ISSN 1560-0904, Polymer Science, Series B, 2017, Vol. 59, No. 4, pp. 437–442. © Pleiades Publishing, Ltd., 2017.

CHEMICAL TRANSFORMATIONS

Reactive Blending Toughened PLA by In Situ Formation of Polyurethane Crosslinked Elastomer[1]

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Received September 4, 2016;
Revised Manuscript Received March 1, 2017

Abstract—Polylactide (PLA)/polyurethane (PU) composites were prepared by reactive blending method with in-situ formation of PU particles via the reaction between polyester polyol (PPG) and toluene-2,4-diisocyanate (TDI). The interfacial compatibility and adhesion between the PLA and PU phases were greatly improved by the reaction of the terminal hydroxyl groups of PLA and N=C=O groups of TDI forming graft copolymer, as confirmed by FTIR spectroscopy. The elongation at break and notch impact strength of PLA/PU composites increased considerably with increasing PU content, and the tensile strength of PLA/PU composites decreased slightly compared with that of pure PLA. The excellent interfacial adhesion, dispersed PU elastomeric particles acting as stress concentration areas and the triggering of large matrix shearing yielding and many fibrils by internal cavitation were the main mechanical toughening mechanisms.

DOI: 10.1134/S156009041704011X

INTRODUCTION

Polylactide (PLA) has attracted considerable attention in both scientific research and industrial applications due to its excellent biocompatibility, biodegradability and mechanical properties. It has been widely used in many applications such as biomedical devices, packaging and consumer goods [1]. However, PLA has inherent shortcoming that limit its widespread application: brittleness with short elongation at break and low impact strength [2]. Therefore, many strategies have been adopted to improve the toughness of PLA, with polymer blending shown to be a more cost-effective approach for achieving this goal than plasticization and copolymerization.

Kowalczuk [3] represented a new perspective application materials of (bio)degradable poly(ester-urethane)s containing PLA. The (bio)degradable poly(ester-urethane)s containing PLA and poly[(1,4-butylene terephthalate)-*co*-(1,4-butylene adipate)] (BTA) segments in the main chain were prepared and butanediol (BD) used as a polymer chain extender. The poly(ester-urethane)s that were examined had a single glass transition temperature T_g, which pointed to a one-phase system. And various polymers, such as poly(butylene succinate) (PBS) [4], poly(ε-caprolactone) [5], poly(butylene adipate-*co*-teraphthalate) [6], and thermoplastic polyolefin elastomer [7], have been used to blend with PLA in order to improve its toughness. Unfortunately, high performance materials cannot be prepared in this approach due to the poor compatibility and interfacial adhesion in the blend systems. Therefore, suitable compatibilizers must be added in order to improve the interfacial compatibility and further enhance the tensile strength and elongation at break of PLA blends. However, to data, additions of compatibilizers have not let to sufficient improvement in impact toughness while greatly decreasing the tensile strength. Bartczak [8] reported that blending of PLA with biodegradable atactic poly([R,S]-3-hydroxy butyrate) (a-PHB) leads to significant improvement of drawability and impact strength. The thin-film tensile impact resistance increases from about 50 kJ/m^2 in neat PLA to nearly 120 kJ/m^2.

Reactive blending [9] is a more effective approach for the preparation of high performance polymers than simple blending due to the improved compatibility obtained by in-situ reactive blending. Mohanty [10] fabricated multiphase blends of PLA, ethylene-methyl acrylate-glydidyl methacrylate (EMA-GMA) terpolymer, and a series of renewable poly(ether-*b*-amide) elastomeric copolymers (PEBA), and investigated the

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phase morphology and performance of supertoughened renewable PLA reactive multiphase blends system. The synergistic effect of good interfacial adhesion and interfacial cavitations triggering high shear yielding of matrix was the main toughening mechanism. Zeng [11, 12] reported a novel method for toughening PLA by in situ formation of a crosslinked polyurethane. Super-tough polylactide/crosslinked polyurethane binary blends were prepared by reactive blending of PLA with poly(ethylene glycol) (PEG) and polymeric methylene diphenylene diisocyanate. Super-tough poly(L-lactide)/crosslinked polyurethane blends were also prepared by reactive blending of PLA with PEG, glycerol, and methylenendiphenyl diisocyanate. The morphology of blends plays an important role in notched impact strength and can be controlled by adjusting the content of glycerol. Binary and ternary composites were prepared in which the in-situ formed crosslinking polyurethane was dispersed in the PLA matrix, thus enabling the tailoring of the physical properties. The in situ crosslinked formation of polyurethane to toughen PLA is a novel and effective method that has been investigated in only a few studies.

In this paper, PLA/polyurethane (PU) composites with high toughness were prepared via in-situ reactive blending of PLA with polyester polyol (PPG) and toluene-2,4-diisocyanate (TDI). The in-situ reaction of PPG and TDI formed the polyurethane particles that were dispersed in the PLA matrix. The morphologies and interfacial compatibility of PLA/PU composites were investigated and it was found that the mechanical properties of these composites can be adjusted by changing the PU content.

EXPERIMENTAL

Material and Methods

PLA (4032D) was purchased from Natureworks LLC, and dried under vacuum at 50°C for 12 h prior to use. The industrial grade PPG and TDI were supplied by Huntsman Chemical R and D Center (Shanghai China) and were used without any further purification and processing. The weight ratio of PPG and TDI is 10 : 4 and corresponding to the molar ratio of hydroxyl group in PPG and in isocyanate group TDI is 1 : 1.

PLA/PU Composites Preparation

All PLA composite samples were prepared by reactive blending in a HAAKE rheometer (HAAKE 90, Germany). First, PLA and PPG were premixed in an internal mixer at 170°C and the rotor speed of 60 rpm for 5 min, and then TDI was added into the PLA/PPG blends for 10min. The PLA/PU composites were labeled as PLA/PU-x, where x represents the polyurethane content. Pure PLA was prepared under the same experimental conditions. All samples were hot-pressed into 1 and 4 mm thick samples under 10 MPa and 180°C for 5 min for tensile and impact tests, respectively.

Fourier Transform Infrared Spectroscopy (FTIR)

To prove the occurrence of the reaction between PLA and TDI, a FTIR spectrometer (Iso10, Nicolet USA) with a resolution of 4 cm^{-1} and a scanning number of 32 was used to obtain infrared spectra. The sample films of PLA/PU composites were prepared by using the hot-press method. And the PLA sample was extracted from the PLA/PU composites (91/9) by Soxhlet extraction, and the extracted PLA was also characterized to verify the reaction between PLA macromolecular hydroxyl group(OH) and N=C=O of TDI, and formation of PU-g-PLA or PPG-g-PLA graft copolymers.

Scanning Electron Microscopy (SEM)

The morphologies of cryo-fractured and impact fractured surface were examined by SEM (JSM-6390LV, JEOR Japan) at an accelerating voltage of 30 kV. The 4 mm thick hot-pressed samples were cryofractured in liquid nitrogen.

Mechanical Properties Measurements

The tensile test was performed according to the international standards ISO 527-2 using a CMT-4204 Electrical Tensile Instrument (Shenzhen SANS, China) with the speed of 5 mm/min.

The impact-test specimens were notched on one side with a depth of around 0.8 mm. The notched impact test was performed according to international standards ISO 179-1 using a mechanical impact tester (SJJ-50, Chengde Jinjian, China). The average values for at least five specimens were reported for all tests.

RESULTS AND DISCUSSION

Structure Characterization of PLA/PU Composites and In Situ Formed Graft Copolymers

FTIR spectroscopy was used to prove the in situ formation of polyurethane and the chemical reaction between the terminal hydroxyl group of PLA and N=C=O of isocyanates [11]. New absorption peaks that were absent in the PLA FTIR spectra appeared at approximately 1593, 1536, 1500, 1414 and 819 cm^{-1} for all blends (Fig. 1). These peaks were ascribed to the characteristic peaks of the conjugated double bonds of the benzene ring (for peaks in the 1500–1600 cm^{-1} range) and urethane linkage, and the C–H bonds of the benzene ring, respectively. While the characteristic isocyanate group at around 2270 cm^{-1} was not detected, the new absorption peak at around 1414 cm^{-1} was ascribed to the C–N vibration peak. All of these results suggested that diisocyanate was completely

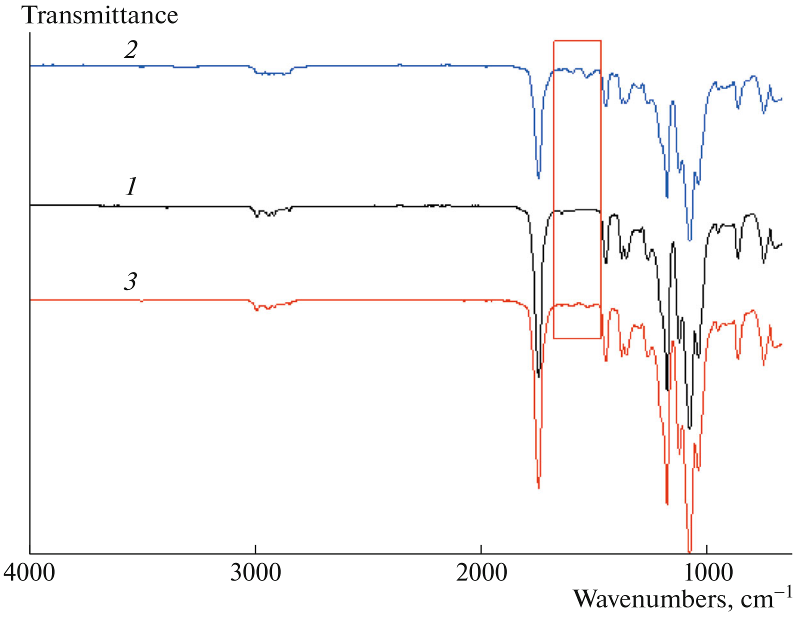

Fig. 1. (Color online) FTIR spectra of (*1*) PLA, (*2*) PLA/PU composites and (*3*) extracted PLA.

consumed during the molten blending process. The PLA macromolecular hydroxyl group (OH) reacted with N=C=O of TDI to graft the PLA chain segment onto the surface of PU or some non-crosslinked PPG component to form PU-*g*-PLA or PPG-*g*-PLA graft copolymers. The formed graft copolymers are located at the interface between the PLA matrix and dispersed PU phase and thus improved their interfacial adhesion and compatibility.

Cryo-Fractured Surface Phase Morphologies

The cryogenically fractured morphology of PLA was that of one uniform phase with a smooth surface (not shown here). Figure 2 shows the cryogenically fractured morphology of PLA/PU blends. Examination of the images shows that all PLA/PU blends exhibit rough surfaces and phase separated morphologies with PU particles dispersed in the PLA matrix. Some voids due to the pullout of dispersed PU particles were also observed, which is agreement with the results obtained in other toughened PLA reactive multiphase blends [10, 11]. And partially miscible and phase-separation phenomenon leading to excellent impact toughness was also accordance with PLA/poly([R,S]-3-hydroxy butyrate) (a-PHB) composites reported by Bartczak [8].

As PU content increased, the gap between the PLA and PU phases decreased and the phase boundary became more obscure with increasing the content of PU; meanwhile, the dimension of dispersed PU gradually increased and the shape of PU particles was more irregular, suggesting that there was a good interfacial compatibility. The reaction probability of TDI with PLA and the content of in-situ formed graft copolymers increases with increasing the content of PU components. The formed graft copolymers increases with increasing content of PU components, and the generated graft copolymers self-assemble into a subinclusion microstructure in the PLA phase, when the PU component content increased to 15 wt %, indicating excellent compatibility between PLA and PU in the blends. The appearance of clusters with interlinked PU particles suggested the improved continuity of the PU phase, implying the formation of a quasi-cocontinuous phase-separation morphology.

Impact Fractured Surface Morphologies and Toughening Mechanisms

The morphologies for the impact fractured surfaces of PLA/PU composites are shown in Fig. 3. The fracture surface of neat PLA was smooth with few slightly stressed whitening areas, indicating typical brittle fractured corresponding to the impact strength (not shown). The fractured surfaces of PLA/PU composites showed much rougher surfaces with many stress whitening zones and fibrils, indicating the gradual transition from brittle to tough impact fracture. The fractured surfaces of PLA/PU composites exhibited a large shear zone and many fibrils with increasing PU content, suggesting larger plastic deformation and the formation of large failure areas. In case of PLA/PU composites, fibril threads were noticed, which served as a clear evidence for ductile fracture [10]. Compared to the neat PLA samples, the PLA/PU composites showed much tougher morphologies, and denser plastic deformation domains and fibrils, thus improving

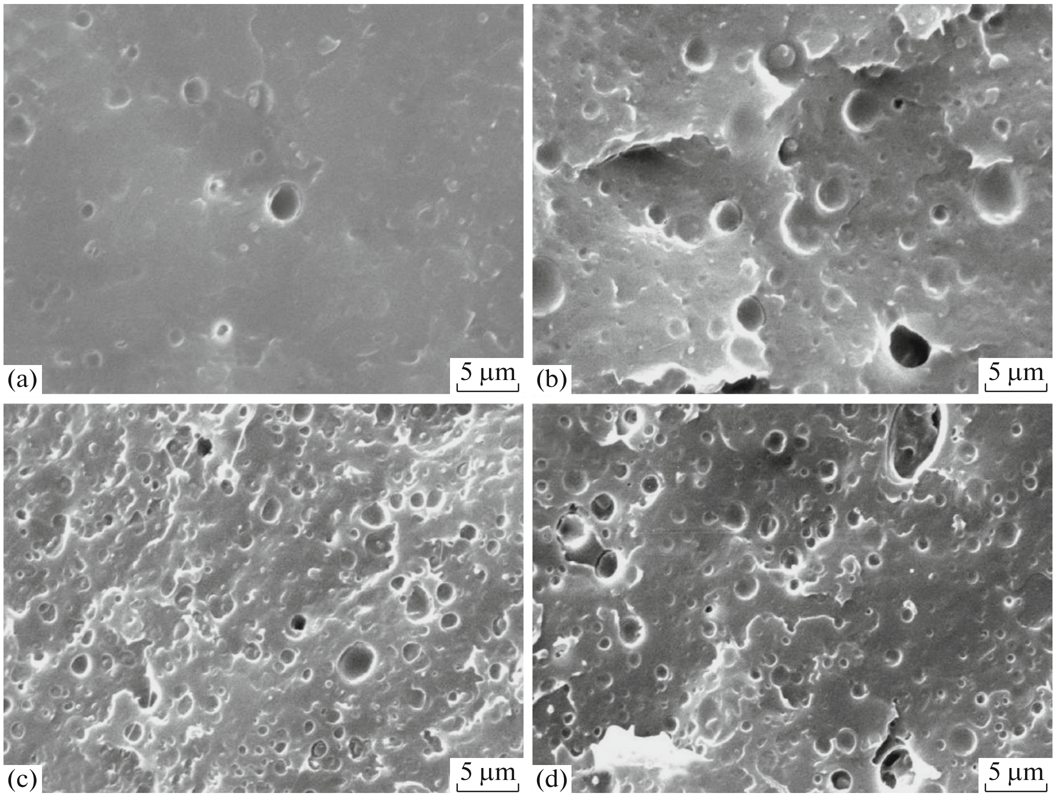

Fig. 2. SEM micrographs for the cryo-fractured surface of PLA/PU blends: (a) PLA-PU-6, (b) PLA-PU-12, (c) PLA-PU-15, and (d) PLA-PU-18.

the impact strength through higher energy absorption. The in situ formed crosslinking PU particles were an elastic polymer, and acted as stress concentration areas in the PLA matrix to induce high shear yielding and many fibrils, that could absorb large impact energies.

The PLA/PU composites exhibited ductile properties with a large area of stress whitening through cold drawing continuously and as observed in impact tests, resulting in considerable energy dissipation. To study the toughening mechanism, the sides of impact fracture samples were cryo-fractured longitudinally for SEM observation. Figure 4 shows the SEM micrographs of the side of impact fracture samples. Cavitations could be clearly observed with randomly arrayed cavities in the wider areas. These random cavities become well-oriented with elongated shapes in the impact process, and the PLA matrix around the cavities oriented to some extent due to the matrix shear yielding, indicating excellent ductility of blends during impacting. The elongated voids and oriented cavities with hollow cylinder-like shapes and elliptic-shaped of micro scale revealed the toughening mechanism of microvoids triggering the shear yielding. Some studies have suggested that internal cavitation only occurs when the interfacial adhesion is sufficiently strong [10, 13]. The interfacial adhesion between the PLA matrix and dispersed PU particles was greatly enhanced through interfacial compatibilization by in situ formed PU-*g*-PLA or PPG-*g*-PLA graft copolymers. The excellent interfacial adhesion, the dispersed PU elastomeric particles acting as stress concentration areas and triggering of large matrix shearing yielding and many fibrils by internal cavitation were the main mechanical toughening mechanisms.

The Tensile Strength, Elongation at Break and Impact Strength of PLA/PU Blends

The mechanical data for PLA, and PLA/PU composites were summarized in Fig. 5. Examination of the data shows that the tensile strength, elongation at break, and notch impact strength of PLA are 64.3 MPa, 6.5%, and 2.0 kJ/m^2, indicating brittle fracture behavior of PLA. The elongation at break and notch impact strength of PLA/PU composites increased considerably with increasing PU content, suggesting the transition from the rigid and brittle PLA to ductile PU-containing materials. The tensile strength of PLA/PU composites decreased continuously, which should be due to the increased plasticization with the increasing PU content. The PLA/PU-3, PLA/PU-6, PLA/PU-9, PLA/PU-12, PLA/PU-15, PLA/PU-18, PLA/PU-21 samples exhibited tensile

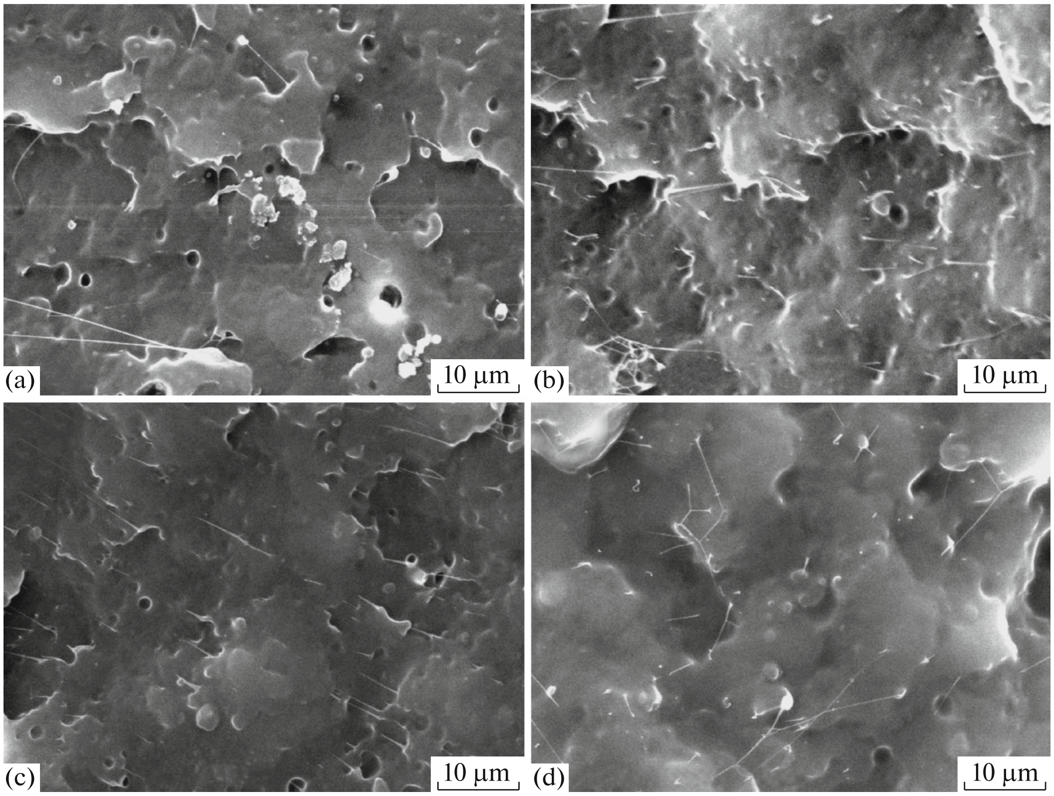

Fig. 3. SEM micrographs for impact fractured surface of PLA/PU: (a) PLA-PU-6, (b) PLA-PU-12, (c) PLA-PU-15, and (d) PLA-PU-18.

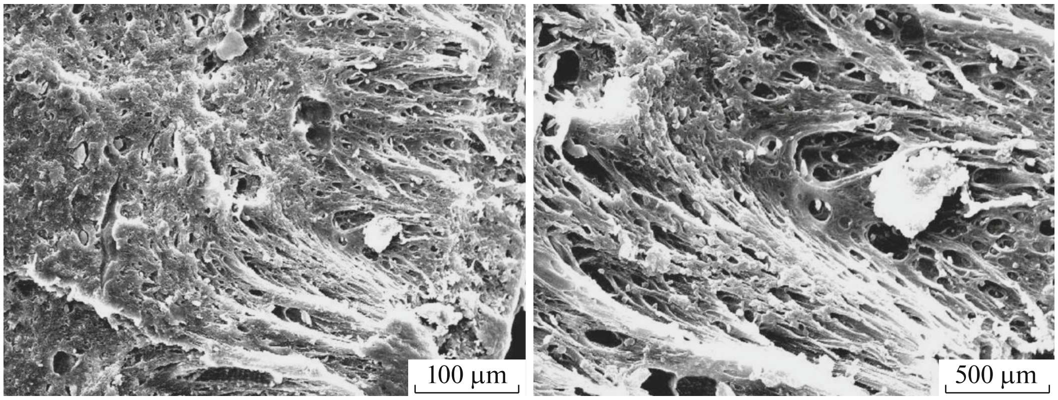

Fig. 4. SEM micrographs of the side of impact fracture surface of PLA/PU-12 composites.

strength of 61.7, 57.4, 55.8, 48.7, 42.0, 35.4, and 37.1 MPa, respectively. Compared with that of neat PLA (64.3 MPa), the tensile strength of PLA/PU composites were decreased by 4.0, 10.7, 13.1, 24.3, 34.7, 44.9, and 42.3%, respectively. At the same time, the value of elongation at break increased firstly and then decreased with PU content. The elongation at break of the PLA/PU composites were more than 90%, which were much higher than that of neat PLA, indicating a significant improve in tensile toughness by reactive blending with the in situ formed PU. The PLA/PU-9, PLA/PU-12, PLA/PU-15 and PLA/PU-18 samples exhibited elongation at break of 147.2, 175.2, 138.9, and 105.6%, respectively, approximately 22.7, 27, 21.4 and 16.2 times that of neat PLA (6.5%). PLA showed an impact strength of 2.0 kJ/m^2 indicating a brittle fracture during the impact test. The notch impact strength increased firstly and then decreased slightly with increasing PU content. The maximum impact strength was reached for PLA/PU-12

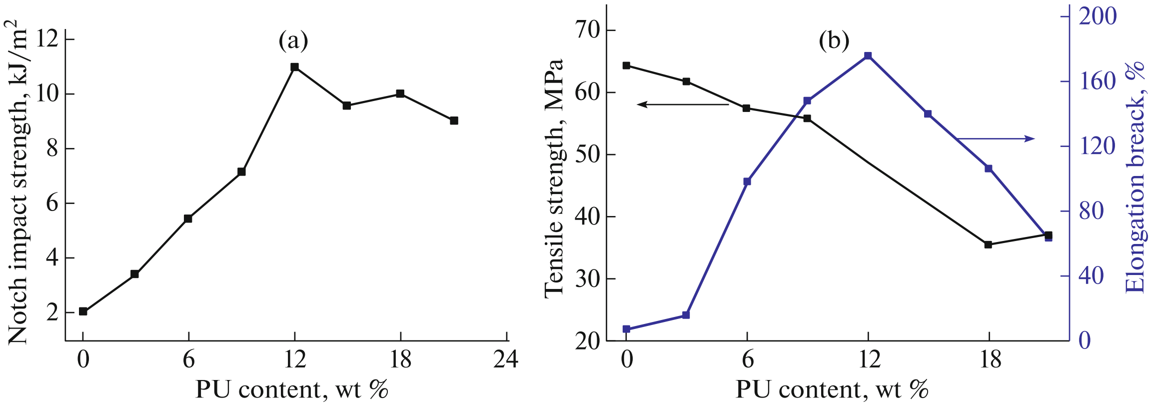

Fig. 5. (Color online) The effect of PU content on the mechanical properties: (a) impact strength, (b) tensile strength and elongation at break of PLA/PU blends.

with the value of 11.0 kJ/m^2, which was about times that of neat PLA, suggesting a considerable improvement in impact strength of PLA. Upon addition of 12 wt % PU, the elongation at break and notch impact strength increased to 175.2% and 11.0 kJ/m^2, respectively, about 27 and 5.5 times greater than the values for neat PLA. The tensile strength decreased only slightly to 48.7 MP due to the plasticization of PPG with increasing PU content. Thus, the in-situ formation of PU via the molten reactive blending offers a simple industrial method to obtain toughened PLA with a good overall balance of properties. The results should be due to the different interfacial interactions between the two phases and the different plasticization effects of PU content on the PLA matrix.

CONCLUSIONS

The PLA/PU composites were prepared by molten reactive blending method with the in-situ formed PU particles obtained via the reaction of PPG and TDI. The reaction between the terminal hydroxyl groups of PLA and N=C=O groups of TDI formed the graft copolymer, leading to improve interfacial compatibility. The interfacial adhesion between the PLA matrix and dispersed PU particles was greatly enhanced through interfacial compatibilization by in situ formed PU-*g*-PLA or PPG-*g*-PLA graft copolymers. The excellent interfacial adhesion, dispersed PU elastomeric particles acting as stress concentration areas and the triggering of large matrix shearing yielding and many fibrils by internal cavitation were the main mechanical toughening mechanisms. The composites have excellent overall properties and in particular show high elongation at break and excellent impact strength. Upon addition of 12 wt.% PU, the elongation at break and notch impact strength increased to 175.2% and 11.0 kJ/m^2, respectively, about 27 and 5.5 times greater than the corresponding values for neat PLA. The tensile strength decreased to 48.7 MPa only slightly.

AKNOWLEDGMENTS

The research was supported by the granted of National Natural Science Foundation of China (51273060, 21174108), Key Project of Hubei provincial Department of Education (D20111407), the Open Fund of Hubei Provincial Key Laboratory of Green Materials for Light Industry, and the National College Students' Innovative Entrepreneurial Training Program.

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