Asian Journal of Chemistry; Vol. 26, No. 6 (2014), 1745-1747

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17342

Ionic Liquid [Bmim]PF_6 Plasticize Polylactic Acid†

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Published online: 10 March 2014; AJC-14883

Room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) was studied as novel plasticizers for polylactic acid. The mixture process was carried out in molten state. [Bmim]PF_6 were found to be excellent plasticizers for polylactic acid, with improved thermal stablity and plasticity. The microstructure indicated that novel plasticizer make agglomeration of $CaCO_3$ particles and phase separation easy, which might be due to the reduction of melt viscosity and the [Bmim]PF_6 concentration on the $CaCO_3$ particles.

Keywords: Ionic liquid, Polylactic acid, Mechanical properties, Thermal stability.

INTRODUCTION

Polylactic acid (PLA) is one of the most studied biodegradable polymers mainly because of its high mechanical properties and easy production from its monomer. At present, the monomer of PLA is produced by fermentation from agricultural products. Polylactic acid is eco-friendly and exhibits interesting physical properties, which can be further modulated by simply blending with selected additives in the molten state. In spite of all these advantages, its range of application is still limited by high production cost, brittleness and low thermal stability[1].

Plasticizers are added to polymer formulations to reduce glass transition temperature and impart flexibility to materials under conditions where they are normally used. Dioctyl phthalate (DOP) is the most widely used plasticizer, as it is highly compatible with polymers[2]. Dioctyl phthalate is being questioned worldwide because of their potential toxicity to humans and the environment, so it is a huge challenge to develop new plasticized materials that have better performance in harsh environments, longer lifetimes and reduced toxicity. In this context, ionic liquids (ILs) are currently being presented as interesting alternatives to replace plasticizers[1-6]. The general properties of ionic liquids, such as negligible vapor pressure, non-flammability, chemical and thermal stability, enable their use as solvents, thermal fluids, lubricants, dispersants and surfactants, antimicrobial agents and so on. Moreover, ionic liquids have already been proved to be a efficient plasticizers for both synthetic[1-7] and natural-based polymers[8].

In this study, ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) was used as plasticizer of PLA. The effect of [Bmim]PF_6 dosage on mechanical properties, processing performance and thermal stability have been evaluated by tensile and impact strength test, TGA/DTA and SEM.

EXPERIMENTAL

Polylactic acid (PLA706) was purchased from Zhejiang Hisun Biomaterials Co., Ltd. [Bmim]PF_6 was purchased from Lanzhou Institute of Chemical Physics. Polylactic acid was dried at 60 ºC for 24 h before use. Reagents were used as received without further purification. Direct addition of [Bmim]PF_6 into the molten PLA in the mixing process. The concentrations of ionic liquids was 0, 0.4, 0.8, 1.2 and 2 %, respectively. Melt-kneading continued 6 min at 130 ºC. The blends of PLA/[Bmim]PF_6 was forming a sheet of 4 mm after melt-kneading.

Techniques used to analyze the plasticized polymer samples included Impact Tester (Tanhor, TCJ-25J, CHN), Universal Testing Machine (Kaiqiangli, WDW-50,CHN), Melt Indexer (Tanhor, RZY-400, CHN), Thermogracimetric Analysis (TA, SDT2960, USA) and Scanning Electron Microscopy (Hitachi, S-3000N, JPN). Mechanical properties was tested according to GB/T 1040-1992 and GB/T 1043-1992.

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

Melt Indexer was tested according to GB/T 3682-2000. TG was conducted using a thermal ramp rate of 10 K/min from 30-400 ℃.

RESULTS AND DISCUSSION

Polylactic acid materials are stiff, brittle and limited extendibility, [Bmim]PF_6 modified PLA substantially improved the ductile mechanical properties, as shown in Fig. 1. The prepared new ductile materials showed higher impact strength with the dosage of ionic liquids, but lower tensile strength. For the PLA modified with 2 % [Bmim]PF_6, impact strength was increased from 15.97 to 36.31 KJ/m^2, tensile strength was decreased from 53.0 to 41.8 MPa. Mechanical properties and the amount of ionic liquids showed linear trend in our experiments.

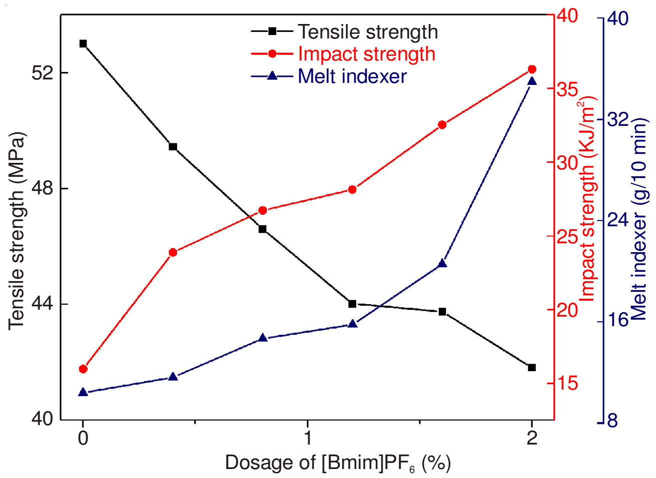

Fig. 1. Mechanical properties of [Bmim]PF_6 modified PLA materials

We evaluated the thermal stability of polylactic acid based on the TG/DTG. The thermal decomposition temperatures at 20 % (A point) and 50 % (B point) weight loss was connected with a line, which crossed with the baseline at C point. The temperature of C point was named as decomposition temperature of the PLA samples. The peak of DTG curve (D point) was the maximum weight lose rate temperature. In previous studies of ductile PLA, general plasticizers improved the ductility of PLA, but reduced the thermal properties of PLA. In contrast, the addition of [Bmim]PF_6 maintained the good thermal stability of PLA (Fig. 2) while improving the ductile mechanical properties of PLA (Fig. 1). the PLA/[Bmim]PF_6 showed much better thermal stability than pristine PLA. The decomposition temperature raise 10-36 ℃ and the maximum weight lose rate temperature raise 16-20 ℃, which can be attributed to the high temperature stability of ionic liquids.

The morphology was elucidated by SEM to investigate the microstructure of modified materials. In Fig. 3a, pristine PLA showed a smooth and dense morphology. The white particles in the images was $CaCO_3$ particles which was mixed in the PLA in their produce process. When PLA was modified with [Bmim]BF_6 to prepare the ductile polymer material, the morphology of the fracture surface changed substantially. The $CaCO_3$ particles agglomerated and phase separation between PLA and $CaCO_3$ particles became difficult. The agglomeration

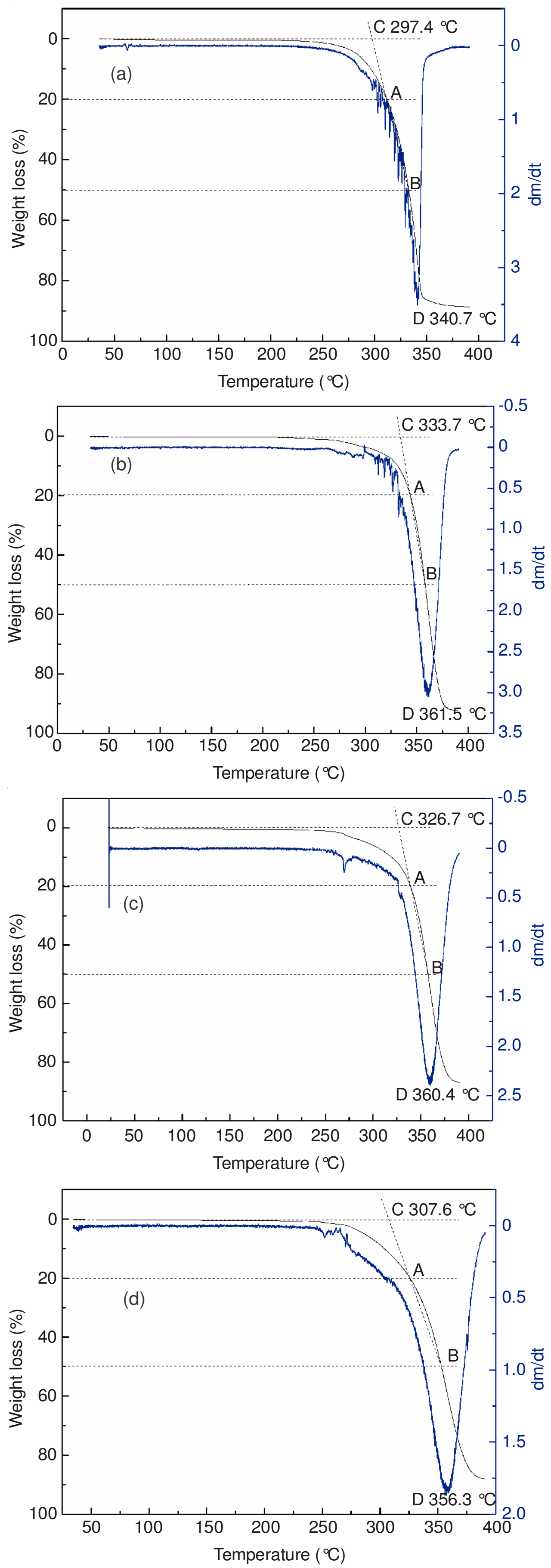

Fig. 2. TGA scan of PLA/[Bmim]PF_6 samples, A: 0 % [Bmim]PF_6; B: 0.4 % [Bmim]PF_6; C: 1.2 % [Bmim]PF_6; D: 2.0 % [Bmim]PF_6;

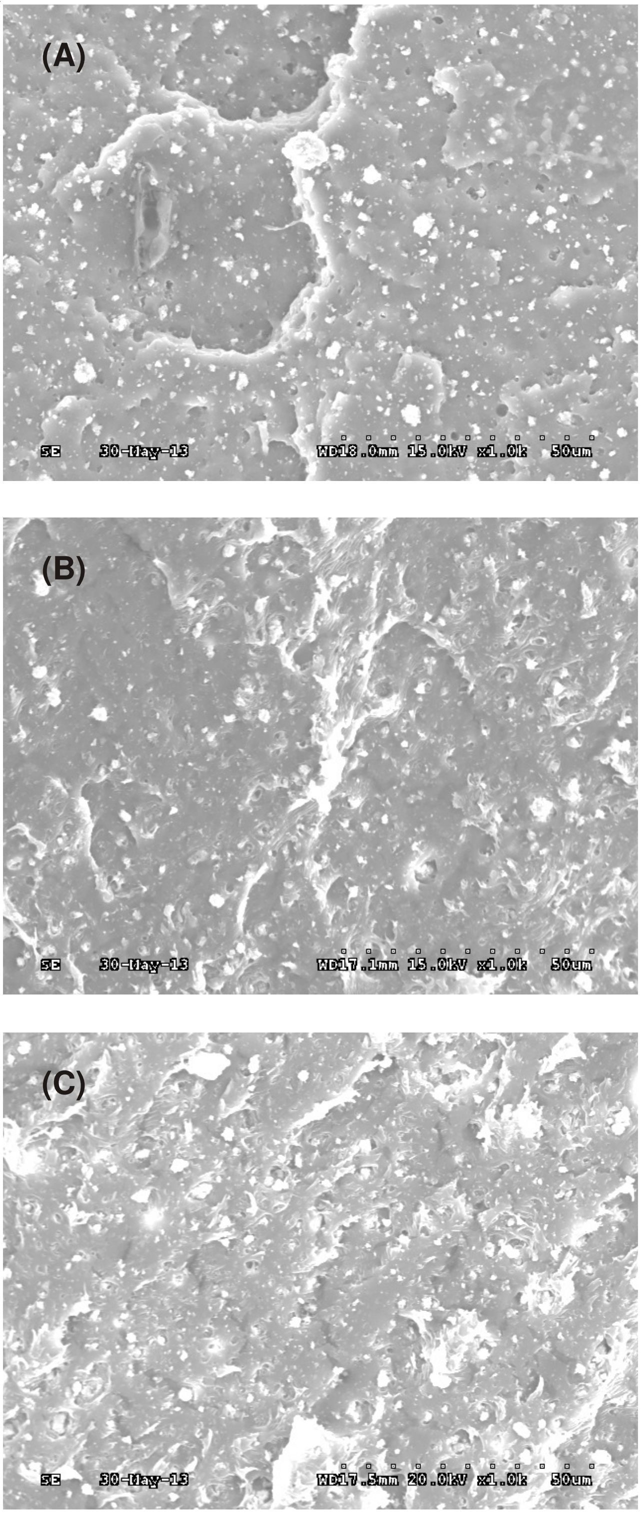

Fig. 3. SEM morphology of the samples fracture surface, A: 0 % [Bmim]PF_6; B: 0.4 % [Bmim]PF_6; C: 1.2 % [Bmim]PF_6

of $CaCO_3$ particles occurred in the course of plasticizing, the melt viscosity of PLA caused a strong reduction after the addition of [Bmim]PF_6, that had been proved based on strong increase of melt indexer (Fig. 1). That might make $CaCO_3$ particles agglomerate easy. The phase separation between PLA and $CaCO_3$ Particles might due to ionic liquids trend to concentrate on $CaCO_3$ Particles.

Conclusion

Ionic liquid [Bmim]PF_6 modified PLA demonstrated markedly improved ductile mechnical properties. The thermal stability of PLA became better, the decomposition temperature raise 10-36 ºC and the maximum weight lose rate temperature raise 16-20 ºC. Agglomeration of $CaCO_3$ particles and phase separation were found at samples fracture surface, which might due to the reduction of melt viscosity and the [Bmim]PF_6 concentration on the $CaCO_3$ particles. Ionic liquids as plasticizers may revolutionize the usage of flexible polymers at high temperatures, without brittleness or loss of mechanical strength. However, the ionic liquids is still expensive compared general plasticizers and limit its widespread application, the potential threat of ionic liquids to human and environment is still not clear.

ACKNOWLEDGEMENTS

This work is financially supported by Young Teacher Research Fund of Anhui University of Science and Technology (2012QNZ03).

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