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Application of ionic liquid [bmim]PF_6 as green plasticizer for poly(L-lactide)

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Abstract: Ionic liquid [bmim]PF_6 (1-butyl-3-methylimidazolium hexafluoro phosphate) was synthesized and characterized. It was used as the plasticizer for poly(L-lactide) (PLLA). The glass transition temperature (T_g) and the thermal stability of the plasticized PLLA samples were measured by thermogravimetry (TG) and differential scanning calorimetry (DSC). Compared with poly(ethylene glycol) having M_w of 300 g/mol (PEG_{300}), TG results showed that the thermal stability of PLLA plasticized with ionic liquid was better than that of PLLA plasticized with PEG_{300}. The T_g of plasticized PLLA decrease with increasing the content of ionic liquid [bmim]PF_6 from 2 wt.% to 10 wt.%. The T_g of PLLA can be reduced to 40 ^oC when the content of ionic liquid [bmim]PF_6 was 10 wt.%. The materials of PLLA with plasticizer were also investigated using polarizing microscope (POM), the results of which indicate that the movements of PLLA chains were improved when ionic liquid plasticizer was used.

Keywords: ionic liquid, poly(L-lactide), plasticizer, crystallization.

Introduction

Recently, biodegradable polymers have attracted great interest for their environmental friendly applications [1]. The most popular and important biodegradable polymers are aliphatic polyesters, such as polylactide (PLA), poly(glycolic acid) (PGA), poly(ε-caprolactone) (PCL) and poly(β-hydroxybutyrate) (PHB). Among these biodegradable polymers, polylactide was studied extensively because it is producible from renewable resources such as starch and is biodegradable and compostable without any harmful effects on the environment. Moreover, it has high mechanical performance comparable to those of commercial polymers such as polyethylene and polystyrene [2, 3]. PLA has already been applied in biomedical, pharmaceutical and other fields [4-7]. Due to its higher cost, the initial focus of PLA as a packaging material has been in high value films, rigid thermoforms, food and beverage containers and coated papers [8]. Recent advances in polymerization technologies mean that the previously expensive PLA-polymers now have a good chance of being introduced in such low-priced packaging applications [9].

However, PLA is a rather brittle and rigid polymer. In order to improve the processability, flexibility and ductility of glassy polymers, plasticizers are widely used in the processing of thermoplastic material. Low volatility and thermal stability are crucial characteristics of practical plasticizers. The common used plasticizers such as phthalates had limited use for PLA owing to their leaching and migration [10]. The lactide monomer is an excellent plasticizer for PLA, however it tends to migrate at the material surface, causing the surface to turn sludgy. Poly(ethylene glycol) (PEG) has been reported as plasticizer for PLA [11-13], but its thermal stability is not satisfactory yet.

Ionic liquids (ILs) are salts consisting entirely of ionic species that are fluid at room or near-room temperature [14-15], with many fascinating properties such as negligible vapor pressure, a wide liquids range, high thermal and chemical stability and excellent solubility for many compounds. They are also emerging as a new class of ‘green solvents’ or soft materials especially enormous attention for alternative environmentally benign reactions [16-17] and separation processes [18-19]. Recent studies indicate ionic liquids have a great potential to be used as performance additives [10, 20-22].

In this paper, ionic liquid [bmim]PF_6 (1-butyl-3-methylimidazolium hexafluoro phosphate) was synthesized and characterized. The studies focus on its new applications as the plasticizer for poly(L-lactide). The effect of plasticization was determined by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and polarizing microscope (POM).

Results and discussion

Structure analysis of [bmim]PF6

The chemical structure of [bmim]PF_6 is described in Fig. 1. Its structure was confirmed by FT-IR and ^{1}H NMR.

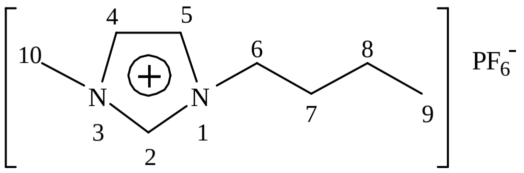

Fig. 1. Molecular structure of ionic liquid [bmim]PF_6.

Thermal stability of PLLA and plasticized PLLA

The TG curves of PLLA and PLLA plasticized with PEG_{300} are shown in Fig. 2. It can be found that the onset temperature of pure PLLA was about 300 ^oC and the 50% weight loss temperature was 345 ^oC; the sample was decomposed completely as temperature reached over 410 ^oC. Fig.2 shows that the onset temperature of PEG_{300} was approximately 200 ^oC and PEG_{300} decomposed completely as temperature got beyond 300 ^oC. It clearly indicates that the thermal stability of PEG_{300} is less than PLLA. 50% weight loss temperature was also an evaluating method for thermal stability; the 50% weight loss temperatures of each plasticized PLLA were 337 ^oC, 334 ^oC, 319 ^oC, 293 ^oC, 266 ^oC, when the weight ratios of PLLA/PEG_{300} were 98/2, 97/3, 96/4, 95/5, 90/10 respectively. The decomposition temperature decreases when the content of PEG_{300} increased. The thermal stability of PLLA plasticized with PEG_{300} become worse due to the decomposed temperature of PEG_{300} being lower than that of PLLA, so that the application of PLLA/PEG_{300} is limited in some high temperature environment.

For [bmim]PF6 being used as PLLA plasticizer, the TG curves of plasticized PLLA are shown in Fig. 3. It can be found that [bmim]PF_6 showed little evaporative loss from 0 °C to 350 °C and the 50% weight loss temperature was 427 °C. As shown in Fig. 3, all PLLA plasticized with [bmim]PF_6 were more stable than that of pure PLLA.

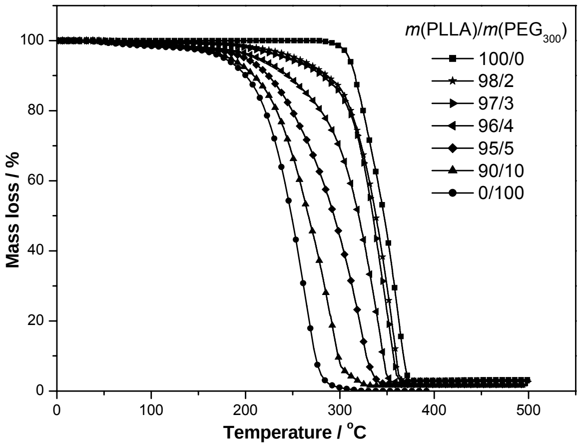

Fig. 2. Thermal stability of PLLA with PEG_{300} as plasticizer.

The 50% weight loss temperature of each plasticized PLLA were 347 °C, 355 °C, 362 °C, 369 °C, 380 °C, in which case the weight ratios of PLLA/[bmim]PF_6 were 98/2, 96/4, 94/6, 92/8, 90/10 respectively. When the content of [bmim]PF_6 increase, the decomposition temperature of PLLA samples increase correspondingly. [bmim]PF_6 provide a significant advantage over PEG for plasticization, especially for PLLA that are used at high temperature.

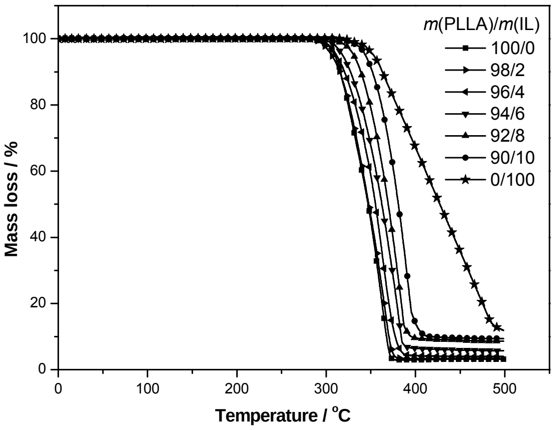

Fig. 3. Thermal stability of PLLA with [bmim]PF_6 as plasticizer.

Glass transition of PLLA and plasticized PLLA

The glass transition temperature (T_g) is crucial for polymeric materials because the properties of thermoplastic polymers were determined by T_g. Plasticizers are often used in polymers to reduce the glass transition temperature (T_g), so that the polymer's processing can be successfully performed. Furthermore, the effects of plasticization can be evaluated by T_g. The glass transition temperatures of PLLA and plasticized PLLA can be measured by DSC. Some studies of PLLA plasticized with poly(ethylene glycol) (PEG) have proved that low molecular weight PEGs can reduce the T_g of PLLA efficiently [11-13]. The T_g of PLLA plasticized with PEG is reduced to 45 °C when the PEG content was 10 wt. %.

The DSC curves of pure PLLA and PLLA plasticized with [bmim]PF_6 are shown in Fig. 4, from which it can be found that the T_g of pure PLLA is about 58 °C. The T_g of plasticized PLLA decreased with increasing amounts of [bmim]PF_6, e.g. the T_g of plasticized PLLA decreased to 55 °C, when the [bmim]PF_6 content was 2 wt. %; when the [bmim]PF_6 content was 10 wt. %, the T_g of plasticized PLLA reduced to 40 °C remarkably. [bmim]PF_6 does indeed act as a plasticizer for polymer with a performance that is comparable with that of conventional plasticizers which function by reducing the normal intermolecular forces in a resin thus permitting the macromolecules to slide over one another more freely. All samples of PLLA plasticized with [bmim]PF_6 were transparent and DSC curves exhibited single peaks of T_g indicating that [bmim]PF_6 was compatible with PLLA.

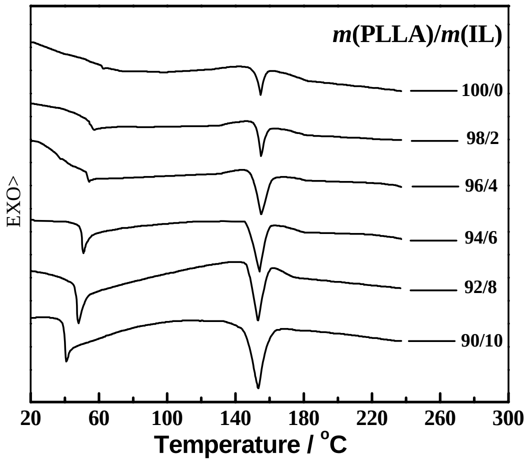

Fig. 4. DSC results of PLLA with [bmim]PF_6 as plasticizer.

Polarized optical microscopy analysis

Polarized optical microscopy of pure PLLA and plasticized PLLA are shown in Fig. 5. It can be seen that for neat PLLA, the structure consists of a large number of small spherulites, when [bmim]PF_6 were added to the semicrystalline PLLA, the spherulitic structure of PLLA dominated and the spherulite size increased with increasing concentrations of [bmim]PF_6. The crystallization rate of plasticized samples increased obviously, and the degree of crystallinity also augmented. It is coincident with the DSC results that melting crystal peaks broaden with increasing [bmim]PF_6 content. It is known that the crystal growth was inhibited in the presence of amorphous polymers in the systems of crystal polymers/amorphous blends. But the movement of molecular chains can be enhanced because the viscosities of plasticizers were far lower than that of polymers and their good compatibility. So [bmim]PF_6 accelerates the growth of spherulitic crystal.

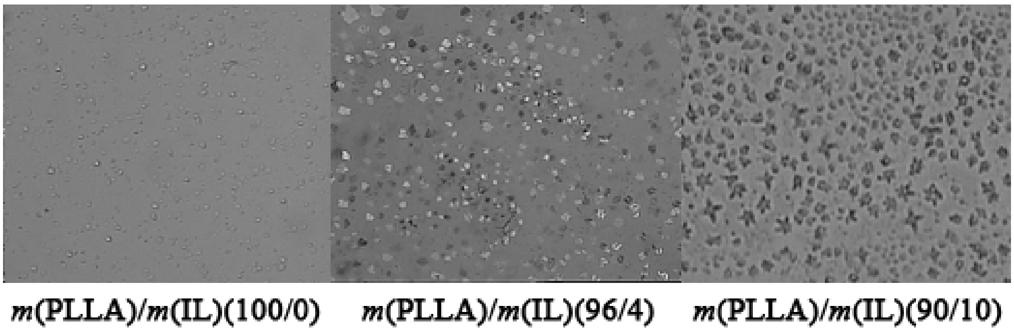

Fig. 5. Polarized optical micrographs of wide range PLLA/IL samples.

Conclusions

The results presented here represent the feasibility of using ionic liquids as plasticizers for PLLA. The glass transition temperature (T_g) of plasticized PLLA decreased with increasing ionic liquids contents. Plasticized PLLA also exhibit excellent thermal stability at high temperatures.

Experimental part

Materials

1-methylimidazole, [mim] (Acros, AR) and hexafluorophosphoric acid (Acros, 60 wt.%, solution in water) were used without further purification. PLLA (M_w=8.05×10^4 g/mol, PDI=1.34), PEG_{300}, 1-chlorobutane, ethyl acetate and AIBN were commercially obtained and were used as received.

Sample preparation

[bmim]PF6 was synthesized according to the literature [18, 20] (yield 75%). The molecular structure of [bmim]PF6 was identified by Nicolet AVATAR-360 FT-IR spectrometer (KBr pellet), and ^{1}H NMR were recorded on a Bruker AVANCE 400 spectrometer, using $CDCl_3$ as the solvent.

The typical FT-IR spectrum value of specific peaks of [bmim]PF_6 are as follows: 3171.73cm^{-1}, 3125cm^{-1} [v(C-H), aromatic], 2966.24cm^{-1}, 2873.37cm^{-1}[v(C-H), acyclic], 838.69cm^{-1}[v(P-F)], 1576.05cm^{-1} and 1466.82cm^{-1}[v(C=C)].

The ^{1}H NMR results of [bmim]PF_6 are as follows: δH 8.440(s, 1H, CH); 7.100(s, 1H, CH); 7.011(s, 1H, CH); 3.896(t, 2H, CH_2); 3.624(t, 3H, CH_3); 1.652(m, 2H, CH_2); 1.158(m, 2H, CH_2); 0.661(t, 3H, CH_3).

Plasticized samples of PLLA were prepared using a solvent casting method. The weight ratios of PLLA/ionic liquid mixtures were 98/2, 96/4, 94/6, 92/8 and 90/10 respectively. All samples were solubilized in tetrahydrofuran (THF), the solutions (20 g/L) were cast on glass petri dishes, and the solvent was allowed to evaporate at room temperature. All obtained films were further dried overnight under vacuum at 40 °C to eliminate residual solvent.

Thermogravimetry

A Mettler Toledo 851^e TGA/SDTA thermogravimetric analyzer was used to monitor weight loss of pure and plasticized PLLA samples. Approximately 5 mg samples were placed in aluminum pans where the test was carried out under nitrogen atmosphere. For temperature ramp experiments, the samples were heated from 0 °C to 500 °C at 10 K/min, with the weight data collected continuously.

Differential scanning calorimetry

The glass transition temperatures of pure and plasticized PLLA samples were measured using Mettler Toledo DSC822^e differential scanning calorimetry. Polymer samples of 5-8 mg weight were placed in aluminium pans, against an empty reference pan, and T_g was determined by the inflection in heat flow as the temperature increased. The samples were subjected to an initial temperature ramp to 250 °C to remove their thermal history, then recooled quickly using liquid nitrogen, and finally heated at 10 K/min to 250 °C, during which the T_g was determined.

Polarizing microscope

The samples was observed using Leica DMLP polarizing microscope. Samples were heated to 250 °C for 2 min and cooled to 120 °C. Then the micrographs were recorded.

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