Effects of 1-*n*-Tetradecyl-3-methylimidazolium Bromide on the Properties of Polypropylene

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ABSTRACT: In this study, 1-*n*-tetradecyl-3-methylimidazolium bromide ([C$_{14}$mim]Br), one kind of imidazolium ionic liquids (imi-IL), was incorporated into polypropylene (PP) via melting blend. The structure and properties of PP/[C$_{14}$mim]Br blend were investigated by differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), and thermogravimetric analysis (TGA). DSC results show that the [C$_{14}$mim]Br has effects on the melting and crystallization process so that PP and PP/[C$_{14}$mim]Br blends (weight ratio is 100/3) have different melting and crystallization temperature. Results of DMA show that the [C$_{14}$mim]Br has the effects on the plasticization and crystallization of PP, and the glass transition temperature (T_g) of PP decreases around 11°C when 3 weight shares of [C$_{14}$mim]Br were incorporated into 100 weight shares of PP. Moreover, both tensile strength and impact strength of PP have been improved reasonably in this situation. TGA also shows the thermal stability of PP is not affected by the [C$_{14}$mim]Br, which was incorporated into it though its molecule is small. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1138–1142, 2008

Key words: imidazolium ionic liquid; polypropylene; blend; glass transition temperature; mechanical properties; thermal properties

INTRODUCTION

Ionic liquids (ILs), most of them are molten salts at ambient temperature, are collecting keen interests for their quite unique characteristics such as nonvolatility, nonflammability, high thermal stability, and so on.[1] ILs were initially found to have better compatibility with poly(methyl methacrylate) (PMMA) than di(2-ethylhexyl) phthalate (DEHP), a good all-round performance plasticizer.[2] It was also found that they were capable of lowering the T_g of PMMA much more than DEHP does, while improving the high temperature stability of PMMA and also providing a wide temperature range of flexible PMMA-based plastics.[2–5] So, ILs existed in the polymer matrix could affect its structures and properties.

Poly(propylene) (PP) is quite a versatile material exhibiting crystallinity, which is responsible for its stiffness. Because its glass transition (typically at about 0°C) is high, the application scope of PP is limited especially at room temperature or even lower. To extend the PP working temperature range and increase its properties, the pristine PP should be modified. Filling inorganic particles into PP matrix to form PP composites or blending PP with other polymers to form PP blends are the two main popular ways. But it is difficult to toughen and reinforce the PP matrix at the same time and get the modified PP with good processing properties.[6] Based on the special properties of ILs and its effect on the aggregative structure and properties of polymer, PP could be modified by incorporated ILs into it.

In this study, 1-*n*-tetradecyl-3-methylimidazolium bromide ([C$_{14}$mim]Br) whose chemical structure is shown in Figure 1, was incorporated into PP matrix by melting blend, and the aim of this work is to investigate the influences of [C$_{14}$mim]Br on the PP structure and its properties.

EXPERIMENTAL SECTION

Materials

PP(grade Q/SHYZ-251) used for this study was procured from Sinopec Co. (Beijing, China). Antioxidant (grade 1010) was obtained from Ncm Hersbit Chemical Co. (Shanghai, China) [C$_{14}$mim]Br was synthesized in our laboratory.

Preparation of PP/[C$_{14}$mim]Br blend

[C$_{14}$mim]Br was kept drying under vacuum at 80°C for 24 h before use. PP and [C$_{14}$mim]Br were mixed
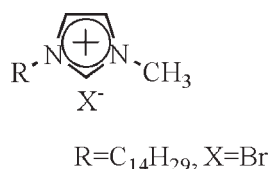
R=C$_{14}$H$_{29}$, X=Br

Figure 1 Molecule structure of 1-*n*-tetradecyl-3-methylimidazolium bromide.

in a cold twin-roll mill with weight ratio of 100/3 for about 5 min, and then the resulting mixture of PP and [C$_{14}$mim]Br were hot-molded in a mold with the compression molding press under 177°C, 2.5 MPa for 10 min. Finally, the mold with the blend of PP/[C$_{14}$mim]Br was moved to another compression molding press to cool to room temperature with the pressure of about 2 MPa, to obtain the PP/[C$_{14}$mim]Br blend for preparing samples.

To obtain a reference, samples of neat PP were also processed in the same way of PP/[C$_{14}$mim]Br blend.

Characterization

Differential scanning calorimetry

Differential scanning calorimetric (DSC) measurements were pursued on a DSC 7 (Perkin–Elmer Co., USA) calorimeter. About 7 mg were sealed in the aluminum pan with a lid. All samples were heated from −10 to 210°C at 15°C/min, under dry nitrogen atmosphere, and held at this temperature for 5 min, and then cooled to room temperature.

Dynamical mechanical analysis

Dynamic mechanical thermal analysis (DMA) was collected on a Rheometric Scientific DMTA Mark IV running in tensile mode at an oscillation frequency of 1 Hz from −60 to 120°C. A gaseous nitrogen purge and a heating rate of 5°C/min were used. Rectangular samples were used with approximate length of 5 mm, width of 2 mm, and thickness of 0.2 mm. The strain amplitude was set to 0.1% strain, well within the linear viscoelastic range.

Mechanical properties

Tensile strength of samples was determined by the electronic tensing machine (LJ-1000) at ambient temperature, relative humidity (RH) 63%, and a crosshead speed of 50 mm/min. Rectangular samples were used with length of 90 mm, but the virtual length of 50 mm, width of 10 mm, and thickness of 4 mm. The tests were carried out in conformity with GB/T1040-92 for at least three times for each specimen and the results were averaged arithmetically.

Impact strength testing of samples was performed on the impacting machine (IZOD UJ-4). Rectangular samples were used with length of 80 mm, width of 10 mm, thickness of 4 mm, and the V-shaped gap of 2 mm in the middle of samples. The tests were carried out at least five times for each specimen and the results also were averaged arithmetically.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on Perkin–Elmer-7 thermal analysis system, and the testing was carried out at the heating rate of 20°C/min under a flow of nitrogen in a temperature range of 50–650°C.

RESULTS AND DISCUSSION

Effects of [C$_{14}$mim]Br on the melting and crystallization of PP

DSC curves of PP/[C$_{14}$mim]Br blend and neat PP are presented in Figure 2. From this, we can find that the melting point of PP/[C$_{14}$mim]Br blend (centered at about 176°C) is higher than that of neat PP (centered at about 165°C), whereas the crystallization temperature of PP/[C$_{14}$mim]Br blend (centered at about 97°C) is lower than that of neat PP (centered at about 109°C). During the melting blend process of preparing the PP/[C$_{14}$mim]Br blend, the moving activity of PP chains should be affected by the existence of [C$_{14}$mim]Br in PP matrix, so that the crystallinity and the crystal structure should be affected. Higher activity of PP chains makes PP crystal more perfectly in the cooling process of PP/[C$_{14}$mim]Br blend preparation, so that in the heating process of DSC testing, the PP in the PP/[C$_{14}$mim]Br blend has higher melting point and a narrower half width of melting peak than neat PP. On the other hand, the PP in the PP/[C$_{14}$mim]Br blend crystallizes at lower temperature than neat PP during the cooling process of DSC testing, which is also attributed to the
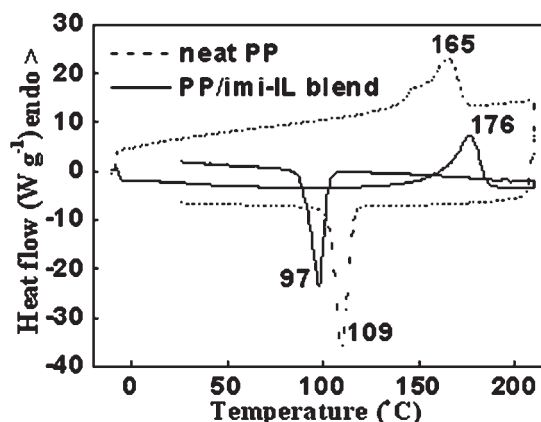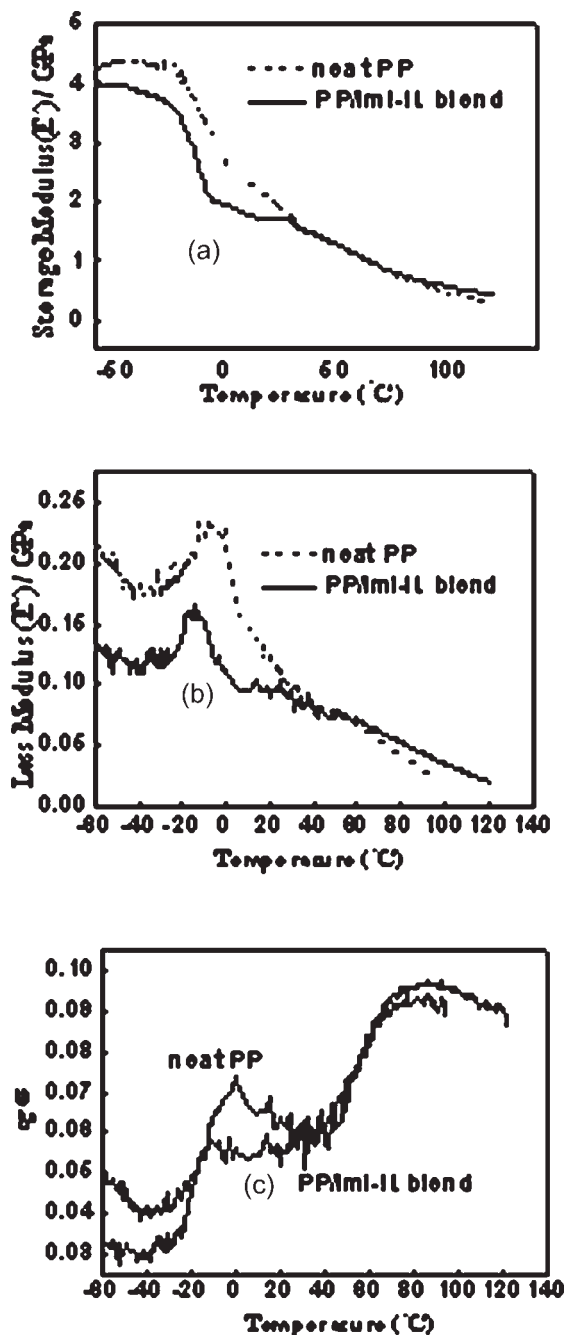

Figure 2 DSC curves for PP and PP/[C$_{14}$mim]Br blend.

Figure 3 DMA curves for PP and PP/[C$_{14}$mim]Br blend. (a) Storage modulus (E′), (b) loss modulus (E″), and (c) tan δ.

increasing of PP chains moving activity. This indicated the [C$_{14}$mim]Br existed in the PP matrix made the PP chains have higher moving activity. Moreover, there are only a melting peak and a crystallization peak in the DSC thermogram of PP/[C$_{14}$mim]Br blend showing a high compatibility of [C$_{14}$mim]Br with PP matrix in our experiment.

Dynamic mechanical thermal analysis

The effect of [C$_{14}$mim]Br on the PP molecular motions associated with the internal changes that

occur in PP/[C$_{14}$mim]Br blend can be investigated by DMA. The DMA spectroscopy, normalized for storage modulus(E′), loss modulus(E″), and tan δ as function of temperature for PP/[C$_{14}$mim]Br blend and neat PP were shown in Figure 3(a–c). In Figure 3(a), for neat PP there are two changes observed in the slope of the curve over the temperature range from −60 to 120°C. The first change corresponds to the segmental motions of the PP chain backbone which is due to the increase in the free volume of the PP with temperature, and the second is assigned as the glass transition temperature (T_g). In the E′ curve of PP/[C$_{14}$mim]Br blend (weight ratio of PP to [C$_{14}$mim]Br is 100/3), there are also two notable changes observed, but a rubbery plateau appeared after the second change between the temperature range of 10–25°C. This plateau could also be seen in E″ and tan δ curves depicted in Figure 3(b,c) signifying the existence of the rubbery state in PP relaxation process and the effects of [C$_{14}$mim]Br on the elastic contribution to PP. In lower temperature region of −60 to −20°C, neat PP shows a gradual change in the elastic contribution, whereas rapid change in PP/[C$_{14}$mim]Br blend. This infers the change in E′, therefore, the stiffness of PP can be modified with [C$_{14}$mim]Br. E′ of neat PP showed a sharp change than PP/[C$_{14}$mim]Br blend with increasing of temperature from 60 to 95°C, and modulus of neat PP could not be measured at 95°C for it began to flow. But the PP/[C$_{14}$mim]Br blend could retains modulus up to 120°C. This difference may be attributed to the effect of [C$_{14}$mim]Br on PP crystalline structure, which makes the PP crystal more perfectly and have higher melting temperature as we discussed in DSC results.

The appearance of peaks in the E″ or tan δ curves presented in Figure 3(b,c) is linked with increasing in the free volume, which is associated with the glassy-to-rubbery transition. As PP is the major component of PP/[C$_{14}$mim]Br blend, the main transitions observed in both E″ and tan δ are due to the glass transition of the amorphous region of the PP in the blend. However, the glass transition temperature (T_g) of PP changed from about −4 to −15°C (centered point of peak) since the 3 shares of [C$_{14}$mim]Br was incorporated into PP matrix via melting blend. These results indicate that the [C$_{14}$mim]Br has the effects on the plasticization and crystallization of PP.

TABLE I
Mechanical Properties of PP and PP/[C$_{14}$mim]Br Blend

	Neat PP	PP/[C$_{14}$mim]Br blend
Tensile strength MP	24.77	29.38
Impact strength (kJ/m^2)	1.64	2.27
Elongation at break	7.5	7.39

Mechanical properties of PP/[C$_{14}$mim]Br blend

Tensile strength and impact strength of neat PP and PP/[C$_{14}$mim]Br blend are listed in Table I. Tensile strength of neat PP and PP/[C$_{14}$mim]Br blend is the ultimate strength. The way of preparing neat PP and PP/[C14mim]Br blend, including their preparation of samples has been introduced in the experiment section.

Neat PP exhibited typical brittle fracture during the tensile experiment. Necking was observed in the neat PP, but the addition of [C$_{14}$mim]Br to the PP suppressed its tendency to neck. Both tensile strength and impact strength of PP matrix in the PP/[C$_{14}$mim]Br blend have been improved since the 3 shares of [C$_{14}$mim]Br was incorporated into 100 shares of PP. Whereas the elongation at break of the PP/[C$_{14}$mim]Br blend shows lower value than neat PP. This is a phenomenon of antiplasticization. Because the interactions of [C$_{14}$mim]Br-matrix affect the mobility and the physicochemical properties of PP chains, the free volume of PP chains gets larger, which improves the moving activity of PP chains. PP chains in the noncrystallization spaces create new crystal, and PP resin becomes more orderly and stiffer. The impact strength of PP depends on the moving activity of PP chains. An apparently increase of impact strength of PP in the PP/[C$_{14}$mim]Br blend was expected due to better moving activity of PP chains from the exist of [C$_{14}$mim]Br in PP matrix. The role of crystal structure of PP in its tensile strength, the effect of [C$_{14}$mim]Br on the crystal structure of PP matrix leads to higher tensile strength than neat PP.

Thermal stability of PP/[C$_{14}$mim]Br blend

To compare the thermal properties of the PP/[C$_{14}$mim]Br blend with neat PP, TGA curves, and their first derivatives (DTG) were shown in Figure 4(a,b). In Figure 4(a), the result indicates the onset decomposition temperature (T_{onset}) of PP/[C$_{14}$mim]Br blend is 384°C, which is almost the same with the T_{onset} of neat PP, indicates that the thermal stability of PP matrix is not declined by the incorporating of [C$_{14}$mim]Br, though the molecular weight of [C$_{14}$mim]Br is lower. DTG curves of PP/[C$_{14}$mim]Br blend and neat PP were presented in Figure 4(b). The DTG curve of PP/[C$_{14}$mim]Br blend presents almost same with that of neat PP, and its maximal weight loss point is about 485°C, relatively small difference with that of neat PP, which maximal weight loss point is about 480°C. Results of TGA suggest that the thermal stability of PP is not decreased by incorporating the [C$_{14}$mim]Br into it via melting blend, and the decomposed velocity of PP/[C$_{14}$mim]Br blend and neat PP is almost same.
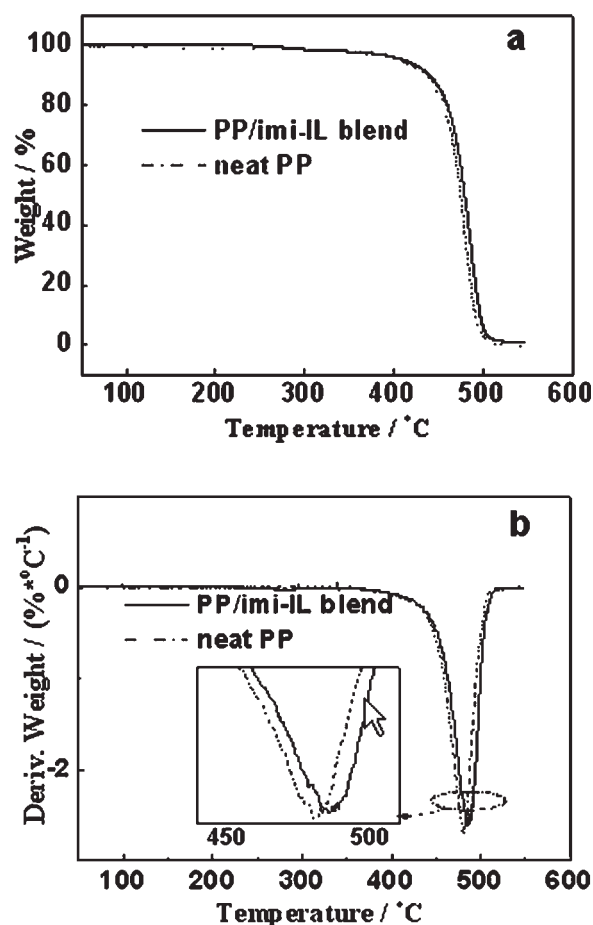

Figure 4 (a) TGA curves for PP and PP/[C$_{14}$mim]Br blend and (b) DTG curves for PP and PP/[C$_{14}$mim]Br blend.

Moreover, there is only one peak in the DTG curves of the PP/[C$_{14}$mim]Br blend indicates the high compatibility of [C$_{14}$mim]Br and PP matrix in the PP/[C$_{14}$mim]Br blend. The high thermal stability of [C$_{14}$mim]Br has also been concluded,[7] so that the properties of PP/[C$_{14}$mim]Br blend should not be down within its processing temperature range, even if there exists little uncommon decomposition and volatilization of [C$_{14}$mim]Br.

CONCLUSIONS

In this article, effects of [C$_{14}$mim]Br on the PP structures and properties were characterized by DSC, DMA, tensile testing, and impacting testing. Results show that the 3 shares of [C$_{14}$mim]Br incorporated into 100 shares of PP via melting blend have the effects on the plasticization and crystallization of PP, so that the PP/[C$_{14}$mim]Br blend has better tensile and impact strength than those of neat PP. TGA result shows PP/[C$_{14}$mim]Br blend have good thermal stability over a wide range of temperature (T_{onset} is 384°C) and the thermal stability of PP ma-

trix was not affected by incorporating the [C$_{14}$mim]Br into it, though its molecular weight is lower.

References

1. Sarbu, T.; Matyjaszewski, K. Macromol Chem Phys 2001, 202, 3379.
2. Scott, M. P.; Brazel, C. S.; Benton, M. G.; Mays, J. W.; Holbrey, J. D.; Rogers, R. D. Chem Commun 2002, 13, 370.
3. Scott, M. P.; Benton, M. G.; Rahman, M.; Brazel, C. S. In Ionic Liquids as Green Solvents: Progress and Prospects; Rogers, R. D.; Seddon, K. P., Eds.; American Chemical Society: Washington, DC, 2003; p 468. American Chemical Society Symposium Series Vol. 856.
4. Scott, M. P.; Rahman, M.; Brazel, C. S. Eur Polym J 2003, 39, 1947.
5. Rahman, M.; Benton, M. G.; Scott, M. P.; Brazel, C. S. Proc Green Chem Eng Conf 2003, 7, 180.
6. Karian, G. H. Handbook of Polypropylene and Polypropylene Composites; Marcel Dekker: New York, 2003; p 155.
7. Ding, Y. S.; Zha, M.; Zhang, J.; Wang, S. S. Colloids Surf A 2007, 298, 201.