Transparent and ductile poly(lactic acid)/poly(butyl acrylate) (PBA) blends: Structure and properties

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Abstract

Poly(butyl acrylate) was prepared by the free radical polymerization of butyl acrylate as an initiator in the presence of 2,2′-Azoisobutyronitrile (AIBN) and the average molecular weight, polydispersity and thermal stability were evaluated. PLA and PBA were melt blended using a Haake Rheometer, and the light transmission, thermal properties, dynamic rheological properties, mechanical properties, phase morphology of blends and toughening mechanism were investigated. Dynamic rheology, SEM and DSC results show that the PLA is partial miscible with PBA. The PBA component improved the crystallization ability of PLA and the crystallinity of PLA increased with content of PBA (<15 wt.%). With the increase of PBA, the tensile strength and modulus of the blend decreased slightly while the elongation at break and toughness were dramatically increased. With the addition of PBA, the failure mode changes from brittle fracture of neat PLA to ductile fracture of the blend. Rheological results revealed the complex viscosity and melt elasticity of the blends decreased with increasing content of PBA and phase segregation occurred at loading above 11 wt.% PBA. UV–vis light transmittance showed that PLA/PBA blends with a high transparency, and the transmittance decreased with the amount of PBA.

1. Introduction

Today, pollution caused by the enormously large amount of application and improper disposal of petroleum based plastic materials is a serious and critical problem all over the world. Biopolymers are expected to be an alternative for conventional plastics due to environmental and economic concerns associated with waste disposal and intensifying expenses of petroleum production. Poly(lactic acid) (PLA), a biodegradable polymer, possesses many physical characteristics that make it suitable for replacing petroleum-based polymers. Among its advantages are high strength, biocompatibility, thermoplastic fabricability, good crease-retention, grease and oil resistance and excellent aroma barrier [1–4]. Therefore, PLA represents a good candidate to produce biodegradable packaging materials for food and consumer goods (transparent bottles, meat trays, bags, etc.) with the polymer typically discarded after use [5]. These applications benefit from its ability to decompose relatively quickly in landfill or compost environments. Unfortunately, with the glass-transition temperature ranging from 55 to 65 °C, PLA is too stiff and brittle for room-temperature applications, which greatly limited its widespread implementation. For example, extruded film may be too brittle for handling in continuous moving equipment without breakage.

Many approaches, such as toughening with rigid particle [6], adding plasticizers [2,7–9] and blending with flexible polymer [4,10–13], have been developed to improve its ductile properties. PLA toughened by inorganic particles can reduce the cost and improve the heat distortion temperature, but the essential transparent characteristic, which is important for food packaging and other consumer products, is generally sacrifices [1]. Addition of plasticizer can effectively decrease the stiffness of PLA and keep its transparency generally, but the low molecular weight
plasticizer has a tendency to migrate and decrease the
glass transition temperature ($T_g$) significantly. For exam-
ple, PLA blend containing 15 wt.% acetyl triethyl citrate
(ATC) resulted in a material with a $T_g$ well below room
temperature [14]. Consequently, the ductile properties
deteriorate during storage, and the use temperature is fur-
ther limited.

Alternative approaches, more economic and practical,
to improve ductile properties is blending PLA with other
flexible polymers that are known to undergo plastic flow
in tension rather than exhibit crazing. The most widely
preferred route, however, is the incorporation of a substan-
tial volume fraction (typically 10%) of an elastomeric com-
ponent in the form of a block or graft copolymer [15]. PLA
has been blended with a variety of biodegradable and
biocompatible rubbery polymers such as poly(butylene
adipate-co-terephthalate) [16], poly(ether-urethane) elast-
tomer, [11,17,18] poly(ethylene glycol), polyhydroxylalk-
avoate [19], and poly(butylene succinate),[20] These
rubbery polymers are relatively expensive, which increase
costs of the resulting PLA blends. To reduce the cost
and expand its commercial applications, improving the
toughness of PLA by direct mechanical blending with
inexpensive non-degradable polymers such as poly(ethyl-
ene oxide), poly(vinyl acetate), polyisoprene, elastomeric
ethylene-butyl acrylate-glycidyl methacrylate terpolymer
(EBA-GMA) [12,21], and ethylene/acrylate copolymer
(EAC)[22] has also been explored. In many applications
especially in packaging, the transparency of the material
is necessary. However, to the best of our knowledge, there
are no published results on transparent and ductile PLA
blend, probably due to their poor transparency compared
to the pristine polymer. Blending polymers with different
refractive indexes could sacrifice the transparency of the
resulted material. So, the majority of these PLA blends
studied by other researchers are opaque due to the differ-
ence of the refractive index between components.

Therefore, it is very important to find a cost-effective
toughening agent that can effectively improves the tough-
ness of PLA at low concentrations to maintain its bio-
dergradability, and maintains the essential transparency
of PLA. Poly(butyl acrylate) (PBA) is a very ductile (~2000%
elongation at break), sticky, colorless and transparent rub-
bery material. The refractive index of the PBA chosen in
this study is 1.474, very close to that of the PLA matrix
(1.45) [23]. In view of their complementary properties,
bending PLA with PBA is a natural choice to improve prop-
erties including ductility of PLA without compromising its
transparency.

The objective of the present study was to explore the
possibility of toughening PLA by PBA and to obtain trans-
parent blend with improved flexibility for potential use
in packaging material. The PBA used was synthesized
through a free radical polymerization reaction. The misci-
bility, phase morphology, mechanical properties and rheo-
logical properties of the PLA/PBA blends were evaluated.
The tensile toughness of the blends was probed, and a
direct correlation between the morphology and toughness
was revealed.

2. Materials and methods

2.1. Materials

Butyl acrylate (BA, 128 g/mol) and 2, 2’-Azoisobu-
tyrionitrite (AIBN) were purchased from Aladdin-Reagent
Chemical Factory. Ethanol, acetone and calcium hydride
(CaH₂) used in this study were supplied by Yingda Sparse-
ness and Noble Reagent chemical factory (Tianjin, China).
Polylactide (PLA) resin (2002D) was purchased from
Nature-works Company.

2.2. Synthesis of poly(butyl acrylate) (PBA)

2,2’-Azoisobutyronitrile (AIBN) was recrystallized
twice from ethanol before use. BA was dried over CaH₂
and distilled under vacuum prior to use. BA (1 mol,
128 g) and AIBN (1.28 g) were dissolved in 100 mL of eth-
anol, and then added in a dry three-necked glass flask,
equipped with a stirrer and heating bath. Thereafter,
the mixture was stirred; the reaction temperature was in-
creased to 80 °C at 1 °C/min under N₂ atmosphere. After
3 h reaction under stirring, the mixture was cooled to room
temperature and poured into 1 L deionized water and stir-
ed; then the product was precipitated. After filtration, it
was washed by 10% alcohol for 5 times to remove the unre-
acted reagents. The product was dried under vacuum at
80 °C for 3 days.

2.3. Preparation of PLA blends

PLA was dried under vacuum at 40 °C for 24 h to re-
move water before blending. PLA/PBA blends containing
different PBA contents (0, 5, 8, 11 and 15 wt.%) were pre-
pared in the mixing chamber of a Haake Rheometer XSS-
300 at 175 °C, and a mixing rotation of 50 rpm for 7 min.
In the following part of this paper, the blends are denoted
as BA followed by the mass fraction of the PBA (wt.%). For
example, BA-5 indicated PLA/PBA blend with 5 wt.% PBA.
The blends were preheated at 175 °C for 3 min and then
hot pressed into 1 mm thickness sheets for 2 min using a
compression molding machine.

2.4. Characterization

Thermogravimetric analysis (TGA) was performed with
a WRT-2P thermogravimetric analyzer from ambient tem-
perature to 600 °C at a heating rate of 10 °C/min, under a
steady flow of nitrogen of 100 mL/min.

The light transmittance of the neat PLA and PLA/PBA
sheets were measured with a UV–vis spectrophotometer
instrument (721, Shanghai Jinhua Group Co., Ltd., China)
in the range of 500–900 nm at room temperature. The
sheets used for characterization were prepared by melting
and then quick quenching into a thickness of 0.5 ±
0.02 mm.

Thermal analysis was carried out on a differential scan-
ing calorimeter (DSC) Instruments (DSC-204F1, Netzsch,
Germany) under nitrogen. Both temperature and heat flow
were calibrated with indium. About 5 mg samples taken from the tensile samples were heated to 180 °C at a heating rate of 10 °C/min. The crystallinity of PLA ($\chi_c$) was estimated using the following equation:

$$\chi_c = \frac{\Delta H_m \times \Delta H_c}{w_f \times \Delta H^0_m} \times 100\%$$

Where $\Delta H_m$ and $\Delta H_c$ are the enthalpies of melting and cold crystallization during the heating, respectively; $\Delta H^0_m$ is the enthalpy for 100% crystalline PLA homopolymers (93.7 J/g), and $w_f$ is the weight fraction of PLA component in the blend.

The morphologies of blends were examined by a JSM-5900LV scanning electron microscopy (SEM, JEOL Ltd., Akishima, Japan) at an accelerating voltage of 20 kV. All the samples were fractured after immersion in liquid nitrogen for about 10 min. The fracture surface was then coated with a thin layer of gold prior to observation. Different zones of the specimens after tensile tests were also examined.

Mechanical properties of samples were measured with an Instron universal tester (model 4302), and the measurement was conducted at 25 °C with a cross-head speed of 20 mm/min in accordance with ISO527 (type 5). Five replicates were tested for each sample and the average value results were reported here.

Dynamic rheological properties of the PLA and PLA/PBA blends were assessed using a strain-controlled rheometer (AR 2000EX, TA Instruments, USA). Samples were tested using a parallel-plate geometry ($d = 25$ mm) operated at 190 °C. A dynamic frequency sweep test was performed to determine the rheological properties of the blends. The strain and frequency range used during testing were 5% and 80–0.01 Hz, respectively.

### 3. Results and discussion

#### 3.1. Characterization of PBA

The average molecular weights and polydispersity of the synthesized PBA were measured by gel permeation chromatography (GPC) on an Agilent 1100 series liquid chromatography equipped with a refractive index detector (RID A). Tetrahydrofuran was used as the mobile phase at a flow rate of 1.0 ml/min, and the column calibration was performed with polystyrene standards. The result shows that the average weight and polydispersity of poly(butyl acrylate) are 13.16 kg/mol and 4.202, respectively.

To evaluate the thermostability of PBA in the blending process with PLA, the thermogravimetric analysis of PLA and PBA was performed (Fig. 1). The TG characteristic temperatures of PLA and PBA are included in Table 1. It is evident that the thermal degradation of virgin PLA and PBAT started at 358.3 and 348.8 °C, respectively, and the characteristic temperatures of $T_{0.1}$ is 373.8 and 409.5 °C as shown in Table 1. As shown in Fig. 1, the TGA curves of PBA sample gives a slower decomposition velocity compared to that of PLA. Clearly, the thermostability of PBA matches up to PLA during processing.

#### 3.2. Rheological properties

Dynamic melt rheological properties of neat PLA and PLA/PBA blends are measured to elucidate the interaction between both phases and the melt processibility of the blends. The complex viscosities, $\eta'$, of pure PLA and blends as a function of frequency, $\omega$, are shown in Fig. 2. It can be seen that plain PLA exhibits typical Newtonian behavior in the low-frequency region and slight shear thinning from about 10 rad/s, which was a characteristic for linear polymers [25]. Compared with PLA melt, the complex viscosities of PLA/PBA melts show a shear-thinning tendency at
lower frequencies and the tendency became stronger with PBA content. The dynamic complex viscosities of blends are substantially lower than that of neat PLA and decrease with PBA content (<15 wt.%), which is a typical plasticizing effect. It indicates that the PBA in the blends acts as plasticizer and causes the increase of the free volume and the chains’ mobility of PLA. [26] The decreased complex viscosity of the blend means that the processability of PLA is improved apparently. It was intriguing that the complex viscosity of PLA/PBA blend with 15 wt.% PBA increased compared with that of the blend containing 11 wt.% PBA. Such an increase of the complex viscosity may be caused by strong physical interaction between ester groups of PBA and PLA. That is, the physical bonding through ester groups may lead to the formation of pseudostructures, [25] which can withstand the shear force [27].

The miscibility of polymer blends could be analyzed by Cole–Cole plot, representing by the relationship between the real (\(g_0\)) and the imaginary (\(g_00\)) parts of complex viscosity [28]. A smooth, semicircular shape of the plotted curves would suggest good compatibility and phase homogeneity in the melt, and any deviation from this shape shows a nonhomogeneous dispersion and phase segregation due to immiscibility [29]. The Cole–Cole plot for PLA blend at 190 °C is presented in Fig. 3. It indicates that dispersed PBA particles in the blends with 5 and 8 wt.% PBA were finely distributed (miscible), as can be evidenced from the smooth semicircular shape of the plots. It is very interesting that, above 8 wt.%, a clear deviation from the semicircular curve is observed. It means that dispersed PBA particles in the blends are unevenly distributed. The blend PLLA/PBA is compatible but not highly miscible. The probability of the coalescence of PBA domains increases with PBA content. Thus, the driving force toward demixing is strong when compared to the shear forces that lead to dispersion [30]. Consequently, the Cole–Cole plot shows a nonhomogeneous dispersion in high PBA content (>8%) of the blend.

The variation of the storage modulus, \(G'\), and loss modulus, \(G''\), with small-amplitude oscillatory frequency for neat PLA and the blends is given in Fig. 4. A homopolymer with narrow molecular weight distribution usually shows a characteristic terminal behavior of \(G'(\omega) \propto \omega^{1.58}\) [31]. Pure PLA deviates from the terminal behavior markedly (\(G'(\omega) \propto \omega^{1.58}\)). The values are in consistency with the results reported in literatures [16,32]. The \(G'\) of PLA/PBA blends slightly deviates from the terminal behavior, from \(G'(\omega) \propto \omega^{1.51}\) for the blend with 5 wt.% PBA to \(G'(\omega) \propto \omega^{1.2}\) for the blend with 15% PBA. Molecular weight distribution strongly affects the shape of the terminal region. Chains of different sizes relax to equilibrium at different times, which "smears out" the typical relaxation behavior of a monosized polymer melt. The relatively broad molecular weight distribution of PBA (\(PI = 4.202\)) likely accounts for the different relaxation behavior.[33] On the other hand, the partially miscible characteris of blends might be the other reason for the deviation.[34] The incorporation of PBA affected the storage moduli and loss moduli of the melts at all frequencies; they decreased with the increase of PBA content as compared with pure PLA, except that the \(G'\) of BA-15 increased at low frequencies. For the blend with 15 wt.% PBA, the lower slope values and higher absolute values of dynamic modulus indicate the formation of entanglement structures in PLA/PBA melts [16]. It is known that molecular chain PBA is more flexible than that of PLA and is easier to entangle. The entanglement density was higher than that of PLA, leading to high reversible elastic deformation (\(G'\)) of the BA-15 melts [16].
3.3. Thermal properties

Neat PLA and the blends exhibit very similar thermograms, all showing cold crystallization of PLA and subsequent melting of PLA crystals. DSC results of PLA and blends are shown in Table 2, including the degree of crystallinity. Because the crystalline state of the PLA molded samples finally influences the mechanical properties of the blends, only the DSC data from the first heating scan are presented.

From Table 2, the difference in melting temperature ($T_m$) between neat PLA and PLA in the blends is not significant and seems to be independent of loading of PBA. The glass transition temperature ($T_g$) slightly decreases with the increasing of PBA. It also indicates that PBA is partially miscible with PLA [35], which well accords with the SEM observation. However, the cold crystallization peak temperature ($T_{cc}$) and characteristic temperature $\Delta T = T_{cc} - T_g$ of PLA in blends is slightly decreased with the increase of PBA content. Such decrease in $T_g$ and enhanced cold crystallization process are commonly observed for plasticized PLA systems and are due to the increased segmental mobility of the PLA chains by plasticization [36,37]. The decrease of characteristic temperature ($\Delta T$) suggests that the blend shows higher kinetic crystallizability and crystallization rate than pure PLA [38]. As shown in Table 2, the crystallinity of the PLA matrix increases with increasing content of PBA except for BA–15 sample. It is well known that for polymer blends containing a semi-crystalline component, the variations in the values of $\chi_c$ are usually due to the interactions between components. In fact, the interface of the phase-separated domains may provide favorable nucleation sites for crystallization and, therefore, the crystallization rate of PLA promotes by a lower nucleation barrier than that of pure PLA melt.[30] Therefore, the enhanced crystallization rate of PLA is resulted from the increase in the nucleation rate.

3.4. Morphology

Since the mechanical properties of multiphase polymer blends depend largely on the phase morphologies, SEM was employed to identify the phase structure of the binary blends. Fig. 5 shows cryo-fracture surface SEM micrographs of various PLA-based blends. As observed from Fig. 5, the round particles indicated the PBA phases distributed within the PLA matrix. As shown in Fig. 5 (a), the oval particles were well dispersed in PLA matrix for the blend containing 5 wt.% PBA. With increasing content of PBA, the amount of the big rubber particles increases. It can be seen that the interface between PBA and PLA phases is indistinct (Fig. 5). This indicates that in the present blends a relatively strong interaction between PBA and PLA matrix exists. The interaction is thought to be a hydrogen bond among polar groups like –C=O of PBA and PLA [2,4].

![Fig. 5. Cryo-fractured SEM images of blends: (a) BA-5, (b) BA-8, (c) BA-11 and (d) BA-15.](image-url)
3.5. Mechanical properties and toughening

The stress–strain curves of neat PLA and the blends are shown in Fig. 6, and the details of the tensile properties are given in Table 3. From Table 3, it can be found that the fracture behavior of the specimens in the tensile tests changes from brittleness of neat PLA to ductile fracture of binary blends. It is also demonstrated in the stress–strain curves as shown in Fig. 6. Neat PLA deforms in brittle fashion and is very rigid and brittle. On the other hand, the binary blends show an initial strain softening after yielding and then undergo considerable cold drawing. The stress–strain curve after the yield point shows a combination of strain softening and cold drawing. In this region, there is competition between the orientation of PLA chains and crack formation. Hence, there is a drop in stress with increasing strain. After about 10–15% of strain, cold drawing dominates at a constant stress. This suggests that large energy dissipation occurs owing to the presence of PBA in the binary systems.

The elongation at break of PLA blends is improved dramatically with the increase of PBA content. The elongation at break of the blends increases from 4% for neat PLA to 31% for the blend containing 5 wt.% PBA, and reaches the maximum of 174.52% for the blend containing 15 wt.% PBA. The tensile toughness also increases with PBA content dramatically from 2.13 MJ/m³ for neat PLA to 47.02 MJ/m³ for the PLA/PBA blend with 15 wt.% PBA. This is quite an unusual result, as PLA/PBA blend maintains a quite high tensile modulus value of 1.33 GPa even with 15 wt.% PBA. The tensile strength of the binary blends decrease slowly with the continuous increase of PBA content (Table 3). The tensile strength is still 41.01 MPa for the blend containing 15 wt.% rubber, which is still greater than that of general petroleum based package polymer, such as PE and PP. The result is very significant in obtaining a bio-based transparent material with remarkable stiffness-toughness balance.

To elucidate the reason why PBA toughens PLA, the morphologies of the fracture surface and the skin of the stretched samples were observed by SEM, and the micrographs of the samples are shown in Fig. 7. The presence of the rubber domains alters the deformation mechanism. As shown in Fig. 7(a–d), there are many voids in the PLA matrix that occurred in uniaxial extension. The micrographs of fractured surface of the blend show a ductile fracture which is evident from the presence of more and longer fibrils pulled out during the test. For the blend with 5 wt.% PBA, it can be seen that a few fibrils are formed during crazing (Fig. 7e). For the blend with PBA more than 5 wt.%, the fracture surfaces show more features because of larger plastic deformation caused by more crazes with increasing rubber contents. On the fracture surface of blends numerous fibrils are drawn out of the polymer, with cavities residing among them, as shown in Fig. 7(e–h). The SEM observation is well consistent with the results of mechanical properties.

Plastic deformation in rubber-toughened glassy polymers can occur through several mechanisms including crazing, cavitation of the rubber phase, and shear yielding. Inelastic deformation occurs via the phenomenon of shear yielding, multiple crazing, and cavitation in the softer dispersed phase. Dispersed rubber phase can provide control over nucleation and growth of crazes and increase craze plasticity in glassy polymers leading to the decrease in brittleness. The true stress acting on the craze fibrils is inversely proportional to the volume fraction of the craze [39]. So increasing the volume fraction of the craze can reduce the true stress on an individual craze. Thus, if the small size of the rubber domains in the PLA matrix causes the critical stress for cavitation to be greater than that of an alternative deformation mechanism (e.g., matrix crazing), the matrix phase may yield prior to cavitation. [40] Consequently, the phenomenon of multiple crazing was likely the possible energy dissipation mechanism.

3.6. Transparency of PLA blends

An effective way to judge the miscibility is the optical clarity of the blend; immiscible blends usually are cloudy
or milk white in appearance because of the different refractive indices of the components. In Fig. 8(a–d) show the photos of PLA and PLA blends. PLA sheet is completely transparent and the blends maintain high transparency. However, the blends containing PBA show a reduction of optical clarity compared to pure PLA with increasing rubber content. In spite of this, the blends still show very high transparency even at high loading of PBA, which meets the requirements of transparent package material.

To further study the effect of the PBA rubber on the transparency of the binary, the visible light transmittance of PLA and PLA/PBA were measured by a UV–vis spectrophotometer instrument (Fig. 9). It is obvious that the transmittance decreases with increasing content of PBA, which is in consistent with the optical observation. But the transmittance of the blends is still above 75% in the range of 500–900 nm, also indicating that the blends are miscible or semi-miscible [41].
4. Conclusions

Poly(butyl acrylate) rubber was successfully prepared by the free radical polymerization of butyl acrylate in the presence of 2,2’-Azisobu-tyronitrile (AIBN); and the average molecular weight, polydispersity and thermal stability were evaluated. Then, PLA/PBA binary blends were prepared by melt blending to investigate the effects of rubber loadings on the optical transparency, thermal properties, mechanical properties, phase morphology and dynamical rheological properties of the blends. Dynamic rheology, SEM and DSC results show that the PLA was semi-miscible with PBA. Rheological results reveal the complex viscosity and melt elasticity of the blends decrease with the concentration of PBA. In addition to toughening PLA, PBA increases the processability of PLA by acting as a plasticizer. Phase segregation occurred at PBA loading above 11 wt.%. DSC results showed the addition of PBA accelerates the crystallization rate of PLA and the crystallinity increased slowly with the increase of PBA content (>15 wt.%). The mechanical test shows that the material changed from brittle (PLA) to ductile failure with the addition of PBA; the elongation at break and toughness increase with increasing loading of PBA. The tensile toughness of the PLA blends is greatly improved without severe loss in tensile strength and modulus. SEM micrographs reveal that a debonding-initiated shear yielding mechanism is involved in the toughening of the blend. Visible light transmittance show that PLA/PBA blends is transparency, and visible light transmittance was slightly decreased with the amount of PBA. Thus, for transparent packaging application, the toughness of PLA is improved greatly by blending with PBA and the transparency of the blends is maintained.

Acknowledgment

The authors are grateful to the National Natural Science Foundation of China (Grant No. 51033003) and the Fundamental Research Funds for the Central Universities (Grant No. 2011SCU04A03) for the financial support.

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