the moisture. This indicates that thermal stability enhances as OPC content increases in geopolymer matrix.

The addition of OPC to CF-reinforced geopolymer composite and its influence on thermal stability can be seen in Fig. 11. The CF-reinforced geopolymer composite containing OPC showed lower weight loss and better thermal stability than those without OPC. Compared to the weight loss of 10% for composite containing CF without OPC, the weight loss of CF-reinforced geopolymer composite with 10 wt% OPC was only 4.64% at 200 °C. This enhancement of thermal properties is the result of formation of CSH. In addition, the presence of OPC in geopolymer composites may provide a thermal barrier which reduces the ingress of air and the resultant oxidative degradation; therefore, the resistance to thermal degradation of cotton fibre reinforced composites can be improved by the addition of OPC.

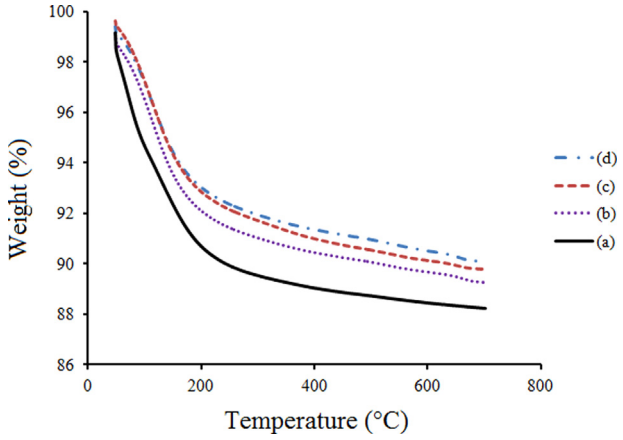

Fig. 10. TGA curves of geopolymer matrix containing (a) 0 wt% OPC; (b) 5 wt% OPC; (c) 8 wt% OPC and (d) 10 wt% OPC.

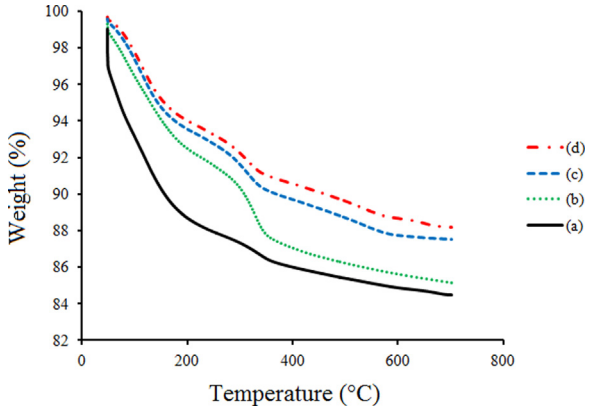

Fig. 11. TGA curves of CF-reinforced geopolymer composites containing (a) 0 wt% OPC; (b) 5 wt% OPC; (c) 8 wt% OPC and (d) 10 wt% OPC.

4. Conclusions

In this study, ambient cured fly-ash based geopolymer matrices and CF reinforced geopolymer composites containing OPC were fabricated and studied in terms of flexural strength, impact strength and fracture toughness. The addition of OPC was found to be effective in improving the fibre–matrix adhesion, increasing both the flexural strength and impact strength of the composites due to the formation of additional C-S-H gel in geopolymer matrix. This product is formed and filled the pore to make the dense and strong geopolymer. XRD analysis showed that the addition of OPC with fly ash produced C-S-H in the geopolymeric system, which improved the fibre–matrix interfacial bonding and thereby increased the flexural strength and impact strength. The addition of OPC also improved the thermal stability of geopolymer composites. However, the increases in OPC content beyond 5 wt% caused a reduction in the fracture toughness due to the reduction in

energy dissipation processes such as interfacial debonding, fibre pull-out and crack-bridging. The SEM micrographs also support this observation.

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3.5 Synthesis and Mechanical Properties of Cotton Fabric Reinforced Geopolymer Composites

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Synthesis and mechanical properties of cotton fabric reinforced geopolymer composites

T. Alomayri [a,b], F.U.A. Shaikh [c], I.M. Low [a,*]

[a] Department of Imaging & Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] Department of Physics, Umm Al-Qura University, Makkah 21955, Saudi Arabia
[c] Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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ABSTRACT

Geopolymer composites reinforced with different layers of woven cotton fabric are fabricated using lay-up technique. Mechanical properties, such as flexural strength, flexural modulus, impact strength and fracture toughness of geopolymer composites reinforced with 3.6, 4.5, 6.2 and 8.3 wt% cotton fibres are studied. The fracture surfaces of the composites are also examined using scanning electron microscopy. The results show that all the mechanical properties of the composites are improved by increasing the cotton fibre contents. It is found that the mechanical properties of cotton fabric reinforced geopolymer composites are superior to pure geopolymer matrix.

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1. Introduction

Geopolymers are inorganic compounds that can be cured and hardened at near-ambient temperatures to form materials that are effectively low-temperature ceramics with typical temperature resistance and strength [1]. In recent years, geopolymers have emerged as an alternative to cements [2,3]. However, despite their many desirable attributes, such as relatively high strength, elastic modulus and low shrinkage, geopolymers suffer from brittle failure like most ceramics. Nevertheless, this limitation can be overcome by the introduction of reinforcing materials, including short fibres or unidirectional long fibres into the geopolymer matrix. For this purpose, various inorganic fibres have been previously used as reinforcement in geopolymer composites [4–7].

However, contemporary concerns over environment and climate change have given rise to an increasing interest in natural materials to produce environmentally friendly composite materials for construction. Natural fibres are very attractive for composite materials as they have several useful characteristics, such as low cost, low density, availability, recyclability, and renewability. In addition, they possess excellent mechanical properties like high values of toughness, flexibility, specific modulus and specific strength [8,9].

For these reasons, natural fibres are more attractive to researchers and scientists as an alternative source of reinforcement to develop organic polymer composites. As an illustration, cellulose fibres have been used to reinforce various organic matrices like polyester, vinyl ester, and epoxy matrices [10–13]. However, at present there has been limited published research on the use of natural fibres to reinforce inorganic matrices despite the advantages they offer in terms of low cost, ready availability, low toxicity and good mechanical strength [14]. In a previous report, the authors studied the mechanical properties of short cotton fibre-reinforced geopolymer composites. Results showed that further increases in short cotton fibre content beyond 0.5 wt% caused a reduction in the mechanical properties due to poor workability which led to formation of voids and fibre agglomerations [15,16]. In a follow-up work by the same authors [17], similar behaviour has been reported in cotton fabric-reinforced geopolymer composites, with the exception that the mechanical properties decreased beyond 2.1 wt% cotton fibres. This decrease was attributed to poor bonding between the cotton fibre and matrix due to insufficient amount of geopolymer matrix in the composites containing more than 2.1 wt% cotton fibres.

In the present study, woven cotton fabrics (CF) have been impregnated (wet out) with geopolymer paste, stacked, and compressed by a roller to force the paste to penetrate the fabric and to remove most of the trapped air. The aim was to investigate the possibility of applying the above technique to manufacture geopolymer composites with cotton fabrics for structural applications, and to examine the basic mechanical properties through experimental testing. Useful results have been gathered for composites with various cotton fibre contents (0, 3.6, 4.5, 6.2 and

* Corresponding author. Tel.: +61 892667544; fax: +61 892662377.
E-mail address: j.low@curtin.edu.au (I.M. Low).

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8.3 wt%) under three-point bending tests. The results show that the addition of cotton fibres improves the mechanical properties of geopolymer composites such as flexural strength, flexural modulus, impact strength and fracture toughness. Synchrotron radiation diffraction (SRD) and scanning electron microscopy (SEM) were used to characterise the phase composition, microstructure, and failure mechanisms of woven cotton fibre reinforced geopolymer composites.

2. Experimental investigation

2.1. Materials

Cotton fabric (CF) of 30 cm × 7.5 cm was used to reinforce the geopolymer. This fabric is made up of yarns with a density of 1.54 g/cm^3, tensile strength of 400 MPa, and Young's modulus of 4.8 GPa. Low calcium fly-ash (ASTM class F), collected from Collie power station in Western Australia, was used as the source material of the geopolymer matrix. The chemical composition of fly-ash (FA) is shown in Table 1. The alkaline activator for geopolymerisation was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes with 98% purity were used to prepare the solution. The chemical composition of sodium silicate used was 14.7% Na_2O, 29.4% SiO_2 and 55.9% water by mass.

2.2. Preparation of geopolymer composites

To cast the composite samples, five wooden moulds with open tops were prepared and greased to avoid the samples sticking during de-moulding. The fabrics were pre-dried for 60 min at 70 °C. An 8 M concentration of sodium hydroxide solution was prepared and combined with the sodium silicate solution one day before mixing. The fly ash and alkaline solution were mixed in a Hobart mixer to form a homogeneous paste. A thin layer of geopolymer paste was first spread in the wooden mould and the first layer of woven fabric was carefully laid on that layer. The fabric was then fully impregnated (wet out) with geopolymer paste by a roller and the process repeated for the desired number of cotton fibre layers. Each specimen contained different layers of cotton fabric (see Table 2) with final layer being geopolymer paste. The alkaline solution to fly ash ratio was fixed at 0.35 whereas the ratio of sodium silicate solution to sodium hydroxide solution was maintained at 2.5. The composite specimens were placed on a vibration table in order to ensure better penetration of the matrix between the fabric openings and to remove the entrapped air voids. Then, the composite specimens were pressed under 25 kg load for 3 h. Subsequently, the specimens were covered with plastic film and cured at 80 °C in an oven for 24 h. The samples were de-moulded and kept in room condition for 28 days before testing. The mechanical properties of unreinforced geopolymer used in this study were measured and used for comparison purpose. Typically, the compressive strength of the geopolymer paste is 21 MPa with density of 1.9 g/cm^3.

2.3. Characterisation

2.3.1. Synchrotron radiation diffraction (SRD)

The Powder Diffraction beamline at the Australian Synchrotron was used to collect the diffraction patterns of fly-ash and the geopolymer composites. The diffraction pattern of each sample was collected using a wavelength of 0.825 Å over the 2θ range of 5–45°.

Table 1
Chemical composition of fly ash.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
50%	28.25%	13.5%	1.78%	0.89%	0.38%	0.32%	0.46%	1.64%

Table 2
Formulations of samples.

Sample	Fabric layers	Fibre content (wt%)
Composite 0	0	0
Composites 1	5	3.6
Composites 2	10	4.5
Composites 3	20	6.2
Composites 4	40	8.3

2.3.2. Scanning electron microscopy (SEM)

The microstructures of geopolymer composites were examined using a Zeiss Evo 40XVP scanning electron microscope. The specimens were mounted on aluminium stubs using carbon tape and then coated with a thin layer of platinum to prevent charging before the observation.

2.4. Mechanical properties

2.4.1. Flexural strength

Rectangular bars with a length of 60 mm were cut from the fully cured samples and subjected to three-point bend tests to evaluate their flexural strength. The tests were performed in a LLOYD Material Testing Machine (50 kN capacity) with a displacement rate of 0.5 mm/min. Five specimens of each composition were tested. The flexural strength (σ_F) was determined using the following equation [9]:

$$\sigma_F = \frac{3}{2}\frac{P_m S}{BW^2} \tag{1}$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width and W is the specimen thickness (depth).

Values of the flexural modulus (E_F) were computed using the initial slope of the load–displacement curve, $\Delta P/\Delta X$, using the following formula [9]:

$$E_F = \frac{S^3}{4BW^3}\left(\frac{\Delta P}{\Delta X}\right) \tag{2}$$

2.4.2. Impact strength

The impact strength was determined using a Zwick Charpy impact tester with a 7.5 J pendulum hammer. Five bars of 60 mm long were utilised. The impact strength (σ_i) was calculated using the following equation [18]:

$$\sigma_i = \frac{E}{A} \tag{3}$$

where E is the impact energy required to break a sample with a ligament of area A.

2.4.3. Fracture toughness

Rectangular bars of 60 mm long and cross-sectional dimension of 20 × 20 mm were used in the fracture toughness measurements. A crack with a length to thickness (depth) (a/W) ratio of 0.4 was introduced into the specimen using a 0.4 mm diamond blade to evaluate the fracture toughness. The fracture toughness K_{IC} was calculated using the following equation:

$$K_{IC} = \frac{p_m S}{BW^{3/2}} f\left(\frac{a}{W}\right) \tag{4a}$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width, W is the specimen thickness

(depth), a is the crack length where $f(a/W)$ is the polynomial geometrical correction factor given by [9]:

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}\left[1.99 - (a/W)(1 - a/W) \times \left(2.15 - 3.93a/W + 2.7a^2/W^2\right)\right]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \quad (4b)$$

3. Results and discussion

3.1. Synchrotron radiation diffraction

The synchrotron radiation diffraction (SRD) patterns of class F fly ash, cotton fibres, and geopolymer composites containing 0, 3.6, 4.5, 6.2 and 8.3 wt% of cotton fibres, are shown in Fig. 1. The crystalline phases present were indexed using Powder Diffraction Files (PDFs) from the Inorganic Crystal Structure Database (ICSD). The diffraction pattern of cotton fibres shows typical characteristic peaks, indicating the presence of cellulose. The SRD pattern of fly ash shows that the major crystalline phases are quartz, mullite and hematite. These crystalline phases are the main component of fly ash. When comparing the SRD pattern of the original fly ash with those of the hardened geopolymeric materials shown in Fig. 1, it is seen that the crystalline phases of quartz, mullite and hematite remain unchanged and have not been visibly altered by the activation reaction. This finding confirms that the crystalline phases are not reactive or involved in geopolymerisation, but simply present as inactive fillers in geopolymer network [18–21]. In this case, however, amorphous aluminosilicate phases are more reactive and dissolvable in alkaline solution during the formation of a geopolymer [22–24].

3.2. Mechanical properties

3.2.1. Flexural strength and modulus

Flexural tests are often used to characterise the mechanical properties of layered materials since they provide a simple means of determining the bending response. This provides useful information on the performance of layered fabric-based composites [25]. The test results show that the flexural strength of cotton fabric reinforced composite increases as the wt% of cotton fibres increases (see Fig. 2). The composite containing 8.3 wt% woven cotton fibres exhibited the highest flexural strength among all composites. The flexural strength of the composites increased from 8.2 MPa to 31.7 MPa compared to pure geopolymer. This indicates that increasing the number of woven cotton fibres leads to considerable improvement in flexural strength in the composite. This finding can be justified from the fact that the flexural strength is controlled by the number of reinforcement layers. The lower weight of cotton fabrics allows multiple layers of fabric in the composite, to resist the shear failure and contribute in sustaining the applied load to the composites. This permits greater stress transfer between the matrix and the cotton fibres, resulting in improved flexural strength [26].

In previous studies [15,16], the authors studied the flexural behaviour of short cotton fibre reinforced geopolymer composites and observed minimum improvement in the flexural strength over that of the unreinforced specimens due to poor dispersion of short cotton fibres in the matrix. In fact, agglomerations of cotton fibres were noticed which degraded the interfacial adhesion between the fibre and the matrix as shown in Fig. 6. In present study, the utilisation of continuous fibres as reinforcement for geopolymer composites has shown better mechanical properties than short cotton fibres, owing to their ability to effectively bridge the cracks due to their alignment in the direction of tension which resulted in greater stress transfer at the interface of the composites. The improved performance of cotton fabric–geopolymer composites can be explained by observing the SEM microstructure images as shown in Fig. 7(f). This shows good penetration of geopolymer paste into the filament of the cotton bundle making up the fabric, thus providing improved bonding between the fabric and the geopolymer matrix and leading to an improvement in flexural strength.

The flexural modulus of geopolymer composites is shown in Fig. 3 and indicates similar trends to flexural strength values. In reality, the addition of woven cotton fibres in the geopolymer matrix increases the flexural modulus over plain geopolymer matrix. The flexural modulus is a measure of resistance to deformation of the composite in bending. It was observed that none of the specimens are completely broken at peak load. This could be due to the crack bridging by long continuous fibres, which makes their flexural modulus higher than un-reinforced geopolymer. Such fibres are able to withstand a higher load and are capable of undergoing multiple cracks throughout the loading process, thus preventing brittle failure of the specimens. Similar results have been

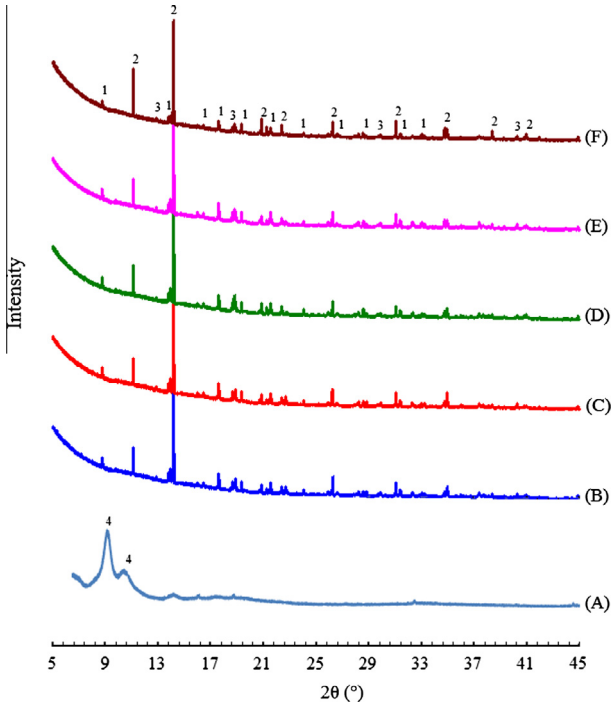

Fig. 1. Synchrotron radiation diffraction patterns of (A) cotton fibres (CF), (B) fly-ash, and geopolymer composite with (C) 3.6 wt% CF, (D) 4.5 wt% CF, (E) 6.2 wt% CF and (F) 8.3 wt% CF. [Legend: 1 = mullite (PDF 15-0776), 2 = quartz (PDF 05-0490), 3 = hematite (PDF 13-0534), 4 = cellulose (PDF 00-060-1502)].

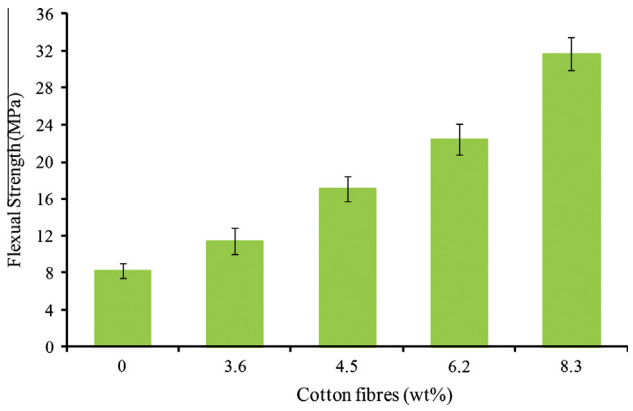

Fig. 2. Flexural strength of geopolymer composites as a function of fibre content.

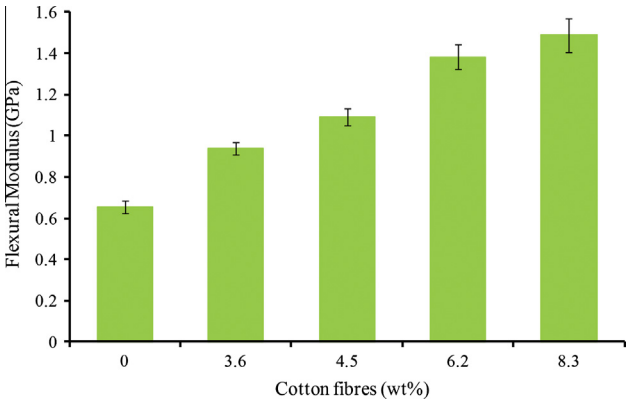

Fig. 3. Flexural modulus of geopolymer composites as a function of fibre content.

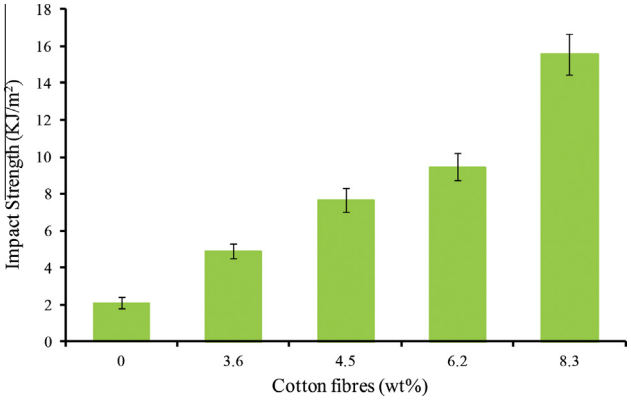

Fig. 4. Impact strength of geopolymer composites as a function of fibre content.

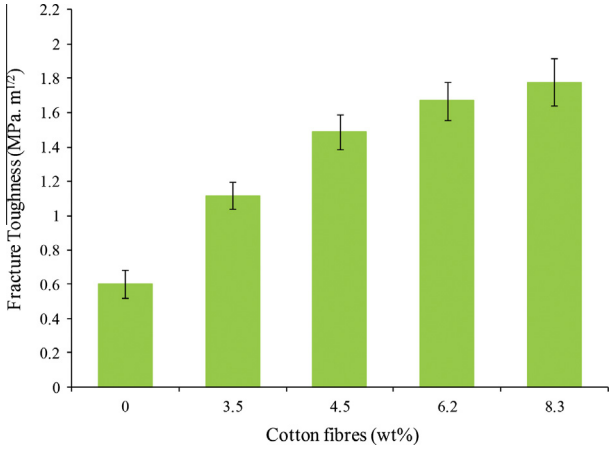

Fig. 5. Fracture toughness of geopolymer composites as a function of fibre content.

reported by Low et al. [9] when testing the mechanical properties of cellulose fibre-reinforced epoxy laminates using the three point bending tests. They reported an increase in both flexural strength and modulus as the fibre contents increase.

The increase in woven cotton fibre content was exceptionally useful in terms of improving the flexural strength and modulus of this inorganic polymer matrix.

3.2.2. Impact strength

Impact strength is an essential dynamic property of engineering material that gives an indication of its resistance against sudden impact. The impact strength of fibre reinforced polymer is

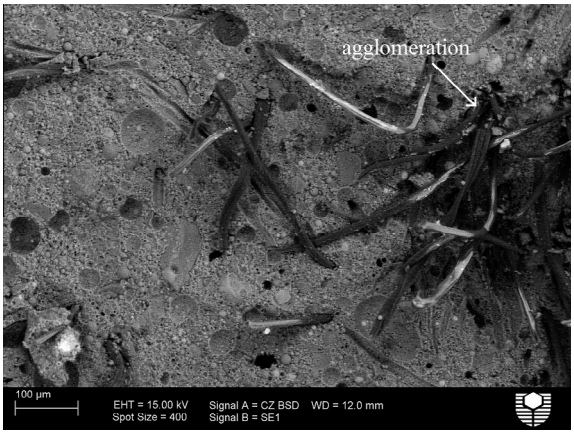

Fig. 6. SEM showing agglomeration of short fibres in cotton fibre/geopolymer composites loaded with 1.0 wt%.

governed by the matrix–fibre interfacial bonding, and properties of matrix and fibres. When the composites undergo a sudden force, the impact energy is dissipated by the combination of fibre pull outs, fibre fracture and matrix deformation [27,28]. The experimental results presented in Fig. 4 indicate that the impact strength of the composites increases as cotton fibre content increases. The impact strength of the neat geopolymer increased from 2.1 to15.6 kJ/m^2 after the addition of 8.3 wt% woven cotton fabric to the geopolymer composite. This significant enhancement in impact strength could be attributed to the use of applied load on the top surface of the geopolymer composites during sample preparation, which expelled the trapped air from the sample and forced the geopolymer paste into the voids and pore spaces. As a result, the bonding between the fabrics and the matrix is enhanced, and results in increased impact strength.

This improvement in impact strength may also be attributed to the fibrillation of cotton layers that creates branches in the fibre (see Fig. 7g), resulting in the formation of microfibrils which increase the fibre specific surface area [29,30]. This leads to an enhanced fibre–matrix interaction, and a strong bonding between the microfibrils and the geopolymer matrix. Therefore, better stress transfer from the matrix to the microfibrils results in increased fibre–matrix bonding. Similar remarkable improvements in impact strength were reported by Graupner [31] where the addition of cotton fibre increased the impact strength of pure poly (lactic acid) (PLA) matrix. He concluded that the increase was due to greater elongation of cotton fibres at break. Natural fibres containing cellulose generally have high elongation at break values. Cotton fibres have a cellulose content of about 88–96%. Generally, elongation at break and impact strength are directly correlated. The high elongation at break of cotton fibres increased the elongation at break in the composites, leading to higher impact strength.

3.2.3. Fracture toughness

Generally, crack deflection, debonding and bridging of fibres slows down the crack propagation in fibre reinforced composites and increase the fracture energy [32–37].

Fig. 5 shows the influence of cotton fabric content on the fracture toughness of the composites, the composite containing higher cotton fibre content exhibits higher fracture toughness. The greatest improvement in fracture toughness (from about 0.6 MPa m$^{1/2}$ in the unreinforced matrix to about 1.8 MPa m$^{1/2}$) was obtained with 8.3 wt% cotton fibre reinforcement. This extraordinary enhancement is due to the unique properties of woven cotton fibre to resist fracture resulted in increased energy dissipation from crack-deflection at fibre–matrix interface, fibre-debonding, fibre-bridging, fibre pull-out and fibre-fracture. The high values

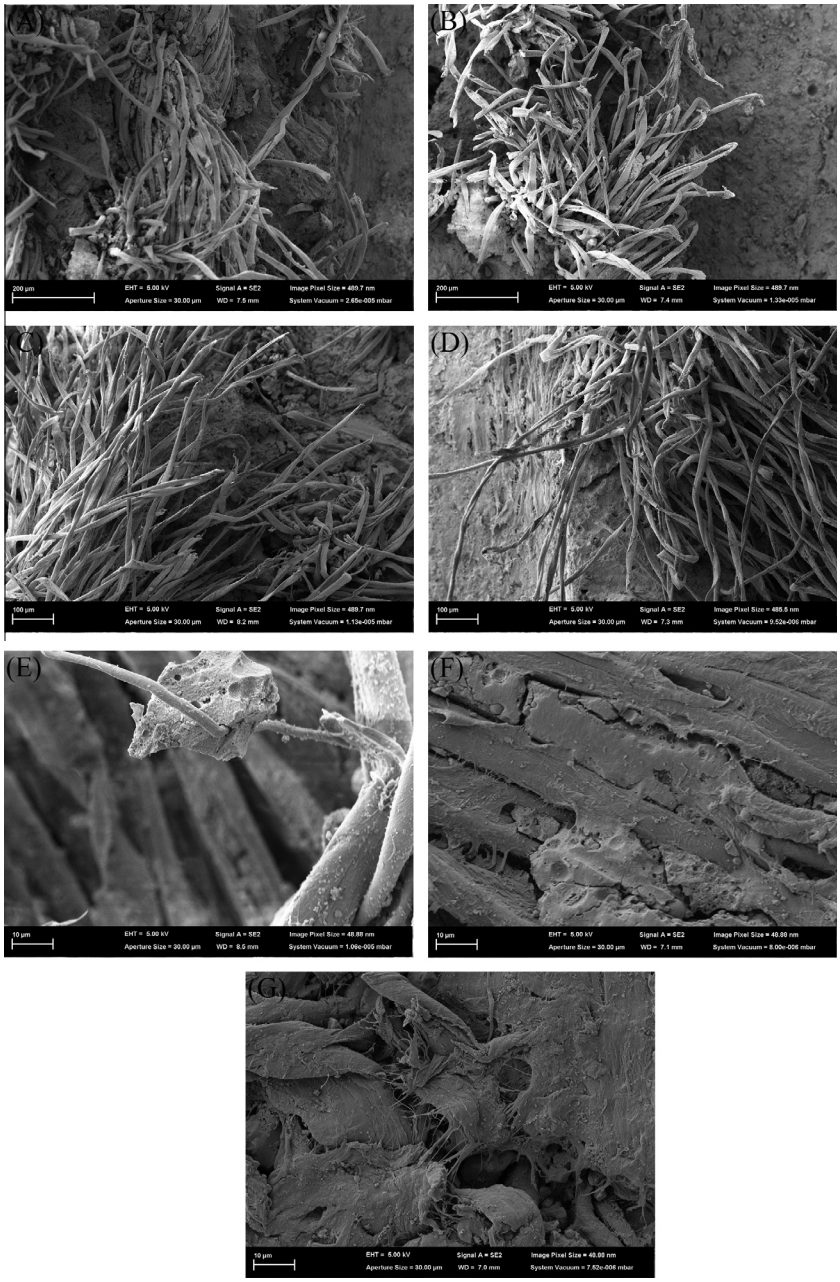

Fig. 7. SEM images of the fracture surface for geopolymer composites reinforced with varying content of cotton fibres (A) 3.6, (B) 4.5, (C) 6.2 and (D and E) 8.3 wt%. The micrographs of (F) penetration of the geopolymer matrix into cotton fabrics and (G) microfibrillation of cotton fibres.

of fracture toughness obtained in geopolymer composites with woven cotton fibres were due to better interface interaction between fibre and matrix as shown in Fig. 7. The improved interfacial adhesion enabled higher stress transfer between the fibres and matrix and reduced the chance of fibre de-bonding. Accordingly, the load required to break the sample increases when the content of cotton fibre is increased. Therefore, the fracture toughness of geopolymer composites increases with increasing wt% of cotton fibres.

Fig. 7E demonstrates selected scanning electron micrographs of fracture surface of geopolymer composite and explains the fracture toughness behaviour. It can be seen from Fig. 7E that small pieces of geopolymer paste were attached to the fibre surface of cotton fibre/geopolymer composites. Hence, retention of the matrix on the fibre surfaces shows the good adhesion between cotton fibres and geopolymer matrix. Additionally, it was observed that geopolymer composites with woven cotton fibres did not completely break into two pieces due to close spacing of woven cotton fabric which lead to fibres bridging the cracks and enhancing the crack propagation resistance. The tortuous pathway of the crack propagation indicates that high energy is absorbed by the cotton fibre layers (see Fig. 8).

3.3. Microstructure characteristics

The fracture surfaces of the woven cotton fibre reinforced geopolymer composites have been studied under SEM and are shown in Fig. 7. Generally, fibre pullout, fibre-debonding, fibre breakage and matrix fracture are observed after the fracture test of all composites. In fact, such toughening mechanisms increased the fracture properties of samples reinforced with woven cotton fibres.

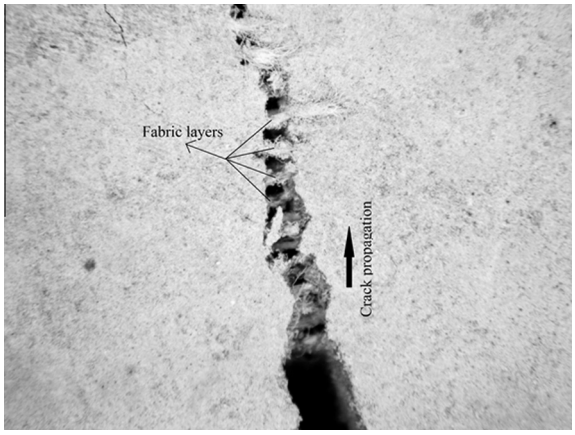

Fig. 8. Optical image of crack propagation in cotton fabric/geopolymer composites loaded with 8.3 wt% fibre.

The effect of fibre content on the fracture surface is clearly seen in Fig. 7A and B. Composites filled with lower fibre content (3.6 and 4.5) wt% show an increase in matrix-rich regions compared to composites filled with higher fibre content. An increase in matrix rich regions means that the matrix is not reinforced by enough fibres. Therefore, there are insufficient fibres to transfer the load from the matrix [37]. Due to this reason, the geopolymer composites with low fibre content exhibited low fracture toughness and mechanical properties. However, Fig. 7C and D illustrate the fracture surfaces of the geopolymer composites with higher fibre content. It can be seen that there are higher fibre-rich regions of composites filled with 6.2 and 8.3 wt% cotton fibres. An increase in fibre-rich regions means greater stress-transfer from the matrix to the cotton fibres thereby resulting in the improvement of mechanical properties.

Therefore, these observations indicate that the woven cotton fabrics can be used as potential material to reinforce geopolymer composites due to their good mechanical properties.

4. Conclusions

This study on mechanical properties of cotton fabric-reinforced geopolymer composite has shown that the presence of cotton fabric layers in the geopolymer composites significantly increases the flexural strength, flexural modulus, impact strength and fracture toughness when compared to neat geopolymer. This remarkable enhancement is due to the unique properties of cotton fibres in withstanding greater bending and fracture forces than the more brittle geopolymer. SEM micrographs show a number of toughness mechanisms which include crack bridging, fibre pullout and fibre fracture, and matrix fracture. These toughening mechanisms are the major factors contributing to the enhanced mechanical properties of cotton fabric-reinforced geopolymer composites. Cotton fibres appear to be uniquely suited to reinforce geopolymer composites since they can be easily processed using conventional manufacturing techniques to yield a product with good mechanical properties at low cost. They can be classified as desirable performing composites that offer benefits to engineers, particularly in less developed countries or countries that need low-cost construction materials. Possible applications for cotton fibre-reinforced geopolymer composites include slabs or shingles for siding, certain types of roofing, and some interior uses in the building structure. They may also be used for other applications such as pipes and cooling towers.

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3.6 Effect of Fabric Orientation on Mechanical Properties of Cotton Fabric Reinforced Geopolymer Composites

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Effect of fabric orientation on mechanical properties of cotton fabric reinforced geopolymer composites

T. Alomayri [a,b], F.U.A. Shaikh [c], I.M. Low [a,*]

[a] Department of Imaging & Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] Department of Physics, Umm Al-Qura University, Makkah 21955, Saudi Arabia
[c] Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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ABSTRACT

This paper presents the thermal, mechanical and fracture behaviour of fly-ash based geopolymer composites reinforced with cotton fabric (0–8.3 wt.%). Results revealed that fly-ash based geopolymer can prevent the degradation of cotton fabric at elevated temperatures. The effect of cotton fabric orientation (i.e., horizontal or vertical) to the applied load on flexural strength, compressive strength, hardness and fracture toughness of geopolymer composites is also investigated. The results showed that when the fabrics are aligned in horizontal orientation with respect to the applied load, higher load and greater resistance to the deformation were achieved when compared to their vertically-aligned counterparts.

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1. Introduction

In recent years, environmental awareness in construction industry has focused on finding environmentally friendly alternative material for Portland cement which is the main cause of the global warming. The use of Portland cement as the main component in the production of concrete is responsible for about 6% of the CO_2 emission worldwide [1,2].

In recent years, a new class of environmental-friendly and sustainable inorganic aluminosilicate polymers (also known as geopolymers) has emerged as an alternative to cements. These inorganic compounds improve the greenness of normal concrete and at the same time maintain comparable and even better properties. They possess good mechanical properties, inflammability, acid resistance and durability, and thus can be readily prepared at room temperature with less CO_2 emission than Portland cement [3–6].

Although geopolymers have desirable thermal stability and other favourable attributes, they suffer from brittle failure like most ceramics. This limitation can be readily overcome by the incorporation of short fibres or unidirectional long fibres into the geopolymer matrix. These fibres are able to improve the mechanical properties of the matrix by preventing the microcracks from propagating and thus enable them to fail in ductile mode rather than brittle mode, which increase their range of applications [7–9]. Hitherto, the most common fibre reinforcements used in geopolymer composites is based on inorganic fibres such as carbon and basalt fibres [10–13].

Current concerns over the environment and climate change have given rise to an interesting interest in replacing the synthetic fibres currently used in geopolymer composites or other brittle matrices with natural fibres. Natural fibres are low cost, low density, less health risk, renewable, recyclable and display good mechanical properties when compared to man-made fibres [14–19]. However, the conventional methods of mixing of natural fibres into the resins have usually been based on mechanical blending or stirring. This process does not allow the incorporation of large volume fraction of fibres and also has the tendency to cause fibre damage, fibre agglomeration and/or generation of air-bubbles during sample preparation [20].

In the present work, the authors report the use of cotton fabric to reinforce the geopolymer matrix, and verify the viability of developing a green composite material, using geopolymer as matrix and cotton fabric as the reinforcement. The cotton fabric reinforced geopolymer composites were subjected to flexural and impact tests, in order to determine their flexural strength, fracture toughness and impact strength. Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to investigate their thermal behaviour, microstructure and failure mechanisms. Results suggest that this is a promising area of investigation, adding significantly to the body of literature on natural and green alternatives to concrete.

* Corresponding author.
E-mail address: j.low@curtin.edu.au (I.M. Low).

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Table 1
Chemical composition of fly-ash.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
50%	28.25%	13.5%	1.78%	0.89%	0.38%	0.32%	0.46%	1.64%

Table 2
Formulations of samples.

Sample	Fabric layers	Fibre content (wt.%)
Composite 0	0	0
Composites 1	10	4.5
Composites 2	20	6.2
Composites 3	40	8.3

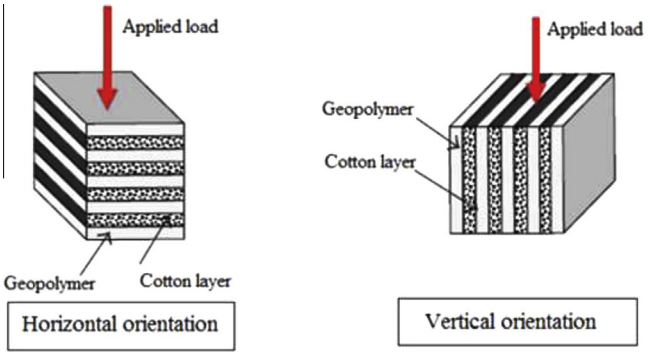

Fig. 1. Schematic drawing showing the orientation of cotton fabrics with respect to the applied load.

2. Materials and experiments

Cotton fabric (CF) of 30 cm × 7.5 cm was used to reinforce the geopolymer composites. Low calcium fly-ash (ASTM class F), collected from Collie power station in Western Australia, was also used as the source material of the geopolymer matrix. The chemical composition of fly-ash (FA) is shown in Table 1. The alkaline activator for geopolymerisation was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes with 98% purity were used to prepare the solution. The chemical compositions of sodium silicate used were 14.7% Na_2O, 29.4% SiO_2 and 55.9% water by mass.

Composite samples were prepared by spreading a thin layer of geopolymer paste in a well-greased wooden moulds followed by carefully laying the first layer of woven cotton fabric on that layer. Thereafter, the fabric was fully impregnated (wet out) with geopolymer paste by a roller with the process repeated for the desired number of cotton fibre layers. Each specimen contained different layers of cotton fabric (see Table 2). For each specimen, the final layer was geopolymer paste. The alkaline solution to fly-ash ratio was fixed at 0.35 whereas the ratio of sodium silicate solution to sodium hydroxide solution was maintained at 2.5. The composite specimens were placed on a vibration table in order to ensure better penetration of the matrix between the fabric openings and to remove the entrapped air voids. The specimens were also pressed under 25 kg load for 3 h. Subsequently, the specimens were covered with plastic film and cured at 80 °C in an oven for 24 h. The samples were de-moulded and kept in room condition for 28 days before testing.

3. Characterisation

3.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out for cotton fibres, unreinforced geopolymer and cotton fabric reinforced geopolymer composites at a heating rate of 10 °C/min under atmospheric condition. The temperature range scanned between 50 °C and 1000 °C. The weight of all specimens was maintained around 15 mg.

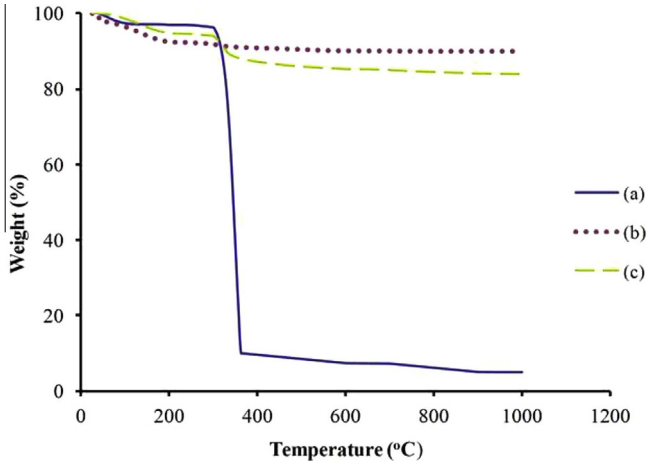

Fig. 2. TGA curves of: (a) cotton fibres, (b) pure geopolymer and (c) geopolymer composite.

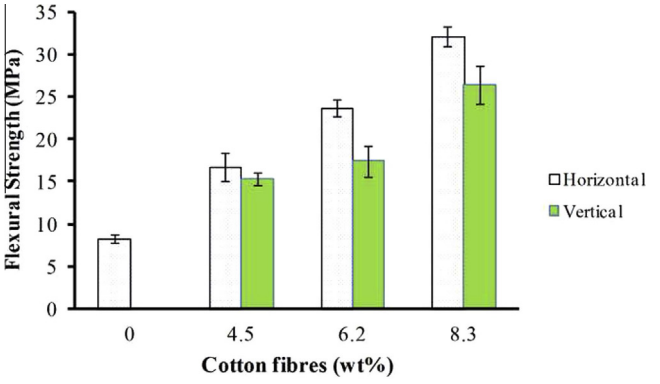

Fig. 3. Flexural strength of geopolymer composites as a function of fibre content.

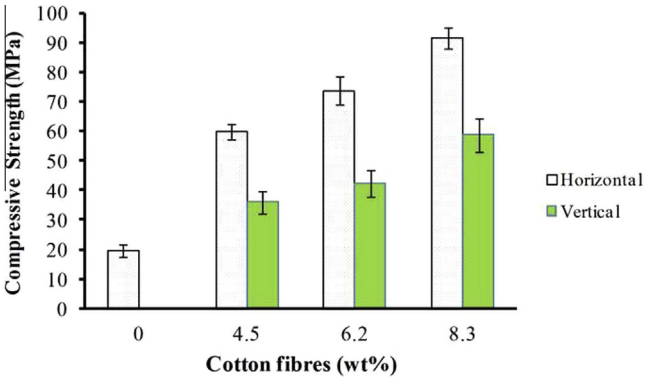

Fig. 4. Compressive strength of geopolymer composites as a function of fibre content.

3.2. Scanning Electron Microscopy (SEM)

A Zeiss Evo 40XVP scanning electron microscope was used to examine the microstructures of fly-ash and geopolymer composites. The specimens were mounted on aluminium stubs using car-

bon tape, and then coated with a thin layer of platinum to prevent charging during observation.

4. Mechanical properties

Mechanical properties of composites were studied in terms of flexural strength, compressive strength, hardness and fracture toughness. In these measurements, the samples were tested in two directions as the fabrics were aligned either horizontal or vertical to the applied load (see Fig. 1).

4.1. Flexural strength

Five specimens, measuring 80 mm × 20 mm × 10 mm, were cut from the fully cured samples and subjected to three-point bend tests to evaluate their flexural strength. The tests were performed in a LLOYD Material Testing Machine (50 kN capacity) with a displacement rate of 0.5 mm/minute. The flexural strength (σ_F) was determined using the following equation:

$$\sigma_F = 3P_m S/2BW^2 \quad (1)$$

where P_m is the maximum load, S is the span of the sample, while B is the specimen width and W is the specimen thickness.

4.2. Compressive strength

The compressive strength of the geopolymer composites was measured using a LLOYD Material Testing Machine (50 kN capacity). The cubes were tested according to ASTM C109, but instead of using the recommended 50 mm cube specimens, 20 mm cubes were used for the determination of compressive strength [21].

The compressive strength (C) of the sample was calculated using the following formula:

$$C = P/A \quad (2)$$

where P is maximum load on the sample at failure and A is the surface area of the specimen.

4.3. Rockwell hardness

The hardness of geopolymer composites was measured on the Rockwell H scale using an Avery Rockwell hardness tester. Before measurement, the samples were polished with emery paper to achieve flat and smooth surfaces.

4.4. Fracture toughness

Rectangular bars were used in the fracture toughness measurements. A crack with a length to thickness (depth) (a/W) ratio of 0.4 was introduced into the specimen using 0.4 mm diamond blade to evaluate the fracture toughness. The fracture toughness K_{IC} was calculated using the following equation:

$$K_{IC} = \left(\frac{P_m S}{BW^{3/2}}\right) f(a/W) \quad (3a)$$

where P_m is the maximum load at crack extension, S is the span of the sample, while B is the specimen width, W is the specimen thickness, and a is the crack length where $f(a/W)$ is the polynomial geometrical correction factor [14]:

$$f(a/W) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)}{2(1 + 2a/W)(1 - a/W)^{3/2}} \quad (3b)$$

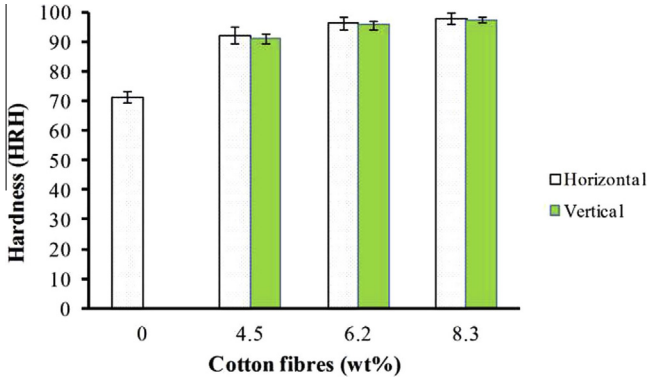

Fig. 5. Hardness of geopolymer composites as a function of fibre content.

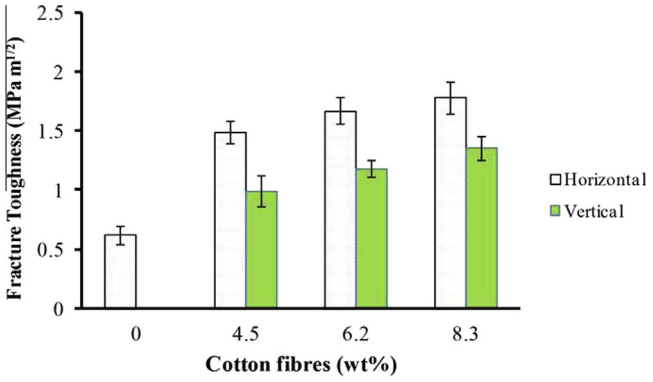

Fig. 6. Fracture toughness of geopolymer composites as a function of fibre content.

5. Results and discussion

5.1. Thermal properties

Thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability of the composites. The thermograms of pure geopolymer, geopolymer composite and cotton fibre are shown in Fig. 2. It can be seen that the unreinforced geopolymer matrix shows weight loss at between 50 and 300 °C, which resulted from water loss due to evaporation of free water. The composite also shows similar trend with slight additional mass loss above 300 °C which may be attributed to the decomposition of cotton fibres.

As observed in Fig. 2, pure cotton fibre degrades through three main stages. The first transition occurs from 50 to about 250 °C, which was attributed to the release of absorbed moisture in the cotton fibres by evaporation of water in the fibre. In this stage, the weight loss is approximately similar with the decomposition behaviour of other natural fibres, such as kenaf [22], jute [23] and wood [24]. The second transition occurs from 250 to 370 °C. In this stage, the cotton fibre displays a large weight loss, which is attributed to the degradation of cellulose [25]. The third stage occurs above 370 °C, and the cotton fibre starts to decompose with a lower rate of the weight loss. In this stage, all the volatile materials are driven off from the sample resulting in the residual char.

However, it is obvious that a higher temperature would be required to decompose the cotton fibres since they are protected by geopolymer matrix. Thus, this can be confirmed by the amount of weight loss of cotton fibres against the geopolymer composite. It can also be observed that the weight loss of cotton fibres is higher than that of the geopolymer composites. This, therefore, is attributed to the ability of geopolymer matrix to encapsulate the fibres as a barrier to reduce the ingress of air and the resultant

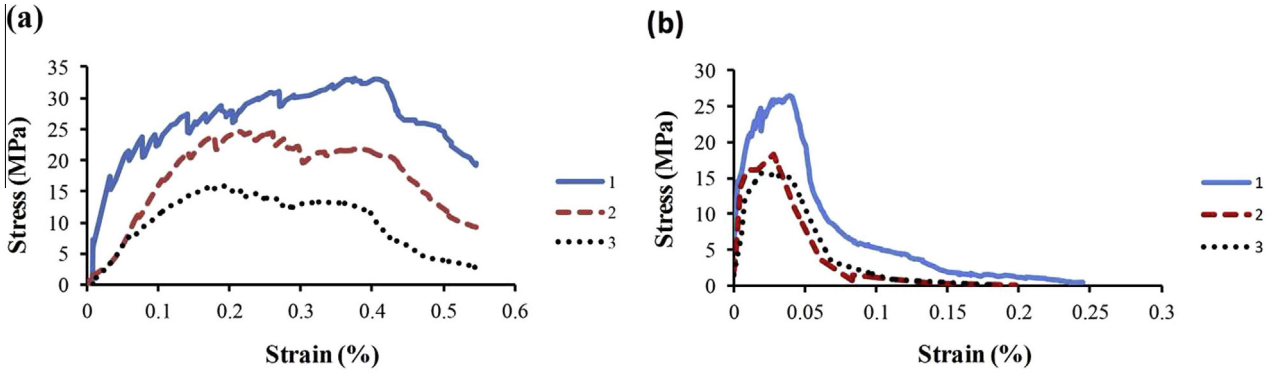

Fig. 7. Typical stress–strain curves of geopolymer composites with the cotton fabric: (a) horizontally aligned and (b) vertically aligned to the applied load. [Legend: (1) = 8.3 wt.%, (2) = 6.2 wt.%, (3) = 4.5 wt.%].

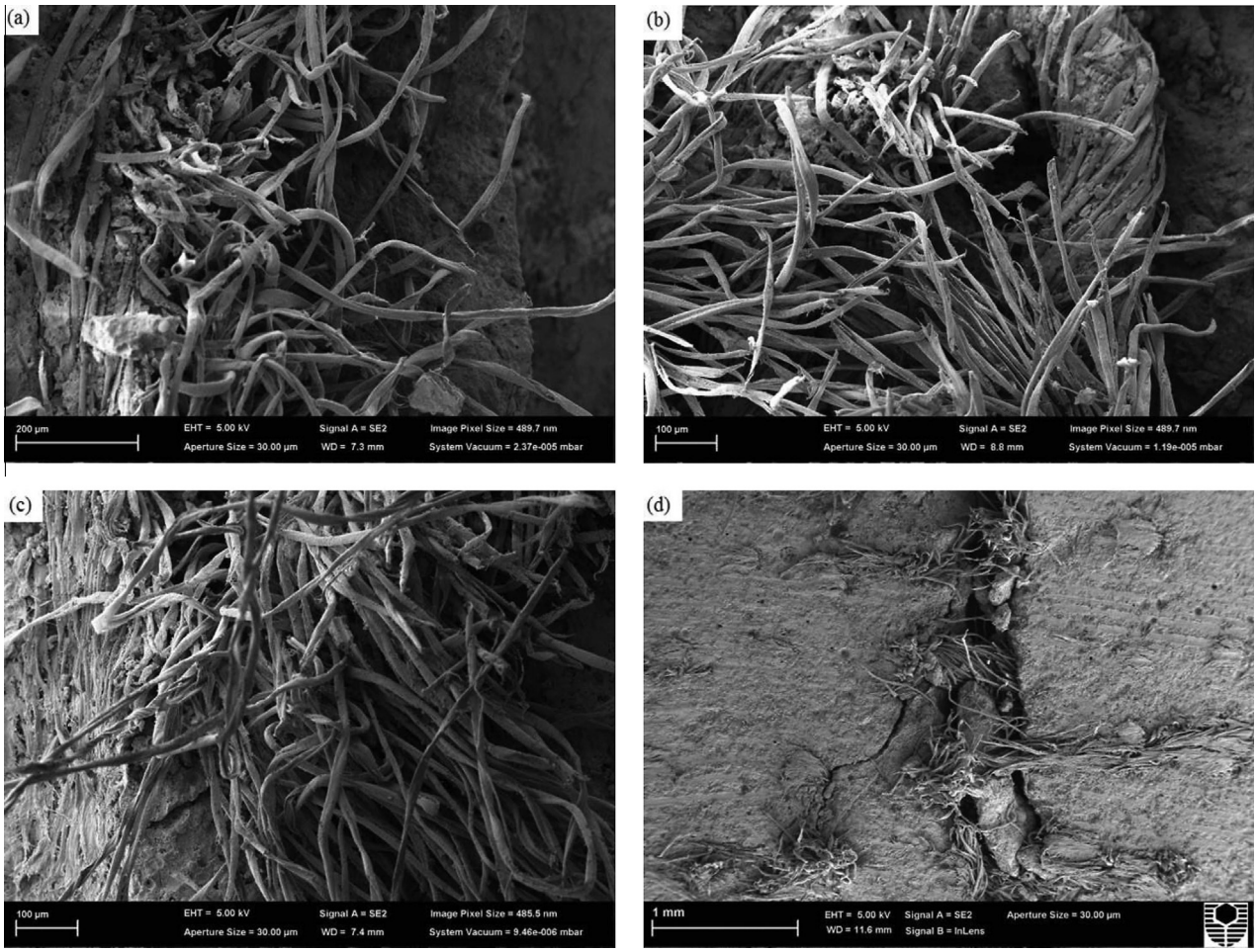

Fig. 8. SEM images showing the fracture surfaces of geopolymer composites reinforced with varying content of cotton fibres: (a) 4.5, (b) 6.2 and (c) 8.3 wt.%. The evidence of crack-bridging by cotton fabrics is shown in (d).

oxidative degradation. Hence, the thermal degradation resistance of cotton fibres can be improved by the use of geopolymer paste.

5.2. Mechanical properties

5.2.1. Flexural strength

The effect of cotton fibre content and fibre orientation on flexural strength is shown in Fig. 3. It is observed that the incorporation of cotton fabric layers has significantly increased the flexural strength of the composites. Thus, there is a significant difference between the flexural strength of cotton fabric reinforced geopolymer composites and the control specimens. This is observed in both horizontal and vertical directions of the cotton fabrics, indicating the advantage of using cotton fibres to reinforce geopolymer composites as previously discussed in earlier publications [26,27]. Fig. 3 also shows the effect of fabric direction on the flexural strength of the composites. The results showed that the composites with horizontal fabric layers (i.e., load normal to fabric

layers) have higher flexural strength than those with vertical fabric layers (i.e., load parallel to fabric layers). The higher flexural strength in composites with horizontally laid cotton fabric can be attributed to better uniformity in load distribution among the consecutive layers of cotton fabric.

5.2.2. Compressive strength

The compressive strength of geopolymer composites containing cotton fabrics laid in both horizontal and vertical directions are presented in Fig. 4. The results showed that the compressive strengths are affected significantly by the fabric direction. The compressive strength of composites is higher in the case of horizontally oriented fabric compared to that laid in vertical direction. This can be due to the ability of horizontally laid cotton fabric to directly absorb and distribute the load uniformly throughout the cross-section [28]. In addition, this significant enhancement of compressive strength in the horizontal direction is due to the fact that the interface between the fabric and the matrix is not exposed to any shear loading which in turn reduces the possibility of fabric detachments or delamination from the matrix at high loads. However, the scenario is different when fabric is oriented vertically to the compressive load where delamination between the cotton fabric and matrix can happen, which will result in inefficient stress transfer between the fabric and matrix.

Moreover, the results in Fig. 4 show that the compressive strength of the composites containing cotton fabric increases with increase in fabric layers (i.e. the fibre contents) oriented in both directions. The increase in compressive strength with fibre loading may be due to the ability of the cotton fibres to absorb the stress transferred from the matrix. Therefore, the results of compression test in this study revealed that addition of cotton fabric enhances the compressive strength of fly-ash-based geopolymer composites.

5.2.3. Hardness

The hardness values of cotton fabric reinforced geopolymer composites are shown in Fig. 5. The results show that the hardness of composites increases with increase in the fibre loading. This is true for both horizontally and vertically laid fabrics. It can also be seen that the hardness of composites with horizontally laid cotton fabric exhibited slightly higher hardness than those containing vertically oriented fabric. This is due to the uniform distribution of the load on cotton fibres which decreased the penetration of the test ball to the surface of the composite and consequently increased the hardness of composite [28].

5.2.4. Fracture toughness

In general, processes such as crack deflection, debonding and bridging of fibres will slow down the crack propagation in fibre reinforced composites and increase the fracture energy [29–32].

Fracture toughness of geopolymer composites containing cotton fabric in horizontal and vertical directions are shown in Fig. 6. It can be seen that the fracture toughness increases as the content of cotton fibre increases. This significant enhancement of facture toughness is due to fibre pull-out, fibre fracture and fibre-bridging, as clearly shown in the SEM images of Fig. 8a–c.

Fig. 7a and b shows the flexural stress–strain curves of geopolymer composites containing cotton fabric in horizontal and vertical directions. It can be seen that the composites containing horizontally laid cotton fabrics exhibited non-catastrophic fracture behaviour. All horizontally reinforced cotton fabric reinforced composites exhibited strain hardening behaviour as can be seen in Fig. 6a. The flexural strength and strain at peak load increase with increase in cotton fabric layers. On the other hand, the composites containing vertically aligned cotton fabrics showed some nonlinearity at very low strain, followed by strain softening after the peak load. This suggests the feasibility of using horizontal layers of cotton fabrics to mitigate the brittle failure of geopolymers. Moreover, the areas under the curves give an indication that the composite containing horizontal cotton fabric layers achieved higher fracture toughness than samples with vertically aligned cotton fabric layers. In the case of composite containing horizontal cotton fabric layers, the fabrics are stretched and the crack developed through the fabric layers in graceful failure behaviour, leading to a high degree of ductility. Also, the contribution of the reinforcing cotton fabric to crack arresting and bridging was clearly observed. The crack propagates through the thickness of the specimen from one fabric layer to the next. Such crack arresting, bridging mechanisms and crack deflection were responsible for the significant enhancement in fracture toughness as seen in Fig. 8d. On the contrary, at vertical loading the crack developed along the fabric layer mainly through the geopolymer matrix leading to a more brittle behaviour [33].

Similarly, this enhancement of fracture toughness in the horizontal direction has been reported by other researchers when dealing with natural fibre based composites. Low et al. [20] reported that cellulose fibre-reinforced epoxy composites in the horizontal direction to the applied load achieved higher fracture toughness when compared to samples with fibre sheets in the vertical direction to the applied load. Thus, they concluded that the higher fracture toughness in the horizontal could be attributed to the pronounced display of interfacial crack-deflection, leading to a very tortuous crack path. Hence, the composite sample failed in a more graceful manner with discontinuous or multiple "stick-slip" fracture. In contrast, the composite samples in the vertical direction showed continuous crack growth. Therefore, the phenomenon of multiple "stick-slip" fracture is attributed to the repeating occurrence of crack initiation, arrests and de-bonding at the cotton fabric/geopolymer interfaces.

6. Conclusions

The effect of fibre orientation on the mechanical properties of woven cotton fabric reinforced geopolymer composites was investigated. It was observed that the mechanical properties of the composites were greatly affected by the direction of the fabric to the applied load. In the case of the vertical orientation, the composites suffered from detachments and delamination which resulted in low strength of the composites. In contrast, when the fabrics were in horizontal orientation with respect to the applied load, higher load and resistance to the deformation was achieved. The fly-ash based geopolymer matrix also protected the degradation of cotton fabrics at high temperatures.

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3.7 Effect of Water Absorption on the Mechanical Properties of Cotton Fabric-reinforced Geopolymer Composites

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Effect of water absorption on the mechanical properties of cotton fabric-reinforced geopolymer composites

T. Alomayri[a,b], H. Assaedi[a,b], F.U.A. Shaikh[c], I.M. Low[a,*]

[a] Department of Imaging & Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] Department of Physics, Umm Al-Qura University, Makkah 21955, Saudi Arabia
[c] Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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ABSTRACT

Cotton fabric (CF) reinforced geopolymer composites are fabricated with fibre loadings of 4.5, 6.2 and 8.3 wt%. Results show that flexural strength, flexural modulus, impact strength, hardness and fracture toughness are increased as the fibre content increased. The ultimate mechanical properties were achieved with a fibre content of 8.3 wt%. The effect of water absorption on mechanical and physical properties of CF reinforced geopolymer composites is also investigated. The magnitude of maximum water uptake and diffusion coefficient is increased with an increase in fibre content. Flexural strength, modulus, impact strength, hardness and fracture toughness values are decreased as a result of water absorption. Scanning electron microscopy (SEM) is used to characterise the microstructure and failure mechanisms of dry and wet cotton fibre reinforced geopolymer composites.

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1. Introduction

Geopolymers are aluminosilicate inorganic polymers formed by polymerisation of aluminosilicates with alkaline solutions. Geopolymers have several desirable attributes which include good mechanical properties and durability [1]. They are environmentally friendly, being derived from natural materials, and because they can be prepared at room temperature they do not emit the high levels of carbon dioxide associated with the preparation of Portland cement [2,3]. However, despite their many desirable attributes such as relatively high strength, elastic modulus and low shrinkage, geopolymers suffer from brittle failure like most ceramics. This limitation may be readily overcome with fibre reinforcement as in high performance polymer–matrix composites. Hitherto, the most common fibre reinforcements used in geopolymer composites have been based on carbon, basalt, glass and polyvinyl alcohol fibres [4–7].

Current concerns over the environment and climate change have given rise to an increasing interest in replacing the synthetic fibres currently used in geopolymer composites or other brittle matrices with natural plant fibres [8,9]. The advantages of natural plant fibres over traditional glass fibres are low density, low cost, biodegradability, acceptable specific properties, less wear during processing and low energy consumption during extraction. The wide variety of natural fibres available locally is an added benefit to manufacturers the composites [10,11].

Natural fibres have a few disadvantages when used as reinforcements, such as higher moisture absorption which brings about dimensional changes thus leading to micro-cracking and poor thermal stability. The moisture absorption by the composites containing natural fibres had several adverse effects on their properties and affected their long-term performance. Water absorption can lead to swelling of the fibre, forming voids and micro-cracks at the fibre–matrix interface region which may result in a reduction of the mechanical properties and dimensional stability of composites [12–14]. Several studies in the use of natural fibre reinforced polymeric composites have reported that water molecules act as a plasticiser agent in the composite material, which normally leads to a decrease in the mechanical properties of the composites after water absorption [15–17].

Moisture diffusion in composites may degrade mechanical properties by three different mechanisms [18,19]. The first mechanism involves the diffusion of water molecules inside the micro gaps between polymer chains. The second mechanism involves capillary transport into gaps and flaws at interfaces between fibre and matrix. The third mechanism involves swelling effects which propagate microcracks in the matrix. In general, moisture diffusion

* Corresponding author. Tel.: +61 892667544; fax: +61 892662377.
E-mail addresses: j.low@curtin.edu.au, low246@gmail.com (I.M. Low).

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Table 1
Chemical analysis of cotton.

	Cellulose (%)	Water (%)	Hemicelluloses and pectin (%)	Proteins (%)	Waxes and fats (%)
Cotton fibre	80–90	6–8	4–6	0–1.5	0.5–1

in a composite depends on factors such as volume of fibre, voids, viscosity of matrix, humidity and temperature.

In order to promote the wider use of such materials in high-performance applications, it is essential to consider the effect of moisture absorption and water uptake on their physical and mechanical properties. However, according to the best knowledge of authors, no research was reported about the effect of water absorption on the mechanical properties of cotton fabric (CF) reinforced geopolymer composites. In this research, CF-reinforced geopolymer composites with different fibre contents (4.5, 6.2 and 8.3 wt%) have been successfully fabricated. The effect of fibre content on the mechanical properties has been investigated in terms of flexural strength, modulus, impact strength, hardness and fracture toughness. The effect of water absorption on the mechanical properties of composites has also been studied as a function of fibre content. Scanning electron microscopy (SEM) has been used to investigate the morphology, micro-structure and failure mechanisms of CF-reinforced geopolymer composites.

2. Experimental procedure

2.1. Materials

CF of 30 cm × 7.5 cm was used as a reinforcing material for the fabrication of geopolymer composites. The chemical composition and the physical properties of CF are shown in Tables 1 and 2 respectively [20]. Low calcium fly-ash (ASTM class F), collected from the Collie power station in Western Australia, was used as the source material of the geopolymer matrix. The chemical compositions of fly-ash are shown in Table 3. The alkaline activator for geopolymerisation was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes of 98% purity were used to prepare the sodium hydroxide solution. The chemical composition of sodium silicate solution was 14.7% Na_2O, 29.4% SiO_2 and 55.9% water by weight.

2.2. Sample preparation

To prepare the CF-reinforced geopolymer composites the fabric was initially pre-dried for 60 min at 70 °C in an oven. A thin layer of geopolymer matrix was spread into the wooden mould and the first layer of CF was laid upon it and fully impregnated (wet out) with geopolymer paste with a roller before placing the next layer. This process was repeated for the desired number of cotton fibre layers. In each specimen, the final layer was geopolymer matrix. Pure samples of geopolymer were prepared as controls by slowly adding dry fly ash to the alkaline solution in a Hobart mixer until the mixture became homogeneous. This was then poured into a wooden mould. The alkaline solution to fly-ash ratio was kept at 0.35, and the ratio of sodium silicate solution to sodium hydroxide solution (8 M concentration) was fixed at 2.5.

After casting, each sample was pressed with a 20 kg load for 5 h, after which the specimens were covered with plastic film cured at 80 °C in an oven for 24 h and then allowed them to cool down to laboratory conditions before being removed from the mould. Then rectangular bars with dimensions of 80 mm × 20 mm × 20 mm for both dry and wet conditions were prepared.

Table 2
Properties and structure of cotton fabric.

Fabric thickness (mm)	0.41
Fabric geometry	Woven (plain weave)
Yarn nature	Bundle
Filament size (mm)	0.0413
Number of filaments in a bundle	24
Bundle diameter (mm)	0.23
Opening size (mm)	0.5
Fabric density (g/cm^3)	1.6
Tensile strength (MPa)	287–597

Table 3
Chemical composition of fly-ash.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
50%	28.25%	13.5%	1.78%	0.89%	0.38%	0.32%	0.46%	1.64%

2.3. Water absorption test

The composite specimens used for moisture absorption test were immersed in a water bath at room temperature for longer period to reach equilibrium. At regular intervals, the specimens were taken out from the water and wiped with filter paper to remove surface water and weighed with digital scale (AA-200, Denver Instrument Company, USA). The samples were re-immersed in water to permit the continuation of sorption until saturation limit was reached after 133 days. The weighing was done within 30 s, in order to avoid the error due to evaporation. The percentage of the water content (M_t) was determined using the following equation [21]:

$$M_t\,(\%) = \left(\frac{W_t - W_o}{W_o}\right) \times 100 \tag{1a}$$

where W_t is the weight of the sample at time t and W_o is the initial weight of the sample.

The water absorption behaviour in the samples can be studied as Fickian behaviour. Therefore, the following formula has been used [21,22]:

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi h^2}\right)^{1/2} \tag{1b}$$

where M_t is the water content at time t, M_∞ is the equilibrium water content, D is the diffusion coefficient and h is the sample thickness.

2.4. Mechanical testing

2.4.1. Flexural strength and modulus

Rectangular bars with a length of 40 mm were cut from the fully cured samples and subjected to three-point bend tests to evaluate their flexural strength and modulus. A LLOYD Material Testing Machine (50 kN capacity) with a displacement rate of 1.0 mm/min was employed to perform the tests. In total, five specimens of each composition were tested. The flexural strength (σ_F) was determined using the following equation:

$$\sigma_F = \frac{3}{2}\frac{P_m S}{BW^2} \tag{2}$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width and W is the specimen thickness or depth. The flexural modulus was computed using the initial

slope of the load–displacement curve, $\Delta P/\Delta X$, using the following formula:

$$E_F = \frac{S^3}{4WD^3}\left(\frac{\Delta P}{\Delta X}\right) \quad (3)$$

2.4.2. Impact strength

A Zwick Charpy impact tester with a 1.0 J pendulum hammer was employed to determine the impact strength. For each composition, five bars of 40 mm length were tested. The impact strength (σ_i) was calculated using the following equation:

$$\sigma_i = \frac{E}{A} \quad (4)$$

where E is the impact energy required to break a sample with a ligament of area A.

2.4.3. Rockwell hardness

The hardness of geopolymer composites was measured using an Avery Rockwell hardness tester at hardness scale H. Before measurement, the surfaces of test samples were polished using a Struers Pedimat polisher, finishing with 10 μm grade diamond paste.

2.4.4. Fracture toughness

Rectangular bars of 80 mm in length with a cross-sectional dimension of 20 mm × 20 mm were used in fracture toughness measurements. Subsequently, a crack with a length to thickness (depth) (a/W) ratio of 0.4 was introduced in each specimen by means of a 0.4 mm diamond blade. The fracture toughness (K_{IC}) was calculated using the equation proposed by Low et al. [23]:

$$K_{IC} = \frac{p_m S}{BW^{3/2}} f\left(\frac{a}{W}\right) \quad (5a)$$

where P_m is the maximum load at crack extension, S is the span of the sample, B is the specimen width, W is the specimen thickness (depth), a is the crack length and $f(a/W)$ is the polynomial geometrical correction factor given by the equation below [23]:

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \quad (5b)$$

2.5. Microstructure examination

SEM was carried out using a Tescan Lyra SEM machine. The SEM investigation was performed in detail on the fractured surfaces of the composites. In order to avoid charging, the specimens were coated with a thin layer of gold before observation.

3. Results and discussion

The results obtained from this experimental study can be divided into two parts. The first part considers water absorption behaviour of CF-reinforced geopolymer composites and the second evaluates the effects of water absorption at room temperature on the mechanical properties.

3.1. Water absorption behaviour

Fig. 1 shows the percentage of water uptake as a function of square root of time of geopolymer composite samples reinforced with 0, 4.5, 6.2 and 8.3 wt% CF due to immersion in tap water for 133 days at room temperature. It can be seen that the water absorption increases with increase in fibre contents. The increase in water absorption is due to the hydrophilic nature of natural fibre and the greater interfacial area between the fibre and the matrix [15]. The maximum water uptake and the diffusion coefficient values increased for all composite specimens as the cotton fibre content

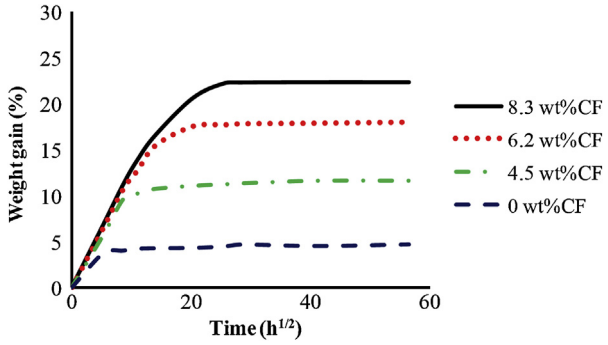

Fig. 1. Water absorption behaviour of cotton fibre-reinforced geopolymer composites.

increased (see Table 4). The water absorption of all specimens was high in the early stages of exposure, after which it slowed down and reached saturation level after prolonged time, following a Fickian diffusion process. The initial rate of water absorption and the maximum water uptake increase, as the fibre loading increases in all natural fibre composite samples [15]. This phenomenon can be explained by considering the water uptake characteristics of cotton fibre. When natural fibre-reinforced composite is exposed to moisture, the hydrophilic nature of fibre, in this case cotton, causes the fibre to absorb water and swell. As a result, micro-cracking of the geopolymer composite occurs. The high cellulose content in cotton fibre absorbs extra water that penetrates the interface through these micro-cracks, creating swelling stresses that lead to composite failure [24]. The more the composite cracks, the more capillarity and transport via micro-cracks become active. The capillary mechanism involves the flow of water molecules along fibre–matrix interfaces and diffusion through the bulk matrix. Water molecules actively attack the interface, resulting in de-bonding of the fibre and the matrix [15].

3.2. Effect of water absorption on mechanical properties

The effect of water absorption on the mechanical properties of CF-reinforced geopolymer composites was investigated after placing specimens in water for 133 days at room temperature and comparing them with samples of the same composites kept in dry conditions.

3.2.1. Flexural strength

The effect of fibre content on the flexural strength of dry CF reinforced geopolymer composites is shown in Fig. 2. In dry condition, the flexural strength increased as fibre content increased. The flexural strength of neat geopolymer increased from 8.3 to 15.8, 19.7 and 28.1 MPa due to the addition of 4.5, 6.2 and 8.3 wt% CF, respectively. This enhancement in flexural strength of CF-reinforced geopolymer composites is due to the ability of natural

Table 4
Maximum water uptake and diffusion coefficient (D) of CF/geopolymer composites.

Sample	CF content (wt%)	M_∞ (%)	$D \times 10^{-6}$ (mm^2/s)
Geopolymer (GP)	0	4.72	4.26
CF/GP1	4.5	11.74	5.42
CF/GP2	6.2	17.98	6.16
CF/GP3	8.3	22.32	8.4

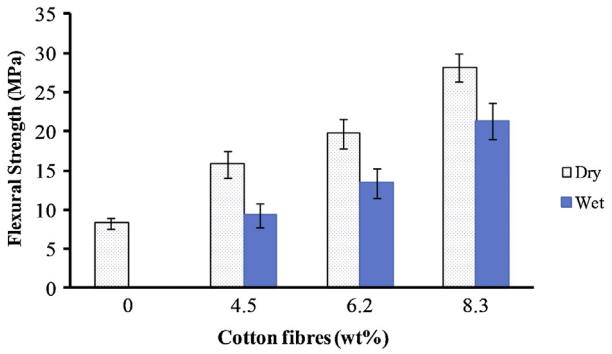

Fig. 2. Flexural strength of geopolymer composites in dry and wet conditions.

fibre to resist bending forces and good stress transfer from the matrix resulting in improve strength properties [25].

The effect of water absorption on flexural strength of CF reinforced geopolymer composites is also shown in Fig. 2. It can be seen that the flexural strength of composites decreased markedly after water absorption. Compared to the dry composites, the flexural strength of the composites reinforced with 4.5, 6.2 and 8.3 wt% CF deceased from 15.8, 19.7 and 28.1 to 9.3, 13.4 and 21.4 MPa, respectively. This could be due to the fact that the immersion of the composite samples in water affects the interfacial adhesion between fibre and matrix and creates de-bonding, leading to a decrease in mechanical properties. When the fibre–matrix interface was accessible to moisture in the environment the cotton fibres swelled. This resulted in the development of shear stress at the interface, and led to the ultimate de-bonding of the fibres, delamination and loss of structural integrity [26].

Water absorbed in polymers is generally as either free water or bound water as reported by Azwa et al. [27] (see Fig. 3). Water molecules which are relatively free to travel through the micro voids and pores are identified as free water, while those dispersed in the polymer matrix and attached to the polar groups of the polymer are designated as bound water [28]. In a wet environment,

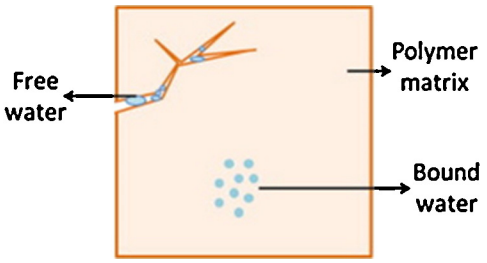

Fig. 3. Free water and bound water in polymer matrix [27].

water molecules penetrate in natural fibre-reinforced composite through micro-cracks and reduce interfacial adhesion of fibre with the matrix. This causes swelling of the fibres, which may create micro-cracks in the matrix and may eventually lead to debonding between the fibre and the matrix [27]. A schematic illustration of this process is presented in Fig. 4.

Dry cotton fibre constructed from fibrils of cellulose is fairly stiff and rigid. The cellulose molecules are held tightly together inside the fibrils by bonds established between molecules lying closely alongside one another. Water, however, can penetrate this cellulose network and move into the capillaries and spaces between the fibrils. In this situation, water molecules tend to force the cellulose molecules apart, reducing the forces that hold them together and destroying their rigidity, because water acts as a plasticiser and permits the cellulose molecules to move. Consequently the mass of the cellulose is softened, and this changes the dimensions of the fibre under applied force [15,16]. According to Ray and Rout [29], water molecules attract the hydrophilic groups of natural fibres and react with the hydroxyl groups (—OH) of the cellulose molecules to form hydrogen bonds. A schematic illustration of moisture absorption by natural fibres is presented in Fig. 5.

3.2.2. *Flexural modulus*

The flexural modulus values of different cotton fibre reinforced geopolymer composites in dry and wet conditions are shown in

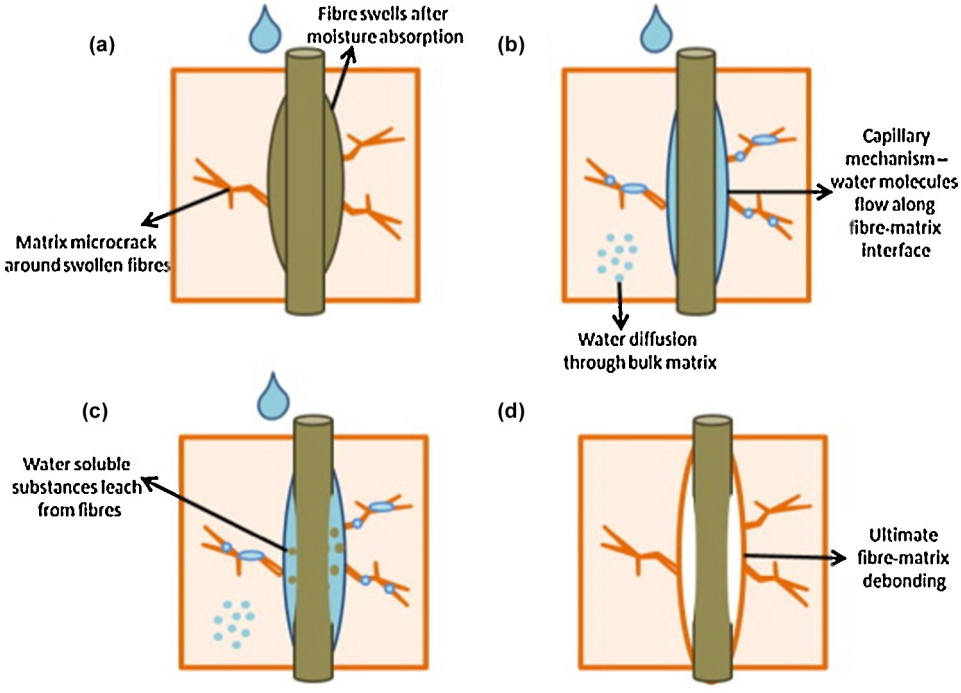

Fig. 4. Effect of water on fibre–matrix interface [27].

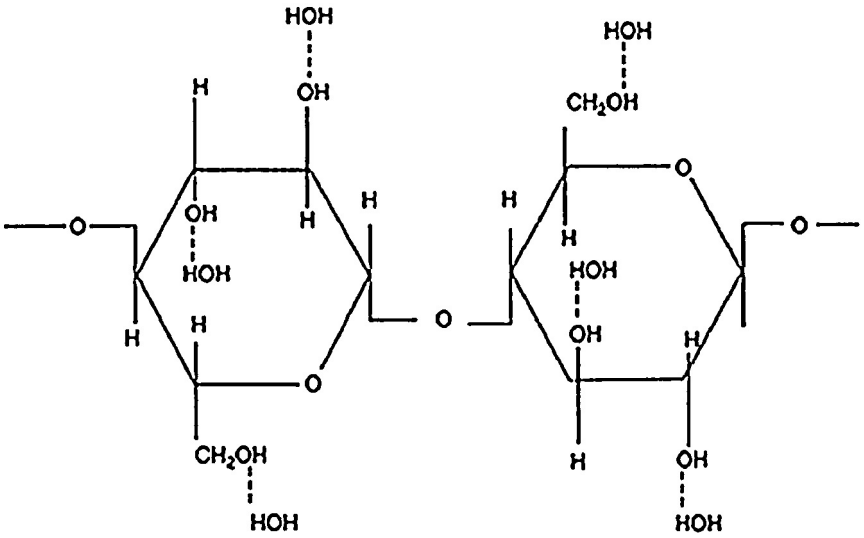

Fig. 5. Schematic of moisture absorption by natural fibre [29].

Fig. 6. In the dry samples, the flexural modulus increased as the fibre content increased. The addition of 4.5, 6.2 and 8.3 wt% CF increased the flexural modulus from 0.87 to 1.23, 1.4 and 1.74 GPa, respectively, compared to pure geopolymer: thus, an increase in the fibre content of the composite material resulted in an increase in flexural modulus. The improvement in flexural modulus is believed to be due to the higher initial modulus of the natural fibres acting as backbones in the composites [30,31]. This is supported by earlier studies, which have reported significant increases in the flexural modulus of natural fibre-reinforced polymer composites. For example, Ma et al. [32] reported that the flexural modulus of winceyette fibre-reinforced thermoplastic starch composites increased from 45 MPa for neat resin to approximately 140 GPa as the fibre content increased from 0% to 20%.

The influence of water absorption on the flexural modulus of CF reinforced geopolymer composites is also shown in Fig. 6, which shows a considerable decrease in the flexural modulus of the wet samples when compared to the dry samples. The reason for this is that in the wet samples absorbed water molecules and reduced the intermolecular hydrogen bonding between cellulose molecules in the fibre and established intermolecular hydrogen bonding between the cellulose molecules and water molecules in the fibre, thereby reduced the interfacial adhesion between the fibre and the matrix and resulting in decreased flexural modulus [15]. Fig. 7 illustrates the typical flexural stress–strain curves for geopolymer composites before and after being placed in water. It can be observed that the maximum stress in dry composite significantly decreased after immersion in water for a

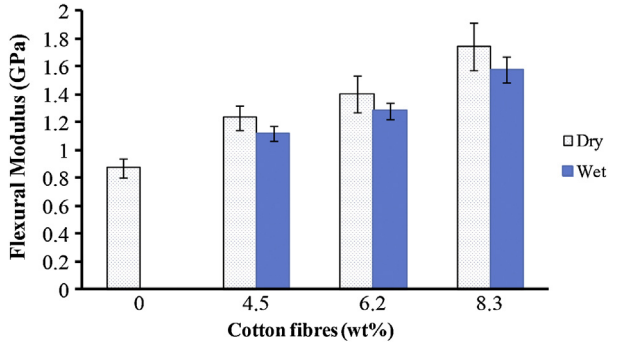

Fig. 6. Flexural modulus of geopolymer composites in dry and wet conditions.

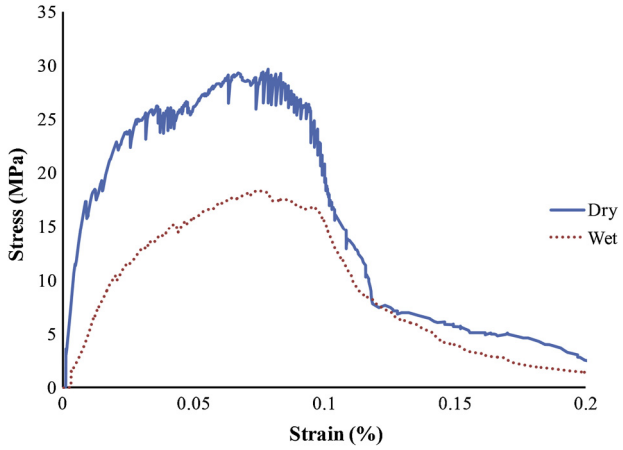

Fig. 7. Typical stress–strain curves of geopolymer composites in dry and wet conditions.

prolonged period. This drop can be attributed to degradation in the fibre–matrix interfacial bonding caused by the water absorption [11].

3.2.3. *Impact strength*

Impact strength is an important property that gives an indication of overall material toughness. Impact strength of fibre-reinforced polymer is governed by the matrix–fibre interfacial bonding, and the properties of both matrix and fibre. When the composites undergo a sudden force, the impact energy is dissipated by the combination of fibre pullouts, fibre fracture and matrix deformation [10]. Normally in fibre-reinforced polymer composites, the impact strength increases as fibre content increases because of the increase in fibre pull out and fibre breakage [33].

The effect of fibre contents on the impact strength of dry and wet cotton fibre-reinforced geopolymer composites is shown in Fig. 8. It can be seen that impact strength significantly increased as the CF content increased in dry composites. The presence of CF layers in the matrix increases the ability of these composites to absorb impact energy. In dry conditions, the addition of CF with contents of 4.5, 6.2 and 8.3 wt% increases the impact strength from 1.9 to 6.2, 8.5 and 13.4 KJ/m^2, respectively compared to unreinforced geopolymer. Similar remarkable improvements in impact strength were reported by Graupner [24], who observed that the addition of

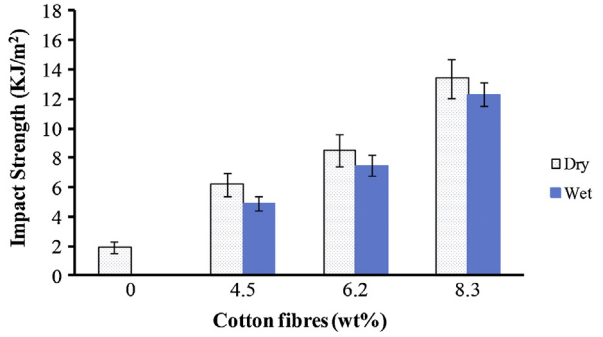

Fig. 8. Impact strength of geopolymer composites in dry and wet conditions.

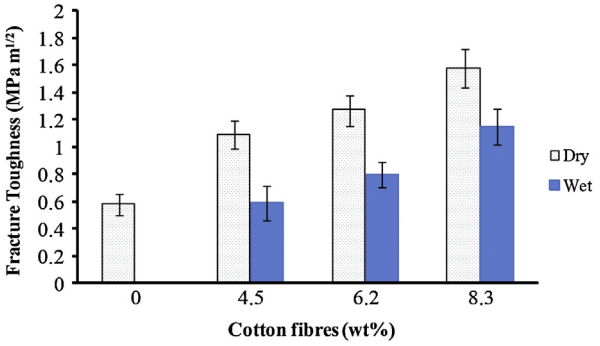

Fig. 10. Fracture toughness of geopolymer composites in dry and wet conditions.

cotton fibre increased the impact strength of pure poly(lactic acid) matrix. He concluded that the increase was due to greater elongation of cotton fibres at break. Fibres containing much cellulose generally have high elongation at break values. Cotton has a cellulose content of about 88–96%. Elongation at break and impact strength are directly correlated. The high elongation at break of cotton fibres increased the elongation at break in the composites, leading to higher impact strength.

However, impact strength is adversely affected by water absorption. The decrease in impact properties after water immersion can be related to the weak fibre–matrix interface, which resulted in a reduction of the mechanical properties and dimensional stability of composites [14].

3.2.4. Hardness

The effect of cotton fibre contents on the hardness of the cotton fibre-reinforced geopolymer composites is presented in Fig. 9. The hardness of geopolymer composites reinforced with 4.5, 6.2 and 8.3 wt% CF increased from 65.5 to 87.22, 92.32 and 86.4 HRH, respectively relative to the neat geopolymer. This enhancement in hardness is caused by the distribution of the test load on the fibres, which decreased the penetration of the test ball on the surface of the composite material and consequently improved the hardness of this material [34].

However, hardness is affected by water absorption, as shown in Fig. 9. Hardness decreases in all cotton fibre-reinforced samples in wet condition, and is associated with the weakening of interface between the geopolymer matrix and the cotton fibre caused by the water absorption. This decrease has been reported by other researchers working with natural fibre-based composites. Dhakal et al. [35] reported that as water absorption increased, the hardness of flax fibre-reinforced composites decreased, and found that the deformation depth increased for water-immersed specimens compared to dry ones, due to the hydrophilic nature of the fibres, and eventually led to the formation of a weak fibre–matrix interface. In

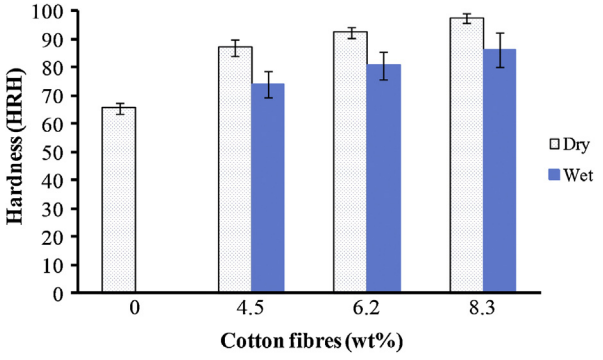

Fig. 9. Hardness of geopolymer composites in dry and wet conditions.

the case of cotton fibre-reinforced geopolymer composites when water uptake reaches saturation level, the bound water and the free water remain in the composite as a reservoir. This leads to softening of the fibres and weakening of the fibre matrix adhesion, resulting in reduced material properties.

3.2.5. Fracture toughness

The effect of cotton fibre contents on the facture toughness of geopolymer composites is presented in Fig. 10. The addition of cotton fibre gradually increased the fracture toughness of CF reinforced geopolymer composites compared to net geopolymer. Cotton fibres play a significant role in enhancing the facture toughness of the matrices through several energy-absorbing characteristics such as fibre rupture, fibre–matrix interface debonding, fibre pull-out and fibre-bridging, which slow crack propagation and therefore increase the fracture energy [36–40]. The fracture toughness of geopolymer reinforced with 4.5, 6.2 and 8.3 wt% CF increased from 0.57 to 1.09, 1.27 and 1.58 MPa $m^{1/2}$, respectively compared to neat geopolymer. This significant enhancement in facture toughness at higher CF content is due to extensive fibre pull-out, fibre fracture and fibre-bridging of cotton fibres.

The effect of water absorption on fracture toughness of CF-reinforced geopolymer composites is also shown in Fig. 10. The fracture toughness for all wet composites considerably decreased compared to the dry composites, as a result of the severe damage to fibre structure and interfacial bonding between the cotton fibre and the geopolymer matrix caused by the absorbed water. Typical load–displacement curves for the composites before and after immersion in water are shown in Fig. 11. It can be seen that the maximum peak load of dry composite significantly decreased after immersing in water for a prolonged period. The areas under the curve indicate that the wet composite achieved lower fracture toughness than the dried composite. This reduction can be

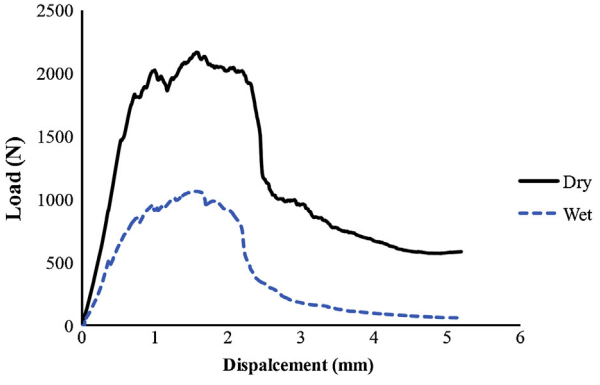

Fig. 11. Typical load–displacement curves of geopolymer composites in dry and wet conditions.

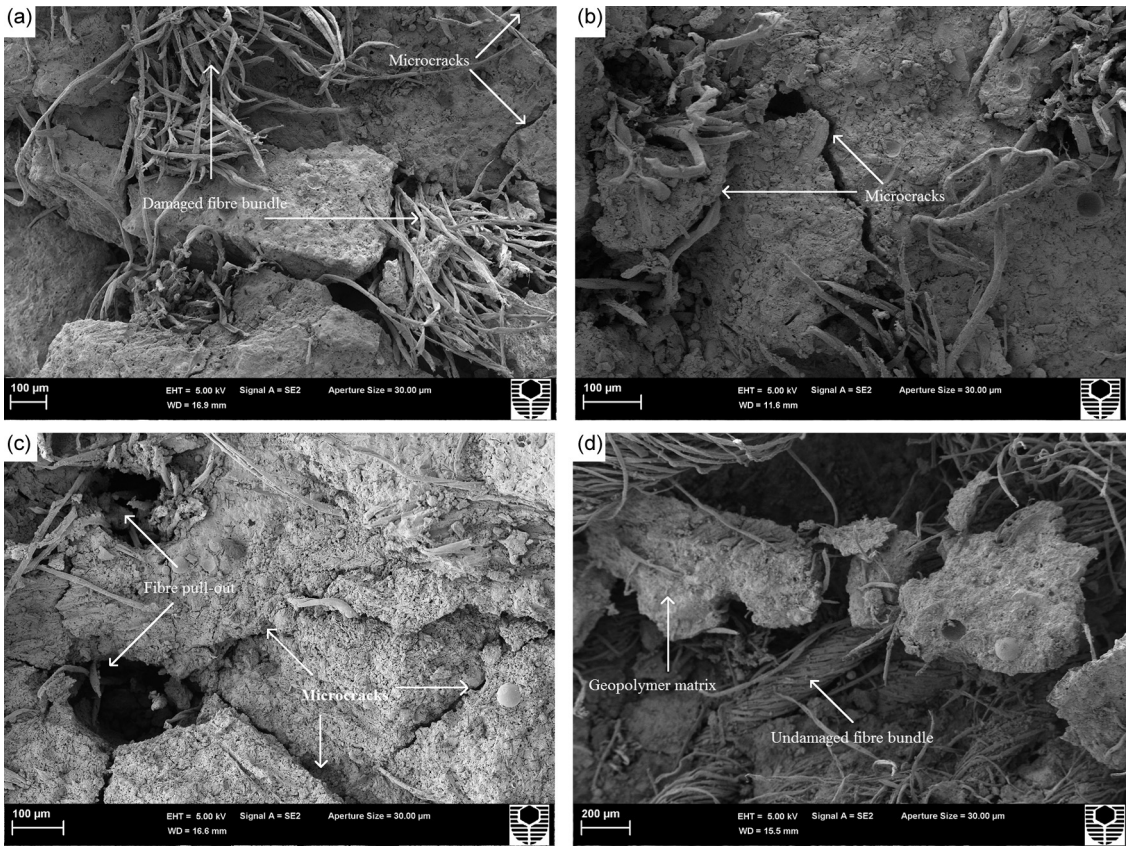

Fig. 12. SEM micrographs showing (a) separation of the cotton fibre bundles into finer fibrils, (b) matrix cracking, (d) fibre pull-out and (c) small pieces of matrix attached to the fibre.

explained as the effect of moisture absorption causing swelling of fibres, which creates micro-cracks in the sample, leading to lower fracture toughness [24]. In addition, water molecules diffuse into the fibre–matrix interfaces through these micro-cracks, which cause debonding of the fibres and thus weakens the fibre–matrix interface [14].

The reduction in fracture toughness can be attributed to internal pore water pressure which developed in the limited pore spaces of the wet geopolymer composites. Water does not move into a pore when adjacent pores are completely filled with water. As a result, a very high disjoining pressure is produced due to the capillary action, leading to early crack propagation under external loading. The fracture resistance of wet geopolymer composites thus becomes lower than that of dry composites [41].

The microstructures of dry and wet composites reinforced with 8.3 wt% CF are shown in Fig. 12a–d. Fig. 12a and b shows severe matrix cracking and degradation of the interfacial adhesion between the fibres and the matrix in wet composites characterised by the appearance of gap between fibre and matrix. Water penetrates into the cotton fibre bundle and causes the breaking down of the composite fibre bundle into finer fibrils due to decrease in bundle coherence when subjected to flexural loads, as shown in Fig. 12a. It can also be observed extensive fibre pull-out and no evidence or traces of matrix adhering to the fibre which are an indication of poor fibre–matrix adhesion as shown in Fig. 12c of wet composite. In contrast, prior to exposure to water, SEM micrographs showed almost no fibre pull-out, undamaged fibre bundle and small pieces of geopolymer paste were attached to the fibre surface of cotton fibre. These observations are indicative of strong bond between the fibres and the matrix in dry composite as shown in Fig. 12d.

4. Conclusions

CF reinforced geopolymer composite has been fabricated and the effect of water absorption on the mechanical properties of the composite is evaluated. The presence of CF layers in the geopolymer composite significantly increased all mechanical properties (e.g., flexural strength, flexural modulus, impact strength, hardness and fracture toughness) compared to un-reinforced geopolymer. This remarkable enhancement is due the unique properties of cotton fibre in withstanding the bending force and resisting fracture force compared to brittle geopolymers.

However, cotton fibres are hydrophilic in nature and hence have a poor resistance to water absorption. The water absorption of CF-reinforced geopolymer composites at room temperature was found to increase with increasing fibre content. Exposure to moisture for an extended period causes a reduction in flexural strength, flexural modulus, impact strength, hardness and fracture toughness. A plausible explanation for this would be that bonding at the fibre–matrix interfaces is degraded as a result of water absorption. SEM micrograph of fractured wet composite also showed damage of cotton fibre–geopolymer matrix interface and damage of cotton thread into ruptured cotton fibrils.

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3.8 Mechanical Properties of Cotton Fabric Reinforced Geopolymer Composites at 200–1000 °C

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Research Article

Mechanical properties of cotton fabric reinforced geopolymer composites at 200–1000 ℃

Thamer ALOMAYRI[a,b], Les VICKERS[a], Faiz U. A. SHAIKH[c], It-Meng LOW[a,*]

[a]*Department of Imaging & Applied Physics*, *Curtin University*, *GPO Box U1987*, *Perth*, *WA 6845*, *Australia*
[b]*Department of Physics*, *Umm Al-Qura University*, *Makkah 21955*, *Saudi Arabia*
[c]*Department of Civil Engineering*, *Curtin University*, *GPO Box U1987*, *Perth*, *WA 6845*, *Australia*

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Abstract: Geopolymer composites containing woven cotton fabric (0–8.3 wt%) were fabricated using the hand lay-up technique, and were exposed to elevated temperatures of 200 ℃, 400 ℃, 600 ℃, 800 ℃ and 1000 ℃. With an increase in temperature, the geopolymer composites exhibited a reduction in compressive strength, flexural strength and fracture toughness. When heated above 600 ℃, the composites exhibited a significant reduction in mechanical properties. They also exhibited brittle behavior due to severe degradation of cotton fibres and the creation of additional porosity in the composites. Microstructural images verified the existence of voids and small channels in the composites due to fibre degradation.

Keywords: geopolymer composites; microstructures; mechanical properties; fracture toughness

1 Introduction

Portland cements are used in many building and construction applications because of their good mechanical performance. However, the emission of greenhouse gases associated with their manufacture is a serious problem. In recent years, a new class of environmentally friendly and sustainable inorganic aluminosilicate polymers (known as geopolymers) has emerged as an alternative to Portland cements. These inorganic compounds do not use Portland cements as binder, but instead employ a material such as fly-ash, rich in silicon (Si) and aluminium (Al), which reacts to alkaline liquids to produce binder [1–4]. Geopolymers have attracted the interest of scientists due to their low cost, low curing and hardening temperatures, and excellent thermal stability at high temperatures [5–9]. However, despite these desirable attributes, they suffer from brittle failure like most ceramics. This limitation may be readily overcome through fibre reinforcement as in high-performance polymer-matrix composites. Hitherto, the most common fibre reinforcement used in geopolymer composites is based on steel, carbon, polypropylene (PP) and polyvinyl alcohol (PVA) [10–15].

Current concerns over the environment and climate change have given rise to an increasing interest in replacing the synthetic fibres currently used in geopolymer composites or other brittle matrices with natural plant fibres [16,17]. Investigations of natural fibres such as sisal, coconut, bamboo, jute, banana, coir and hemp fibres have revealed desirable effects on

* Corresponding author.
E-mail: j.low@curtin.edu.au

the mechanical and physical properties of brittle organic and inorganic matrices [18–27]. For example, the mechanical and thermal properties of geopolymer resin have been significantly improved as a result of natural wool fibre reinforcement [28,29]. Similarly, Teixeira-Pinto *et al*. [30] found that jute fibres are effective in improving the mechanical properties of geopolymer composites, and Al Bakri *et al*. [31] observed a similar desirable effect in wood-fibre reinforced geopolymers.

In recent years, investigations into the resistance of geopolymer concrete to elevated temperatures have been of particular interest, and many promising results have been obtained [32]. One of the requirements for safety when designing construction structures is the ability to resist elevated temperatures which can lead to spalling because of reduced permeability and increased brittleness. In high-performance concrete, fibres are often added to overcome the adverse effects of fire-induced spalling, as they melt or degrade at certain temperatures and form dehydration pathways for escaping water, preventing pore pressure build-up. However, the presence of porosity and small channels created by fibre melting or degrading may reduce the mechanical strength of the composites [33,34].

According to the literature, the effect of elevated temperature on the mechanical properties of cotton fabric reinforced geopolymer matrix composites has not yet been reported so far. In the present work, therefore, cotton fibre/geopolymer composites were prepared and then heated at different temperatures ranging from 200 ℃ to 1000 ℃. Mechanical properties such as flexural strength, compressive strength and fracture toughness were evaluated. Thermogravimetric analysis (TGA), optical microscopy and scanning electron microscopy (SEM) were used to investigate their thermal behavior, microstructure and failure mechanisms. Results suggest that this is a promising area of investigation, adding significantly to the body of literature on natural and green alternatives to concrete.

2 Experimental

2.1 Preparation of geopolymer composites

Cotton fabric (CF) of 30 cm × 7.5 cm was used to reinforce the geopolymer composites. Low-calcium fly-ash (ASTM Class F), collected from Collie power station in Western Australia, was also used as the source material of the geopolymer matrix. The chemical composition of fly-ash (FA) is shown in Table 1. The alkaline activator for geopolymerisation was a combination of sodium hydroxide solution and sodium silicate grade D solution which were supplied by PQ Australia. Sodium hydroxide flakes with 98% purity were used to prepare the solution. The chemical composition of sodium silicate used was 14.7% Na_2O, 29.4% SiO_2 and 55.9% water by weight.

Composite samples were prepared by spreading a thin layer of geopolymer paste in a well-greased wooden mould, followed by carefully laying the first layer of woven cotton fabric on that layer. Thereafter, the fabric was fully impregnated (wet out) with geopolymer paste by a roller before placing the next layer. This process was repeated for the desired numbers of cotton fabric layers. Each specimen contained different layers of cotton fabric. For each specimen, the final layer was geopolymer paste. The alkaline solution to fly-ash weight ratio was fixed at 0.35, whereas the weight ratio of sodium silicate solution to sodium hydroxide solution was maintained at 2.5. The composite specimens were placed on a vibration table in order to ensure better penetration of the matrix among the fabric openings and to remove the entrapped air voids. The specimens were also pressed under 25 kg load for 3 h. Subsequently, the specimens were covered with plastic film and cured at 80 ℃ in an oven for 24 h.

After curing, the composite samples with different weight percentages of fibres (0 wt%, 4.5 wt%, 6.2 wt% and 8.3 wt%) were heated in a ventilated furnace to assess their strength retention at temperatures of 200 ℃, 400 ℃, 600 ℃, 800 ℃ and 1000 ℃. The heating was carried out at a rate of 5 ℃/min until the target temperatures were reached; these final temperatures were held for 2 h. The specimens were left to cool naturally inside the furnace before being removed to room temperature. Their dimensions were measured using a digital vernier calliper to determine drying shrinkage (D) using the following equation:

$$D = \frac{L_0 - L}{L_0} \times 100\% \quad (1)$$

where L_0 is the initial length of specimens before

Table 1 Chemical composition of fly-ash in weight percentage (Unit: wt%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Others	LOI
50	28.25	13.5	1.78	0.89	0.38	0.32	0.46	2.78	1.64

heating; and L is the length of specimens after heating.

2.2 Characterisation

2.2.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out for cotton fibres, unreinforced geopolymer and cotton fabric reinforced geopolymer composites at a heating rate of 10 ℃/min under atmospheric condition. The temperature range scanned between 50 ℃ and 1000 ℃. The weight of all specimens was maintained around 15 mg.

2.2.2 Porosity

Porosity tests were performed according to ASTM C20 [35]; the value of apparent porosity (P_s) was calculated using the following equation [35]:

$$P_s = \frac{W_a - W_d}{W_a - W_w} \times 100\% \quad (2)$$

where W_d is the weight of the dried sample; W_w is the weight of the sample saturated with and suspended in water; and W_a is the weight of the sample in air.

2.2.3 Optical microscopy and scanning electron microscopy

The microstructures of the samples were studied under a Nikon SMZ 800 stereo microscope. This was undertaken to take advantage of the color contrast provided by optical microscopy.

A NEON 40EsB (Zeiss, Germany) field-emission SEM was used to examine the microstructures of the prepared samples. The fracture samples were mounted on aluminium stubs using carbon tape and coated with a thin layer of platinum to prevent charging during the observation.

2.3 Mechanical properties

Rectangular bars measuring 60 mm × 20 mm × 20 mm were cut from the fully cured samples and subjected to three-point bend tests performed in a LLOYD material testing machine (50 kN capacity) with a displacement rate of 0.5 mm/min. Five specimens of each composition were tested. The flexural strength (σ_f) was determined using the following equation [9]:

$$\sigma_f = \frac{3}{2}\frac{p_{max}S}{BW^2} \quad (3)$$

where p_{max} is the maximum load at crack extension; S is the span of the sample; B is the specimen width; and W is the specimen thickness (depth).

The compressive strength of the composites was measured using LLOYD material testing machine (50 kN capacity). The cubes were tested according to ASTM C109 [36]. The compressive strength (C) was calculated using the following formula:

$$C = \frac{p}{A} \quad (4)$$

where p is the total load on the sample at failure; A is calculated area of the loaded surface of the specimen.

Rectangular bars of 60 mm long and a cross-sectional dimension of 20 mm × 20 mm were used in the fracture toughness measurements. A crack with a length to thickness (depth) ratio (a/W) of 0.4 was introduced into each specimen using a 0.4 mm diamond blade, and the fracture toughness K_{IC} was calculated using the following equation:

$$K_{IC} = \frac{p_{max}S}{BW^{3/2}} f(a/W) \quad (5)$$

where p_{max} is the maximum load at crack extension; S is the span of the sample; B is the specimen width; W is the specimen thickness (depth); a is the crack length; and $f(a/W)$ is the polynomial geometrical correction factor given by [17]:

$$f(a/W) = \frac{3(a/W)^{1/2}}{2(1+2a/W)(1-a/W)^{3/2}} \times [1.99 - (a/W)(1 - a/W)(2.15 - 3.93a/W + 2.7a^2/W^2)] \quad (6)$$

3 Results and discussion

3.1 Thermal properties

The thermal stability of the composites was studied using the thermogravimetric analysis (TGA); thermograms of pure geopolymers, geopolymer composites and cotton fibres are shown in Fig. 1. The geopolymer matrix undergoes weight loss between 50 ℃ and 250 ℃ due to the evaporation of free water. The composites show a similar trend, with a slight additional weight loss above 250 ℃ which may be attributed to the thermal decomposition of the cotton fibres.

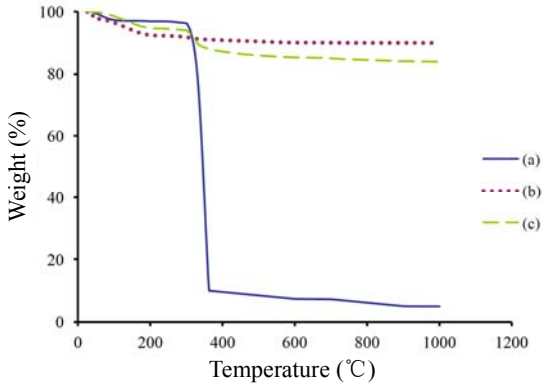


Fig. 1 TGA curves of (a) cotton fibres, (b) pure geopolymers and (c) geopolymer composites.

As shown in Fig. 1, pure cotton fibres degrade in three main stages. The first transition occurs from 50 ℃ to about 250 ℃, with the release of absorbed moisture from the fibre by evaporation. In this stage, the weight loss of cotton fibres is roughly similar to that of other natural fibres such as kenaf, jute and wood [37–39]. The second transition occurs between 250 ℃ and 370 ℃ when a large weight loss occurs, attributable to the degradation of cellulose. The third stage occurs above 370 ℃ when the fibres start to decompose, but shows a lower rate of weight loss. In this stage, all volatile materials are driven off, resulting in the formation of residual char in the sample. Similar degradation stages of cotton fibres were observed by Babu *et al*. [40] when they studied the thermal decomposition characteristics of cotton fibres using the thermogravimetric analysis.

3.2 Temperature effects on drying shrinkage

Figure 2 shows that the shrinkage of geopolymer composites increases with an increase of cotton fibres in the matrix. This tendency is observed for all samples at various temperatures. In all the three composites containing cotton fibres (4.5 wt%, 6.2 wt% and 8.2 wt%), the drying shrinkage increases as temperature increases.

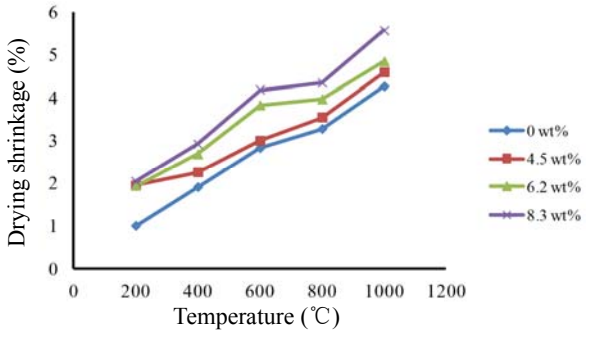


Fig. 2 Drying shrinkage of geopolymer composites at various temperatures.

This is in contrast with reports of reduced shrinkage in geopolymer composites containing a small quantity of synthetic fibres such as carbon at elevated temperatures [41]. Shrinkage of geopolymer composites is influenced by many factors, including fibre type and fibre content when drying begins. The results here indicate that the addition of cotton fibres increases the matrix porosity (Fig. 3) and contributes to a higher drying shrinkage. This is due to more moisture paths being created into the matrix, which is also reported by Toledo Filho *et al*. [42] in their study of the effect of vegetable fibres on drying shrinkage of cement mortar composites.

3.3 Change in color with temperature

After heating at various temperatures, the samples were assessed visually to determine the color change. Photographs of the geopolymer composite samples before and after heating at various temperatures are shown in Fig. 4.

All samples exhibit a change in color after exposure to elevated temperatures as follows: grey at 200 ℃,

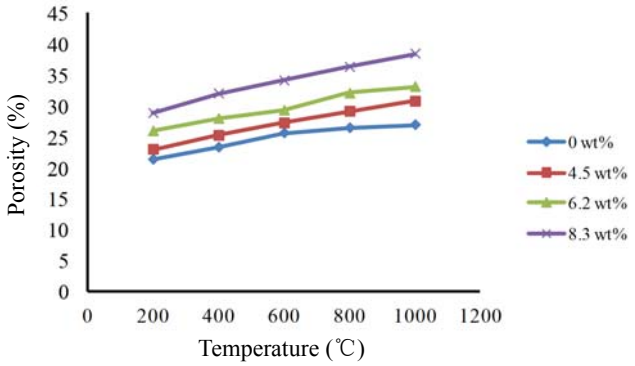


Fig. 3 Porosity of geopolymer composites at various temperatures.

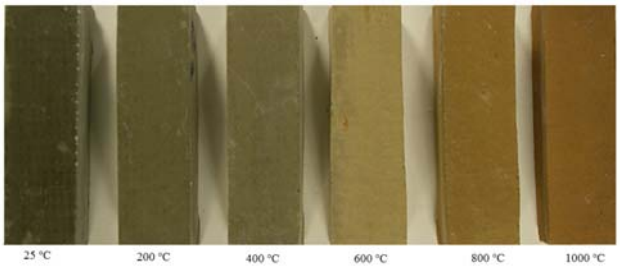


Fig. 4 Geopolymer composites loaded with 8.3 wt% CF before and after heating at various temperatures.

yellowish grey between 400 ℃ and 600 ℃, pink up to 800 ℃, and reddish brown at 1000 ℃. High temperature exposure causes the oxidation and liberation of iron species present in the fly-ash particles, where similar observations were also reported by Rickard *et al*. [43] when testing the color change of Collie fly-ash geopolymers at elevated temperatures. Such color changes are a useful tool for estimating temperatures easily which have been reached after exposure to fire. They can also be used as an indication of significant loss in mechanical properties and are useful since the appearance coincides with a significant reduction in strength as a result of heating [44].

3.4 Crack analysis

It is well known that cracks occur in concrete during fire because of the internal pressure of evaporable moisture, characterised by hairline cracks over the surface at low to medium temperatures and extending deep into the specimen at higher temperatures. The result is a significant reduction in structural integrity and load-carrying capacity [45]. One of the primary mechanisms responsible for concrete cracking is low porosity, which slows the migration of water vapour and offers few escape channels, leading to higher pore pressures [46].

In this study, networks of hairline cracks are observed on un-reinforced geopolymer specimens heated at 400 ℃ and 600 ℃. Beyond 600 ℃, severe cracking occurs on the surfaces, as shown in Fig. 5. It is probable that cracking is initially due to the normal thermal contraction of geopolymer paste, causing local changes to the geopolymer microstructure. An increment in temperature leads to additional contraction in the matrix as water is driven off. This phenomenon has been observed to occur in the geopolymer gel during dehydroxylation between 300 ℃ and 600 ℃ [47]. However, when cotton fibres are incorporated, no crack is found in the surface of geopolymer composites as shown in Fig. 4. This indicates that cotton fibres are very effective in prevention of cracking caused by high temperatures due to the formation of small cavities inside the matrix created by the fibre degradation. The structure of the composites becomes more porous, and the expanded water vapour escapes without substantial damage to the microstructure.

Fig. 5 Photograph of the geopolymer composites loaded with 0 wt% CF after heating at 1000 ℃.

Such degradation of the cotton fibres may be beneficial to the behavior of geopolymer composites under thermal exposure. At high temperatures, when all water is not expelled fast enough from the composites, internal vaporisation may create high pressures inside the matrix. The porosity and small channels created by the degradation of the cotton fibres may lower internal vapour pressures and thus reduce the likelihood of cracking.

3.5 Effects of temperature on mechanical properties

3.5.1 Compressive strength

The influence of elevated temperature on compressive strength of geopolymer composites is exhibited in Fig. 6. The compressive strength of all geopolymer composites decreases after exposure to temperatures between 200 ℃ and 1000 ℃. This reduction in compressive strength is probably because of the persistent deterioration of the geopolymer hydrates, which contributes most of the compressive strength of the composites, as temperature increases. Moreover, this decreasing tendency in compressive strength also results from increasing porosity as temperature increases. The total porosities of the composites heated to 800 ℃ and 1000 ℃ are higher than those at 200 ℃, 400 ℃ and 600 ℃ (Fig. 3). The hydrophilic nature of cotton fibres enables the composites to take up moisture from the surrounding environment, increasing their water content. Upon heating, dehydration causes weight loss as is evident in Fig. 1. At low temperatures, dehydration is slow, but as temperature increases, so does the dehydration rate, leading to greater weight loss and the formation of a large quantity of voids that damage the bond between fibre and matrix and act as stress concentration points, resulting in a loss in load-bearing capacity [17]. Some authors carried out compressive tests on concrete containing polypropylene (PP) fibres and reported that, the strength properties decrease with the increase of temperature, due to the additional porosity and small

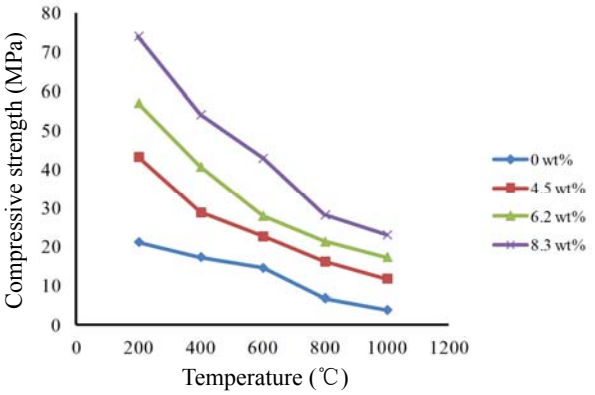


Fig. 6 Compressive strength of geopolymer composites at various temperatures.

channels created by the melting of the PP fibres [48–50].

3.5.2 Flexural strength

Like compressive strength, the flexural strength of all the composites decreases with an increase in temperature. As shown in Fig. 7, the reduction in flexural strength of the composites at 800 ℃ and 1000 ℃ is greater than those at 200 ℃, 400 ℃ and 600 ℃. The main cause of this strength reduction may be attributed to fibre degradation, or to burning and void formation. When temperature increases, more fibres may degrade and more voids form, leading to a continual decrease in flexural strength. SEM examinations reveal some cotton fibres surviving inside the specimens heated between 200 ℃ and 600 ℃ (Figs. 8(a)–8(c)): the possible reason for the higher flexural strength of these composites than those heated at 800 ℃ and 1000 ℃ where most of fibres degrade (Figs. 8(d) and 8(e)).

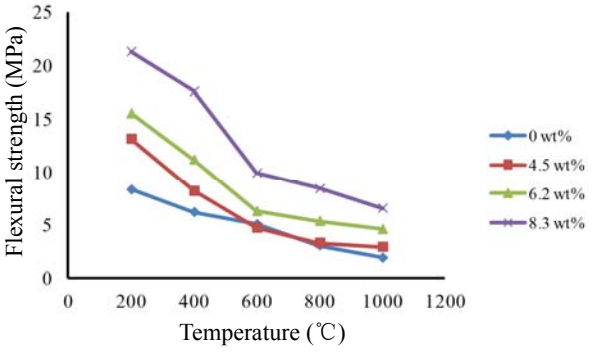
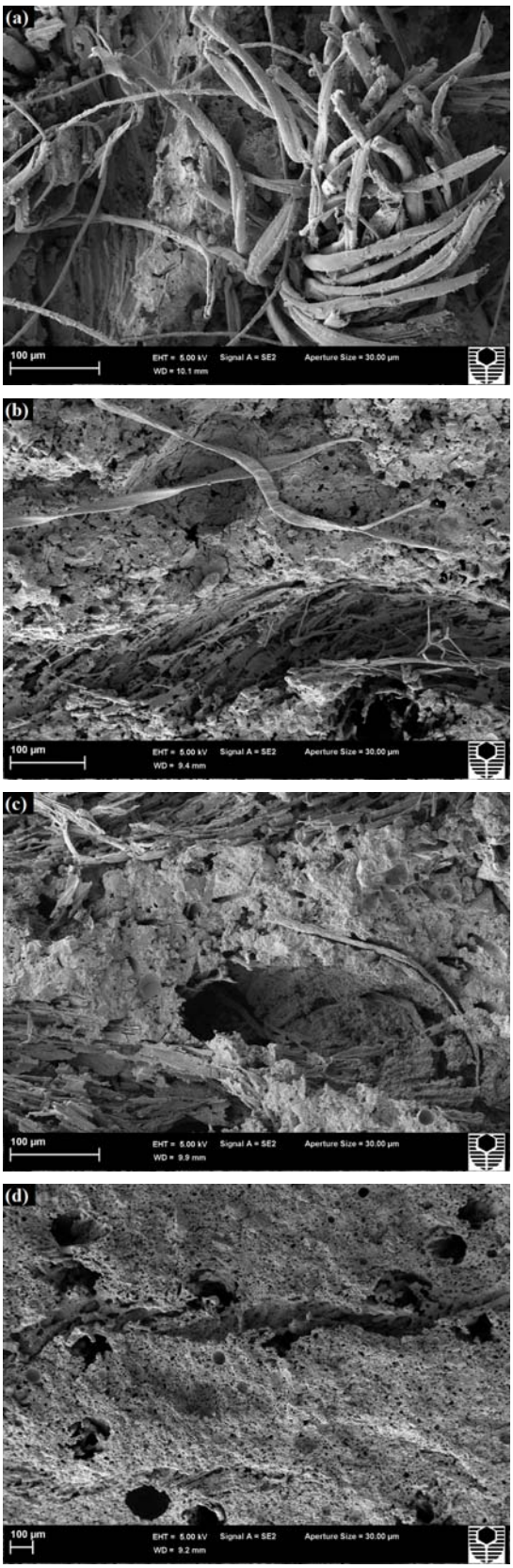


Fig. 7 Flexural strength of geopolymer composites at various temperatures.



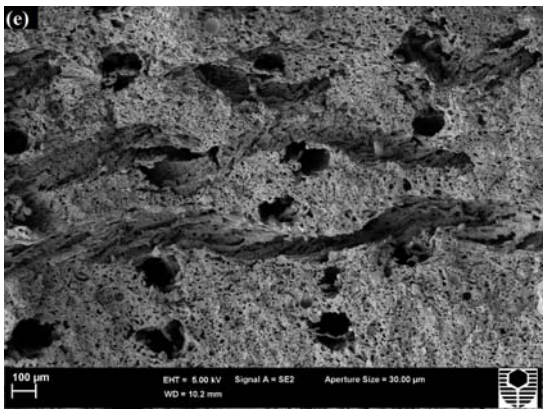


Fig. 8 SEM images of the fracture surface for geopolymer composites loaded with 8.3 wt% CF at various temperatures: (a) 200 ℃, (b) 400 ℃, (c) 600 ℃, (d) 800 ℃ and (e) 1000 ℃.

Of the few reported investigations of the flexural strength of geopolymer composites at high temperatures, Lin *et al.*'s study [41] of elevated temperature on carbon fibre reinforced geopolymer composites found that flexural strength decreases with increasing temperature. They concluded that microcracking is the primary mechanism causing fibre degradation, occurring when high temperatures cause both free and hydration water to evaporate and leave voids, leading to lower flexural strength.

3.5.3 Fracture toughness

In general, natural fibre–polymer composites display crack deflection, de-bonding between fibre and matrix, fibre pull-out and fibre-bridging, all of which contribute to improving fracture toughness [51,52].

Figure 9 shows that an increase in temperature of the geopolymer composites causes a decrease in fracture toughness. This can be explained by the very high porosity caused by the oxidation and consequent degradation of the cotton fibres, becoming more severe as temperature increases. At the highest temperatures tested (800 ℃ and 1000 ℃), enhanced porosity formation in the matrices is observed, the probable result of the cotton fibre burning as shown in Figs. 8(d) and 8(e). The images show high porosity in the composites as consequence of cotton fibre degradation due to oxidation effects, thus resulting in low fracture toughness because no fibre pull-out or fibre-fracture is observed. At testing temperatures below 800 ℃, the higher fracture toughness of the composites may account for the presence of toughening mechanism such as fibre-bridging, fibre pull-out and fibre-fracture as only evident in the specimens exposed to 200–600 ℃ and confirmed by SEM observations (Figs. 8(a)–8(c)).

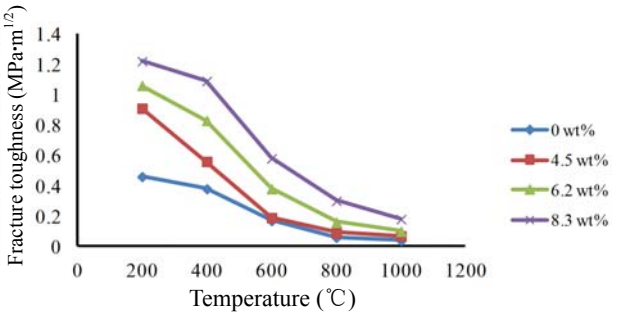
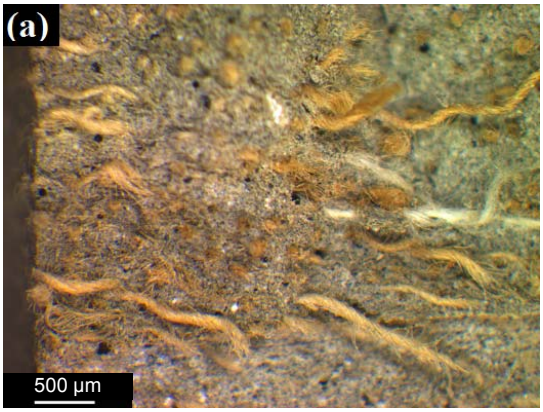


Fig. 9 Fracture toughness of geopolymer composites at various temperatures.

3.6 Microstructure analysis

To observe changes in microstructure at moderate length scales, microscopy at low magnification and with a large field of view was conducted; Figs. 10(a)–10(c) show the optical micrographs of specimens exposed to elevated temperatures from 200 ℃ to 600 ℃. A significant amount of oxidation appears as dark "burns out" areas along the outer perimeter of the samples; but the centres remain pristine because oxygen is quickly depleted at the edge of the sample and no oxygen remains to react with the cotton fibres inside. The good condition of the interior fibres indicates that the geopolymer paste aids in stopping or significantly decreasing the supply of oxygen to the interior of the composites.

The matrix is effective in cutting off the oxygen supply to the fibres at temperature up to 600 ℃ (Figs. 10(a)–10(c)); however, as the specimen is heated further, many voids and caverns form around the edge and along the matrix (Figs. 10(d) and 10(e)), probably owing to the severe degradation of cotton fibres caused



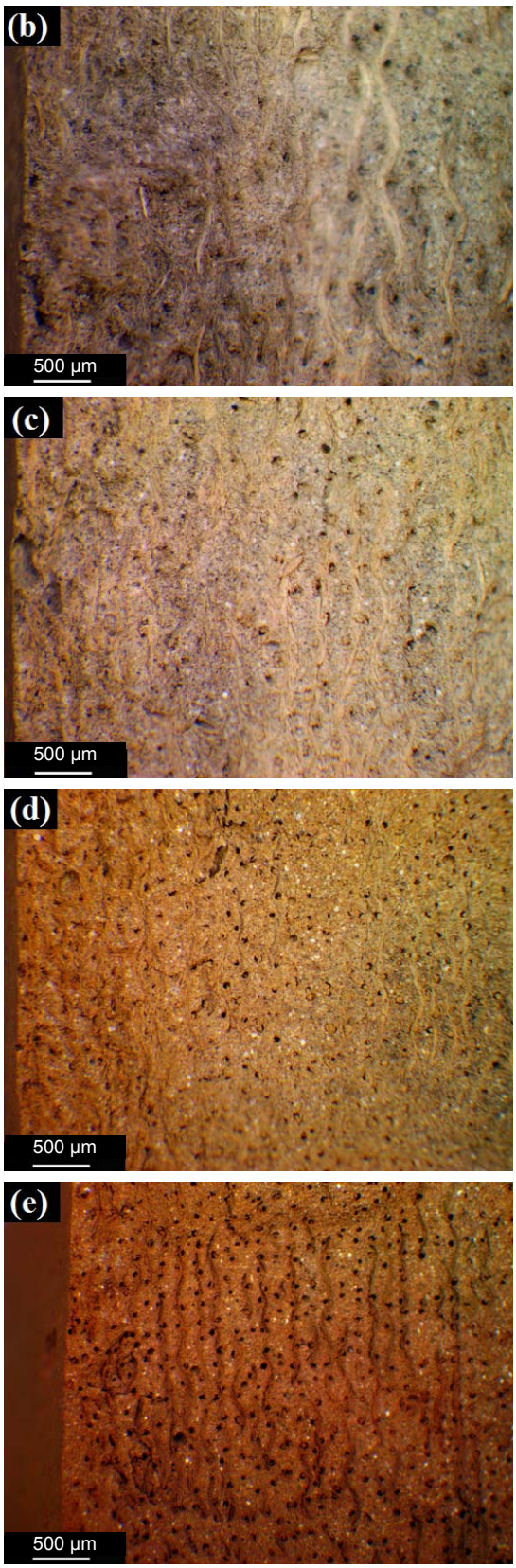


Fig. 10 Optical micrographs of geopolymer composites loaded with 8.3 wt% CF at various temperatures: (a) 200 ℃, (b) 400 ℃, (c) 600 ℃, (d) 800 ℃ and (e) 1000 ℃ .

by oxidation along the edge and deep into the interior of the sample. As the temperature approaches 800 ℃ and 1000 ℃, oxygen is better able to diffuse into the interior and react with the fibres, leading to complete fibre burnout. However, no crack is observed in any of the specimens at these temperatures, possibly because the degrading cotton fibres form the dehydration pathways along which water could escape, preventing the build-up of pore pressures.

Therefore, the addition of cotton fibres to a geopolymer matrix has a positive influence, enhancing the temperature resistance and the mechanical and fracture properties of the composites. This makes them suitable for use in technological applications which are likely to be exposed to extreme high temperatures during wildfire: underground structures and reinforcement of mine works (adits, tunnels, etc.) are possibilities, as railroad and road tunnel constructions are.

4 Conclusions

The effect of temperature (200–1000 ℃) on the mechanical properties of cotton fabric reinforced geopolymer composites was investigated. Physical degradation mechanisms resulting from exposure to high temperatures were identified by monitoring color change, cracking and microstructure of the composites. The addition of cotton fibres has been shown to prevent matrix cracking after exposure of the geopolymer composites to high temperatures because of the additional porosity and small channels being created as they degrade.

The results also show that compressive strength, flexural strength and fracture toughness all decrease after exposure to high temperatures (200–600 ℃). A severe loss in strength was observed on specimens heated at 800 ℃ and 1000 ℃ due to fibre degradation and formation of a large quantity of voids.

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4 CONCLUSIONS AND FUTURE WORK

4.1 Short Cotton Fibre Reinforced Geopolymer Composites

Short cotton fibre-reinforced geopolymer composites with a range of fibre contents from 0 to 1.0 wt.% were prepared by adding short cotton fibres in fly ash based geopolymer paste. The fabricated composites were investigated to identify and assess the effect of fibre reinforcement on the flexural modulus, flexural strength, impact strength, hardness, compressive strength and fracture toughness. It was found that the addition of cotton fibre reinforcements increased the flexural modulus, flexural strength and impact strength of geopolymer composites. For example, while pure geopolymer showed a flexural strength of 10.4 MPa, reinforcement with 0.3 and 0.5 wt.% cotton fibre exhibited flexural strengths of 11.2 and 11.7 MPa, respectively.

The enhancements in flexural strength and flexural modulus of the geopolymer composites compared to geopolymer matrix are believed to be underpinned by good dispersion of cotton fibres throughout the matrix, which helps to increase the adhesion at the matrix/cotton fibre interface and permits the stress transfer from matrix to the fibres, resulting in an improvement of strength properties.

The addition of cotton fibres to 0.3 and 0.5 wt.% was found to increase impact strength from 1.9 kJ/m^2 to 3.2 and 4.5 kJ/m^2, respectively. This enhancement in impact strength is believed to be due to the ability of the cotton fibres to transfer impact stress using energy dissipation mechanisms, primarily by fibre pullout, fibre fracture, and matrix deformation. Results were similar to compressive strength. Geopolymer composites with 0.3 and 0.5 wt.% cotton fibres were increased from 18 MPa to 27 and 45 MPa, respectively.

The addition of short cotton fibres also improved the fracture toughness. For example, while the fracture toughness of pure geopolymer was recorded as 0.6 $MPa.m^{1/2}$, after the addition of 0.3 and 0.5 wt.% cotton fibres, the fracture toughness was increased to 0.9 $MPa.m^{1/2}$ and 1.12 $MPa.m^{1/2}$, respectively. This improvement in fracture toughness is attributed to crack deflection, energy dissipation, and fracture resistance properties provided by the cotton fibres.

However, when the fibre content increases to more than 0.5 wt.% a different pattern emerged. The mechanical properties (flexural strength, flexural modulus, compressive strength, hardness, impact strength and fracture toughness) were not improved at this fibre content. It is believed that a high content of cotton fibres inhibits the non-homogeneity within the matrix so that agglomerations of fibres (confirmed with SEM) are formed, degrading interfacial adhesion between fibre and matrix. In addition these agglomerations may act as stress concentrators, causing further reductions in flexural strength, flexural modulus, compressive strength, hardness, impact strength and fracture toughness. It was observed that increasing the content of cotton fibre caused a discernible increase in matrix viscosity. This was compensated for by increasing the water content of the mix, and overcoming one problem in this way may have led to other adverse effects, such as an increase in porosity and microcracking. These usually lead to the reduction in bonding at the fibre–matrix interface, which results in lower stress transferred from the matrix to the fibres.

4.2 Cotton Fabric-reinforced Geopolymer Composites

Geopolymer composites with different fibre loadings of cotton fabric (CF) were produced by the hand-layup technique. The amount of binder varies as the quantity of fabric increases. Mechanical properties as function of fibre content were investigated. It was found that the increase in the cotton fibre content in geopolymer composites led to an enhancement of the mechanical properties of the composites. The flexural strength, flexural modulus, impact strength and fracture toughness are increased at an optimum fibre content of 2.1 wt.% (i.e., three layers of cotton fabric). However, further increase in cotton fibre content beyond this level caused a reduction in mechanical properties, which is attributed to poor bonding between the fibre and matrix because of the higher porosity and the formation of voids trapped beneath the cotton fabric sheets during casting. With respect to thermal properties, it was found that the use of geopolymer binder improved the cotton fibre's resistance to thermal degradation. The geopolymer binder protects the cotton fibres, acting as barrier to reduce the ingress of air and the resultant oxidative degradation.

The addition of Ordinary Portland Cement (OPC) enhanced the bonding, reduced the porosity and improved the mechanical properties of CF/geopolymer composites. By increasing the OPC content to 5, 8 and 10 wt.% the flexural strength increased from 14.7 MPa for pure geopolymer to 16.2, 16.6 and 17.1 MPa, respectively. Similarly, the addition of OPC at 5, 8, and 10 wt.% also increased the impact strength from 6.9 kJ/m^2 for pure geopolymer to 7.3, 7.5 and 7.8 kJ/m^2, respectively. The enhancement in flexural strength and impact strength of the CF/geopolymer composites with added OPC compared to those without is attributed to an enhancement in interfacial adhesion between fibre and matrix. This superior interfacial adhesion is believed to be caused by a filling effect, whereby the OPC particles fill voids or pores in the geopolymer paste making the microstructure of the matrix denser than that of the paste without OPC, and also by a pozzolanic reaction, in which the OPC with fly ash produces C-S-H gel in the geopolymeric system (confirmed by XRD and SEM), and reduces porosity, thereby enhancing mechanical properties.

When OPC content increased beyond 5 wt.% the fracture toughness is decreased. It has already been considered that the OPC addition results in desirable strength properties as a result of an improvement in fibre–matrix adhesion; but this also makes the composite brittle, as indicated by the lower fracture toughness in all the samples. The addition of OPC improves the fibre–matrix adhesion, but hinders the energy absorption mechanisms provided by fibre pullout and fibre de-bonding. For example, in composites with 10 wt.% OPC, the SEM confirmed that cotton fibres were ruptured rather than pulled out.

With respect to thermal stability, the CF-reinforced geopolymer composites containing OPC showed lower weight loss and better thermal stability than those without OPC. This enhancement of thermal properties is the result of the formation of calcium silicate hydrate (CSH). In addition, the presence of OPC in geopolymer composites was found to provide a thermal barrier reducing the ingress of air and inhibiting oxidative degradation; thus, the addition of OPC to cotton fibre-reinforced composites was found to improve the fibre's resistance to thermal degradation.

The forced impregnation-hand layup process, which involved rolling and brushing the woven cotton fabric with geopolymer paste and then stacking the fabric/paste

layers to a required thickness, was found to be the most effective method of making multiple layers while ensuring complete penetration of the matrix into the fibre bundles. This impregnation method was found to lead to the fabrication of composites with lower void content and good fibre–matrix adhesion. Several following conclusions were derived from the experiment.

- The flexural strength and modulus of geopolymer composites increase with the addition of woven cotton fibres, compared to pure geopolymer. It was observed that at peak load none of the specimens was completely broken. This could be because the crack bridging by long continuous fibres caused the flexural strength and modulus of woven cotton fibre-reinforced geopolymer composites to be higher than pure geopolymer. The flexural strength of geopolymer composites increased from 8.2 MPa to 31.7 MPa as fibre content increased from 0 to 8.3 wt.%; these enhancements are attributed to the ability of the fibres to resist shear failure and contribute in sustaining the applied load to the composites. The resistance of shear failure permits greater stress transfer between matrix and cotton fibres, resulting in improved flexural strength of the composites.
- The impact strength of the composites also increases as the cotton fibre content increases. The impact strength of the geopolymer is increased from 2.1 to 15.6 kJ/m^2 after the addition of 8.3 wt.% cotton fibres. This improvement in impact strength may be attributed to the fibrillation of cotton layers creating branches in the fibre (confirmed by SEM), resulting in the formation of microfibrils which increase the specific surface area of the fibre. Increasing the surface area leads to enhanced fibre–matrix interaction and bonding between the microfibrils and the geopolymer matrix; thus, increased fibre–matrix bonding leads to superior stress transfer from the matrix to the microfibrils.
- Fracture toughness increases with higher fibre content. The composites with higher cotton fibre content exhibited higher fracture toughness. The greatest improvement in fracture toughness (from about 0.6 MPa $m^{1/2}$ for the unreinforced matrix to about 1.8 MPa $m^{1/2}$) was obtained

with 8.3 wt.% cotton fibre reinforcement. This enhancement is because of the unique properties of woven cotton fibre to resist fracture through increased energy dissipation from crack-deflection at the fibre–matrix interface, fibre-debonding, fibre-bridging, fibre pullout and fibre-fracture.

- The hardness of composites increases with higher fibre loading. This is because the uniform distribution of the load on cotton fibres decreases the penetration of the test ball to the surface of the composite and consequently increases the hardness of composite.
- The compressive strength of composites increases with the addition of cotton fibres. From 19.8 MPa for pure geopolymer, reinforcement with 8.3 wt.% CF increased compressive strength to 90 MPa. This is attributed to the superior ability of the cotton fibres to absorb stress transferred from the matrix, compared to that of the pure geopolymer.

Fibre orientation in relation to the applied load was found to be an important factor affecting the mechanical properties of cotton fabric-reinforced geopolymer composites. The mechanical properties of those composites with horizontal fabric layers (i.e., load normal to fabric layers) were higher than those with vertical fabric layers (i.e., load parallel to fabric layers). This may be because of the ability of horizontally laid cotton fabric to directly absorb and uniformly distribute the load throughout the cross-section. In addition, this enhancement of strength in the horizontal direction is due to the absence of shear loading at the fabric-matrix interface, which reduces the possibility of fabric detachment or delamination from the matrix at high loads. When composites contain horizontal cotton fabric layers, the fabrics are stretched and cracks develop through fabric layers in a graceful failure behaviour, leading to a high degree of ductility.

The contribution of the reinforcing cotton fabric to crack arresting and bridging was also observed. The crack propagates through the specimen from one fabric layer to the next. Such crack arresting, bridging mechanisms and crack deflection are believed to be responsible for the significant enhancement in fracture toughness. However, when fabric is oriented vertically to the applied load, fabric delamination

and detachment from the matrix can occur, resulting in inefficient stress transfer between fabric and matrix. In addition, at vertical loading the cracks develop along the fabric layers mainly through the geopolymer matrix, leading to a more brittle behaviour.

The water absorption of CF-reinforced geopolymer composites at room temperature is increased with increasing fibre content. Reductions in flexural strength, flexural modulus, impact strength, hardness and fracture toughness are caused by exposing the composite to water for a prolonged period. The deterioration of mechanical properties is attributed to degradation of the bonding at fibre–matrix interfaces as an effect of water absorption. Water penetrates the cotton fibre bundles and decreases their coherence, causing them to break down into finer fibrils. SEM micrographs show extensive fibre pullout and no evidence or trace of the geopolymer paste adhering to fibre. The observation is indicative of poor fibre–matrix adhesion in wet composites. In contrast, prior to exposure to water, SEM micrographs show almost no fibre pullout, undamaged fibre bundles, and pieces of geopolymer attached to the surface of the cotton fibre. Such observations are indicative of strong fibre–matrix bonding in dry composites.

Exposure to high temperatures (200 to 1000°C) also leads to reduced mechanical performance (compressive strength, flexural strength and fracture toughness) in cotton fabric-reinforced geopolymer composites. As the samples were heated to 200 and 600 °C, it was found that some of the cotton fibres survived (confirmed by SEM); however, once specimens were heated to 800 °C and 1000 °C, a severe loss in strength was observed. The explanation for this is that as the temperatures increase beyond 600 °C, the oxidation and consequent degradation of the cotton fibres causes the sample to become highly porous (as confirmed by SEM and optical images). Furthermore, networks of hairline cracks were observed on pure geopolymer samples heated to 400 and 600 °C. Beyond 600 °C, severe cracking occurred on the surfaces.

When cotton fibres were incorporated, no such cracks were found in the surface of geopolymer composites. This suggests that cotton fibres are effective in preventing cracking caused by high temperatures. This prevention is due to the formation of small cavities inside the matrix, created by the fibre degradation, which prevent

crack propagation. In this case, the structure of the composite becomes more porous, and expanded water vapour escapes without substantial damage to the microstructure. In addition, all samples exhibited a change in colour after exposure to elevated temperatures as follows: grey at 200 °C, yellowish grey between 400 °C and 600 °C, pink at 800 °C, and reddish brown at 1000 °C. These changes in colour are a result of the oxidation and liberation of iron species present in the fly ash particles. Such colour changes will be a useful tool for estimating temperatures reached after exposure to fire.

It is concluded that cotton fibre in the textile woven form is effective reinforcement for geopolymers. The mechanical properties of woven cotton fabric-reinforced geopolymer composites are comparable with or superior to those of geopolymer composites with short cotton fibres. The geopolymer composite made of woven cotton layers exhibits greater load-bearing capacity than that with short cotton fibre composites. This is believed to be because of better wetting by the geopolymer paste, and therefore better fibre–matrix bonding. In addition, since the precise content of short cotton fibres in geopolymers composites is an important parameter affecting the performance of these composites, an advantage of impregnated woven fabrics with geopolymer paste is that the fibre content in geopolymer composites can be increased without the adverse outcomes observed in the short cotton fibre composites: thus, by increasing the number of cotton layers significant strength improvement is attained. Natural fibres in textile form, as in cotton fabric-reinforced geopolymer composites, can be regarded as a good alternative to synthetic fabrics. These natural fibre fabric composites, with their good mechanical, environmental and economic properties, are a suitable choice for load-bearing applications.

4.3 Recommendations for Future Work

There is a need to continue investigating the potential of cotton fibres as reinforcement for geopolymers. The following recommendations have been formulated to help guide further study:

- In this research, no chemical or physical treatment was used on cotton fibre; the use of coupling agents should be considered to improve the fibre/geopolymer interfacial bonding and provide better mechanical and thermal properties of the composites.
- The thermal expansion of the composites because of changes in temperature should be assessed. Expansion during heating introduces stresses which can weaken or damage the structure of geopolymer matrix.
- Fibres could be pressure-treated with a low-viscosity chemical solution that penetrates the amorphous regions of the fibre and bonds with available OH groups. This would likely to reduce the hydrophilicity of natural fibres and improve the water resistance of natural fibre-reinforced composites.
- In the case of engineering materials, a key consideration is long-term mechanical performance. It is recommended that the long-term mechanical behaviour of cotton fibre-reinforced geopolymer composites be investigated. This will help determine if the composite loses or gains strength as time progresses
- A combination of short fibres and woven cotton fabrics as a reinforcement of the geopolymer matrix should be studied. This technique would give better reinforcement than woven cotton fabric alone because the spaces between the fabric layers and geopolymer matrix will be filled with short cotton fibres.
- The degradation of cotton fibre under alkaline conditions should be investigated. This will help determine the effect of highly alkaline environments on the fibres, particularly with respect to any dissolving of the lignin and hemicellulose phases and the likely weakening of the fibre structure.

APPENDICES

APPENDIX I: Statements of Contributions of Others

Statement of Contribution of Others to "Characterisation of Cotton Fibre-Reinforced Geopolymer Composites".

5 December 2014

To Whom It May Concern

I, Prof. I.M. Low, contributed by project supervision and manuscript editing to the paper/publication entitled

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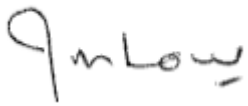

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I.M. Low

(Signature of First Author)

Thamer Alomayri

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(Signature of Co-Author)

F. U. A. Shaikh

(Signature of First Author)

Thamer Alomayri

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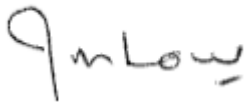

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I.M. Low

(Signature of First Author)

Thamer Alomayri

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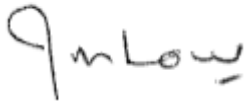

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I.M. Low

(Signature of First Author)

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(Signature of Co-Author)

F. U. A. Shaikh

(Signature of First Author)

Thamer Alomayri

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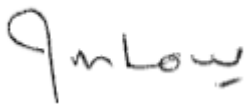

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I.M. Low

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Thamer Alomayri

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(Signature of Co-Author)

F. U. A. Shaikh

(Signature of First Author)

Thamer Alomayri

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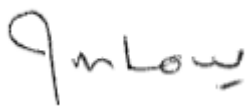

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I.M Low

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(Signature of Co-Author)

F. U. A. Shaikh

(Signature of First Author)

Thamer Alomayri

Statement of Contribution of Others to "Effect of Fabric Orientation on Mechanical Properties of Cotton Fabric Reinforced Geopolymer Composites"

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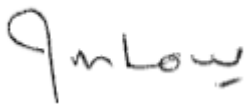

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(Signature of Co-Author)

F. U. A. Shaikh

(Signature of First Author)

Thamer Alomayri

Statement of Contribution of Others to "Effect of Water Absorption on the Mechanical Properties of Cotton Fabric-Reinforced Geopolymer Composites".

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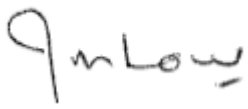

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I.M. Low

(Signature of First Author)

Thamer Alomayri

Statement of Contribution of Others to "Effect of Water Absorption on the Mechanical Properties of Cotton Fabric-Reinforced Geopolymer Composites".

5 December 2014

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I, Dr. F.U.A. Shaikh, contributed by project supervision and manuscript editing to the paper/publication entitled

ALOMAYRI, T. ASSAEDI, H., SHAIKH, F. U. A. and LOW, I. M. 2014. Effect of water absorption on the mechanical properties of cotton fabric-reinforced geopolymer composites. *Journal of Asian Ceramic Societies*, 2, 223-230.

Undertaken with Thamer Alomayri

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F. U. A. Shaikh

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Thamer Alomayri

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I, Mr. Hasan Assaedi provided technical assistance during the preparation and testing of geopolymer composite samples to the paper/publication entitled

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(Signature of Co-Author)

Hasan Assaedi

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I, Prof. I.M. Low, contributed by project supervision and manuscript editing to the paper/publication entitled

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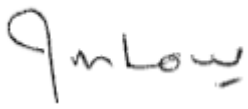

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I, Mr. Les VICKERS, provided interpretation of the thermal analysis results for the paper/publication entitled

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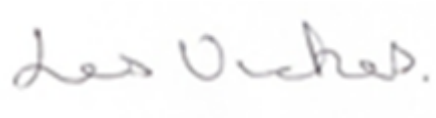

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Thamer Alomayri

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