

Toughening of poly(propylene carbonate) using rubbery non-isocyanate polyurethane: Transition from brittle to marginally tough



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ABSTRACT

To overcome the brittleness of poly(propylene carbonate) (PPC), rubbery non-isocyanate polyurethane (NIPU) with rich hydrogen bonding moiety was synthesized for toughening PPC. Debonding phenomenon of NIPU was observed during the impact process of PPC/NIPU blends, which was beneficial for toughening PPC. When the NIPU loading increased to 10 wt%, the unnotched impact strength increased 3 times compared with neat PPC. The NIPU dispersed uniformly and a transition from brittle to marginally tough occurred when L/d reached a critical value, 1.74, where L and d were center-to-center distance and the diameter of the particle, respectively. The debonding of NIPU accounted for the increase of toughness, and shear yielding of the matrix was limited around the microvoids. When the NIPU loading reached 13 wt%, NIPU flocculated in the matrix leading to decline in toughness. The equilibrium between self-associating hydrogen bonding and intermolecular one formed between PPC and NIPU affected their miscibility and thereby the morphology of the blends.

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1. Introduction

Poly(propylene carbonate) (PPC) is an alternating copolymer of carbon dioxide and propylene oxide, it has received intensive attention not only for it comes from cheap, abundant CO₂, but also it is biodegradable polymer [1–4]. Possible application of PPC has been reported, such as tissue scaffolding [5,6], polymer electrolyte [7], adhesive agents, etc. In addition, considering its remarkable barrier property of oxygen and water, PPC can also be used as packaging material [8–10]. However, PPC is a brittle polymer, since its elongation at break was below 10% at 20 °C, which severely limits its practical application.

To modify the mechanical properties of PPC, especially the brittleness, plasticizer such as diallyl phthalate [11] or low molecular weight urethane compound [12], etc., has been employed through blending, and the elongation at break of PPC has been improved significantly. However, the tensile strength and the glass transition temperature decreased meanwhile because the low

molecular weight plasticizer acted as lubricant leading to more prone to move for PPC chain.

Rubbery particles, which have different elastic property with the matrix, have been proved to be effective in toughening brittle polymers. Generally, toughness of a polyblend is related to its morphological structure, while the toughening mechanism is quite complicate. A commonly accepted view is that the rubbery particles alter the stress state in the matrix around the particles, and special structure such as multiple crazes [13–15], microvoids [16,17], shear bands [18,19], appears during the impact process. Multiple crazes have been observed during the impact process of high impact polystyrene (HIPS) [13], the size of rubbery particles, along with the adhesion between rubbery particles and the matrix, is of vital importance because the rubbery particles must act as craze initiators and craze stoppers. While in nylon/rubber blend, matrix yielding is believed to be the main factor contributing to its toughness [18]. Interparticle distance is the critical parameter determining the brittle–ductile transition, and the adhesion between the matrix and rubber is necessary. Enhanced matrix shear yielding has been observed due to the formation of microvoids in ABS [17] and polycarbonate [16]. Although only a small part of energy dissipated through cavitation, it played an important role in initiating further plastic deformation [20,21]. Because the stress

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state around the particles is important in the toughening mechanism, the morphology of the polyblend becomes the definitive factor. As far as we have known, there are few articles discussing the effect of rubbery particles on the toughness of PPC.

Non-isocyanate polyurethane (NIPU), which can be prepared by reaction of bis(cyclic carbonate)s and diamines, is non-toxic and CO₂-based with utilization of CO₂ in the synthesis of bis(cyclic carbonate)s [22,23]. Because of the randomly existing units containing primary and secondary hydroxyl groups, it is amorphous with low glass transition temperature, making it to be rubbery particles at 20 °C. Moreover, as shown in Scheme 1, it is rich in hydrogen bonding moiety like amine or hydroxyl group, capable of forming hydrogen bonding with carbonyl or oxygen unit in PPC. Another bonus lies in its water solubility, it can be easily removed from the polyblend by water etching, which makes it suitable for prompt morphology study, thereby understanding influence of morphology change on the toughness of polyblend. Therefore, NIPU might be a kind of ideal rubbery particle to toughen PPC and illustrate the toughening mechanism. In this work, three kinds of NIPU were synthesized and used to toughen PPC (Scheme 1). A transition from brittle to marginally tough was observed accompanying with the debonding of NIPU from the matrix. The effect of the morphology and the intermolecular hydrogen bonding between PPC and NIPU on the toughness has also been discussed.

2. Experimental

2.1. Materials

Chemicals like 1, 3-propanediamine, 1, 8-diaminooctane and 1, 6-hexanediamine were purchased from Aldrich and used without further purification. Ethylene glycol diglycidyl ether was purchased from Ruipu Material Co. (China) and distilled under vacuum before use. Bis(cyclic carbonate) based on the coupling reaction of CO₂ and ethylene glycol diglycidyl ether was prepared by iron complex catalysts.

PPC was supplied by Zhejiang Bangfeng Plastic Co. (China), whose technique was licensed under our laboratory. To remove residue rare earth metal ternary catalyst, the copolymer was purified twice by repeated dissolution/precipitation procedure with dimethyl carbonate as a solvent and ethanol as a precipitate. The number-average molecular weight (M_n) and the polydispersity index (PDI) of the purified PPC were determined by gel permeation chromatography (GPC) as 17.3×10^4 g/mol and 3.65, respectively. The carbonate unit content of the purified PPC was 98%, estimated from its ¹H NMR spectrum according to the literature [24,25].

2.2. Synthesis of NIPUs

NIPU was synthesized by the polyaddition of bis(cyclic carbonate) and diamines under N₂ protection. Briefly, bis(cyclic carbonate) (0.1 mol) and diamine (0.1 mol) was added in a flask under N₂ atmosphere, and stirred at 80 °C for 20 min, then the temperature was raised to 100 °C and kept at this temperature for 2 h to complete the reaction. The resultant NIPUs from 1, 3-propanediamine, 1,

6-hexanediamine and 1, 8-diaminooctane were noted as NIPU1, NIPU2 and NIPU3, whose ¹H NMR (*d*₆-DMSO, TMS, 300 MHz) data were listed as follows.

NIPU1: δ (ppm) = 7.24 (–NH, 2H), 4.65 (–OCH(CH₂OH)CH₂–, 1H), 3.34–3.91 (–OCH(CH₂OH)CH₂–, –CH₂O–, –OCH₂CH(OH)CH₂–, 14H), 2.72–2.94 (–NHCH₂, 4H), 1.50–1.53 (–CH₂–, 2H).
 NIPU2: δ (ppm) = 7.12 (–NH, 2H), 4.65 (–OCH(CH₂OH)CH₂–, 1H), 3.37–3.91 (–OCH(CH₂OH)CH₂–, –CH₂O–, –OCH₂CH(OH)CH₂–, 14H), 2.67–2.92 (–NHCH₂, 4H), 1.22–1.48 (–CH₂–, 2H).
 NIPU3: δ (ppm) = 7.11 (–NH, 2H), 4.66 (–OCH(CH₂OH)CH₂–, 1H), 3.35–3.92 (–OCH(CH₂OH)CH₂–, –CH₂O–, –OCH₂CH(OH)CH₂–, 14H), 2.65–2.92 (–NHCH₂, 4H), 1.22–1.48 (–CH₂–, 2H).

2.3. Melt-blending procedure

Prior to the blending, PPC and NIPUs were dried at 45 °C in vacuum for 24 h to get rid of water. Then PPC and NIPU were mixed in calculated weight ratio (NIPU/PPC = 1/99, 2.5/97.5, 5/95, 8/92, 10/90, 13/87, or 15/85). The mixing was operated on a Haake batch-intensive mixer (Haake Rheomix 600) at a speed of 60 r/min for 5 min at 140 °C. All the blends were kept in a desiccator before use.

2.4. Characterization

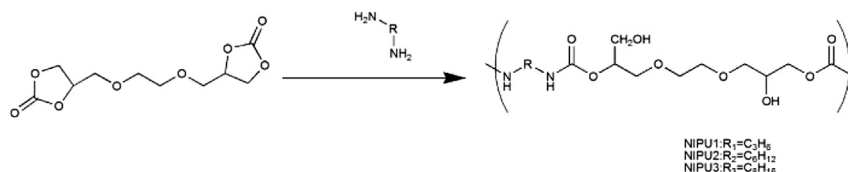
Differential scanning calorimetry (DSC) analysis was performed on a Perkin–Elmer DSC-7 instrument under N₂ atmosphere. The sample was first heated from –50 °C to 50 °C at 10 °C/min and then rapidly quenched to –50 °C, followed by second heating process to obtain the glass transition temperature (T_g) to avoid thermal history.

FT-IR spectra of the samples were recorded on a Bruker TENSOR-27 spectrophotometer using a ZnSe ATR crystal with spectral resolution of 2 cm^{–1}, where the molded blends sheets were pressed directly onto the ZnSe crystal with a close contact.

Tensile performance was evaluated using dumb-bell-shaped sample punched out from the molded sheet in a screw-driven universal testing machine (Z010, Zwick.Co., Germany) equipped with a 10 kN electronic load cell and mechanical grips. The test was conducted at 20 °C using a cross-head rate of 20 mm/min according to the ASTM standard, and the data reported were the mean of the parallel values in five determinations.

The Izod unnotched impact strength of the specimens was carried out with a JJ-20 instrumented impact machine at 20 °C according to the ASTM D4812-115. At least five specimens were tested for each sample to get an average value.

Scanning electron microscopy (SEM) image was obtained on a XL30 ESEM FEG (FEI Co.) with an acceleration voltage of 8 kV. For better observation of the phase morphology, the sample was cryo-fractured in liquid nitrogen and the fractured surface was etched in methanol for 24 h at room temperature and then rinsed with MeOH and water to selectively remove NIPU, followed by vacuum drying at 45 °C for 24 h prior to record its SEM image.



Scheme 1. NIPUs for the modification of PPC.

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