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Influence of chain extension on the compatibilization and properties of recycled poly(ethylene terephthalate)/linear low density polyethylene blends

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ABSTRACT

Polymeric methylene diphenyl diisocyanate (PMDI) was added as chain extender to a blend of recycled poly(ethylene terephthalate) (R-PET) and linear low density polyethylene (LLDPE) with compatibilizer of maleic anhydride-*grafted* poly(styrene–ethylene/butadiene–styrene) (SEBS-*g*-MA). Hydroxyl end groups of PET can react with both isocyanate groups of PMDI and maleic anhydride groups of SEBS-*g*-MA, which are competing reactions during reactive extrusion. The compatibility and properties of the blends with various contents of PMDI were systemically evaluated and investigated. WAXD results and SEM observations indicated that chain extension inhibits the reaction between PET and SEBS-*g*-MA. As the PMDI content increased, the morphology of dispersed phase changed from droplet dispersion to rodlike shape and then to an irregular structure. The DSC results showed that the crystallinity of PET decreased in the presence of PMDI, and the glass transition temperature (T_g) of PET increased with addition of 0–0.7 w% PMDI. The impact strength of the blend with 1.1 w% PMDI increased by 120% with respect to the blend without PMDI, accompanied by only an 8% tensile strength decrease. It was demonstrated that the chain extension of PET with PMDI in R-PET/LLDPE/SEBS-*g*-MA blends not only decreased the compatibilization effect of SEBS-*g*-MA but also hindered the crystallization of PET.

1. Introduction

Poly(ethylene terephthalate) (PET) is widely used in packaging materials especially in beverage packages, owing to its good mechanical properties and excellent barrier properties. Most of these beverage bottles are used only once, which inevitably creates serious resource waste and white pollution. Therefore, with the increased awareness of the environmental protection, governments pay more and more attention to the issue of recycling waste PET.

Compared to other post-consumed plastics, the source of recycled PET (R-PET) is more stable, and R-PET bottles are easier to separate and purified. However, R-PET undergoes a series of degradation problems such as thermal, hydrolytic, mechanical and oxidative degradation during melt processing. This leads to a reduction in molecular weight and intrinsic viscosity, which in turn decreases the mechanical properties of recycled materials [1–5]. In addition, thermal and hydrolytic degradation occur more easily in the presence of contaminants, such as poly(vinyl chloride) (PVC), ethylene-vinyl acetate copolymer (EVA), adhesives, moisture, etc.. It is well known that the recycling of waste PET is to recover the performance of R-PET. In order to improve the mechanical properties and melt strength of R-PET, chain extension has been employed from the past three decades [6–9]. It is very useful to apply chain extension in the reprocessing of R-PET, because the reduction of molecular weight of PET can, in part, be compensated for by introducing the chain extender. Chain extenders are general poly-functional compounds with thermal stability and have the ability of fast reaction with the hydroxyl or carboxyl end groups of PET. The most widely used chain extenders are di- and multi-functional epoxides [10–12], diisocyanates [13–15], dianhydrides [16–18], bis-oxazolines [19–21] and phosphates [22,23].

In our previous work, we have investigated R-PET/LLDPE blends without chain extender by low-temperature solid-state extrusion [24,25]. For R-PET/LLDPE blends, SEBS-*g*-MA is a more effective compatibilizer in improving mechanical properties of the blends than SEBS because the olefin segments of SEBS-*g*-MA are compatible with LLDPE and maleic anhydride groups of SEBS-*g*-MA can react with hydroxyl end groups of PET to synthesize PET-b-SEBS copolymer *in-situ*. With the increase of compatibilizer content,

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elongation at break and impact strength of the blends increased, while tensile properties decreased severely. Therefore, the significant reduction in the tensile strength limited the industrial application of R-PET/LLDPE/SEBS-*g*-MA blends. Moreover, impact strength of the blends was not increased obviously with further increase of SEBS-*g*-MA content.

In order to further improve impact strength of the blends and simultaneously ensure only slight decrease in other mechanical properties, we screened and compared different chain extenders. In this study, polymeric methylene diphenyl diisocyanate (PMDI) was finally chosen as chain extender to modify R-PET/LLDPE/SEBS-*g*-MA blends. The chemical structure of PMDI is shown in Fig. 1. This work systemically investigated the effect of PMDI on the compatibilization effect of SEBS-*g*-MA, as well as the morphology and properties of R-PET/LLDPE/SEBS-*g*-MA blends.

2. Experimental

2.1. Materials

Scraps of recycled PET were from Zijiang Bottle Ltd. (Shanghai, China) with an intrinsic viscosity of 0.71 dL/g. LLDPE was from Panjin Polyethylene industry Co. Ltd. $T_m = 126.0\,^\circ C$, MI = 2.72 g/10 min (265 °C, 2.16 kg). SEBS-*g*-MA (Kraton F1901X), grafted with 1.84 w% maleic anhydride, was supplied by Shell Chemical Company. The ratio of styrene to ethylene–butylene in the triblock copolymer is 30/70 w%. PMDI containing 30–32% isocyanate group, was purchased from Bayer Material Science AG.

2.2. Sample preparation

Scraps of PET were dried in dehumidifier at 120 °C for 10 h before feeding to the extruder; SEBS-*g*-MA and LLDPE were dried under vacuum at 80 °C for 10 h. PMDI contents investigated varied from 0 w% to 1.1 w% with respect to the whole weight fraction of R-PET/LLDPE/SEBS-*g*-MA (72/18/10 w/w/w) blend. The reactive extrusion experiments were implemented on a co-rotating twin-screw extruder ($L/D = 48$, $D = 35$ mm). The barrel temperatures for the extruder from zone 1 to 4 were 100 °C, 150 °C, 200 °C and 240 °C, respectively. The die temperature was 250 °C. The blends were extruded into a water bath and cut into pellets using a pelletiser. The pellets were dried in a dehumidifying dryer at 120 °C for 4 h and then injected to prepare samples by injection moulding. A barrel temperature of 240 °C, a mould temperature of 40 °C, an injection speed of 60 mm/s and an injection pressure of 90 psi were used.

2.3. Characterisation

Tensile properties and flexural properties were tested using a WSN-20KN Mechanical Properties Testing Machine. The cross-head speeds used in the tensile and flexural test were 10 mm/min and 2 mm/min, respectively. Notched Charpy impact strength was measured with a JJ-20 Memorial Impact Tester. Both testing machines were manufactured by Changchun Mechanical Properties Testing Machine Ltd. (China).

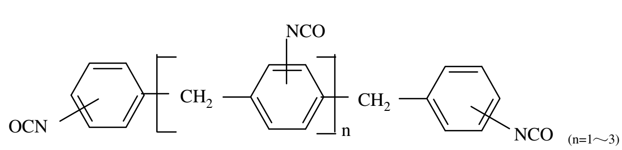

Fig. 1. Chemical structure of PMDI.

Differential scanning calorimeter (DSC) was performed on a Netzsch DSC PC 200 (Germany). The samples (7–10 mg), taken from the injection moulded specimens, were first heated from 50 to 280 °C at 10 °C/min, then cooled at the same rate, and reheated again with a nitrogen atmosphere. Melting temperature, T_m was determined as corresponding to the maximum of the endothermic curve.

Wide-angle X-ray diffraction (WAXD) measurements were carried out with Rigaku (Japan) D/max 2250VB/PC X-ray diffractometer with Cu/$K_{\alpha 1}$ radiation. Diffraction patterns of samples were obtained in the reflection mode from 3° to 50° 2θ.

Fourier-transform infrared (FTIR) spectroscopy with an attenuated total reflectance (ATR) accessory was performed to establish the reaction between PMDI and PET.

The particle size and dispersion of the blends were revealed by a scanning electron microscopy (SEM) instrument (JSM 6100). The samples were cryofractured in liquid nitrogen and coated with gold before testing.

3. Results and discussion

3.1. Chain extension of pure R-PET with PMDI

Because the isocyanate group has high reactivity, PMDI can react with compounds containing active hydrogen such as alcohol, carboxylic acid, amine, etc. The reactive activity is in the order: aliphatic amine > aromatic amine > primary alcohol > water > secondary alcohol > phenol > carboxyl > substituted urea > amide > urethane [26].

To investigate the effect of PMDI on the compatibilized PET-based blends, the chain extension of pure R-PET with PMDI was studied first. When the content of PMDI was less than 0.8 w%, the modified R-PET was soluble in the mixed solvent of phenol/tetrachloroethane (50/50 w/w); When the content of PMDI was more than 0.8 w%, more and more R-PET could not be dissolved with the increase of PMDI content; When the content of PMDI reached 1.1 w%, more than 70 w% R-PET was insoluble but swelled. Isocyanate groups of PMDI can react with both hydroxyl and carboxyl end groups of PET, so the chain extension reaction produces three different chemical structures of PET, including coupled, branched and crosslinked of PET. Due to better reactivity between isocyanate groups and hydroxyl groups, the isocyanate groups of PMDI mainly react with hydroxyl end groups of PET when PMDI content is low, in other words, chain coupling and branching are the major reactions in the chain extension process; with the increase of PMDI content, isocyanate groups of PMDI can react with more and more carboxyl end groups of PET, so crosslinking effect becomes significant, indicating that partial PMDI acts as crosslinking agent for R-PET. With the addition of PMDI, all of these reactions increase the molecular weight or the number of crosslink points of PET and hence hinder the movement of PET chains.

3.2. Competing reactions

For R-PET/LLDPE/SEBS-*g*-MA blends with PMDI, hydroxyl end groups of PET can react with maleic anhydride groups of SEBS-*g*-MA to synthesize PET-b-SEBS-*g*-MA copolymer *in-situ* [24], meanwhile, hydroxyl and carboxyl end groups of PET can react with isocyanate groups of PMDI. The mechanisms of these reactions are described in Fig. 2. On the whole, these reactions play two different roles in the processing of the blends: (i) compatibilization reaction of PET with SEBS-*g*-MA, (ii) chain extension reaction of PET with PMDI. Fig. 3 shows FTIR spectra for PMDI, PET, SEBS-*g*-MA, the R-PET/LLDPE/SEBS-*g*-MA blend and the blend with 1.1 w% PMDI. It can be seen that the peak of isocyanate groups of PMDI at