Chemical Engineering Journal 255 (2014) 513–524

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Ionic liquids: A new way for the compatibilization of thermoplastic blends

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HIGHLIGHTS

- Ionic liquids: new compatibilizers of thermoplastic blends.
- Compatibilizing effect of phosphonium ionic liquids.
- Improvement of thermal and mechanical properties of PP/PA6 blends.

ARTICLE INFO

Article history:
Received 22 February 2014
Received in revised form 17 June 2014
Accepted 20 June 2014
Available online 27 June 2014

Keywords:
Ionic liquids
Polymer blends
Thermoplastic
Compatibilization

ABSTRACT

Ionic liquids based on tetraalkylphosphonium salts combined with different anions (phosphinate versus trifluoromethylsulfonylimide) have been used as new compatibilizers of polymer blends. To highlight the effect of thermostable ionic liquids, a very low amount of ILs (1–10 wt%) have been introduced within a PP/PA blend (80/20) and the polymer blends have been processed in melt by twin-screw extrusion. Transmission electron microscopy (TEM) analysis has been used to investigate the influence of ILs on the different morphologies of these binary blends. In addition to having improved thermal stability, an excellent stiffness–toughness compromise has been obtained (+1400%).

1. Introduction

For many years, it is well known that polymers such as polyolefins (PP, PE) and engineering plastics (PC and PA) are the most recycled polymer materials [1,2]. For this reason, academic and industrial research has focused its attention on improving the properties of the polymer blends. Thus, polymer blends composed of polypropylene (PP) and polyamide 6 (PA6) are most commonly studied in the literature [3,4]. Indeed, many authors have worked on polymer blends composed of PP/PA6 (i) with a phase rich in PA or (ii) with a phase rich in PP in order to combine the properties of the corresponding neat polymers. For example, the addition of PP (minor phase) leads to a decrease of water absorption and to improve the impact resistance of PA. In the opposite, blends with a phase rich in PP, the addition of PA leads to an increase of chemical and heat resistance. Nevertheless, in both cases and due to the immiscibility of these polymers, the bad interactions at molecular level lead to a high interfacial tension. This also induces unstable morphologies with the presence of large domain size for the minor phase and poor interfacial adhesions which are the main causes of poor mechanical performance of polymer blends [5]. For this reason, in order to develop new polymer materials at low cost combined with improved final properties; the use of compatibilizing agents is required. Generally, two main routes were investigated: One is the use of copolymers and ionomers which has a chemical affinity with two immiscible polymers. For example, Ide and Hasegawa used maleic anhydride grafted PP (PP-g-MA) where large amount are needed (20 wt%) to improve the final properties of polymer blends [6]. Different authors have also used ionomers such as Surlyn®9020 which have methacrylic acid functional groups partially neutralized with zinc ions [7]. They concluded that the addition of only 0.5 wt% of the ionomer was sufficient to produce the finest dispersion of the PA minor phase in the PP matrix due mainly to the strong hydrogen bonding interactions occurring between the ionomer and the polyamide. The second way is the use of nanoparticles such as silica [8,9], layered silicates [10–13]

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http://dx.doi.org/10.1016/j.cej.2014.06.080
1385-8947/

and carbon nanotubes [14] to stabilize the morphologies of polymer blends.

Recently, ionic liquids (ILs) especially known for their excellent thermal and chemical stability, their non-flammability and their low saturated vapor pressure are commonly used as surfactant, lubricant, plasticizer, building blocks or processing aids of polymer matrices [15–22]. More recently, Leroy et al. have studied the starch–zein melt processed blends by using an ionic liquid as plasticizer agent [23]. In this study, the ionic liquid in addition to being an excellent plasticizer is also an excellent compatibilizer of biopolymer blends leading to a decrease in the size of the zein aggregates. However, from our knowledge, no paper described the use of ionic liquids as compatibilizing agents of thermoplastic blends.

In this paper, a new route of compatibilization of polymer blends using phosphonium ionic liquids as compatibilizers has been developed and described. Then, their influences in a PP/PA blends as well as the consequences of this structuration on the thermal, physical and mechanical properties have been investigated.

2. Experimental

2.1. Materials

Polypropylene HP500N (density 0.9 g/cm^3, molecular weight 260 kg/mol, polydispersity index 3.3, melt flow index 12 g/10 min [230 °C, 2.16 kg], melting temperature 167 °C) was supplied by LyondellBasell (France). Polyamide 6 (PA6) under commercial name Technyl S-27 BL (density 1.13 g/cm^3, melting temperature 222 °C) was produced by Rhodia Engineering Plastics (France).

The two ionic liquids based on phosphonium cations with different anions and different molar masses were provided by Cytec Industries Inc and are presented in Table 1. They include:

- Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide named as IL-TFSI (Mm = 764 g/mol)
- Trihexyltetradecylphosphonium bis 2,4,4-(trimethylpentyl) phosphinate designated as IL-TMP (Mm = 773 g/mol)

2.2. Processing and instrumental characterization of the polymer blends

Before extrusion, polyamide 6 pellets were dried at 80 °C in a vacuum overnight. Polymer blends based on PP/PA and PP/PA/IL (1–5–10–20% by weight) were prepared under nitrogen atmosphere using a 15 g-capacity DSM micro-extruder (Midi 2000 Heerlen, The Netherlands) with co-rotating screws. The mixture was sheared for about 10 min with a 240 rpm speed at 240 °C and injected in a 10 cm^3 mould at 80 °C to obtain dumbbell-shaped specimens. All the compositions of the blends are shown in Table 2.

Thermogravimetric analyses (TGA) of PP/PA and PP/PA/IL blends were performed on a Q500 thermogravimetric analyser (TA instruments). The samples were heated from 30 to 700 °C at a rate of 20 K min^{-1} under nitrogen flow.

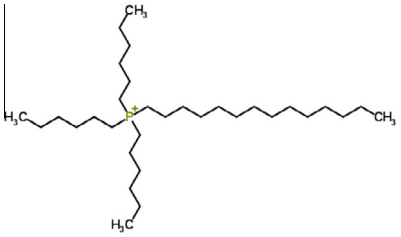
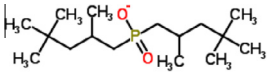
DSC measurements (DSC) of nanocomposites were performed on a Q20 (TA instruments) from 30 to 270 °C for PP/PA and PP/PA/ILs. The samples were kept for 3 min at 270 °C to erase the thermal history before being heated or cooled at a rate of 10 K min^{-1} under nitrogen flow of 50 mL min^{-1}. The integration of the exothermic peaks during the non-isothermal crystallization process was carried out to calculate the relative crystallinity as a function of time. The half crystallization time $t^{1/2}$, represents the time needed to achieve 50% of the entire crystallization kinetics. The crystallinity χ_c (%) of PP and PA6 phases in the blend were calculated by using the following equation:

$$\chi_c(\%) = \frac{\Delta H}{\Delta H^0 \cdot w} \times 100$$

where ΔH is the specific melting enthalpy of the sample measured in the second heating cycle of DSC experiments, ΔH^0 is the theoretical melting enthalpy of the 100% crystalline polymer matrix (209 J/g for PP [24] and 190 J/g for PA6 [25]) and w is the weight fraction of PP or PA6 in the blend.

Surface energy of polymer blends was determined with the sessile drop method using a GBX goniometer. From contact angle measurements performed with water and diiodomethane as probe liquids on discs obtained from anionic clay powders by pressing, polar and dispersive components of surface energy were determined by using Owens–Wendt theory [26].

Table 1
Designation of ionic liquids used.

Commercial name	Abbreviation	Cation structure	Anion structure
CYPHOS® IL104	IL-TMP		
CYPHOS® IL109	IL-TFSI