

Study on Tough Blends of Polylactide and Acrylic Impact Modifier

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Acrylic impact modifiers (ACRs) with different soft/hard monomer ratios (mass ratios) were prepared by semi-continuous seed emulsion copolymerization using the soft monomer butyl acrylate and the hard monomer methyl methacrylate, which were used to toughen polylactide (PLA). The effect of soft/hard ACR monomer ratio on the mechanical properties of PLA/ACR blends was investigated. The results showed that the impact strength and the elongation at break of PLA/ACR blends increased with increasing soft/hard ACR monomer ratio, while the tensile and flexural strengths of PLA had little change. The impact strength of PLA/ACR blends could be increased about 4 times more than that of pure PLA when the soft/hard monomer ratio of ACR was 90/10, which was the optimal ratio for good mechanical properties of PLA. Additionally, the possible mechanism of ACR toughening in PLA was discussed through impact fracture phase morphology analysis.

Keywords: Polyacrylate; Toughening; Polylactide; Impact Strength; Mechanical properties

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INTRODUCTION

In the past few decades, polylactide (PLA) has attracted a great deal of attention due to its intrinsic advantages, including excellent mechanical properties (Ge *et al.* 2011; Feng *et al.* 2013), biodegradability (Wang and Su 2013), biocompatibility (Kakinoki *et al.* 2011), thermoplastic fabricability (Ljungberg and Wesslén 2005), and renewability (Mirabella *et al.* 2013). Early studies of PLA mostly focused on its biomedical applications, such as medical implants (Tisserat and Finkenstadt 2011), drug delivery (Sabo *et al.* 2013), sutures (Jiang *et al.* 2013), and tissue engineering (Jin *et al.* 2012). Recently, with the increased pollution and growing costs of traditional polymeric materials, PLA has been used for the replacement of traditional petroleum-based materials, for example, fiber (Wang and Su 2013) and packaging products (Segerholm *et al.* 2012). However, the brittleness as well as poor thermal stability of PLA still restrict its more widespread applications in general plastics. Melt blending is the most economic method for improving the toughness of PLA (Hassan *et al.* 2013; Ojijo *et al.* 2013). Much research has been carried out to blend PLA with various polymers, including silk fibers (Qu *et al.* 2010), pineapple leaf fibers (Huda *et al.* 2008), sisal fibers (Sun *et al.* 2013), plant oil (Xiong *et al.* 2013), poly(vinyl alcohol) (Caldorera-Moore and Peppas 2009), poly(caprolactone) (Jiang *et al.* 2005), polyethylene (Pai *et al.* 2011), poly (butylene carbonate) (Wang *et al.* 2013), calcium carbonate (Lin *et al.* 2010), and titanium dioxide (Buasri *et al.* 2013). Although some interesting and noteworthy results have been reported on toughening PLA, there are still some defects. For instance, some blends were immiscible, and compatibilizers were needed to increase compatibility to access the desired mechanical properties (Sun *et al.* 2011). In addition, the elongation at break was so low as to limit other potential applications of PLA, and the high toughening modifier content increased the cost of blends (Meng *et al.* 2011). Moreover, some PLA blends

improved impact strength at the expense of reducing the strength and modulus (Ge *et al.* 2011). Therefore, a more economic and effective toughening modifier for PLA is still needed.

Some kinds of acrylic impact modifier have been used to toughen brittle materials, such as epoxy products (Olmos *et al.* 2013), polyvinyl chloride (Pan *et al.* 2005), polyamide (Jin *et al.* 2012), and polycarbonate (Zha *et al.* 2012), and some noteworthy results have been obtained. Moreover, acrylic impact modifiers also have recently been used to toughen PLA. For example, Ge *et al.* (2011) found that the PLA composites with a kind of acrylic impact modifier (BPM) featured a better flexibility compared with pure PLA. However, the notched izod impact strength showed obvious improvement only when the BPM content was over 15 wt%. Nanoparticles of acrylate rubber were blended with PLA in a study reported by Petchwattana *et al.* (2009). The impact strength and elongation at break were increased by 1.8 times and 4 times, respectively, over that of pure PLA, while the tensile and flexural strengths presented a serious decline when the acrylate rubber content was lower than 1%. Though many studies of the relationship between the mechanical properties of PLA and the content of various impact modifiers (Jiang *et al.* 2013) have been reported, the phase behavior of PLA/impact modifier blends and the effect of the monomer ratio of the impact modifier on the mechanical properties of brittle materials have received less attention. In this study, acrylic impact modifiers (ACRs) with different soft/hard monomer ratios were prepared to toughen PLA. The effect of the soft/hard monomer ratio of ACR on the mechanical properties of PLA, including the impact strength, tensile property, and flexural property, were evaluated. The compatibility of PLA and ACR, the possible mechanism by which the ACR toughens PLA, and the thermal stability of the PLA/ACR blends were also considered.

EXPERIMENTAL

Materials

Injection-grade PLA (3051D) with a melt flow rate range of 12 to 20 g/10 min was used. It was purchased from Youli Mstar Technology Company and had a melting point of 165 °C. Methyl methacrylate (MMA) and butyl acrylate (BA), used as the main monomers, were of industrial grade and were purchased from Eastern Petrochemical Company. Potassium persulfate (KPS), used as the initiator, was supplied by Tianyun Chemical Company. Dodecyl sulfonic acid sodium salt (SLS) and alkylphenol ethoxylates (OP-10), used as emulsifiers, were of industrial grade and were supplied by Eastern Petrochemical Company.

Methods

Synthesis of polyacrylate emulsion

Emulsion polymerization was carried out by semi-continuous seed emulsion copolymerization (Song *et al.* 2013) in a 1000-mL four-neck round-bottomed flask equipped with an overhead Teflon stirrer, a reflex condenser, a thermometer, and a calibrated dropping funnel. First, distilled water and a little emulsifier, 0.07 wt.% of total monomers mass, were poured into the flask and stirred slightly. Then, the seed emulsion, taken from the pre-emulsion (10 wt%), was poured into the flask. After heating to 70 °C, some amount of KPS, 0.18 wt.% of total core monomers mass, dissolved in distilled water, was added to the solution. The resulting solution was then heated to 80 °C. The residual pre-emulsion and KPS were added gradually by a delayed process over a period of 4.5 h. The polymerization was continued further for 1 h after the addition of monomers. The polyacrylate emulsion was collected when it was cooled down to room temperature.

Finally, the emulsion was freeze-dried, and the obtained samples were used as impact modifiers for further study.

Blend Preparation

To study the effect of soft/hard ACR monomer ratio on the mechanical properties of PLA/ACR blends, the content of ACR in the various blends was fixed at 10 wt%. Prior to blending, PLA and ACR were dried at 60 °C for 12 h in a vacuum oven. The PLA/ACR blends, including the pure PLA, were prepared by melt mixing in a torque rheometer (PolyLab, Germany) for 10 min at 165 °C with a roller speed of 60 rpm. After blending, the sample was cooled to room temperature and molded into standard specimens with a micro-injection molding machine (MiniJet II, Germany) with an injection temperature of 170 °C and mold temperature of 50 °C.

Characterization

Dynamic light scattering (DLS)

Particle size and distribution were measured by DLS (Nano ZS, UK). The test temperature was controlled at 25 ±1 °C. For the DLS measurement, the samples were diluted in water (1:200 v/v). The particle diameters were taken to be the mean values of the z-average diameters calculated by the cumulative method.

Scanning electron microscopy (SEM)

The morphology of polyacrylic particles and impact fracture surfaces were observed by SEM (Hitachi 3400-I, Japan). All specimens were vacuum coated with gold prior to examination.

Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of samples were measured by DMA (Q800, US) under the multi-frequency-strain module of testing from -100 to 150 °C. The dimensions of the samples were 60 mm × 10 mm × 4 mm. The heating rate was set at 2 °C/min, and a frequency of 1 Hz was employed.

Impact testing

An impact test was performed using an impact tester (XJ-50Z, China) at room temperature with a pendulum hammer of 25 J according to the ISO 179 standard. The dimensions of the sample were 80 mm × 10 mm × 4 mm. Ten samples were tested for each reported value.

Tensile testing

Tensile testing was conducted on a universal testing machine (Instron 4466, US) at a temperature of 25±1 °C according to the ASTM D638 standard. The dimensions of the sample were 60 mm × 3 mm × 3 mm. The capacity of the load cell was 10 kN, while the crosshead speed was set at 10 mm/min. At least five samples were tested for each reported value.

Flexural testing

A three-point bending test was performed at a temperature of 25±1 °C on a universal testing machine (Instron 4466, US) according to the ASTM D 790 standard. The dimensions of the sample were 80 mm × 10 mm × 4 mm. The crosshead speed was set at 4 mm/min. At least five samples were tested for each reported value.

Thermogravimetric analysis (TGA)

TGA was conducted on a thermogravimetric analyzer (TG 209, Germany) under N₂ atmosphere at a flow rate of 20 mL/min. The heating rate was 20 °C/min, and the scanning range was from 35 to 800 °C.

RESULTS AND DISCUSSION**Characterization of Polyacrylic Particles**

Polyacrylate emulsions with different soft/hard monomer ratios were prepared by semi-continuous seed emulsion copolymerization using BA and MMA as the main soft and hard monomers, respectively. The particle size and size distributions of polyacrylate emulsion were measured by DLS, and the results are shown in Table 1. The size of most polyacrylic particles with different soft/hard monomer ratios was in the range of 380 to 390 nm, with a narrow size distribution. The morphology of the particles was investigated using SEM characterization.

Table 1. Particle Size and Size Distribution of Polyacrylate Emulsion

Sample	BA/MMA (wt %)	Particle Size (nm)	PDI
S1	40/60	392.0	0.034
S2	50/50	389.1	0.060
S3	60/40	397.2	0.031
S4	70/30	395.4	0.046
S5	80/20	385.1	0.043
S6	90/10	386.6	0.052

PDI is the dispersion index, the characterization of system dispersion. When PDI < 0.05, the system is considered to be a mono-disperse system.

Figure 1a shows that the size of the resultant particles are about 400 nm, which is consistent with the data from the DLS measurement, and the particles retain a regular spherical structure, without strawberry or sandwich structure. The morphology and structure of polyacrylic particles remained the same after freeze-drying treatment (Fig. 1b). In a further study, dry samples of polyacrylic particles were used as ACR to toughen the PLA materials.

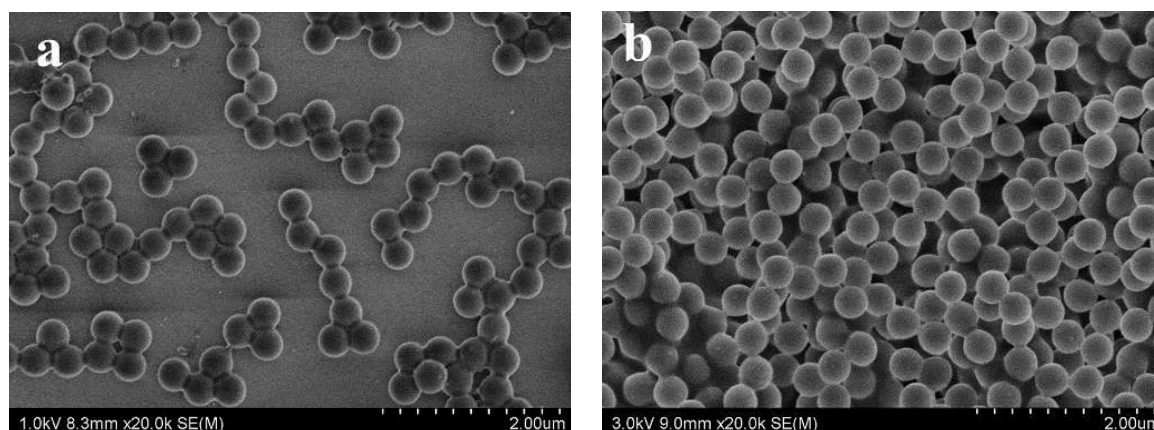


Fig. 1. SEM images of polyacrylate microspheres (sample S1) (a) before freeze-drying and (b) after freeze-drying

Properties of PLA Toughened by ACR

Elastic behavior and compatibility

DMA is a mechanical analytical technique used to measure the dynamic response of materials under a given set of conditions. The dynamic storage modulus (E'), loss modulus (E''), and $\tan\delta$ ($\tan\delta$) curves as a function of temperature for materials can be determined by DMA under the thermal sweep mode. E' measures the elastic behavior of materials, and $\tan\delta$, which is the ratio of E'' to E' , is also particularly useful for qualitatively characterizing the glass transition temperature (T_g) of a polymer (Park *et al.* 2001). Thus, DMA was performed to investigate the elastic behavior and T_g of PLA and PLA/ACR blends.

Figure 2a shows the E' curves of PLA and PLA/ACR blends (S1-S6) as a function of temperature. The E' of each test sample decreased slowly with increasing temperature before reaching the T_g (65 °C) of PLA, but dropped dramatically when approaching the T_g of PLA, which resulted from the softening or segmental mobility of PLA molecules. The addition of ACR (S2-S6) decreased the E' of pure PLA due to the low stiffness of the ACR, suggesting that the stiffness of the PLA could be decreased with the addition of ACR (S2-S6).

It is notable that the E' of blend PLA/S1 was higher than that of pure PLA, indicating that ACR with a higher content of hard monomer (> 60 wt %) could not toughen PLA. Moreover, the high viscosity of 100% PBA will make it difficult to prepare well-distributed mixture with small particle of brittle PLA by melt blending, resulting in low testing repeatability. Therefore, the blends PLA/S1 and PLA/PBA were not considered in the subsequent research.

The E'' curves of PLA and PLA/ACR blends as a function of temperature are shown in Fig. 2b. It can be seen that only one peak was observed for pure PLA, while two distinct peaks for PLA/ACR blends were observed, suggesting that PLA and ACR formed immiscible blends. To further explore the compatibility of PLA and ACR, $\tan\delta$ were measured as a function of temperature, and results are shown in Fig. 2c. Though the weaker peaks of PLA/ACR blends could not be directly observed because the addition of ACR was only 10 wt%, the weaker peaks could be observed after the local curves (temperature from -40 °C to 45 °C) were magnified 10 times.

The T_g of all the samples, obtained from the $\tan\delta$ curves (Fig. 2c), are shown in Table 2. The T_g of the ACR in PLA/ACR blends was much higher than that of pure ACR, while the T_g of PLA in PLA/ACR blends was lower than that of pure PLA (65 °C), implying that the PLA is partially miscible with the ACR (Wang *et al.* 2004; Deng and Zhang 2005). This change in T_g indicated that there may be some possible interactions, such as hydrogen bonding or polar interactions between the carbonyl group and the hydroxyl or carboxyl groups, in the PLA and ACR at the molecular level (Meng *et al.* 2012).

Table 2. The T_g of ACR, ACR in PLA/ACR Blends, and PLA in PLA/ACR Blends

Sample	T_g of ACR, °C	T_g of ACR in PLA/ACR blends, °C	T_g of PLA in PLA/ACR blends, °C
PLA	/	/	65.0
S2	25.1	34.4	62.0
S3	12.0	18.9	58.7
S4	1.7	6.2	61.2
S5	-6.8	-4.6	60.7
S6	-19.6	-17.3	59.1

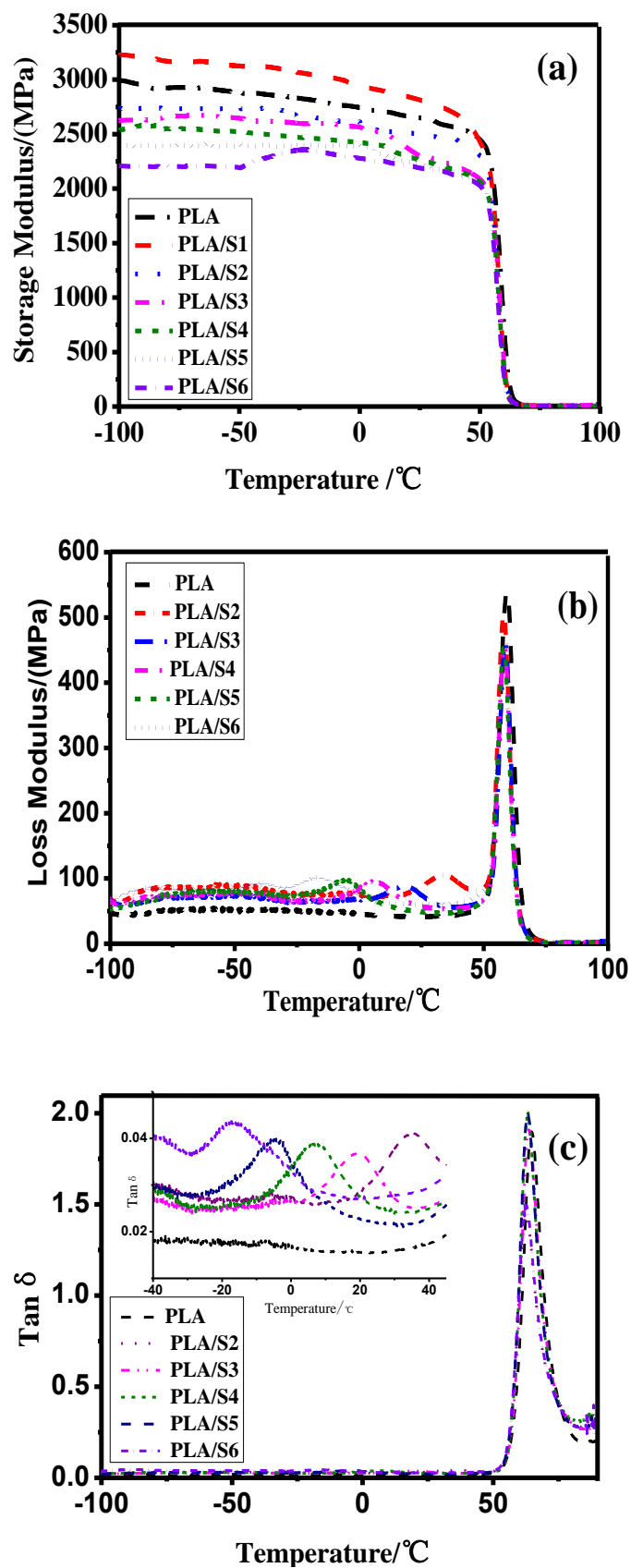


Fig. 2. Dynamic mechanical curves showing (a) storage modulus; (b) loss modulus; and (c) $\tan \delta$ of PLA and PLA/ACR blends

Mechanical properties

In general, the impact strength and the elongation at break are the primary factors for evaluating the flexibility of materials. Therefore, the impact strength, tensile strength, and flexural elongation at break of PLA and PLA/ACR blends were tested. The impact strengths of pure PLA and PLA/ACR blends are depicted in Fig. 3. A gradual increase of the impact strength was observed with increasing soft/hard ACR monomer ratio. With the increasing of soft/hard ACR monomer ratio, the adhesion of PLA/ACR blends and the interactions between the ACR and PLA matrix, which were thought to be hydrogen bonding and polar interactions between carbonyl group and hydroxyl or carboxyl groups of the ACR and PLA at the molecular level (Meng *et al.* 2012), became stronger, so the debonding process required a greater stress, and achieved a better toughening effect. The impact strength was significantly increased from 17 (pure PLA) to 68 kJ/m² (PLA/S6 blend). Compared with other acrylic impact modifiers as reported in previous work (Petchwattana *et al.* 2009), in which the impact strength of PLA generally increased by 1.8 times over that of pure PLA, sample S6 was found to be the most effective impact modifier.

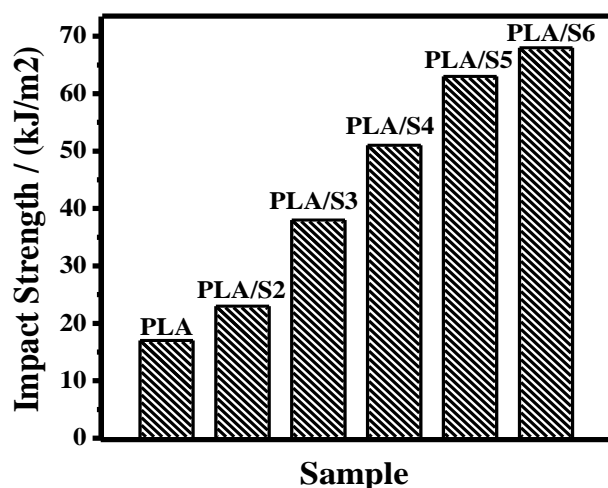


Fig. 3. Impact properties of pure PLA and PLA/ACR blends

The tensile stress-strain curves of the pure PLA and PLA/ACR blends are shown in Fig. 4. The pure PLA was rigid and brittle, with an elongation at break of only about 4.3%. The pure PLA showed a distinct yield point with subsequent failure by neck instability. Correspondingly, the PLA/ACR blends showed a clear yielding and a stable neck growth.

The blends were finally broken at an increased elongation, and the elongation continuously increased with increasing soft/hard ACR monomer ratio. It is notable that in the previous work of Meng *et al.* (2012), the tensile strength of PLA showed a dramatic decrease with the addition of 100% PBA. Here, due to the addition of the hard part of PMMA in ACR, the tensile strength of PLA/ACR exhibited a slight decrease compared to that of pure PLA.

Moreover, the flexural elongation at break of PLA increased with the addition of ACR, as shown in Fig. 5, while the flexural strength of PLA had little change. These results suggest that the brittleness of PLA can be successfully reduced with the addition of ACR.

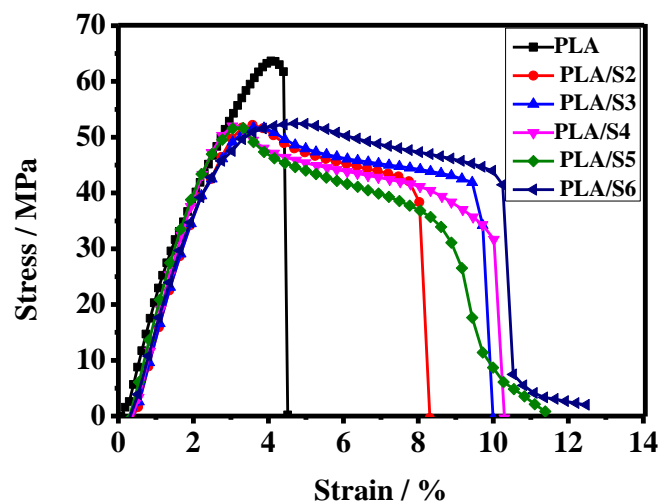


Fig. 4. Tensile properties of pure PLA and PLA/ACR blends

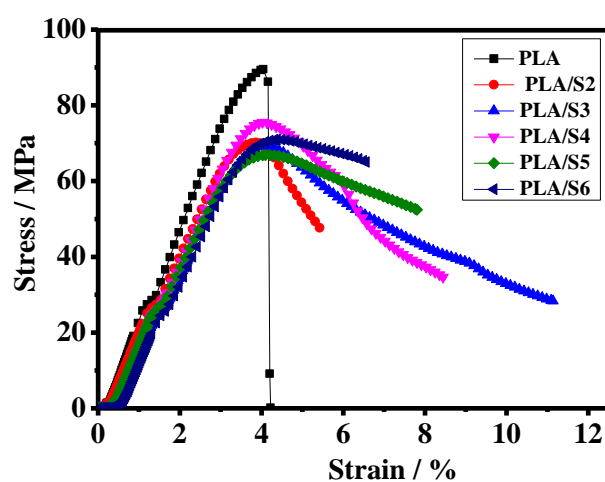
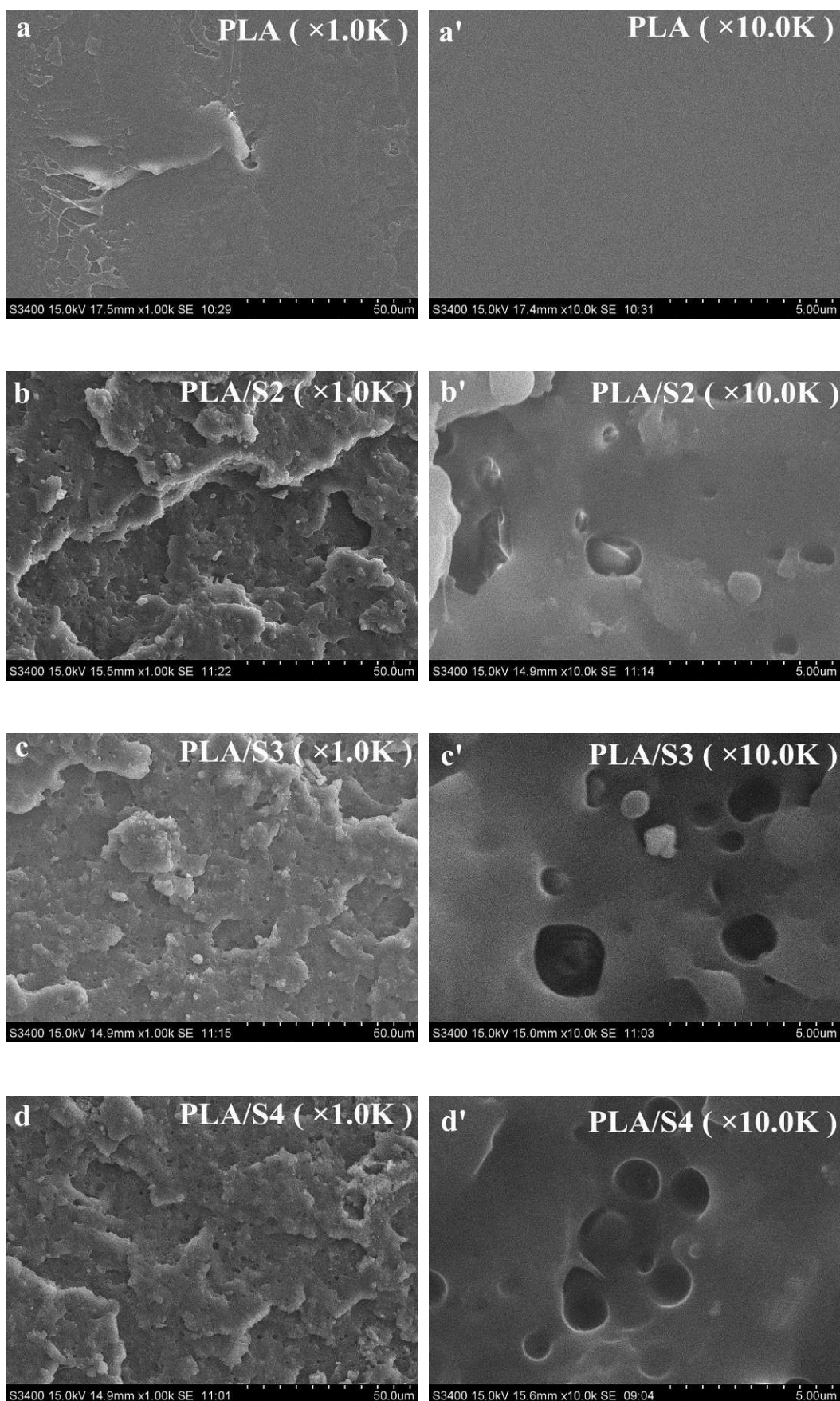


Fig. 5. Flexural properties of pure PLA and PLA/ACR blends

Generally, the mechanical properties of multiphase polymer blends depend on the phase morphologies. To study the possible mechanism by which ACR toughens PLA, SEM characterization was employed to identify the phase structure of the PLA and PLA/ACR blends. For pure PLA, there were only a few lines and a large smooth fracture surface area, as can be seen in Fig. 6a. Compared with the smooth fracture surface of pure PLA, the surfaces of PLA/ACR blends with obvious plastic deformations, as shown in Figs. 6b-6f, appeared rough, and many cavities were observed in the PLA matrix with a relative uniform distribution. Also, the amount of cavities increased with increasing soft/hard ACR monomer ratio. To further investigate the possible toughening mechanism, local magnification images of the impact fracture surfaces were investigated and are shown in Figs. 6a'-6f'. It is clear that the interface between ACR and PLA phases became more and more indistinct with increasing soft/hard ACR monomer ratio. The interactions between the ACR and PLA matrix, which were thought to involve hydrogen bonding and polar interactions between carbonyl group and hydroxyl or carboxyl groups of the ACR and PLA at the molecular level, became stronger with increasing soft/hard ACR monomer ratio. A similar phenomenon has been reported for a PLA/PBA blend (Meng *et al.* 2012).



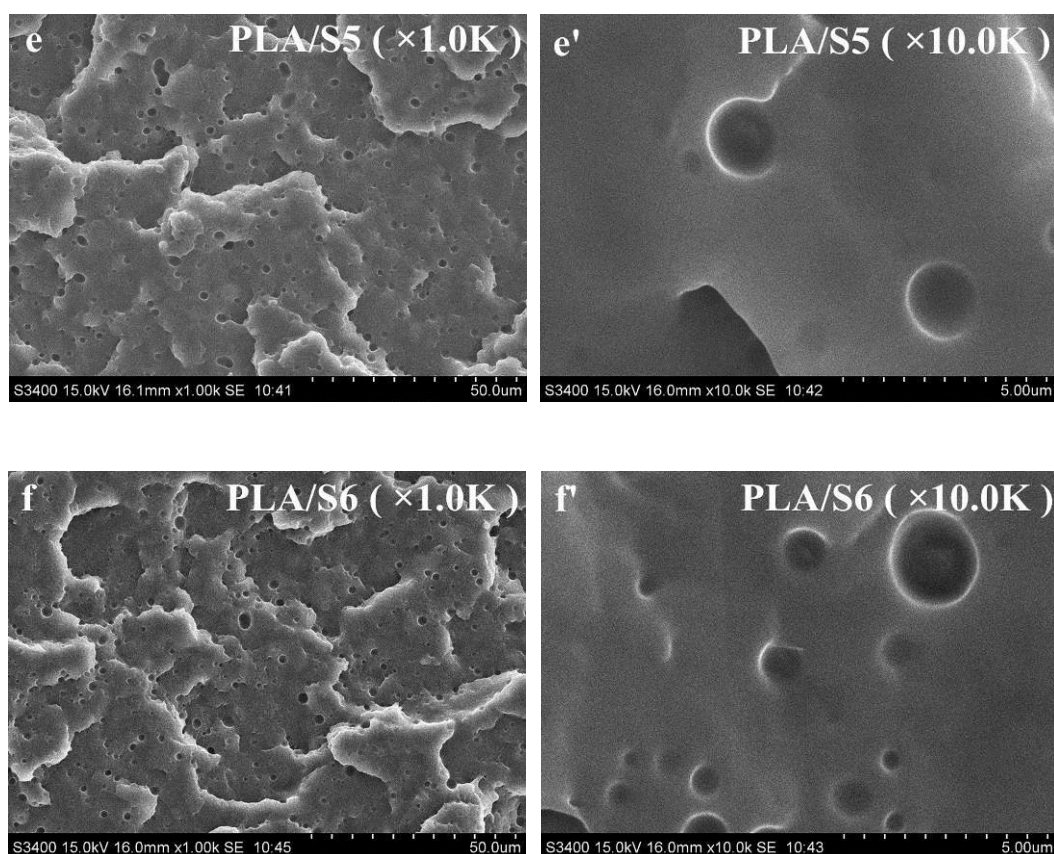
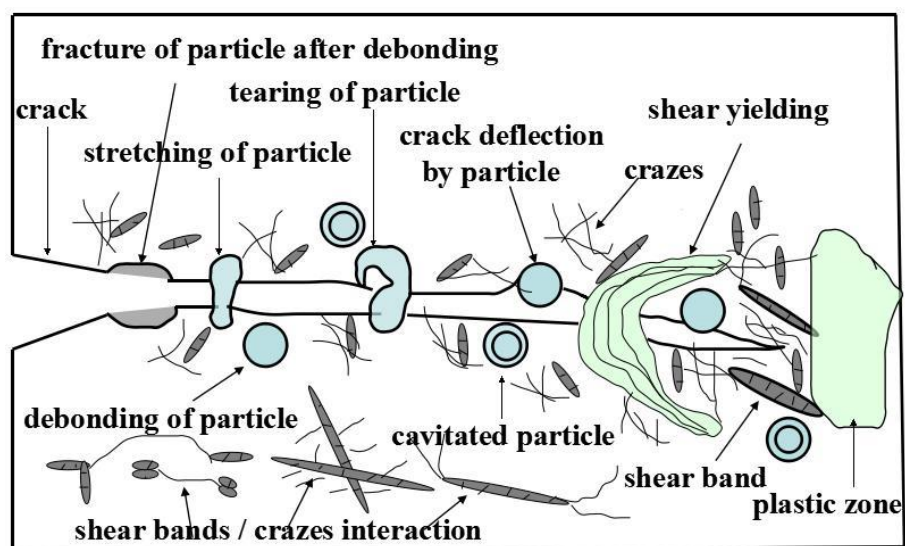


Fig. 6. SEM images of the impact fracture surfaces of PLA and PLA/ACR blends

On the basis of the above discussion, a possible mechanism by which ACR toughens PLA can be simply described as in Scheme 1. On the impact fracture surfaces, ACR in PLA matrix might be present in the following primary forms: stretching of particles, tearing of particles, cavitated particles, debonding of particles, and a kind of particle able to deflect cracking. The spherical elastomeric particles in the PLA matrix acted as stress concentrators because they had an elastic property that differed from the PLA matrix. The stress concentration led to the development of a triaxial stress in the ACR particles. Generally, in rubber-toughened polymeric materials, two types of cavities will come into being: either internal cavities in the rubber domains, when there is a strong interfacial bonding between the components, or debonding cavities at the interface, when the stress is higher than the interfacial bonding strength. Debonding can easily take place at the particle matrix interface in the perpendicular external stress direction because of the lack of phase adhesion (PLA was partially miscible with ACR). Thus, cavities were formed, which can be clearly observed in Figs. 6b-6f. The cavities caused by debonding altered the stress state, and the triaxial tension was locally released. Meanwhile, with the formation of the cavities, crazes and weak shear bands were formed in the PLA matrix and the PLA matrix between the ACR particles deformed more easily to achieve shear yielding. ACR cavitations *via* interfacial debonding and shear yielding induced energy dissipation in the PLA matrix, which retarded crack initiation and propagation and led to an improved impact strength for the brittle PLA, as is evident from Fig. 3. Furthermore, with increasing soft/hard ACR monomer ratio, the adhesion of PLA/ACR blends and the polar interactions between ACR and PLA became stronger, so the debonding process required a greater stress, along with more cavities, as shown in Fig. 6, and achieved a better toughening effect.



Scheme 1. A simple scheme of a possible mechanism by which ACR toughens PLA

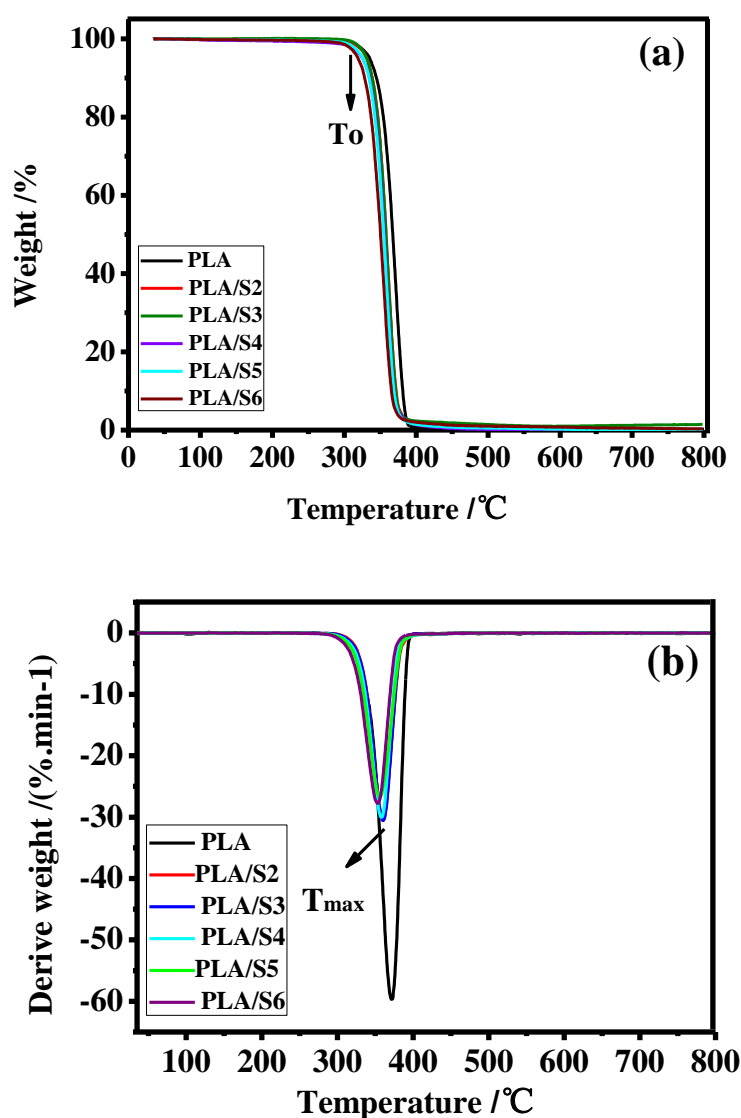


Fig. 7. Thermograms of PLA/ACR composites: (a) TGA thermograms; (b) DTG thermograms

Thermal Stability

To examine the effect of soft/hard ACR monomer ratio on the thermal stability and decomposition behavior of PLA, TGA data under a N₂ atmosphere were obtained and analyzed. Figure 7 shows the TGA and derivative thermogravimetric (DTG) curves of PLA and PLA/ACR blends. All the samples had a single decomposition step in the range of 35 to 800 °C under N₂ atmosphere. Also, only a single peak was observed in the DTA curves (Fig. 7b), which was evidence that complete thermal degradation occurred with a single step. The relevant thermal decomposition data, including the temperature at the beginning of the weight loss (T_o), the temperatures at which 10% weight loss occurred ($T_{10\%}$), and the temperature at the maximum weight loss rate (T_{max}), are presented in Table 3. These values of PLA/ACR blends decreased slightly but still approached that of PLA; thus, it can be deduced that the addition of ACR had almost no influence on the thermal stability of PLA.

Table 3. TGA Data for PLA and PLA/ACR Blends in N₂ Atmosphere

Sample	T_o , °C	$T_{10\%}$, °C	T_{max} , °C
PLA	351.3	381.0	372.0
PLA/S2	343.8	371.4	360.1
PLA/S3	343.2	370.2	360.3
PLA/S4	341.0	369.4	358.0
PLA/S5	339.4	369.3	356.6
PLA/S6	337.0	367.3	356.0

CONCLUSIONS

1. Acrylic impact modifiers (ACRs) with different soft/hard monomer ratios were successfully prepared by semi-continuous seed emulsion copolymerization using the soft monomer butyl acrylate (BA) and the hard monomer methyl methacrylate (MMA) as the main monomers. PLA/ACR binary blends were prepared by melt blending to investigate the effects of soft/hard ACR monomer ratio on the mechanical properties of PLA. The DMA results revealed that PLA and ACR were partially miscible.
2. The brittleness of PLA was diminished by modification with ACR. With increasing soft/hard ACR monomer ratio, the impact strength of PLA/ACR blends was enhanced, and little change was observed in the tensile and flexural strengths. The impact strength of PLA/ACR blends was increased about four times over that of pure PLA when the soft/hard ACR monomer ratio was 90/10. The tensile and flexural stress-strain curves showed that the PLA/ACR blends had gradually increased elongation at break with increasing soft/hard ACR monomer ratio, suggesting that the brittleness of PLA could be successfully improved with the addition of ACR.
3. The SEM characterization revealed that the plastic deformation took place in the PLA matrix. The TGA data showed that the addition of ACR had almost no influence on the thermal stability of PLA.

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