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Synthesis and characterization of TPO–PLA copolymer and its behavior as compatibilizer for PLA/TPO blends

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ABSTRACT

A thermoplastic polyolefin elastomer-*graft*-polylactide (TPO–PLA) was prepared by grafting polylactide onto maleic anhydride-functionalized TPO (TPO–MAH) in the presence of 4-dimethylaminopyridine (DMAP). The characterization of the TPO–PLA copolymers was conducted by FT-IR and ^{1}H NMR. The effects of reaction temperature and concentration of DMAP on the reactivity of graft polymerization were investigated by FT-IR, which revealed that a high reaction temperature and a high DMAP concentration are associated with dramatic depolymerization of PLA and reduction of steric hindrance effect in the graft reaction. A Molau test, SEM observations of cyro-fractured surface morphology and particle size analysis of PLA/TPO blend system demonstrate that this new copolymer, acting as a premade compatibilizer, significantly improved the compatibility of the PLA/TPO blends. As the concentration of TPO–PLA copolymer increased, elongation at break and tensile toughness increased with compatibilizer concentration up to 2.5 wt%, beyond which it declined, but TPO–PLA copolymer did not affect the tensile strength or modulus. The effect of the chemical composition of the TPO–PLA copolymer on the compatibilization efficiency and mechanical properties of the PLA/TPO blends was examined by altering the number of grafting sites and concentration of DMAP, suggesting that DMAP concentration dominated the properties of the ternary blend system. Two compatibilizers, TPO–MAH and TPO–PLA, were used to compatibilize the PLA/TPO blend; the results suggested that TPO–PLA was more efficient in reducing the interfacial tension between the two immiscible polymers and in improving the mechanical properties of PLA/TPO blending specimens.

1. Introduction

Polylactide (PLA), a synthetic aliphatic polyester derived from biomasses, is an environmentally friendly polymer and has been emerging as an alternative to conventional petroleum-based polymeric materials because of its renewability, biodegradability and greenhouse gas neutrality. PLA is most commonly synthesized by the ring opening polymerization of lactide, which is the cyclic dimer of lactic acid. The chirality of the three stereoisomers – L-lactide, D-lactide and D,L-lactide, substantially dominates the properties of PLA: poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA) with high optical purity is semicrystalline with a T_m of 170–180 °C and a T_g of 55–65 °C, and amorphous poly(D,L-lactide) (PDLLA) only has a T_g of 50–60 °C.[1,2] Although PLA is a high-strength and high-modulus polymer analogous to polystyrene, its inherent brittleness and low toughness due to the low entanglement density (V_e) and the high value of characteristic ratio that represents the chain stiffness [3,4] restrict the range of applications.

Among various methods for modifying PLA, such as the copolymerization of lactide with other monomers, blending PLA with immiscible or miscible polymers is a more practical and economical way of toughening PLA [5–8]. However, most of the polymer blends are immiscible, and the multiphase blends show poor mechanical performance because of the low interfacial adhesion between the polymer phases. To solve the problem of immiscibility, compatibilizing agents, such as (i) premade block or graft copolymers that bear constitutive segments that are miscible with the blend components [9,10], or (ii) polymers with complementary reactive groups that can link the matrix with the dispersed phase via covalent bonds formed *in situ* during melt blending process, are utilized to reduce the interfacial tension and elevate interface adhesion between the immiscible phases [11,12].

Poly(ethylene-octene) copolymer is a thermoplastic polyolefin elastomer (TPO), and has been extensively employed as a toughening agent in numerous polymer blending systems, including polyester [13–15], and nylon [16]. These polymer blends, inclusive of PLA/TPO blend, are immiscible due to the high polarity difference between the component polymers. Hillmyer et al. [17,18] synthesized polyethylene-*block*-polylactide and poly(ethylene-*alt*-propylene)-*block*-polylactide via a combination of the anionic

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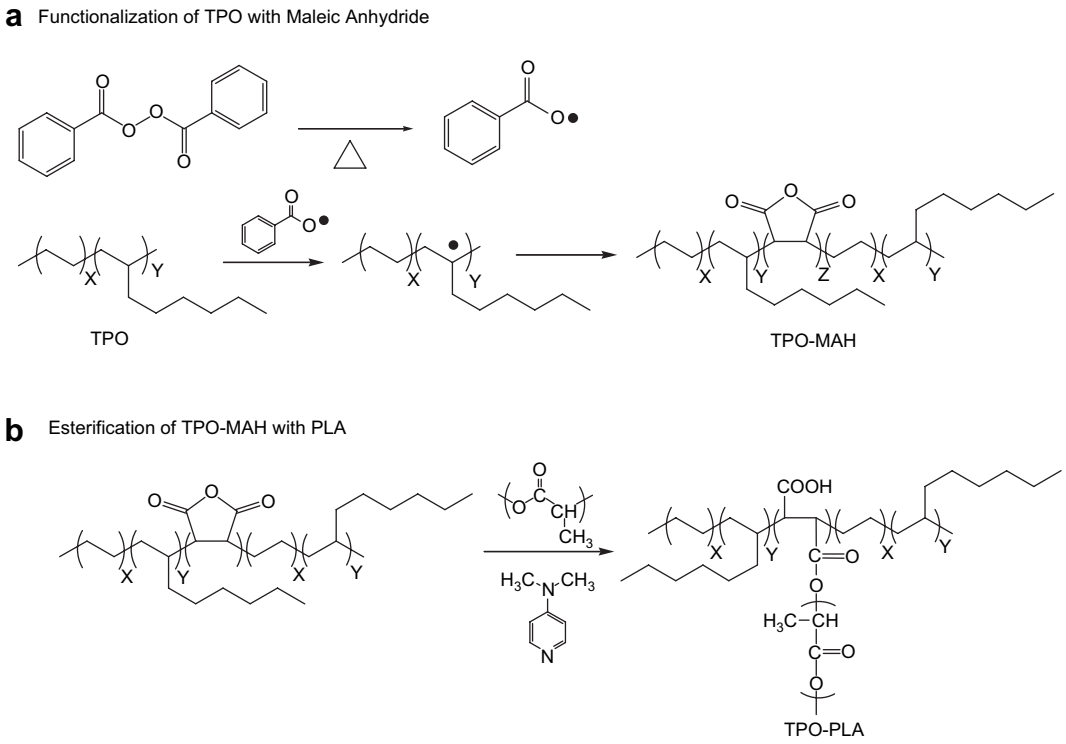

Scheme 1. The synthetic route of TPO–PLA copolymer.

polymerization of butadiene and isoprene and the ring opening polymerization of lactide; they demonstrated that these block copolymers were good compatibilizers for PLLA/LDPE blends. However, ionic polymerization and ring opening polymerization techniques suffer from the stringent requirement for moisture removal and monomer purity, and stannous octoate ($SnOct_2$) that is typically utilized in the PLA synthesis is not easily removed by dissolution and precipitation.

Over the past decades, considerable effort has been made to chemical modification of polyolefin by introducing reactive functional monomers to improve the properties and extend the range of applications of polyolefin, such as poly(polypropylene)-*g*-MAH [19], poly(ethylene)-*g*-MAH [20] and so on. The active functional group can react with numerous reactive groups to form block or graft copolymers acting as *in situ* formed or premade compatibilizers.

In this study, we report an alternative route for the preparation of TPO-*graft*-PLA copolymers that serve as compatibilizing agents for PLA/TPO blends: the maleic anhydride-functionalized TPO (TPO–MAH) reacts with the commercialized polylactide in the presence of 4-dimethylaminopyridine (DMAP). The chemical structures were identified by FT-IR and ^{1}H NMR. The factors influencing the reactivity of grafting PLA onto TPO were discussed. The morphologies and the mechanical properties of the PLA/TPO blends in the presence and absence of compatibilizers were studied, and the effect of the chemical composition of the TPO–PLA copolymers on the mechanical properties was analyzed and discussed. Finally, the mechanical properties and morphologies of PLA/TPO/TPO–MAH ternary blend were compared with those of PLA/TPO/TPO–PLA blend.

2. Experimental

2.1. Materials

PLA (NatureWorks 8300D) utilized in this study was purchased from Cargill–Dow Polymer LLC, and thermoplastic polyolefin elastomer (ENGAGE™ 8411) was obtained from Dow–Dupont elastomer. Acetone, ethyl acetate, and toluene, obtained from TEDIA; maleic anhydride (MAH) obtained from SHOWA; and benzoyl peroxide (BPO) obtained from Lancaster were all used as-received without further purification. 4-Dimethylaminopyridine (DMAP), purchased from Seedchem Company, was purified by recrystallization from toluene.

2.2. Preparation of TPO-graft-PLA copolymer

2.2.1. Functionalization of TPO with maleic anhydride

The reaction was conducted in a two-necked round-bottom flask equipped with a nitrogen gas inlet and a condenser and purged with dry-nitrogen gas. A desired amount of TPO pellets and MAH was added to the vessel, followed by injecting toluene into the flask and immersing the apparatus into an oil bath at 140 °C in sequence. After TPO and MAH were completely dissolved, BPO was added to the solution in an atmosphere of nitrogen. After the reaction mixture had been stirred for approximately 4 h, the reaction solution was poured into acetone to precipitate the functionalized polymer (TPO–MAH). TPO–MAH was further purified by HPLC-grade acetone by Soxhlet extraction overnight and was then dried at 80 °C at reduced pressure for 18 h.

2.2.2. Esterification of TPO–MAH with polylactide

TPO–MAH was added to a two-necked round-bottom flask equipped with a nitrogen gas inlet and a condenser. Toluene was injected and the reaction vessel was placed in an oil bath at 140 °C. After TPO–MAH was entirely dissolved, DMAP was added to the polymer solution. After the DMAP containing solution had been stirred for 1 h, the polylactide pellets were added and the graft reaction proceeded for 16 h. The final product was precipitated into ethyl acetate, and further purification by Soxhlet extraction with HPLC-grade ethyl acetate was accomplished, followed by drying in a vacuum oven at 80 °C for 18 h.