Effects of Radiation-Induced Crosslinking on Thermal and Mechanical Properties of Basalt Fiber-Reinforced Poly(lactic acid) Composites (Postprint)

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Abstract

Poly(lactic acid)/ basalt fiber (PLA/BF) composites were prepared by melt blending with a cross-linking agent, triallyl isocyanurate (TAIC). The thermal and mechanical properties of the composites were investigated through gel fraction, heat defection temperature (HDT), tensile tests and scanning electron microscopy (SEM). Under certain conditions, the HDT of composites was dramatically increased to 140°C after irradiation. Tensile properties were enhanced as well. Both these improvements were consistent with changes of the fracture morphology. Compatibilization and concomitant enhancement of the interfacial adhesive between the polymer matrix and the inorganic fiber were achieved as seen from SEM photos, as a result of the formation of co-crosslinking and grafting structures at the interface according to the determination of gelation extraction.

Full Text

Preamble

Effects of Radiation-Induced Crosslinking on Thermal and Mechanical Properties of Poly(lactic acid) Composites Reinforced by Basalt Fiber

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Abstract

Poly(lactic acid)/basalt fiber (PLA/BF) composites were prepared by melt blending with a cross-linking agent, triallyl isocyanurate (TAIC). The thermal and mechanical properties of the composites were investigated through gel fraction measurement, heat deflection temperature (HDT) testing, tensile tests, and scanning electron microscopy (SEM). Under certain conditions, the HDT of composites was dramatically increased to 140°C after irradiation, and tensile properties were enhanced as well. Both improvements were consistent with changes in fracture morphology. Compatibilization and concomitant enhancement of interfacial adhesion between the polymer matrix and the inorganic fiber were achieved, as seen from SEM micrographs, resulting from the formation of co-crosslinking and grafting structures at the interface according to gelation extraction analysis.

Key words: Poly(lactic acid), Basalt fiber, Irradiation, Triallyl isocyanurate, HDT

Introduction

Polylactic acid (PLA) is a biodegradable polymer produced from renewable plant resources. It is a linear thermoplastic aliphatic polyester with a glass transition temperature of 60°C and a melting point of 175°C, showing outstanding biodegradability, biocompatibility, and processing performance. However, due to obvious drawbacks in heat resistance and impact toughness, applications of PLA have been limited to medical fields such as surgical sutures and drug release carriers.

In recent years, there has been a growing tendency to use PLA as a general polymeric material, driven by increasing feedstock prices for traditional petroleum-derived polymers and reductions in commercial-grade PLA prices. Consequently, numerous studies worldwide have focused on PLA modification through various approaches and techniques. As is well known, fiber reinforcement is usually a powerful method to improve both the mechanical and thermal properties of polymers. The reinforcement effects of bamboo fiber, sugar beet pulp, wood fiber, cellulose fibers, hemp fiber, and hydroxyapatite fibers on PLA properties have been investigated. However, there were differences among the final results due to variations in matrix resins, fiber types, and processing conditions. Some researchers found that the tensile strength of composites decreased with fiber content, while other studies reported that tensile strength first increased and then decreased with fiber content. Literature reports have indicated that adding fiber alone did not directly improve the heat deflection temperature of PLA, attributed to poor interface adhesion between the fibers and PLA matrix. When fiber content exceeded 15%, the HDT reached 107°C after annealing because the crystalline regions acted as physical cross-linking points.

As widely investigated, irradiation-induced crosslinking in polymers is a powerful modification method that has been applied to enhance the thermal properties of PLA. However, high-energy rays have rarely been employed in fiber-reinforced polymer composites (FRPC). In the present work, we used gamma-irradiation to improve the interfacial adhesion of basalt fiber-reinforced PLA composites. The crosslinking agent triallyl isocyanurate (TAIC) was added to the composites by melt-blending, which is the most available accelerating agent for PLA crosslinking. The mechanical properties, gelation fraction, thermal resistance, and fracture surface morphology were determined.

2.1 Materials

PLA (REVODE 101) was supplied by Haizheng Biological Materials Co. Ltd., China, with a density of 1.25 g/cm^3. BF (TEX 7-800) was obtained from Hengdian Group Shanghai Russia Gold Basalt Fiber Co., Ltd., China. TAIC was purchased from Laiyu Chemistry Co. Ltd., China. Chloroform (AR) and absolute alcohol were from Beijing Chemical Plant.

2.2 Sample Preparation and Irradiation

PLA and BF were dried in vacuum at 80°C for 8 h and in circulating air at 120°C for 4 h, respectively. Blending was carried out in a Banbury mixer (HAAKE, Germany) with a rotor speed of 50 rpm at 170°C. The total processing time was 6 min. The blending ratios of PLA/BF were 90/10, 80/20, and 70/30 by weight, and 1, 2, and 5 wt% (relative to the total weight of PLA and BF) of TAIC was added to each composite. The samples were then prepared by hot pressing with a flat vulcanizing machine (XLB-400$×$400, China) at 200°C.

The samples were sealed in polyethylene bags filled with nitrogen and irradiated at a dosage rate of 3.9 Gy/s in a ^{60}Co source at room temperature. The absorbed doses were 5, 10, 30, and 70 kGy.

2.3 Determination of Gel Fraction

The samples covered with nickel mesh were extracted with chloroform in a Soxhlet apparatus at 70°C for 72 h. After washing in alcohol, the extracted samples were dried to constant weight in circulating air at 120°C. The gel fraction was calculated by the formula:

$$G_0 = (W_1 / W_0) \times (1 / (1 - B)) \times 100\%$$

where G_0 is the gel fraction (wt%), W_0 and W_1 represent the dry weight of samples before and after extraction, and B is the fiber content in the composites.

2.4 Heat Deflection Temperature (HDT)

A computer-controlled Heat Deformation Vicat Temperature Testing Machine (WKW-300, China) was used to determine the heat deflection temperature. Samples with dimensions of 10 mm × 10 mm × 1.2 mm were fixed in a holder and heated from room temperature at a rate of 12°C/6 min in silicone oil medium under a constant load of 1000 g. The humidity was 45%. Measurements were recorded when the deformation reached 1 mm according to GB/T1633-2000.

2.5 Mechanical Properties

Tensile strength of various samples was tested with an Instron Universal Testing Instrument (INSTRON 1121, USA) at room temperature. The loading rate was 5 mm/min.

2.6 Scanning Electron Microscopy (SEM)

Specimens were cut from the fracture surface of tension samples and coated with a thin layer of gold, then examined with a Scanning Electron Microscope (SEM) (XL 30, USA).

3.1 Gel Fraction

The gelation fraction of different PLA/BF composites irradiated at various absorbed doses is shown in Fig. 1. No gelation was formed in PLA/BF composites without TAIC as the absorbed dose increased. However, for PLA/BF/TAIC composites, the gel content increased significantly after exposure to gamma-rays, which is consistent with Jin' s study. Irradiation played an important role in the crosslinking of composites as well. Generally, in the presence of TAIC, the gel fraction increased obviously in the low dosage region (5-10 kGy) and then changed moderately with further increases in absorbed dose. BF content had little effect on the ultimate amount of networks. Under optimum conditions, about 60 wt% networks were achieved for composites blended with 5 wt% TAIC.

Fig. 1. Gelation content of irradiated composites with different amounts of TAIC at various absorbed doses: (A) PLA/BF, 90/10 wt/wt; (B) 80/20; (C) 70/30.

3.2 Heat Deflection Temperature (HDT)

The HDT of PLA/BF composites with various blending ratios after irradiation at 5 kGy is shown in Fig. 2. The HDT of PLA/TAIC blends is also given for comparison. The content of basalt fiber had a great impact on the final heat resistance. When the fiber content was less than 20 wt%, the HDT of PLA/BF composites increased by 5-15°C compared with neat PLA and remained mostly unchanged with increasing TAIC content. When the basalt fiber content reached

30 wt%, the HDT of the PLA/BF binary composite improved to 85°C after irradiation. With the addition of TAIC, HDT changed slowly at small TAIC amounts and then dramatically increased to 135°C in the presence of 5 wt% TAIC. Considering density, the volumetric fraction of basalt fiber was much lower than 30% due to the much higher density of basalt fiber compared with neat PLA. The heat resistance of PLA can be improved by enhanced irradiation, and appropriate amounts of basalt fiber and TAIC are necessary.

Fig. 2. Plot of HDT of different PLA/BF composites with TAIC content at 5 kGy.

The effects of absorbed dose on HDT of PLA/BF/TAIC composites are shown in Fig. 3. The TAIC content was fixed at 5 wt%. Similar to Fig. 2, HDT remained almost constant around 65°C with increasing absorbed dose when the basalt fiber content was below 20 wt%. It can also be found that the HDT of the PLA/BF composite (70/30 wt/wt) blended with 5 wt% TAIC was significantly enhanced to 135°C after irradiation, even though the gel fraction of bulk PLA in the composites was less than 50 wt%. However, in N. Nagasawa' s and H. Mitomo' s studies, 80 wt% gelation of PLA was needed to improve HDT obviously. This difference may be due to the formation of PLA-g-BF structure at the interphase during enhanced irradiation, which seriously hindered the movement of PLA chains. The optimum dose was 5-10 kGy, and further increases in absorbed dose resulted in only modest improvement of HDT.

Fig. 3. HDT of different PLA/BF/TAIC composites at various absorbed doses.

3.3 Mechanical Properties

The tensile strength of various PLA/BF/TAIC composites is shown in Fig. 4. The properties of control samples without TAIC are also given. The tensile strength of composites without TAIC decreased with absorbed dose overall, attributed to degradation of PLA chains during gamma-ray exposure. The incorporation of small molecules (TAIC) enhanced tensile strength, even though this was not obvious in the low dose region, especially for composites containing less than 20 wt% basalt fiber. As the absorbed dose reached 70 kGy, the tensile strength of composites with TAIC was significantly higher than that of control samples, which may be attributed to adequate network formation at high dose.

Fig. 4. Tensile strength of PLA/BF composites with different TAIC contents at various doses: (A) PLA/BF, 90/10 wt/wt; (B) 80/20; (C) 70/30.

3.4 Mechanism of Enhanced Radiation Crosslinking

In previous studies, PLA irradiated by γ radiation underwent H-abstraction predominantly on PLA chains. H. Mitomo indicated that if TAIC molecules coexisted with PLA, the double bonds of allyl groups in TAIC would be broken to form a pair of radicals -CH-CH$_2$-, and a complex structure might be generated between PLA and TAIC molecules.

In the present work, it is considered that another crosslinking structure like PLA-g-TAIC-g-BF must form in the composites, besides the network of PLA chains. As is well known, many free radicals were formed on PLA chains during irradiation, and these reactive species would combine with TAIC molecules. At the same time, the fibers also produced free radicals, which would react with the remaining vinyl groups in the TAIC molecules. Finally, a complex crosslinking structure containing both fibers and PLA segments was achieved at the interface. This reaction process is shown in Fig. 5.

Fig. 5. Radiation-induced crosslinking mechanism of PLA/fiber composites with TAIC coexistence.

Based on this speculation, it can be concluded that due to the PLA-g-TAIC-g-BF structures at the interface, the mobile PLA chains were fixed by rigid fibers at high temperature. These conclusions have already been confirmed by the improved heat resistance. Otherwise, because of this compound structure at the interface, the necessary amounts of fiber and gel fraction of PLA were reduced to 20 wt% and 50 wt%, respectively.

3.5 SEM

Figure 6 [Figure 6: see original paper] shows the fracture surface of the composites. From the micrographs, it can be observed that the surfaces of fibers pulled out from the matrix are very smooth, as are the holes in the matrix, regardless of fiber content changes, indicating weak adhesion between the PLA matrix and basalt fiber.

Fig. 6. SEM micrographs of composites without TAIC, non-irradiated: (A) PLA/BF 90/10 wt/wt; (B) PLA/BF 80/20 wt/wt; (C) PLA/BF 70/30 wt/wt.

The fracture surface morphology of enhanced irradiated samples is shown in Fig. 7. Although the surfaces of pull-out fibers are smooth, the holes left in the matrix are less obvious. Some deformation of the PLA matrix during the tension process can be found in the fracture morphology, especially for the sample irradiated at 70 kGy with the blending ratio of 70/30/5 wt/wt/wt. It is considered that a synergistic effect has been obtained between the PLA matrix and filling fibers, and the interface adhesion is improved, resulting from the formation of the above-mentioned structure.

Fig. 7. SEM micrographs of composites: (A) PLA/BF/TAIC 70/30/1 wt/wt/wt, 5 kGy; (B) PLA/BF/TAIC 70/30/5 wt/wt/wt, 70 kGy.

4 Conclusion

The introduction of basalt fiber and enhanced irradiation is an effective approach to improve the heat resistance of PLA. When 30 wt% basalt fiber and 5 wt% TAIC were employed, the HDT was dramatically enhanced to above 135°C after irradiation even at 5 kGy. Tensile strength of composites was improved by enhanced irradiation as well, and the optimum amounts of TAIC and absorbed dose were 5 wt% and 70 kGy, respectively.

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