

Hydrophilic plasticized biopolymers: morphological influence on physical properties

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Abstract

Biopolymers such as amylose, when mixed with plasticizers have excellent potential in forming thin films for various food and packaging applications. In this study, the influences of moisture content, plasticizer type and content have been investigated on the physical tensile elongation and crystalline morphology of starch biopolymeric material. Biopolymeric samples prepared with starch and two types of plasticizer with different molecular weights, namely glycerol ($M_{wt}=92$) and xylitol ($M_{wt}=152$), were employed, which also have different number of hydroxyl (OH) groups (3 for glycerol and 5 for xylitol). A statistical design of experiments (DoE) was performed on the sample responses (i.e. tensile elongation and crystalline morphology) by varying the moisture content, plasticizer type as well as plasticizer content. Plasticizer type and degree of crystallinity have been found to be insignificantly related. However, the plasticizer content has shown a significant effect on both elongation and crystallinity. A clear B-type pattern (peak at $2\theta \approx 20^\circ$) has been observed in most X-ray diffraction (XRD) results.

Keywords: *Thin films; starch; biopolymers; plasticizer; tensile elongation; crystallinity*

1. Introduction

Amylose or amylopectin organized into semi-crystalline granules in starch has high sensitivity to relative humidity (RH) due to its hydrophilic nature [1] and cannot be utilized for making flexible

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films under ambient temperature resulting from its high glass transition temperature (T_g). This can be overcome by introducing plasticizers which could reduce the influence of RH while enhance the flexibility of the matrix [2,3]. However, owing to complex interactions between the hydrophilic plasticizers and the starch, an ‘anti-plasticization’ process takes place with increased stiffness of the matrix. It has been demonstrated that plasticizer molecules with similar structures to the polymer matrix have greater interaction ability [4,5]. As previously mentioned, plasticizers have been shown to influence the overall crystalline morphology of the starch matrix by adsorbing excessive free water [4]. Following this observation, some studies focused on water absorption-isotherm of starch-based polymer [6,7] to understand how the interaction of free water with starch influences the polymer crystalline morphology.

Consequently, a research area of interest arises to understand the relationship between the development of a particular morphology due to starch-plasticizer-water interaction and the macroscopic polymer structure. The complex molecular interactions within the starch-plasticizer-water system are poorly understood and very few reports concentrate on the influence of plasticizer interaction for starch on the matrix crystallinity as well as its influence on the mechanical properties. In this study, a design of experiments (DoE) analysis was reported for the first time to explicitly interpret the complex hydrophilic interaction within the plasticized starch biopolymeric system.

2. Experimental details

2.1. Materials and Testing Procedures

The starch as polymer matrix is labeled as LA, and water, glycerol and xylitol are labeled as W, G and X, respectively. The suffix integer refers to the concentration of the plasticizers by weight. The raw starch and plasticizers were mixed on a dry basis using a Hobart planetary mixer (Model No: N50-619, Hobart, Australia). For example, GLA10 contained 90 g of LA starch and 10 g of glycerol. Melt extrusion was made in a counter-rotating twin-screw extruder ZSK-16 (D=16 mm, L:D=16, Brabender®, Duisburg, Germany) at 140 rpm in the temperature profile of 90/137/110°C. Extruded pellets were allowed to cool to room temperature, ground to fine powders using a bench-top food

grinder, and sealed in polyethylene bags before subjected to controlled humidity conditions. Tensile specimens were prepared by compression molding of the extruded pellets at 135-140°C with 20 tonnes of pressure in a bench-top compression molder (Model: CR100, ENERPAC, UK). Tensile testing was carried out in quintets on an Instron Universal Testing Machine (Model: 4467, Instron Corporation, England) according to ASTM D638. XRD analysis was conducted in a Philips X-ray generator (30 kV accelerating voltage, 30 mA current) with $2\theta = 1.2-10^\circ$ using Ni filtered Cu-K radiation ($\lambda = 0.154$ nm).

2.2. Design of Experiments (DoE)

Taguchi DoE [8,9] is widely used to plan and optimize the processing parameters in the modern manufacturing. This work focused on a 2 level fractional factorial DoE analysis with the three main effects including moisture content (Factor A: 13 and 96 wt%), plasticizer type (Factor B: GLA and XLA), plasticizer content (Factor C: 5 and 20 wt%) and four additional interactions (Factors AB, AC, BC and ABC). Totally 8 runs of experiments (L_8) have been performed to replace the conventional 128 full factorial ones. In order to maximize the tensile elongation as one of DoE major responses, the “larger-the-better” characteristic is utilized with the signal-to-noise (S/N) ratio expressed as

$$S/N = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i} \right) \quad (1)$$

Similarly, a “smaller-the better” characteristic also applies for the minimization of crystallinity as another response with S/N ratio given by

$$S/N = -10 \log \left(\frac{1}{n} \sum_{i=1}^n y_i^2 \right) \quad (2)$$

where n is the number of samples in each trial and y is measured response values, namely tensile elongation and crystallinity degree. Mathematically the greater S/N ratios reflect the more robust quality in DoE work irrespective of the categories of characteristics.

2.3. Analysis of Variance (ANOVA)

Instead of conventionally using more complex ANOVA table and F-test [10,11] with the calculations of the number of degrees of freedom and F-ratios at certain confidence level for statistical significance, a special Pareto ANOVA technique [9] is employed to analyze the significant factorial effects on the performance characteristics of the parameter design. The contribution percentage (CP) can be calculated as

$$CP(\%) = \frac{S_i}{S_T} \times 100\% \quad (3)$$

where S_i is the sum of squared difference from the variability of S/N ratios for the i th factor ($i=1, 2 \dots n$) and S_T is the total sum of squared difference for all factors. The significant factors are gauged on the basis of cumulative CP of about 90% along with the technical and economic considerations for non-significant factors.

3. Results and Discussion

3.1. Water sorption isotherms

Fig. 1 shows the change in overall moisture content (as measured by weight loss) and their water activities A_w (representing the free water content) of the two plasticized starch samples, namely GLA and XLA. The addition of plasticizers clearly influences the overall free water content of the starch matrix. At water activities greater than 0.5, the water absorption is mainly due to the hydrophilicity of the plasticizers where the plasticizers typically absorb a large amount of water [4,5], as compared to the WLA starch sample. Since plasticizers could accommodate free water depending upon their nature [2], comparisons of Fig. 1(a) and (b) indicate that GLA samples have overall greater free water retention than XLA samples despite higher OH groups of xylitol samples, which has been well explained by the excellent hydrophilicity of glycerol [4].

3.2. Morphological analysis using XRD

Table 1 details the crystallinity values of all the plasticized amylose polymer samples. The addition of both plasticizers inclines to reduce the starch crystallinity. Xylitol also shows a greater tendency to suppress crystallinity at higher plasticizer content (~ 20 wt%) relative to glycerol. This

could be attributed to the A-pattern crystallinity (sharp peaks) in XLA20 sample, Fig. 2(b). Only XLA20 sample demonstrates a pattern change from B-type to A-type with sharper and taller peaks, indicating smaller domains of increased well-ordered formation of crystalline structures. Glycerol samples have not presented any A-type pattern shown in Fig. 2(a), suggesting that they resist the largely ordered crystalline morphology within the starch matrix. The fact that glycerol samples have higher moisture content obtained from water sorption experiments indicates that the combination of water and glycerol both with smaller molecules than xylitol has a greater control over the morphology of polymer matrix.

It is most likely that within the large crystalline regions, amylose domains have strong interactions between water and plasticizer molecules, thus forming a rigid-amorphous phase, as previously described [12]. From the XRD crystallinity data, the rigid-amorphous phase was quantified by separating the micro-crystalline peaks from the shoulder as well as from the base using a Gaussian deconvolution method [13]. Table 1 also lists the rigid-amorphous values and it can be seen that varying the plasticizer amount could lead to different rigid-amorphous phase. In addition, the growth of rigid amorphous region is usually linked to the reduction of micro-crystalline phase. Both these morphologies would be responsible for the macroscopic structural responses of the matrix.

3.3. Physical analysis through tensile elongation properties

Since extrusion processing involves excellent shear mixing and is quite biased towards the axial direction (i.e. melt flow direction of extrusion), the tensile elongation properties in the axial direction could be inevitably far greater than those in the transverse direction. To understand the extent of morphological interaction, the ratios of the tensile elongation were obtained in both axial and transverse directions. Their ratios were labeled as the 'elongation ratio' factors against the amount of rigid-amorphous phase and the retained equilibrium moisture content of the matrix, listed in Table 1. As expected, the lower the value of 'elongation ratio', the more isotropic the polymer matrix becomes and thus the greater is the ability to deform in different directions. It appears that the addition of glycerol up to 10 wt% as the plasticizer diminishes the isotropic material behavior with

the elongation ratio of 1.87. Subsequently, this trend has been reversed to the elongation ratio of 1.22 with the inclusion of 20 wt% glycerol. Contrarily, increasing the concentration of xylitol consistently promotes the isotropy of plasticized starch up to 1.12 with 20 wt% xylitol. This isotropy is believed to depend primarily on the rigid-amorphous region and secondarily on the extent of morphological interaction. At the fixed plasticizer concentration beyond 5 wt%, xylitol with a greater number of OH groups offers smaller elongation ratios as close as possible to 1 relative to glycerol, perhaps identified as a good enhancer to tailor plasticized starch with isotropic material properties.

3.4. Statistical analysis

Both moisture content (Factor A) and plasticizer content (Factor C) as the two most significant factors have statistically shown much greater influence than the plasticizer type for elongation and crystallinity, Figs.3 and 4. In terms of increasing the tensile elongation, both Factors C and A achieved CP values of 43.0 and 38.7%, respectively, Fig.3(b), followed by interaction AC (CP: 8.7%) as the third significant factor. As expected, the generally better ability to increase the elongation from XLA becomes manifested with the higher *S/N* ratio for B₂ (Factor B and Level 2), Figure 3(a), and this ability is more visible at lower water activity. An optimal combination of factors of A₂B₂C₂ can be then attained with the maximum elongation of 68.58%. To minimize the crystallinity, Factor A is found to be the most prevalent factor (CP: 68.9%), Figure 4(b). Factor C and its interaction with moisture content (AC) become similarly less significant (CP values of 11.6 and 11.2%, respectively). The overall crystallinity values show that xylitol is able to suppress the crystallinity as compared to glycerol. An optimal combination of factor of A₂B₁C₂ is also determined with the minimum degree of crystallinity of 4.50%. Due to its smallest size, water appears to be the most significant factor, as expected, since its size effect allows greater interaction with the starch.

4 Conclusions

Notwithstanding that plasticizers like glycerol and xylitol typically have the role of increasing the degree of elongation, their interactions with the starch become quite complex. As compared to xylitol, glycerol can retain a greater amount of free water within the starch matrix and thus provide

relatively large elongation ratio values despite its significantly lower rigid-amorphous region. It is suggested that water sorption does not provide a direct relationship with the number of hydrophilic sites (OH groups) in the plasticizer, rather a complex interplay between molecular solubility and matrix crystalline morphology. In terms of tensile elongation and crystallinity, the statistical DoE analysis has provided a quantitative ranking of moisture and plasticizers and overall, the moisture content plays the predominant role in these two responses, followed by the plasticizer content, as expected. In addition, the plasticizer content also dominates the elongation response compared to the degree of crystallinity. Interestingly, plasticizer type is shown to have a minor effect in its manifestation on these responses, but multicomponent interaction between water, plasticizers and amylose chains, has shown significance in crystallinity, which is likely as they are strongly hydrophilic.

References

- [1] Myllärinen P, Partanen R, Seppälä J, Forsella P. *Carb Polym* 2002; 50:355-61.
- [2] Gaudin S, Lourdin D, Botlan L, Ilari J, Colonna P. *J of Cereal Sci* 1999; 29:273-84.
- [3] Cheng LH, Abd Karim A, Seow CC. *J Food Sci* 2006; 71:E62-7.
- [4] Mali S, Sakanaka S, Yamashita F, Grossmann MVE. *Carb Polym* 2005; 60:283-9.
- [5] Chaudhary DS. *J Polym Sci: Polym Phys* 2008; 46:979-88.
- [6] Al-Muhtaseb AH, McMinn WAM, Magee TR. *J of Food Eng* 2004; 62:135-42.
- [7] Müller CMO, Yamashita F, Borges LJ. *Carb Polym* 2008; 72:82-7.
- [8] Lochner RH, Matar JE. *Design for quality: an Introduction to the best of Taguchi and western method of statistical experimental design*. Milwaukee, WI: Quality Resources and ASQC Quality Press; 1990.
- [9] Park SH. *Robust design and analysis for quality engineering*. London: Chapman & Hall; 1996.
- [10] Belavendram N. *Quality by design*. London: Prentice Hall; 1995.
- [11] Condra LW. *Reliability improvement with design of experiments*. 2nd ed. New York: Marcel Dekker; 2001.
- [12] Chaudhary DS, Adhikari BP. *J Appl Polym Sci* 2010; 115:2703-9.
- [13] Klug HP, Alexander LE. *X-ray diffraction procedures*. 2nd ed. New York: John Wiley; 1974.

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Fig. 4. DoE work for the response of degree of crystallinity: (a) estimated factorial effects and (b) contribution percentage in ANOVA.

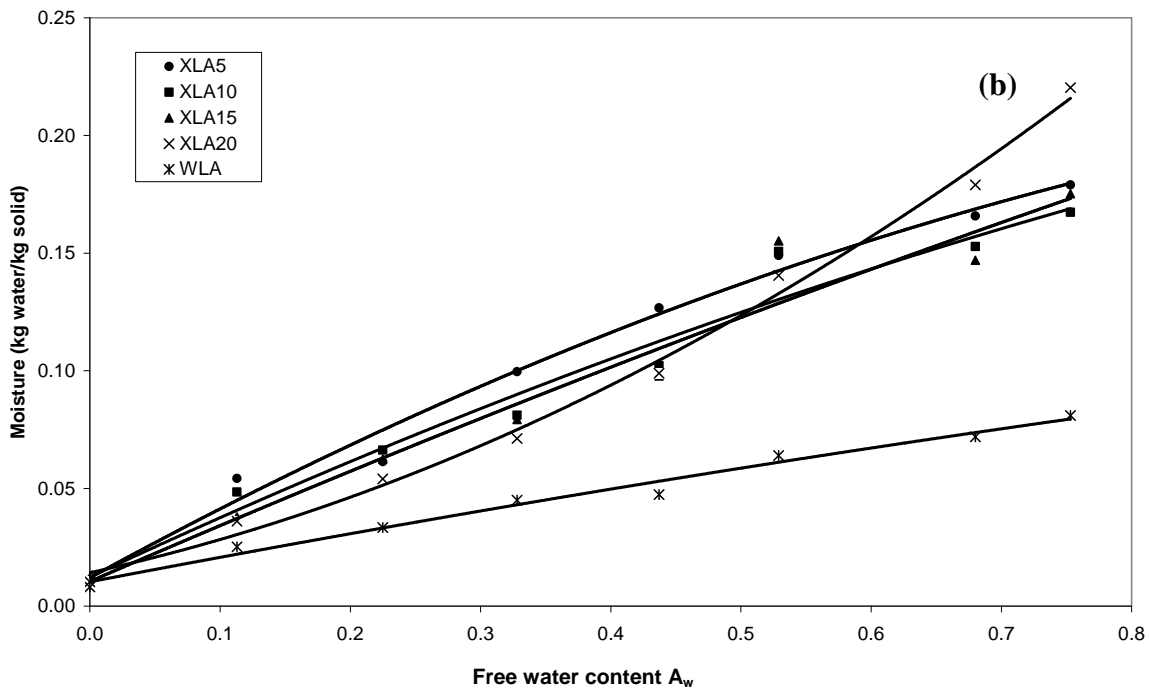
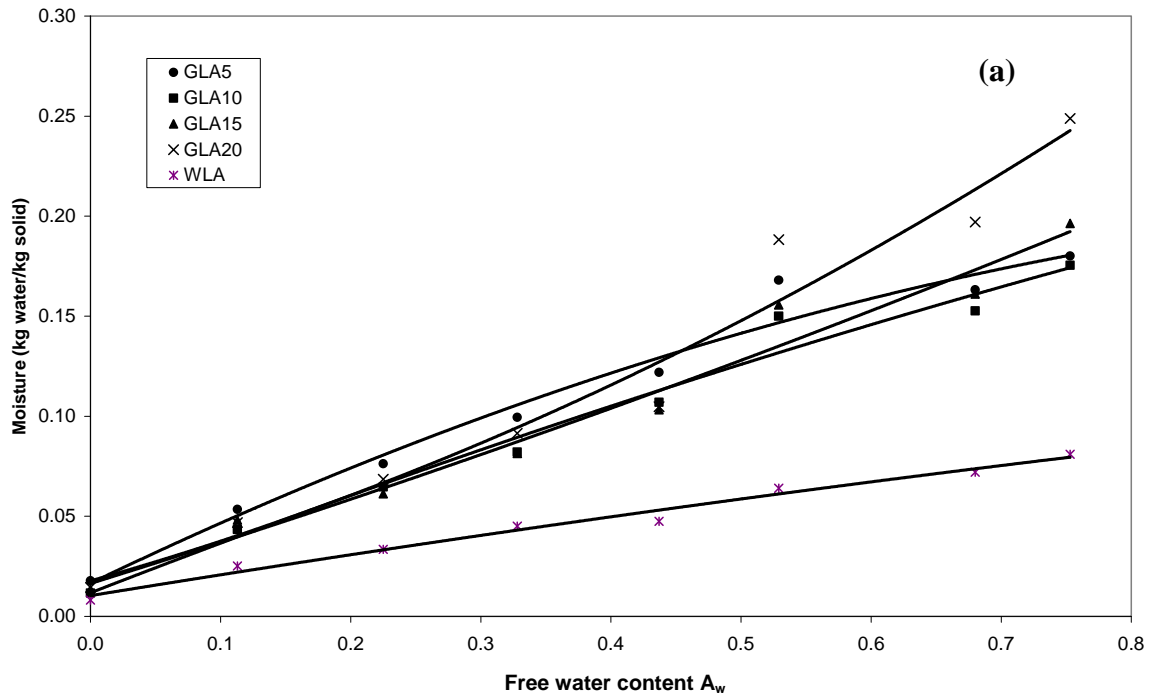


Fig. 1

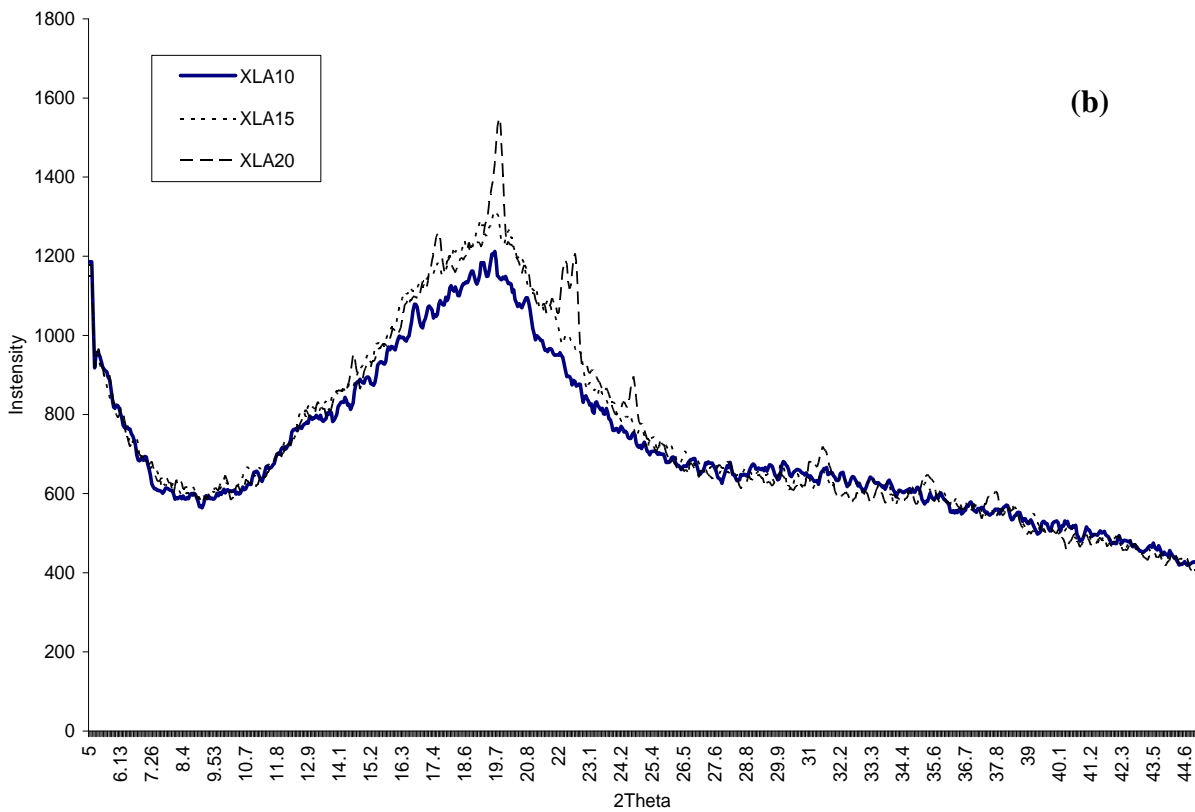
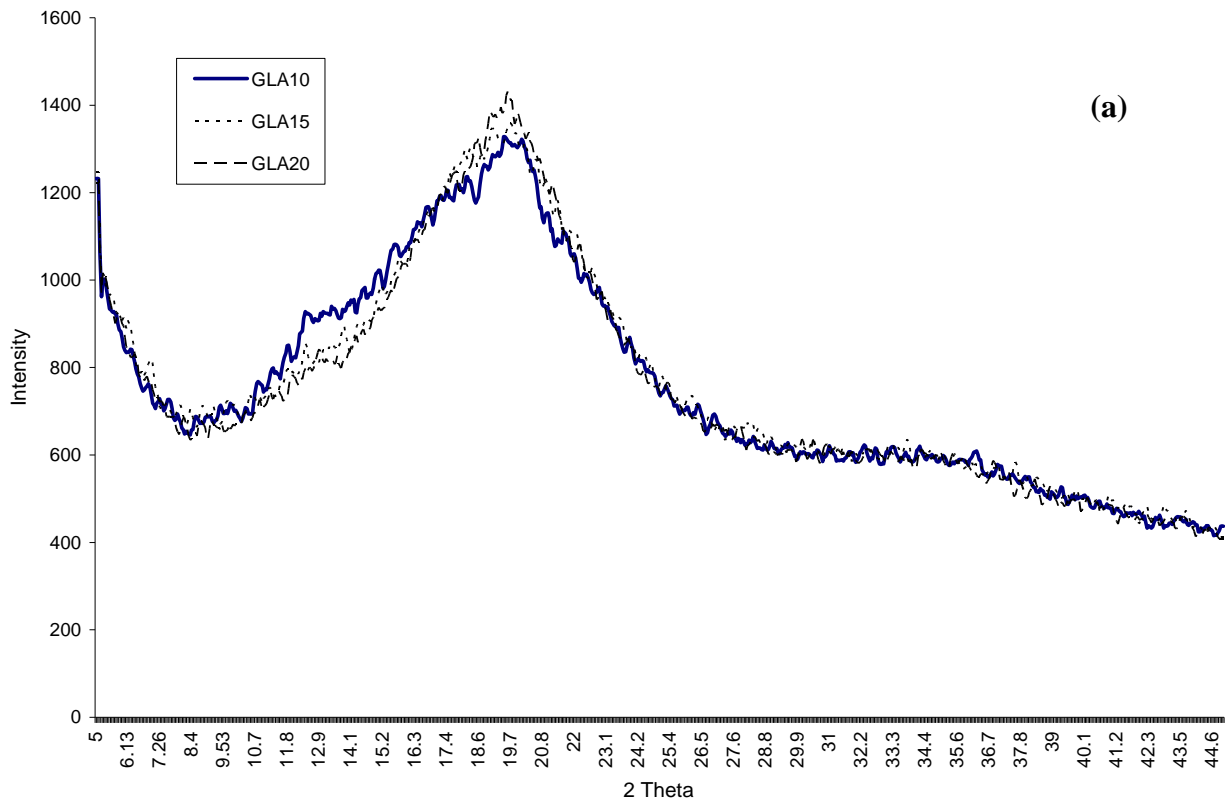


Fig. 2

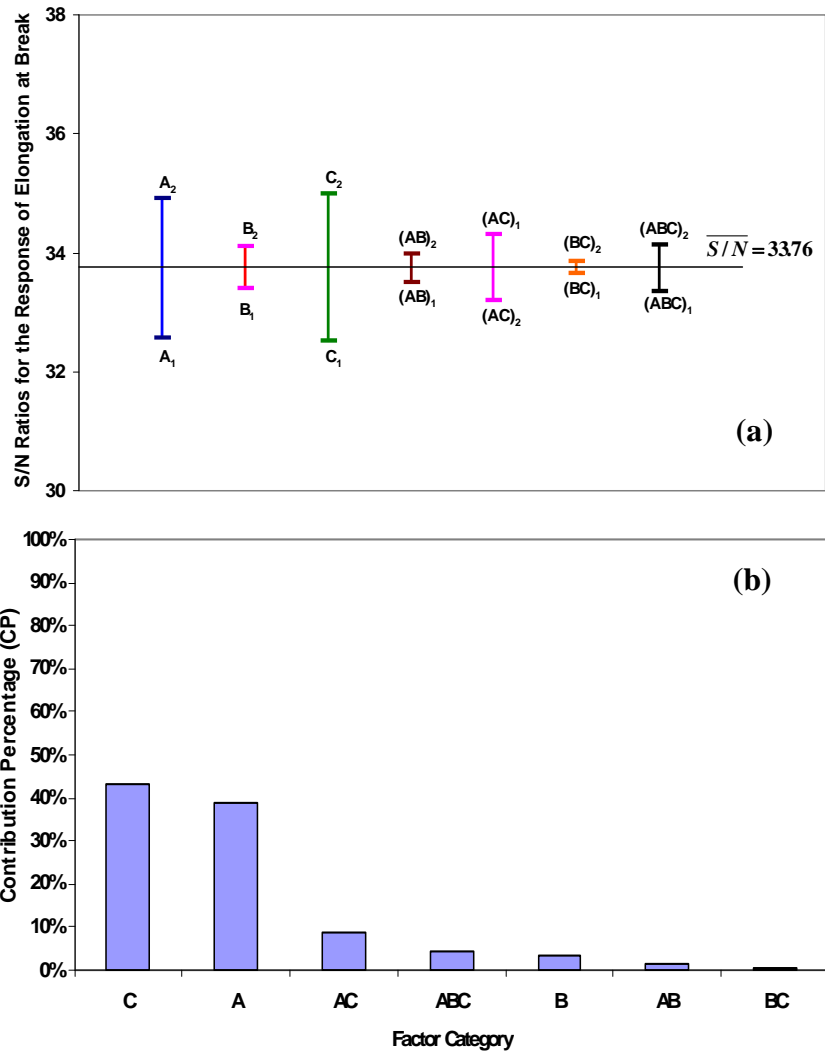


Fig. 3

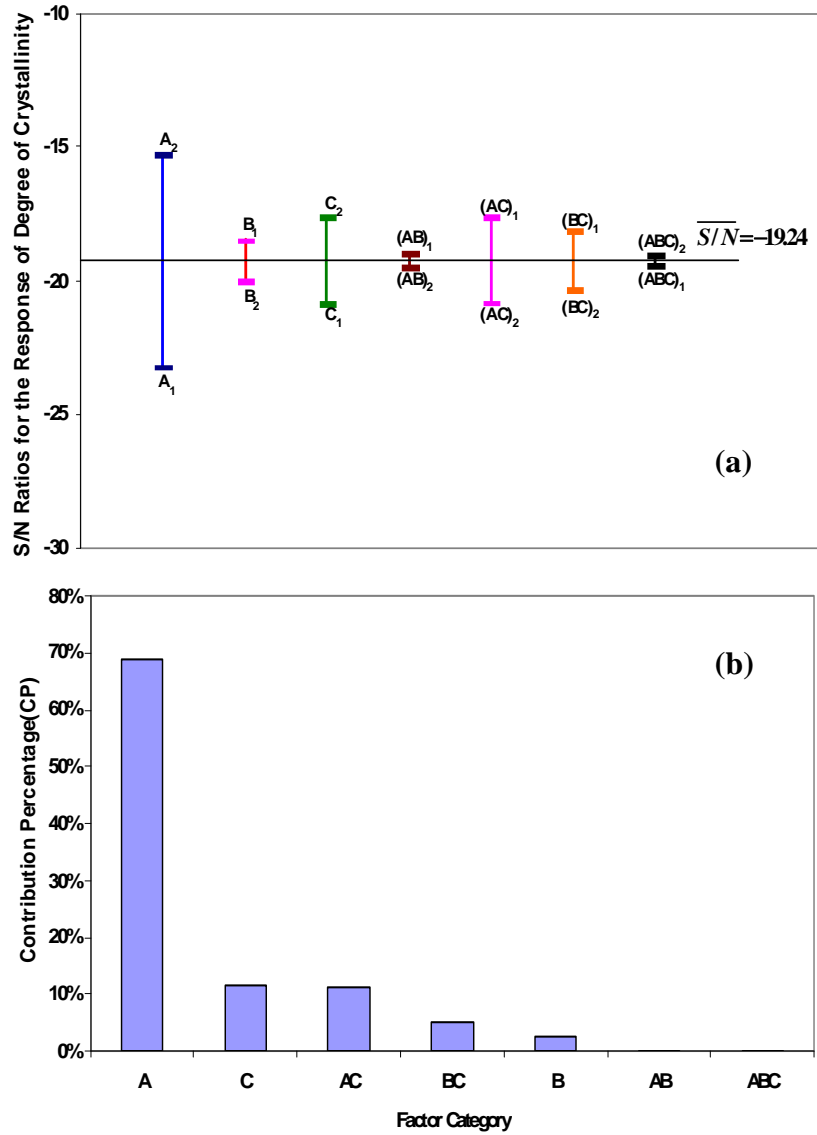


Fig. 4

Table 1 Total crystallinity levels, rigid amorphous contents and elongation ratios of GLA and XLA samples with their mean moisture contents.

Sample type	Moisture (wt%)		Crystalline region%		Rigid-amorphous region%		Elongation ratio $\left(\frac{\varepsilon_a}{\varepsilon_t}\right)^*$	
	mean	SD [†]	mean	SD	mean	SD	mean	SD
GLA5	8.457	(± 0.213)	33.18	(± .073)	4.667	(± 0.051)	1.533	(± 0.123)
GLA10	10.148	(± 0.211)	28.548	(± 0.213)	2.681	(± 0.367)	1.873	(± 0.134)
GLA15	11.263	(± 0.124)	23.486	(± 0.311)	3.301	(± 0.22)	1.641	(± 0.104)
GLA20	14.324	(± 0.336)	22.011	(± 0.116)	11.541	(± 0.193)	1.217	(± 0.103)
XLA5	9.802	(± 0.171)	26.471	(± 0.193)	5.309	(± 0.082)	1.776	(± 0.233)
XLA10	10.041	(± 0.082)	18.586	(± 0.367)	5.872	(± 0.432)	1.225	(± 0.22)
XLA15	10.772	(± 0.092)	14.15	(± 0.122)	9.547	(± 0.124)	1.117	(± 0.051)
XLA20	11.412	(± 0.051)	15.114	(± 0.311)	15.886	(± 0.193)	1.116	(± 0.122)

* ε_a and ε_t are the tensile elongations in the axial and transverse directions, respectively.

† SD= standard deviation