

Characterisation of Mechanical and Fracture Behaviour in Nano-Silicon Carbide Reinforced Vinyl-ester Nanocomposites

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Mechanical and Fracture Properties of Nano-Silicon Carbide Reinforced Vinyl-ester Nanocomposites

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Abstract: In this study vinyl-ester/nano-silicon carbide nanocomposites were synthesised and investigated in terms of their mechanical and fracture properties. Results show that the addition of nano-SiC particles increases modulus and strength, but reduces toughness. The enhancement in strength for nanocomposites was attributed to good interfacial adhesion and good degree of dispersion. The experimental data for elastic modulus were modelled using several theoretical models. The excellent agreement with the experimental data for elastic modulus given by the Guth and Kerner models indicate that the degree of dispersion and the quality of particle/matrix adhesion were both important considerations for the prediction of elastic modulus.

Keywords: Nano-silicon carbide; polymer nanocomposites; mechanical properties; fracture toughness; transmission electron microscopy

INTRODUCTION

Polymer nanocomposites are materials that have at least one phase with dimension in the nano-size range ^[1]. Nanoparticles display extraordinary properties due to their large surface area to mass ratio. The phase interactions that occur at the interfaces of polymer matrix give these composites their remarkable properties ^[2]. The favourable properties of polymer nanocomposites such as mechanical, electrical, optical and thermal have attracted much interest for over 10 years ^[3]. High elastic modulus, increased strength, favourable heat resistance, decreased gas permeability and decreased flammability are some of the useful properties of polymer nanocomposites ^[4].

Vinyl ester resins are a newer thermosetting resin compared to alternatives such as polyester and epoxy resins ^[5]. In terms of industrial applications, the desirable properties of vinyl-ester resins make them suitable for adhesives, coatings, electrical applications, moulding compounds and structural laminates ^[6]. Thus, vinyl-ester resins that combine the most sought-after properties of epoxies and unsaturated polyesters are favoured by the industry ^[7]. In recent years, nanoparticles such as carbon nanotubes ^[8], nano-clay ^[9-11], iron oxide nanoparticles ^[12] and cupric-oxide nanoparticles ^[7] as rigid reinforcements within vinyl-ester matrix have attracted widespread attention. However, few studies have investigated the mechanical properties of vinyl-ester when reinforced with silicon carbide nanoparticles ^[1, 13].

Therefore, this study aims to investigate the mechanical and fracture properties of vinyl ester matrix reinforced with silicon carbide nanoparticles. Particularly, the present work attempts to evaluate the influence of morphological structures such as particle dispersion and particle/matrix interaction on resulting mechanical and fracture properties of vinyl-ester reinforced with nano-silicon carbide.

EXPERIMENTAL

Materials

Silicon carbide nano-particles (n-SiC) had a spherical morphology with a phase purity of >95%, specific surface area of 70–90 m²/g and a particle size of <100 nm. They were purchased from Sigma-Aldrich Co. LLC, Australia. Vinyl-ester resin was supplied by Fibreglass and Aesin Sales Pty Ltd, Australia.

Samples Preparation

Pure vinyl-ester (VER) samples were made as controls to provide the baseline properties. To prepare control samples, 1.0 wt% catalyst (MEKP) was mixed into the vinyl-ester resin and the resultant mixture was then poured into silicon moulds and kept under low vacuum (60 kPa) for two hours. The resultant mixture was then kept for 24 hours at room temperature to cure. Nanocomposite samples were prepared with a dispersion of n-SiC at concentrations of 1, 3, and 5 wt%. First, n-SiC were dried for 60 minutes at 150°C to remove pre-existing moisture. Then a high-speed electric mixer set at 1200 rpm was used to disperse the n-SiC in the resin for 30 minutes. MEKP was then added to the mixture and stirred slowly to minimise the formation of air-bubbles. The resultant mixture was then poured into silicone moulds, degassed for two hours at a vacuum of 60 kPa and then cured at room temperature for 24 hours.

Microstructure Examination

A JEM2011 transmission electron microscope (TEM) was used to study the morphologies of the n-SiC and their dispersion inside the vinyl-ester matrix. A NEON 40ESB scanning electron microscope (SEM) operating at accelerating voltage of 5kV, under secondary

electrons mode was used to examine the dispersion of n-SiC and fracture surfaces. In order to avoid charging, all samples were coated with platinum.

Elastic Modulus and Flexural Strength

Rectangular bars were cut from the fully cured the fully-cured samples for three-point bend tests with a span of 40 mm to evaluate the elastic modulus and flexural strength according to ASTM D790-86. A LLOYD Material Testing Machine (5-50 kN) with a displacement rate of 1.0 mm/min was used to perform the test. Five samples of each batch were used to evaluate flexural strength. The values of were recorded and analyzed with the machine software (NEXYGENPlus) and average values were calculated.

Impact Strength

A Zwick Charpy impact tester with a 2.0 J pendulum hammer was used to determine the impact strengths according to ASTM D 256-06. In total, five 40 mm-span bar samples were used for the measurements. The following equation was used to calculate the impact strength [14].

$$\sigma_i = \frac{E}{A} \quad (1)$$

where σ_i is impact strength and E is the impact energy required to break a sample with a ligament area represented by A .

Fracture Toughness

For fracture toughness (K_{IC}) measurements, the ratio of notch length to width of sample (a/w) used was 0.4 and a sharp razor blade was used to initiate a sharp crack. The flexural tests were performed with a LLOYD Material Testing Machine using a displacement rate of 1.0 mm/min; five samples of each composition were used for the measurements. Five

samples of each group were used and the value of fracture toughness was determined according to ASTM D5045-99 using the following equation ^[15]:

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

where p_m is the maximum load, S is the span of the sample, D is the specimen thickness, w is the specimen width, and a is the crack length, and $f(a/w)$ is the polynomial geometrical correction factor given as ^[15]:

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

Impact Toughness

A Zwick Charpy impact tester with a 2.0 J pendulum hammer was used to determine the impact toughness (G_{IC}). In total, five 40 mm-span bar samples, each with varying notch lengths and razor-cracks, were used. Values of fracture toughness were determined with the following equation ^[15] according to the method of Plati & Williams ^[16]:

$$U = G_{IC} BD\phi + U_0 \quad (4)$$

where U is measured energy, U_0 is kinetic energy, D is specimen thickness, B is specimen breadth and ϕ is the calibration factor for the geometry used.

Mathematical Models for Particulate-Reinforced Composites

There are a number of theoretical frameworks that have been developed to support the prediction of elastic modulus of particulate reinforced polymer composites. These sophisticated theories have been developed according to the requirements of different material or geometric parameters. Conventionally, elastic properties of components of particulate–polymer composites, particle loading, and particle aspect ratio are used in determinations of elastic modulus ^[17, 18]. For example, for spherical particles, when the aspect

ratio of particles equals unity, the modulus of the components and particle loading or particle size will be used to provide the composite modulus. The composite modulus is enhanced by adding particles to matrix since the modulus of inorganic particles is usually much higher than that of the polymer matrix ^[17, 19].

The theories used for predicting the elastic modulus of particulate-reinforced polymer composites are generally satisfactory. However, theories for predicting the strength and fracture toughness of particulate-reinforced systems are much less developed ^[19, 20]. For theories predicting the strength of particulate-reinforced systems, the largest challenge is to accurately predict how the addition of hard particles will affect a composite's interface adhesion, stress concentration and defect size/spatial distributions ^[21, 22]. There is still a lack of development in the understanding of how the characteristics and concentration of the added hard particles lead to the strength of resultant composite. Current theories do not satisfactorily address whether the addition of hard particles will weaken or reinforce the composite ^[23, 24]. Similar, theories for predicting fracture toughness of particulate-reinforced systems have failed to reach consensus among the scientific community, mainly due to the complexity, inefficiency and lack of reliability that has characterised this group of theories so far ^[25].

The focus of this study was limited to the prediction of elastic modulus for particulate reinforced composites. Table 1 provides the names, formulas and nomenclatures of seven elastic modulus prediction mathematical models. To determine the applicability of the empirical relationships, these mathematical models were used to compare experimental data from this study with theoretical data generated from these models. Table 2 provides the parameters corresponding to the material properties of the mathematical model implementation.

RESULTS AND DISCUSSION

Mechanical Properties

Table 3 summarises the mechanical properties of the pure VER and VER/n-SiC nanocomposites with different loadings of n-SiC. The addition of n-SiC particles increases elastic modulus and strength but reduces toughness.

The addition of 1 wt% n-SiC particles increased the elastic modulus and strength to 3.05 GPa and 54.9 MPa, respectively, compared with pure VER (2.9 GPa and 42.4 MPa). Similarly, the nanocomposites reinforced with 3 wt% n-SiC particles showed increases to 3.11 GPa and 59.1 MPa in modulus and strength, respectively. Again, the addition of 5 wt% n-SiC was found to increase elastic modulus and strength to 3.17 GPa and 67.2 MPa, respectively. No further improvement in elastic modulus was observed at 10 wt% (3.2 GPa) and the strength decreased at this concentration (63.2MPa). The results for impact strength were similar. The impact strength for neat VER was 2.6 kJ/m². Adding the n-SiC improved the results for impact strength. At 5wt% impact strength was 3.9 kJ/m². No further improvement in impact strength was observed at 10wt% (3.67 kJ/m²).

The addition of 1%, 3%, 5% and 10% n-SiC led to lower fracture toughness and impact toughness compared to pure VER. These increases in strength and modulus and decreases in toughness due to n-SiC addition are in agreement with the previous studies of Liao et al. [27] and Rodgers et al. [28].

It is well-accepted that the addition of rigid fillers to a polymer matrix enhances elastic modulus [29, 30]. Since n-SiC (457 GPa) has a higher elastic modulus than VER (2.9 GPa), by virtue of the rule of mixtures, an improved elastic modulus was obtained for the resulting nano-composites. This is believed to be a dominant factor that led to increased elastic modulus in the samples. The enhancement in strength depends on particle size, shape, aspect ratio and degree of dispersion [31] and the quality of interfacial bonding between the particles

and matrix ^[32]. These dynamics can each affect the strength of particulate-reinforced polymer composites by determining the extent to which applied stress is transferred efficiently through the reinforcing particles and matrix ^[33, 34].

The SEM and TEM observations, as shown in Figure 1(a-b), confirm that n-SiC particles have a spherical shape and nano-scale size varying from 50 to 150 nm, with an average size of around 100 nm. Thus, n-SiC enables a much higher specific surface area which provides dense interfacial interaction with the polymer matrix. This high interfacial interaction leads to excellent adhesion and bonding between filler and matrix, thereby increasing composite strength ^[35, 36]. It is well accepted that the nature of bonds in composites will determine how a material responds to load. Thus, when a local stress is applied, and the interfacial interaction is good between the reinforcing particles and matrix, the composite will display favourable strength. In contrast, when the interaction is poor between filler and matrix, artificial defects are more likely to form, which leads to marked reductions in composite strength ^[37, 38].

SEM micrographs in Figure 2 show the fracture surfaces of nano-composites with 1, 3 and 5 wt% n-SiC. At the particle/matrix interface, there appeared to be no obvious voids which indicates that nanoparticles had not pull-out from the polymer matrix, thus supporting strong interaction between the nanoparticles and VER matrix. In addition, the images in Figure 2 (a–c) show no agglomerations thus indicating the dispersion of nano-fillers throughout the matrix was quite uniform. Thus, the higher specific surface area inherent with the n-SiC, together with the strong interfacial bonding between n-SiC particles and VER matrix, and the favourable degree of dispersion, effectively facilitate the local stress transfer from VER matrix onto n-SiC particles. Therefore, improved mechanical properties are observed in n-SiC/VER composites.

As previously mentioned, the addition of 10 wt% n-SiC did not lead to further improvements in the modulus and strength properties. The formation of n-SiC

agglomerations at this loading is believed to be the reason for lower modulus and strength properties compared to 5 wt% n-SiC/VER nanocomposite. The small size of n-SiC particles, their hydrophilic surface, and their high surface area can act as driving forces for particle agglomeration ^[13]. When particle agglomeration is present within composites, the load-bearing capability is affected and the elastic modulus is reduced ^[20]. These larger and more loosely assembled areas of particle agglomerations act as stress concentrators, thus reducing strength and limiting elastic modulus enhancement in the resulting composite ^[39, 40]. Moreover, the presence of particle agglomerations adversely affects adhesion quality between the particles and the matrix, causing further reduction of strength properties ^[27]. In this study, particle agglomerations were found to exist in the 10 wt% n-SiC/VER nanocomposite (Figure 3). TEM micrographs (Figure 4) show the difference between the 5 wt% and 10 wt% samples. While the 5 wt% samples show reasonable n-SiC dispersion with minimal agglomerations, the 10 wt% samples exhibit more noticeable agglomeration. Thus, in agreement with previous studies using the direct mixing method for nanoparticle dispersion, this study supports the notion that the addition of nano-fillers beyond 5 wt% is not likely to further improve the overall mechanical properties ^[18, 39, 41].

In contrast, with regards to toughness, the addition of 1, 3, 5 and 10 wt% n-SiC led to lower fracture toughness and impact toughness compared to pure VER. Table 3 shows that, while the addition of 1 and 3 wt% led to noticeable reductions in fracture toughness and impact toughness, only slight reductions in fracture toughness and impact toughness were found with 5 and 10 wt%. Plastic deformations are generally accepted as the dominant contributors to the toughness of polymers and polymer composites. It is worth noting that, when investigating toughening mechanisms, the deformation zone ahead of the crack tip is most often under plane strain condition. This means that the materials are subjected to high levels of plastic constraint. Without vital relief mechanisms, such as plastic deformation, this stress often

causes the material to fracture in a brittle mode with low toughness ^[42, 43]. In this study, the addition of stiff n-SiC, is believed to hinder the mobility of surrounding chains in the polymer, consequently limiting the stress relief provided by plastic deformations. The strong filler/matrix interaction is also a hindrance to the mobility of the matrix component. The strong adhesion between the filler and matrix may also have prevented effective de-bonding of n-SiC particles from the VER matrix, thus reducing energy dissipation ^[44-46]. Therefore, the reduction of toughness is most likely attributed to reduced plastic deformation and the prevention of particle de-bonding. These findings are also supported by previous studies which reported no improvement in toughness in polymer nanocomposites reinforced with nano-fillers ^[29, 47, 48]. However, It has been suggested that fillers need to be larger than 0.1 μ m in order to deflect cracks and to provide the toughening mechanisms of crack bridging, deflection and pinning ^[4, 43].

Figure 5 (a-c) shows the fracture surfaces of pure VER and VER/n-SiC nanocomposites with 5 and 10 wt% addition of n-SiC. Inspection of fracture surfaces (Figure 5a) of pure VER shows crack paths spreading in a radial manner, which is indicative of a large zone of plastic deformation. As plastic deformation is an important toughening mechanism in polymers, pure VER was found to have favourable toughness compared to that of the nanocomposites. In contrast, the fracture surfaces of 5 wt% VER/n-SiC nanocomposite (Figure 5b) reveal more direct crack paths. The shift from radial cracks, in the pure VER, to direct cracks, in the nanocomposites, is indicative of a shift from ductile to brittle behaviour due to enhanced nano-particle/matrix adhesion in nanocomposites ^[27]. The fracture surface of 10 wt% VER/n-SiC nanocomposite (Figure 5c) reveals evidence of brittle behaviour and the existence of some toughening mechanisms. These mechanisms included plastic deformation around the n-SiC clusters (indicated with circles) and n-SiC cluster pull-out (indicated with squares). Voids left by the n-SiC cluster pull-out are also clearly noticeable (indicated with diamonds).

These clusters act like rigid micro-sized inorganic particles, which when confronting cracks, hinder crack propagation and cause crack deflection, twisting and plastic deformation ^[49, 50]. The results of fracture and impact toughness for the 10 wt% VER/n-SiC nanocomposites were higher than those for 5 wt% samples, which seem to confirm the existence of toughening mechanisms in the former that are not present in the latter.

Comparisons with Theoretical Models

Experimental data for the elastic modulus were compared with typical theoretical models (see Figure 6). The Paul model and Ishai-Cohen model assume that two phases of the composite are in a macroscopically homogeneous stress state and that interfacial adhesion is perfect. The Paul model gives the elastic modulus of the particulate composite when uniform stress is applied to the boundary. The Ishai-Cohen model is obtained by applying the uniform normal displacement to the boundary in the Paul model. These models, which are accepted tests of validity, form an approximate theory, identifying upper bound values (the Paul model) and lower bound values (the Ishai-Cohen model) of elastic modulus for particulate-reinforced composites. The validity of elastic modulus for most particulate composites can be tested by comparing the experimental data of the elastic modulus values with the upper bound and lower bound values provided by these models. These models provide upper and lower bounds to the elastic modulus of the composite, and all data lie between the two bounds described by these models ^[17, 19].

All experimental and predicted data values in this investigation, with the exception of those obtained using the Frankle-Acrivos model, fell between the upper bounds and lower bounds. This supports the validity of the elastic modulus data for this study. This finding also indicates that the Paul model and Ishai-Cohen model offer reasonable analytical solutions for validity in this study. While the Paul model and Ishai-Cohen model assume perfect

particle/matrix interaction, experimental data in this study lay closer to the lower bound (Ishai-Cohen model), a finding that is in agreement with previous studies ^[19, 51].

The Guth and Kerner models are in excellent agreement with the experimental data. The Guth model is typically applicable to the assumption of perfect adhesion between the spherical particles and matrix, and perfect dispersion of individual filler particles ^[17, 19]. In this study, the microstructure observation has supported strong adhesion between the spherical fillers and matrix, and good dispersion of n-SiC particles within the matrix. The Kerner model is a measure of validity of the composite system in which the modulus of filler is many times higher than that of the matrix ^[18, 21]. In this study, the elastic modulus of n-SiC (470 GPa), was much more rigid than the matrix, VER (2.97 GPa). The relative modulus ratio of filler to matrix was 151.5, which explains the strong agreement between the theoretical models and the experimental data. When the volume fraction increased to 10 wt%, the Guth model over-predicted the elastic modulus of samples. This discrepancy is probably explained by particle agglomerations. As aforementioned, clusters within the composite can affect the load bearing capability, thus reducing its elastic modulus.

The Counto model, a simpler model, assumes perfect particle/matrix bonding. In this study, this model was found to overestimate the elastic modulus. This model predicts the moduli to be in good agreement with a wide range of experimental data. However, the Counto model tends to be used for concrete systems, which may explain the lack of agreement between the theoretical model and the experimental data of this study ^[16, 18]. The overestimation of the Frankle-Acrivos model, the only model with results outside the upper bounds and lower bounds, clearly did not agree with the experimental data. This model uses a simplistic relative filler volume fraction (V_p/ϕ_{max}), which implies the particle packing efficiency is dominant, and neglects three important factors that influence the elastic modulus: namely, the effect of particle/matrix interfacial interaction, Young's modulus and Poisson's ratio ^[18, 20, 52].

Thus, the degree of dispersion and quality of particle/matrix adhesion seem to be the most important variables in determining composite modulus according to the results of this study and other studies [18, 52-54]. However, it is worth noting that some of the earlier studies of particulate polymer composites reviewed by Ahmed and Jones [17] and Fu et al. [19] proposed that the quality of particle/matrix adhesion was irrelevant. The findings of this study on elastic modulus for particulate polymer composites directly contradict those previous studies.

CONCLUSIONS

Pure VER and VER/HNT composites have been synthesised and characterised in terms of mechanical and fracture properties. The addition of n-SiC particles increased elastic modulus and strength but reduced the toughness. The enhancement in strength for VER/HNT composites was attributed to good interfacial adhesion and a good degree of dispersion. Agglomeration of nanoparticles formed clusters that decreased elastic modulus and strength. Experimental data and predicted data were found to fall within the upper and lower bounds of the Paul model and Ishai-Cohen models supporting the validity of the results of this study. The good agreement of experimental data with Guth and Kerner model suggests that, in addition to dispersion of particles within the matrix, the state of interfacial adhesion between the particles and matrix is a relevant to the prediction of elastic modulus of particulate reinforced composites.

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Tables

TABLE 1

Mathematical models used to compare with experimental data of this study

TABLE 2

Values of parameters used in mathematical modelling

TABLE 3

Mechanical properties of pure VER and VER/n-SiC nanocomposites

Figures Captions

FIG. 1. (a) SEM and (b) TEM micrographs displaying the spherical shape of a n-SiC particle, confirming that the average size of these particles was around 100 nm.

FIG. 2. SEM images of fracture surfaces of VER/n-SiC nanocomposites with (a) 1 wt%, (b) 3 wt%, and (c) 5wt% (arrows indicate the n-SiC particles).

FIG. 3. SEM micrograph displaying n-SiC particle agglomerations within the matrix reinforced with 10 wt% n-SiC.

FIG. 4. TEM micrographs of (a) VER/5 wt% n-SiC, and (b) VER/10 wt% n-SiC.

FIG. 5. SEM micrographs showing the fracture surface of (a) pure VER, (b) VER/5% n-SiC nanocomposite, and (c) VER/10% n-SiC nanocomposite.

FIG. 6. Comparison of experimental data for flexural modulus against n-SiC content with results extrapolated from published models.