

THERMAL AND MECHANICAL PROPERTIES OF POLYLACTIDE TOUGHENED WITH A BUTYL ACRYLATE-ETHYL ACRYLATE-GLYCIDYL METHACRYLATE COPOLYMER*

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Abstract In this work, a specific polylactide (PLA) 4032D was melt-mixed with a new toughener: butyl acrylate (BA), ethyl acrylate (EA) and glycidyl methacrylate (GMA) copolymer (BA-EA-GMA). DMA tests showed that PLA/BA-EA-GMA blends were partially miscible. The degree of crystallinity of PLA increased while the cold crystallization temperature shifted to higher temperatures with increasing BA-EA-GMA content. The SEM micrographs showed that PLA/BA-EA-GMA blends had a good dispersion and this phenomenon was in good agreement with their higher impact strength. The result showed that the adding of BA-EA-GMA has enhanced the flexibility of PLA/BA-EA-GMA blends as compared with pure PLA. The impact strength was changed from 3.4 kJ/m² for pure PLA to 29.6 kJ/m² for 80/20 PLA/BA-EA-GMA blend.

Keywords: Polylactide; Thermal properties; Mechanical properties.

INTRODUCTION

Poly(lactide) (PLA) is a thermoplastic aliphatic polyester which can be produced from annually renewable resources. It has a number of excellent properties including biodegradability, biocompatibility, good mechanical properties and processability. For these reasons, PLA is expected to reduce the impact on the environment caused by production and utilization of petrochemical polymers, and has widely been used in biomedical materials^[1, 2] and general plastics. Nevertheless, the brittleness of PLA has limited its widespread applications. The toughening of PLA has been studied for a long time and different approaches have been used to improve the toughness of PLA^[3–13]. Typically, the impact strength is an indicator of toughness whereas the elongation at break indicates ductility of materials. The impact strength of PLA increases when blending with polycaprolactone, polyurethane, caprolactone/trimethyl carbonate copolymer, caprolactone/lactide diblock copolymer, poly(butylene adipate-co-terephthalate), poly(butylene succinate) and acrylonitrile-butadiene-styrene terpolymer^[13–23]. Linear low-density polyethylene and styrene-ethylene-butylene-styrene triblock copolymer can improve the impact strength as well^[24, 25].

Because most polymer blends do not have the appropriate functional groups, functionalization of the components is very often required^[26–29]. Fortunately, the inherent chemical functionality of PLA makes it an attractive candidate for modification. Some authors have described approaches for improving the toughness of PLA by the reaction of a polymer containing an appropriate chemical functionality with the carboxyl or hydroxyl

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end groups of PLA during melt processing. Functionalized elastomers, such as poly(ethylene-*co*-glycidyl methacrylate (EGMA), have been used to toughen PLA^[30]. The epoxy group of glycidyl methacrylate (GMA) can react *in situ* with the carboxyl and hydroxyl end groups of PLA during melt blending and can lead to an EGMA-grafted PLA copolymer that can compatibilize the blend. Other rubbers containing GMA, such as glycidyl methacrylate grafted poly(ethylene octane) (POE-*g*-GMA) have also been used to toughen PLA by the same mechanism^[30].

In this work, we choose BA-EA-GMA copolymer as a toughener because it exhibits a set of properties suitable for the application. The butyl acrylate (BA), ethyl acrylate (EA) and glycidyl methacrylate (GMA) copolymer was prepared by continuous polymerization method. The right proportion of BA-EA can increase the toughness of PLA. The epoxy group of glycidyl methacrylate (GMA) can react with the carboxyl and hydroxyl end groups of PLA during melt blending^[31, 32]. Such interactions would increase the compatibility between the PLA and BA-EA-GMA. PLA/BA-EA-GMA blends with various blending ratios were prepared by melting mixing at first. The thermal and mechanical properties of the blends were investigated by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), as well as tensile and impact tests. Morphological characterization was performed with scanning electron microscopy (SEM) to identify the toughening mechanism involved.

EXPERIMENTAL

Materials

The PLA (4032D) used in this study comprising around 98% L-lactide was a commercial product of Natureworks Co. Ltd., USA. It had weight-average molecular weight (M_w) of 2.50×10^5 g/mol and polydispersity of 1.70 (by GPC analysis). Butyl acrylate-ethyl acrylate-glycidyl methacrylate copolymer (BA-EA-GMA) (77% butyl acrylate, 20% ethyl acrylate and 3% glycidyl methacrylate) was obtained from Changchun University of Technology. It had weight-average molecular weight (M_w) of 6.6×10^5 g/mol and polydispersity of 10.5 (by GPC analysis).

Preparation of BA-EA-GMA

The butyl acrylate (BA), ethyl acrylate (EA) and glycidyl methacrylate (GMA) copolymer was prepared by continuous polymerization method. First, the reactor was pre-charged with two-thirds of the BA/EA/GMA/toluene/initiator mixture, and then the mixture was heated by an oil bath. The reaction temperature was 130 °C. The BA/EA/GMA/toluene/initiator mixture was continuously injected into the reactor by a feed pump at a given rate, and at the same time, the reaction product in the reactor was continuously pumped into the twin-screw devolatilization extruder by a melt pump at the same rate as the feed pump to remove the solvent and residual monomer, and then the BA, EA and GMA copolymer was obtained. The ratio of GMA in the copolymer was 3 wt%. Di-*tert*-butyl peroxide was used as initiator and the ratio was set at 0.1 wt%.

Sample Preparation

Blends of PLA/BA-EA-GMA were prepared by melt mixing using a twin screw Haake Rheomix 600 at 50 r/min and 190 °C for 5 min. The mixing compositions of the blends were 95/5, 90/10, 85/15 and 80/20 *W/W*. After blending, all the samples were cooled to room temperature under atmosphere air. Also, the pure PLA was subjected to the same mixing treatment so as to obtain a reference material. Films were prepared using a hot press at 190 °C, a hold pressure of 6 MPa and a hold time of 5 min, followed by quenching to room temperature between two thick-metal blocks kept at room temperature. The blocks were cooled on a large metal plate in the air for about 10 min between each quenching round to keep the same processing temperature. A template frame was used to ensure a constant film thickness of 4.0 mm for impact test and 1.0 mm for tensile test, and care was taken to ensure the same thermal history of all films. The specimens were then sealed in plastic bags awaiting the processing and analysis.

Differential Scanning Calorimetry

Thermal properties of the blends were studied by differential scanning calorimetry (DSC) (TA Instruments DSC Q20 USA) on the specimens sliced from compression molded samples. Samples (about 5–8 mg) were placed and sealed in aluminum pans. The samples were then heated first from $-60\text{ }^{\circ}\text{C}$ up to $180\text{ }^{\circ}\text{C}$ at 10 K/min (the first heating scan) and held at $180\text{ }^{\circ}\text{C}$ for 5 min to eliminate their previous thermal history. Following that the samples were quenched to $-60\text{ }^{\circ}\text{C}$ at the same rate and then heated again finally (the second heating scan). Since there are no crystals of BA-EA-GMA, only the contribution of the PLA is considered. The degree of crystallinity of the samples was evaluated from the heat evolved during fusion by the following relationship:

$$x_c = \frac{\Delta H_f}{w_{\text{PLA}} \times \Delta H_f^0} \times 100\% \quad (1)$$

where ΔH_f is the heat of fusion, ΔH_f^0 is the heat of fusion for 100% crystalline PLA (93 J/g)^[33] and w_{PLA} is the weight fraction of PLA.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was performed on a NETZSCH DMA 242C apparatus (Selb, Germany), which provided the plots of the loss tangent and the storage modules. The dimensions of the samples were $20\text{ mm} \times 4\text{ mm} \times 1\text{ mm}$. The experimental was carried out in tension mode at constant heating rate of 3 K/min and a frequency of 1 Hz , from $-70\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$.

Mechanical Properties

The uniaxial tensile tests were carried out at room temperature on an Instron 1121 testing machine (Canton MA). Specimens ($20\text{ mm} \times 4\text{ mm} \times 1\text{ mm}$) were cut from the previously compression-molded sheet into a dumbbell shape. The measurements were conducted at a cross-head speed of 50 mm/min at room temperature according to ASTM D638-2008. At least five runs for each sample were measured, and the results were averaged. Notched Izod impact tests were performed at room temperature according to ASTM D256-2010 on an impact testing machine (CEAST, Chengde, China). The samples with dimensions $63.2\text{ mm} \times 12.0\text{ mm} \times 4.0\text{ mm}$ were obtained from compression-molded specimens. The notch was milled in having a depth of 2.54 mm , an angle of 45° and a notch radius of 0.25 mm .

Morphological Characterization

The phase morphologies of the PLA/BA-EA-GMA blends were characterized by scanning electron microscopy (SEM, model Japan JXA-840 ESEMFE). Before characterization, the samples were kept in liquid nitrogen and then brittle fractured. The fractured surfaces were etched with ethyl alcohol for 30 min at room temperature to dissolve the BA-EA-GMA phase. And a layer of gold was sputter-coated uniformly over all of the fractured surface.

RESULTS AND DISCUSSION

Thermal Properties

DSC heating thermograms of samples are shown in Fig. 1, and the corresponding parameters of PLA/BA-EA-GMA blends are summarized in Table 1. From the thermograms, it can be seen that a single glass transition (T_g) appeared for PLA/BA-EA-GMA blends and it gradually decreased to lower temperature with increasing BA-EA-GMA content in the blends. The T_g decreased from $62.1\text{ }^{\circ}\text{C}$ for pure PLA to $60.8\text{ }^{\circ}\text{C}$ for the 80/20 PLA/BA-EA-GMA blend. The results indicated that BA-EA-GMA was partially miscible with PLA.

In addition to the glass transition temperature, the temperature of the cold crystallization (T_{cc}) was also observed for both pure PLA and PLA/BA-EA-GMA blends. The exothermic peak shifted to higher temperatures with increasing BA-EA-GMA content. Pure PLA exhibited a cold crystallization temperature at $106.2\text{ }^{\circ}\text{C}$. The addition of BA-EA-GMA increased the cold crystallization temperature to $117.7\text{ }^{\circ}\text{C}$ for the 80/20 PLA/BA-EA-GMA blend. It is therefore can be demonstrated that the addition of BA-EA-GMA made the ability of PLA to

crystallize more difficult. According to Byrne *et al.*^[34] the presence of epoxy functionality in the BA-EA-GMA prevented crystallization of PLA during processing. The epoxy functionality groups of the BA-EA-GMA can react with the carboxyl or hydroxyl end groups of PLA and this probably decreases the molecular segmental mobility of PLA reducing the ability of PLA to crystallize and/or recrystallize^[35].

Pure PLA exhibited a single melting peak at 168.6 °C. The addition of BA-EA-GMA separated the melting peak of PLA into two individual peaks for the PLA/BA-EA-GMA blends, as displayed in Fig. 1. This behavior was attributed to the formation of crystallites with different sizes and perfection which was arisen by lamellar rearrangement during crystallization of PLA^[36, 37]. From Table 1, it can be observed that the degrees of crystallinity of PLA/BA-EA-GMA blends increased continuously with the increase of BA-EA-GMA content, the BA-EA-GMA could be acted as heterogeneous nucleation agent and increased the degrees of crystallinity of PLA/BA-EA-GMA blends.

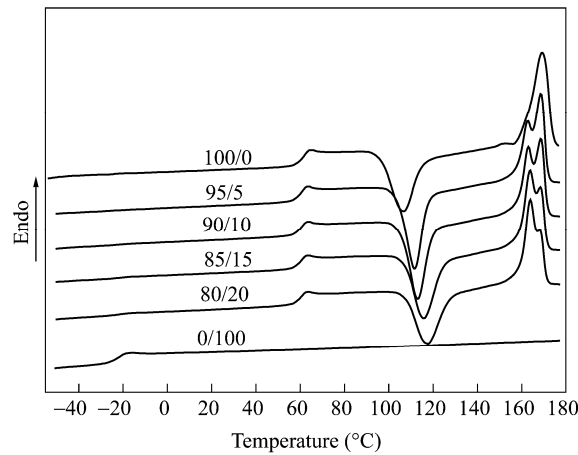


Fig. 1 DSC thermograms recorded during the second heating at the rate of 10 K/min for pure PLA, pure BA-EA-GMA and PLA/BA-EA-GMA blends

Table 1. Crystallization properties of PLA/BA-EA-GMA blends

PLA/BA-EA-GMA (W/W)	Second Heating Run						
	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_f (J/g)	X_c (%)
100/0	62.1	106.2	26.2	—	169.3	32.0	34.4
95/5	61.1	111.7	27.5	162.5	168.9	32.3	36.6
90/10	61.2	113.2	26.6	162.8	168.9	29.5	35.2
85/15	60.9	115.9	26.7	163.6	168.8	28.7	36.3
80/20	60.8	117.7	25.7	163.7	168.6	27.5	37.0
0/100	-21.1	—	—	—	—	—	—

Dynamic Mechanical Properties

DMA was used to analyze the miscibility and modulus changes of the blends. The storage modulus (E') and temperature relation curves of pure PLA and PLA/BA-EA-GMA blends are exhibited in Fig. 2. It can be observed that the E' of the PLA/BA-EA-GMA blends was lower than that of pure PLA. As an example, the E' was significantly decreased from 3484.4 MPa for neat PLA to 1873.9 MPa for the 80/20 PLA/BA-EA-GMA blend at 25 °C (Table 2). The decrease in the E' of the blends can be attributed to the low stiffness of the BA-EA-GMA. It also can be explained that the incorporation of the BA-EA-GMA made more difficult the crystallization of the PLA matrix which has been demonstrated in the DSC section. As shown in Fig. 2 and Table 2, the storage modulus of PLA/BA-EA-GMA blends gradually decreased with increasing temperature. In the regions between -20 °C and 0 °C, an abrupt drop in the E' of the blends was found because of the glass transition of BA-EA-GMA. It can be also observed that the E' had another abrupt drop in the regions between 50 °C and 70 °C because of the glass transition of PLA. Besides, a slight increasing of the E' at temperature

above 100 °C was due to the cold crystallization of PLA.

The $\tan\delta$ and temperature relation curves of pure PLA and PLA/BA-EA-GMA blends are exhibited in Fig. 3. While only one $\tan\delta$ peak was observed for pure PLA and two distinct $\tan\delta$ peaks were observed for PLA/BA-EA-GMA blends. As shown in Fig. 3 and Table 2, the $\tan\delta$ peak of the PLA phase shifted to lower temperatures to some degree, although the change was small, which was different from some investigations, because in most cases, the improvement of miscibility induces the glass-transition temperature shift together. The $\tan\delta$ peak of BA-EA-GMA phase shifted to higher temperatures. Such behaviors observed for both of the glass transition temperatures suggest that PLA and BA-EA-GMA are partially miscible and that there are some interactions between PLA and BA-EA-GMA at the molecular level particularly. These interactions refer to the reactions between the epoxy functional groups of the BA-EA-GMA and the carboxyl and hydroxyl end groups of the PLA^[29].

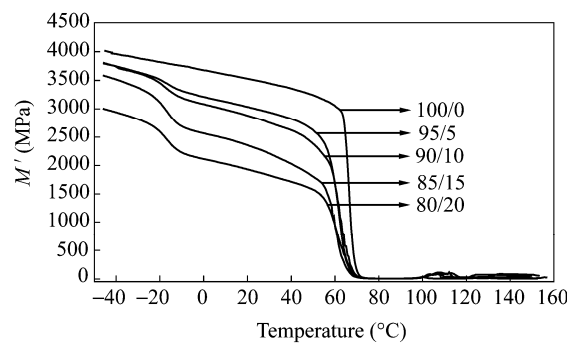


Fig. 2 Dynamic storage modulus of pure PLA and PLA/BA-EA-GMA blends as a function of temperature

Table 2. Thermomechanical properties of pure PLA and PLA/BA-EA-GMA blends

PLA/BA-EA-GMA (W/W)	$\tan\delta$ (°C)		Storage modulus (MPa)		
	1	2	25 °C	40 °C	60 °C
100/0	—	72.4	3484.4	3354.5	3050.8
95/5	-17.2	71.2	2982.3	2817.5	1730.0
90/10	-15.8	72.4	2820.3	2614.6	1570.6
85/15	-16.1	69.8	2286.7	2024.3	902.6
80/20	-15.9	69.4	1873.9	1710.4	914.7

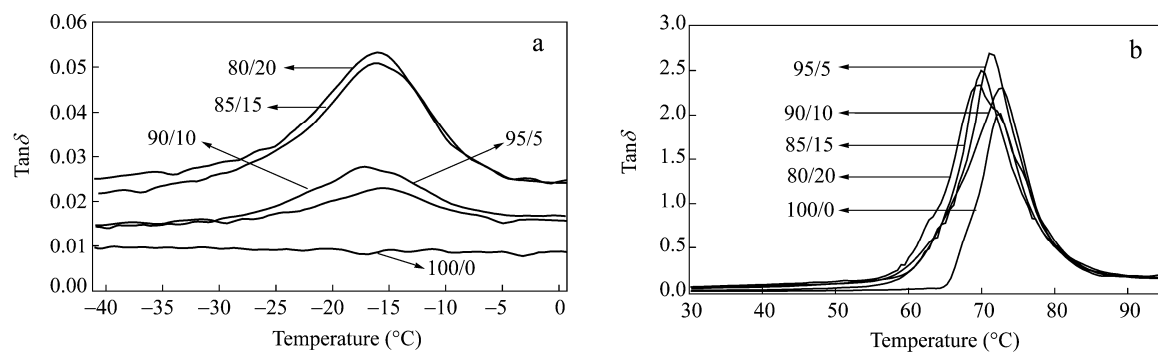


Fig. 3 $\tan\delta$ of pure PLA and PLA/BA-EA-GMA blends as a function of temperature: (a) the enlarged part of the BA-EA-GMA glass transition and (b) the enlarged part of the PLA glass transition

Mechanical Properties

The goal of adding BA-EA-GMA to PLA is to enhance plastic elongation and reduce brittleness and at the same time to maintain maximum polymer strength and stiffness.

The tensile stress-strain curves of pure PLA and PLA/BA-EA-GMA blends are shown in Fig. 4. It can be seen that the addition of BA-EA-GMA significantly changed the tensile behavior of PLA. The brittle fracture of

pure PLA transformed into ductile behavior of the PLA/BA-EA-GMA blends, upon them being subjected to tensile testing. Pure PLA was very rigid and brittle. The elongation at break was only about 5.1% and the tensile strength was 62.0 MPa. However, with the addition of BA-EA-GMA, it was very interesting to find that the 90/10 PLA/BA-EA-GMA blend had a very high elongation at break of 280%, while the tensile strength remained as high as 48.0 MPa. Moreover, the elongation at break continuously increased with increasing BA-EA-GMA content. On the other hand, the tensile strength and the modulus decreased with the addition of BA-EA-GMA, which was due to the lower tensile strength and modulus of BA-EA-GMA than those of pure PLA. These results clearly suggested that the inherent brittle fracture behavior of PLA can be successfully improved with the addition of BA-EA-GMA.

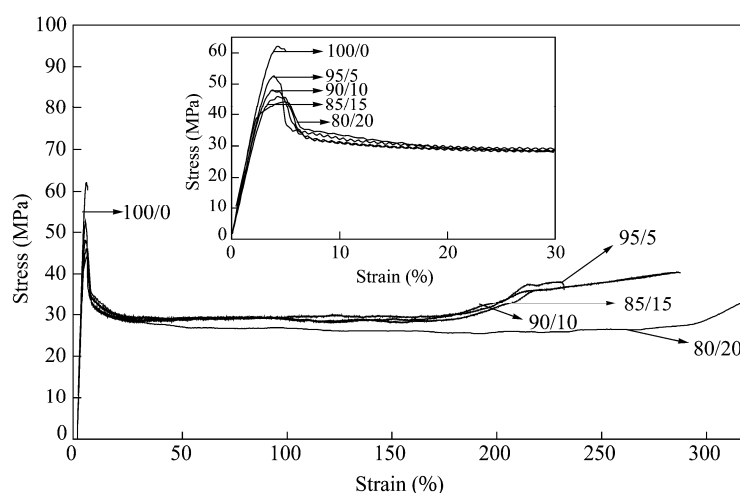


Fig. 4 Stress-strain curves of pure PLA and PLA/BA-EA-GMA blends

Impact strength testing is one of the most widely used methods for investigating polymer toughness, as if it gives information about the high-speed failure of materials. The impact strength of pure PLA and PLA/BA-EA-GMA blends are shown in Fig. 5. It can be observed that the impact strength of pure PLA was only 3.4 kJ/m² and the toughness value was poor. The toughness of PLA improved significantly with the addition of BA-EA-GMA. As for the blend with 20 wt% BA-EA-GMA, the impact strength of 29.6 kJ/m² was achieved, this was about 10 times that of pure PLA and the blend fractures in ductile mode. The obvious improvement of toughness for the blend with 20 wt% BA-EA-GMA may be explained in terms of the slight compatibility between the two phases.

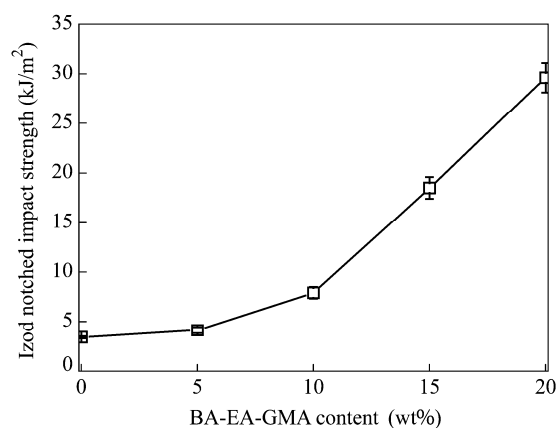


Fig. 5 Izod notched impact strength of pure PLA and PLA/BA-EA-GMA blends

The fractured surfaces of PLA/BA-EA-GMA blends were etched with ethyl alcohol for 30 min at room temperature to dissolve the BA-EA-GMA phase. The SEM micrograms of the samples are shown in Fig. 6. The addition of tougher BA-EA-GMA promotes the aggregated PLA particles to separate from each other during blending. Meanwhile, the BA-EA-GMA permeates into the PLA particles and the PLA molecules tend to disentangle and separate from each other due to the enhanced mobility of PLA chain caused by the toughening of BA-EA-GMA.

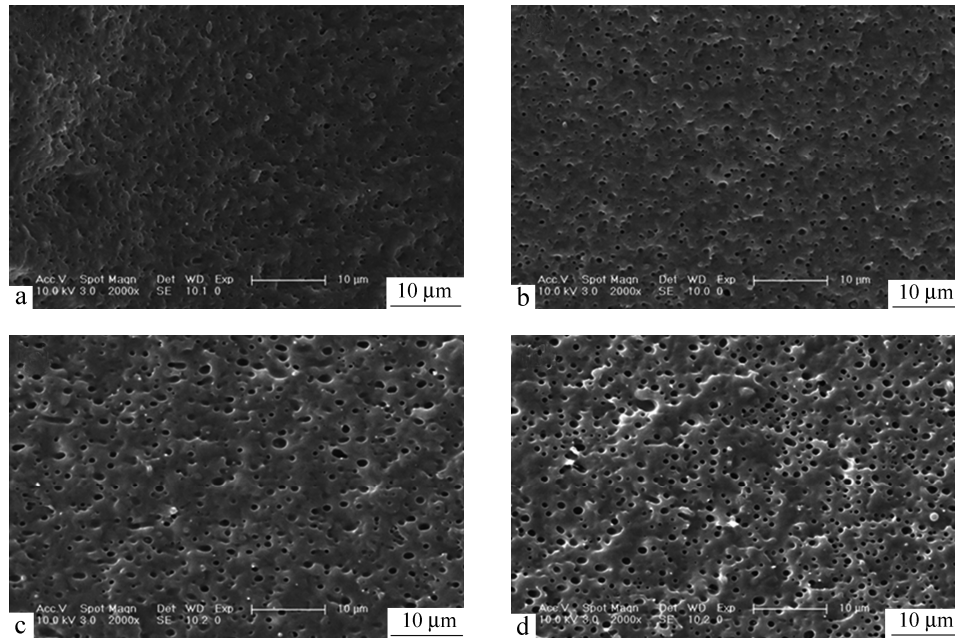


Fig. 6 SEM micrographs of the impact fracture surfaces of PLA/BA-EA-GMA blends: (a) 95/5, (b) 90/10, (c) 85/15 and (d) 80/20

A brittle-ductile transition has been observed in many blend toughened systems. Wu^[38, 39] suggested that the inter-particle distance is the primary controlling factor for toughening in polymer blends. Wu also indicated that if the inter-particle distance is below the critical value, then the blend will be tough; if the inter-particle distance is above the critical value, the blend will be brittle. For PLA/BA-EA-GMA blends, filler dispersions are studied by SEM (Fig. 7) and the distribution in particle size is quantified by image analysis. The average inter-particle distance (τ) for the blend can be calculated with Wu's equation:

$$d = \tau \left[k (\pi / 6 \Phi_r)^{1/3} - 1 \right]^{-1} \quad (2)$$

where d is the number average particle diameter, k is a geometric constant, and Φ_r is volume fraction of these particles. Φ_r can be calculated with Eq. (3):

$$\Phi_r = (M_r / \rho_r) / (M_r / \rho_r + M_p / \rho_p) \quad (3)$$

where M_r is the rubber weight, ρ_r is the rubber density, M_p is the weight of PLA, ρ_p is the density of PLA. For BA/EA/GMA copolymer, the density of BA, EA, and GMA is 0.898, 0.92, and 1.074 g/cm³, respectively.

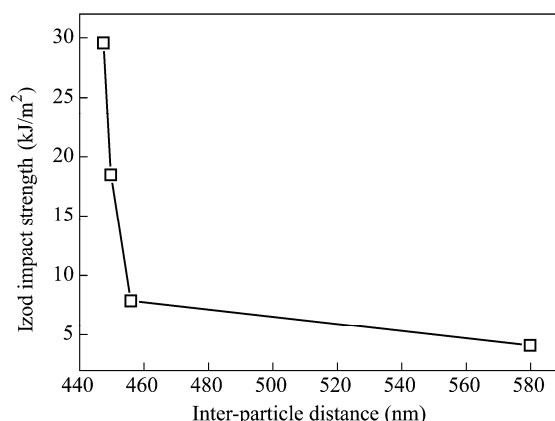


Fig. 7 The impact strength as a function of inter-particle distance of PLA/BA-EA-GMA blends

According to Wu's theory, k is 1 for a cubic lattice. Then, Eq. (2) is simplified to Eq. (4):

$$\tau = d \left[\left(\pi / 6 \Phi_r \right)^{1/3} - 1 \right] \quad (4)$$

The relationship of the Izod notch impact strength and inter-particle distance (τ) obtained by Eq. (4) is described in Fig. 7. A brittle-to-ductile transition marking the onset of toughening efficiency occurs around a critical inter-particle distance, τ_c of about 455.9 nm. Below this critical value, high toughness levels are achieved. The impact strength is increased from 3.4 kJ/m² for pure PLA up to about 29.6 kJ/m² for 80/20 PLA/BA-EA-GMA blend.

CONCLUSIONS

In this study, a new toughener (BA-EA-GMA) was added to PLA matrix with different ratios, such as 95/5, 90/10, 85/15, and 80/20, for toughening PLA.

DMA tests demonstrated that PLA/BA-EA-GMA blends were partially miscible as shifting of the glass transition temperatures of both components slightly towards each other were observed following the increasing of BA-EA-GMA. From the result of DSC, BA-EA-GMA could act as effective heterogeneous nucleation agent for PLA and significantly improved the degree of crystallinity of PLA. The SEM micrographs showed that PLA/BA-EA-GMA blends had a good dispersion. This can be also seen in the result of the impact strength. For example, the impact strength was changed significantly from 3.4 kJ/m² for pure PLA to 29.6 kJ/m² for the 80/20 PLA/BA-EA-GMA blend. Based on the results of this study, BA-EA-GMA may be used to toughen PLA.

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