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Synthesis of polyether imidazole ionic liquid and its modification on polypropylene crystal structure and mechanical properties

Abstract: Polyether imidazole ionic liquid (PIIL) was synthesized from *N*-ethyl iminazole and hydroxyl-terminated polyepichlorhydrin, produced through cationic ring-opening polymerization of epichlorohydrin using $Et_2O{\cdot}BF_3$ as catalyst, and utilized for the modification of polypropylene (PP) by the method of melt blending. The prepared PIIL was characterized by Fourier transform infrared spectroscopy and ^1H nuclear magnetic resonance spectroscopy. The resulting composite of PP and PIIL was characterized by differential scanning calorimetry and X-ray diffraction analyses. With PIIL acting as a nucleating agent, the crystal structure of PP transformed from α to β crystalline form after modification, while crystallization peak temperature was kept unchanged. Comparison test of the mechanical properties of pure PP and PP/PIIL proved that the long flexible chain of PIIL achieved good compatibility with PP and had reinforcing and toughening effects on PP. With the increase of ionic liquid in PP, both the impact strength and the breaking elongation of the PP/PIIL composite were significantly improved.

Keywords: crystal structure; mechanical properties; modification; polyether imidazole ionic liquid; polypropylene.

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1 Introduction

Polypropylene (PP) is one of the thermoplastics with the greatest development future due to its easy machining and extensive use. However, pure PP resin as a crystalline polymer has disadvantages limiting its applications, such as low temperature brittleness, weak age resistance and dimensional stability (1, 2). Hence, modification of PP by melt blending with rubber or other elastic materials was applied to improve its impact strength, while adding cheap inorganic filler increased the dimensional stability and rigidity of PP (3, 4).

New research (5) showed that two types of multi-walled carbon nanotubes (MWCNTs), C70P and C150P, could be incorporated into PP using a melt blending technique that employs a twin-screw extruder to prepare the nanocomposites of PP/MWCNT. The effect of the type and loading of MWCNT on the rheological and electrical properties of nanocomposites was investigated. It was found that the storage modulus, loss modulus, and complex viscosity increased with increasing MWCNT loading. Additionally, the C70P type of MWCNT exhibited a better rheological performance compared to the C150P type. Another study (6) suggested that the mixing intensity of PP was changed by copolymerization and graft routes, two different tracers with polystyrene (PS). The influence of temperature on residence time distribution (RTD) was not significant because of the dominant viscous forces. The overall RTD functions were independent of the tracer types. The shape of residence time distribution was more affected by the melting mechanism than by miscibility.

Many reports were published on the crystallization behavior of PP. For example, Zhu et al. (7) reported that adding nano-mica could increase the crystallization rate of PP and the number of spherulite, implying that nano-mica plays a nucleating role on the crystallization of PP.

Dai et al. (8) suggested that PP nanocomposites filled by MMT and β-MMT exhibited different heterogeneous nucleation. The heterogeneous nucleation of the prepared MMT surface was changed from α-nucleation into β-nucleation, and a novel MMT with a β-nucleating surface was obtained.

The research of Qin et al. (9) indicated that ultrasound-treated calcium sulfate whisker (CSW) could improve the β-nucleated ability, and this resulted in enhancing the content of the β-crystal form.

Due to its special properties and designable structure, ionic liquid has attracted more attention by chemistry

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researchers (10–13). With no saturated vapor pressure, but with good thermal stability and conductivity, a wide electrochemical window, high solvent power, and ability to be used repeatedly, ionic liquid is called a green solvent or green medium (14–16).

Although reports about blending modifications of PP are common, application of polyether imidazole ionic liquid for the modification of the crystal structure and mechanical properties of PP has not yet been reported. In this study, we synthesized polyether imidazole ionic liquid (PIIL) and then mixed it with PP by melting the blend to study the effect of ionic liquid on the crystal structure and the mechanical properties of PP. This work introduced PIIL into organic polymer materials and produced high-performance and environmentally friendly polymer materials, which is completely compatible with the green development theory of polymer materials and has good application value prospects.

2 Results and discussion

2.1 FTIR analysis

In order to gain an insight into the structures of intermediates and products, the FTIR spectra of polyepichlorhydrin (PECH) and PIIL were collected, as shown in Figure 1A and B, respectively.

IR (KBr, cm^{-1}): In Figure 1A, 747 (stretching of Cl-CH_2-), 1108 (stretching of C-O-C), 3451 (stretching of -OH), 1429 (deforming of CH_2-), and 2877 (stretching of CH_2-); in Figure 1B, 3039 (C-H stretching of imidazole ring) and 1592 and 1543 (stretching of imidazole ring skeleton).

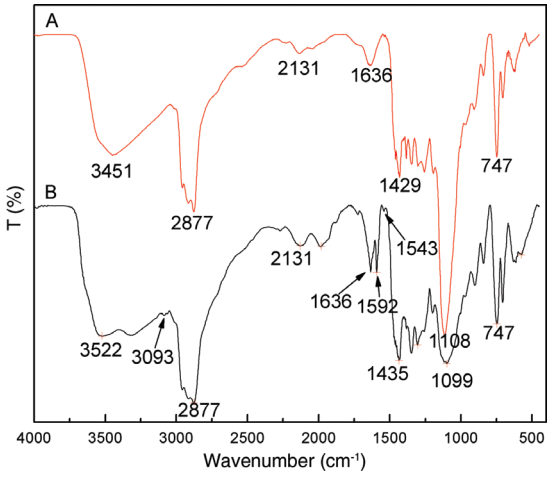

Figure 1 FTIR spectra of (A) PECH and (B) PIIL.

2.2 ^{1}H NMR analysis

The ^{1}H NMR spectrum of the prepared PIIL is illustrated in Figure 2. The peaks around 2.34, 3.69, and 3.63 ppm correspond respectively to the proton resonances of OH at the a position, -CH- at the b position, and -CH_2- at the c position on the main chain of the polyether. The peak around 3.97 ppm can be assigned to the proton resonance of -CH2- at the g position; the site branched the chain of polyether connected with the imidazole ring. Meanwhile, the peaks around 4.36 and 1.42 ppm correspond respectively to the proton resonances of -CH_2- at the h position and -CH_3 at the k position, which are linked with the imidazole ring. The peaks around 7.17, 7.05 and 7.27 ppm are related respectively to the proton resonances of the imidazole ring at the d, e and f positions. The ^{1}H NMR data supported the proposed formulation of PIIL.

2.3 XRD analysis

Figure 3 exemplifies the XRD patterns of pure PP and a PP/PIIL composite. As shown in Figure 3A, the diffraction peaks of the α crystalline form of pure PP are at [110] (14.0°), [040] (16.7°), [130] (18.4°) and [111] (21.7°), while that of the β crystalline form is at [300] (15.8°). The peak at 9.4°, which is attributed to the induced crystallization peak of PP, almost disappeared after the addition of the PIIL, indicating that the PIIL made the crystallization of the PP much easier. The mass fraction of the β crystalline form can be calculated based on the height of the diffraction peak in Figure 3 according to the following equation:

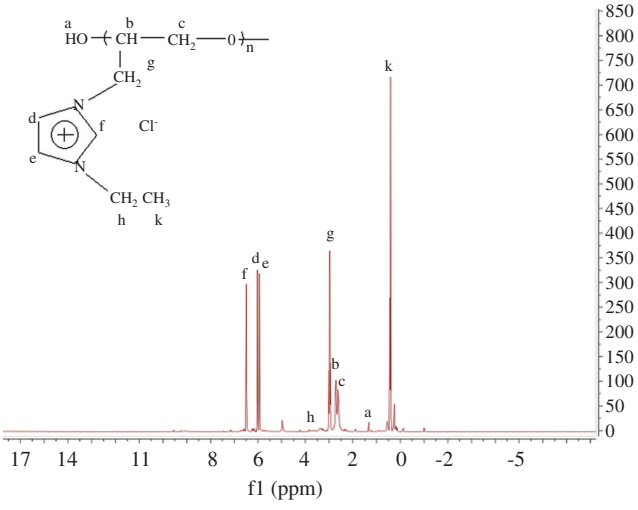

Figure 2 ^{1}H NMR spectrum of PIIL.

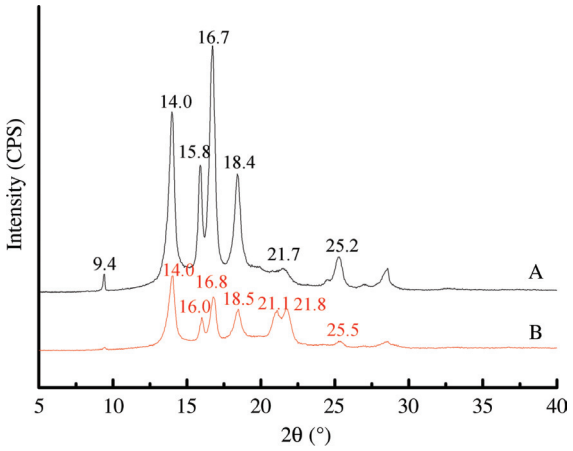

Figure 3 XRD patterns of the (A) PP and (B) PP/PIIL blends (PIIL/PP=3:100).

$$W=\frac{H(300)}{H(300)+H(110)+H(040)+H(130)} \quad [1]$$

The mass fraction of the crystal in β form in the pure PP(a), calculated by Equation [1], was 15%, while that in PP(b) was 20% after the addition of PIIL. This indicated that the PIIL has the effect of β-nucleation on the PP, which is beneficial to the mechanical properties of the modified PP.

2.4 DSC analysis

The thermal properties of pure PP and PP/PIIL composite samples were examined through DSC analysis. The results are shown in Figure 4. It can be seen in Figure 4 that there is only one curing temperature peak of the PP/PIIL composite (172.3°C), which is approximately that of pure PP (171.8°C), indicating that the PIIL has good compatibility with the PP. Moreover, it was also found that the melting peak of the PP was broader and shifted slightly to the area of high temperature, proving that the PIIL acted as a nucleating agent and improved the mechanical properties of PP, which is in accordance with the XRD analysis result in Figure 3 that the amount of the β crystal form increased. In addition, the value of the crystallization enthalpy of the modified PP was increased in Figure 4, which further proved that the thermostability of the PP was improved after the modification by the PIIL.

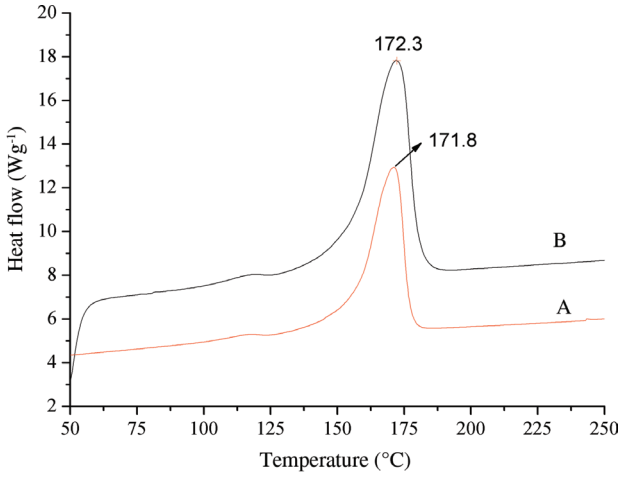

Figure 4 DSC analysis for the (A) pure PP and (B) PP/PIIL composite (PIIL/PP=3:100).

2.5 Analysis of the mechanical properties

The mechanical properties of PP with the addition of PIIL are listed in Table 1.

Table 1 shows that, with the increase in PIIL content, the mechanical property indexes of the modified PP were improved; not only the elongation at break and the impact strength changed regularly, but also the tensile strength and the bending strength reached their maximum when the content of the ionic liquid was 6%, improving by 31% and 11%, respectively. When the content of the ionic liquid was 9%, the impact strength of PP was improved by approximately 132% and the elongation at break was improved from 13.98% to 75.58%. These data show that the long flexible chain of PIIL has plasticizing and toughening effects on PP, which is coincident with the characterization results of XRD and DSC.

3 Conclusions

According to the results of the FTIR and ^{1}H NMR spectroscopy, the target product, PIIL, was synthesized successfully with polyepichlorhydrin and *N*-ethyl iminazole as raw materials.

The results of the XRD and DSC analyses show that PIIL added to PP acts as a nucleating agent for the β

Table 1 Effect of PIIL content on the mechanical properties of PP.

PIIL/PP	0:100	3:100	6:100	9:100
Tensile strength (MPa)	22.65	27.58	29.69	28.52
Elongation at break (%)	13.98	14.09	18.93	75.58
Bending strength (MPa)	30.27	28.37	33.46	29.63
Impact strength (kJ/m^2)	27.24	30.02	51.07	63.09

crystal, which can change the crystal structure of the PP crystal by accelerating the crystallization rate and increasing the crystallinity degree of PP.

The addition of PIIL with its long flexible chain can enhance the mechanical properties of PP. With the increase of PIIL content in PP, both the impact strength and the elongation at break of PP were gradually improved. The values of the tensile strength and bending strength reached the maximum when the amount of PIIL in PP was 6%, and the values of the impact strength reached the maximum when the amount of PIIL in PP was 9%, proving that PIIL has significant reinforcing and toughening effects on PP.

4 Experimental

4.1 Materials

All the chemicals used in the experiments were of analytical reagent grade. Epichlorohydrin was purchased from Luoyang Chemical Reagent Factory (Luoyang, China) and 1,2-dichloroethane from Tianjin Chemical Reagent Factory No. 3 (Tianjin, China). The chemicals ethylene glycol (EG), boron trifluoride etherate, toluene and ether were purchased from China National Medicines Chemicals Reagent Co. Ltd (Shenyang, China). *N*-Ethylinidazole was supplied by Wuxi Zhanwang Chemical Reagent Co. Ltd (Wuxi, China). Particle polypropylene K8303, used as the original PP (pure PP), was offered by Sinopec Beijing Yanshan Company (Beijing, China).

4.2 PECH with low-molecular weight preparation

In a 250-ml, four-mouth and round-bottomed flask equipped with a thermometer, agitator and condenser, ethylene glycol (2.8 ml) and boron trifluoride etherate (2 ml) were added to 1,2-dichloroethane (19.6 ml). The mixture was stirred at room temperature for 30 min, cooled to 0°C with ice-water bath, mixed with epichlorohydrin (39.2 ml) diluted in 1,2-dichloroethane (15 ml) for 3 h, and then stirred at 0°C for 4 h. The mixture turned into a colorless and slightly thickened liquid. After the stirring was stopped and the reaction terminated, the obtained mixture was transferred to a 250-ml separating funnel, washed with deionized water to pH 5.0–6.0 and rested for stratification. The organic phase was evaporated at 50°C under 5 kPa for 3 h to remove the solvent and organic agents with low boiling points; this provided a colorless and slightly thickened liquid of polyepichlorohydrin with a yield of 81% and a viscosity of 30 mPa s measured by a rotational viscometer. The viscosity-average molecular weight measured with an Ubbelohde-type viscometer and the relative molecular weight distribution of the product were 860 and 1.16, respectively.

4.3 PIIL preparation

Polyepichlorohydrin (40 g) in toluene (50 ml) was mixed and reacted with ethylimidazole (68 ml) at 50°C under refluxing and condensation for 10 h. After cooling to room temperature, the mixture obtained after adding diethyl ether (50 ml) was charged into a flask (250 ml) and distilled under a reduced pressure of 0.1 MPa at 90°C for 3 h to remove the solvent and organic materials with low boiling points and to obtain a dense PIIL with a brown-yellow color.

4.4 PP/PIIL composite preparation

PP was premixed with PIIL and an antioxidant according to certain proportions (PP/PIIL/antioxidant=100:3.0–9.0:0.5), then melt blending of the mixture was conducted using an open mill for 5–7 min at 190°C. Afterwards, the molten blended material was molded using an XLB-D400×400×2 plate vulcanization machine (Qingdao Yaxing Machinery Co., Ltd.) at a molding temperature 185°C for 10–12 min. The PP/PIIL composite was obtained after cold pressing using a QLB-350×350×2 plate vulcanization machine (Qingdao Yaxing Machinery Co., Ltd.) under a pressure of 5 MPa.

4.5 Characterization

The tensile properties of the samples were tested by a method that conforms to ISO 527-2:1993 using an LJ-1000 electronic universal testing machine (Xinsansi Materials Testing Co., Ltd.); the impact strength was tested by a method that conforms to ISO 180:2000 on an IZOD-UJ-4 impact tester (Kairui Mechanical Equipment Co., Ltd.); and the bending strength was tested by a method that conforms to ISO 178:2001 at a speed of 2 mm/min.

The ^{1}H NMR spectrum was recorded on a Bruker 300-MHz spectrophotometer (Bruker, Switzerland). FTIR spectra were recorded using a Buck VERTEX70 FT-IR spectrophotometer (Bruker, Germany) with a KBr pellet. The XRD patterns were obtained on a Rigaku D/max-2500 X-ray diffractometer (Japan Science Co., Ltd.) with Cu-Kα

radiation (λ 0.15406 nm, scanning speed 4°/min) and a monochromator (X-ray tube potential 40 kV, tube current 100 mA) over a 2θ range of 5–80° at an ambient temperature. DSC data were taken on a Mettler 821e/400 DSC instrument (Mettler Toledo Company) over a temperature range of 25–350°C at a heating rate of 10°C/min.

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