



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.

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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%).

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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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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/cm³, 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/cm³, 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 cm³ 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.

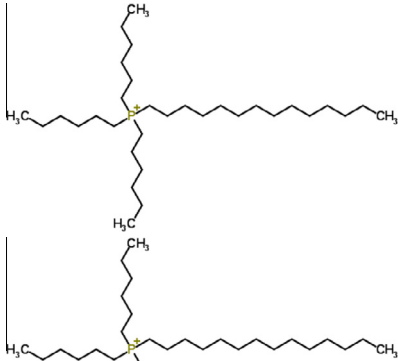
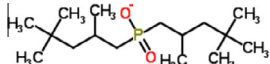
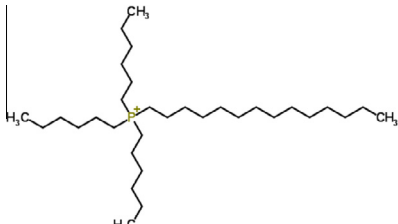

Commercial name	Abbreviation	Cation structure	Anion structure
CYPHOS® IL104	IL-TMP		
CYPHOS® IL109	IL-TFSI		

Table 2

Composition of the PP/PA and PP/PA/IL blends.

Sample	Designation	m(PP):m(PA6): m(IL)
B ₀	PP:PA6	80 :20:0:0
B ₁	PP:PA6:IL-TMP-1%	80 :20:1
B ₂	PP:PA6:IL-TMP-10%	80 :20:10
B ₃	PP:PA6:IL-TMP-20%	80 :20:20
B ₄	PP:PA6:IL-TFSI-1%	80 :20: 1
B ₅	PP:PA6:IL-TFSI-10%	80 :20:10

Transmission Electron microscopy (TEM) was carried out at the Technical Center of Microstructures (University of Lyon) on a Phillips CM 120 microscope operating at 80 kV to characterize the distribution of PA6 phases in PP matrix. The samples were cut using an ultramicrotome equipped with a diamond knife, to obtain 60-nm-thick ultrathin sections. Then, the sections were set on copper grids. ImageJ Software (U.S. National Institutes of Health) was used to estimate the average diameters of PA6 domains and their distribution in each sample.

The dynamic rheological measurements were performed using ARES rheometer (TA Instrument) conducted at 240 °C with plate-plate geometry. A diameter of 40 mm and a gap of 1.0 mm was used to measure the complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') of the blends.

The storage modulus (E') and the loss modulus (E'') and the mechanical loss factor ($\tan\delta = E''/E'$) as a function of temperature (T), were assessed by Dynamic Mechanical Thermal Analysis (DMTA) using on a Rheometrics Solid Analyzer RSA II at 0.1% tensile strain and a frequency of 1 Hz. The heating rate was 3 K/min for the temperature range from –100 to 150 °C.

Uniaxial Tensile Tests were carried out on a MTS 2/M electromechanical testing system at 22 ± 1 °C and $50 \pm 5\%$ relative humidity at crosshead speed of 40 mm min⁻¹. Young's modulus measurements were taken by means of an extensometer using an Instron 4301 machine at a cross-head speed of 1 mm min⁻¹. A minimum of five tensile specimens were tested for each reported value.

3. Results and discussion

3.1. Characterization of polymer blends

3.1.1. Effect of ionic liquids on the morphology of polymer blends

Transmission electron microscopy is the most suitable tool to highlight the influence of ILs on the morphology of polymer blends.

With only 1 wt% of IL-TMP and IL-TFSI, the distribution and dispersion of PA phases in polypropylene matrix are reported in Fig. 1.

Due to the poor interactions at the molecular level and the relatively high interfacial tension between PP and PA6, a phase-separated morphology combined with a poor interfacial adhesion is generated spontaneously. In fact, a continuous PP phase with dispersed PA6 domains has been observed (Fig. 1a). Thus, using image analysis, PA6 phases had diameters in the range of 27.1 ± 8.3 μm .

Then, the influence of the chemical nature of the anion (phosphinate versus bis(trifluoromethylsulfonyl)imide i.e. IL-TMP versus IL-TFSI) has been investigated on the morphologies of polymer blends. In both cases, the use of only 1 wt% of ILs leads to a significant decrease of the PA6 domains. Indeed, for PP/PA6/ILs ternary blends, the morphology changed dramatically where the size and polydispersity of PA6 particles dropped significantly: (i) with 1% of IL-TMP, the diameter of the aggregates of PA6 is smaller than 3 μm whereas (ii) with 1% of IL-TFSI, the mean diameter is 2.8 μm . This phenomenon is commonly encountered in polymer blends when nanoparticles, copolymers or ionomers are used [7,27,28]. For example, Willis et al. have demonstrated that the use of 5% of ionomer composed of 80% PE and 20% of methacrylic acid, partially neutralized with zinc in PP/PA6 (90/10) lead to a decrease in the size of the PA6 phases from 2.69 to 1.11 μm [7]. More recently, Fenouillot et al. have also demonstrated that the use of nanoparticles in a polymer blends act like an emulsifier which stabilize the mixture [29]. Finally, ionic liquids act as nanoparticles because an accumulation of ILs at the interphase leads to a formation of a barrier around the minor phase which prevents the coalescence of PA domains leading to the formation of smaller particles (Fig. 2) [30]. In addition, a small amount of ionic liquid is required to improve the compatibilization of PP/PA blends compared to the use of the copolymer such as maleated propylene (PPgMA) requiring amount of 10–20 wt% [31–33].

Moreover, to confirm these results, the influence of the concentration of ionic liquids in the polymer blend was also studied. TEM micrographs are presented in Fig. 3. The variation of the mean diameter of PA6 nodules in ternary blends are shown in Fig. 4.

When increasing the amount of ionic liquid in the polymer blends, a decrease in the size of the PA6 phases is obtained. In particular, for 10 wt% of ionic liquid introduced into the binary mixtures. In fact, the mean diameter in the presence of 10 wt% of IL-TMP and IL-TFSI lead to size of 1.8–1.9 μm respectively. In the opposite, the use of 20 wt% of ILs induces an increase in the size

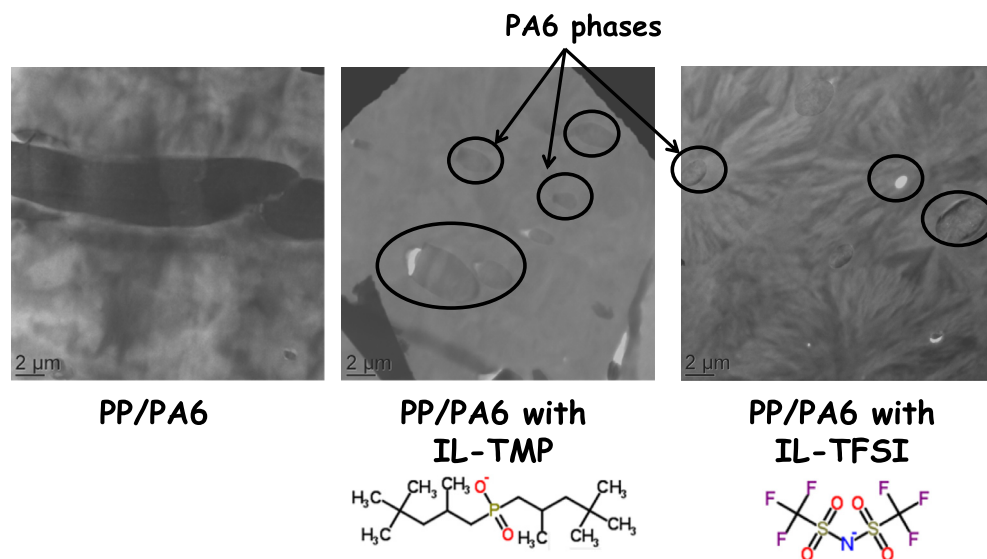


Fig. 1. TEM micrographs showing the influence of the chemical nature of the counter anion on the morphologies of polymer blends (IL-TMP versus IL-TFSI).

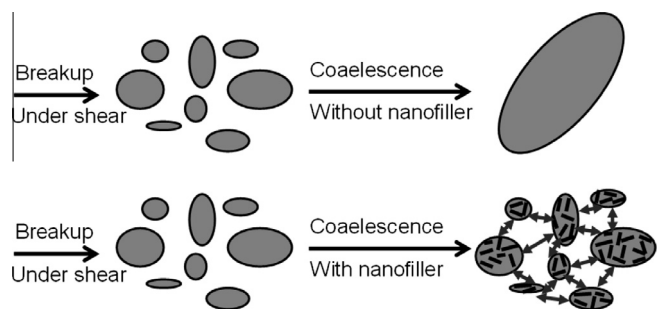


Fig. 2. Schematic representation of the effect of the nanoparticles on the morphology of polymer blends.

of PA6 droplets (3–4 μm). These results can be explained by the fact that ionic liquids act as emulsifiers [29]. In fact, excessive and critical accumulation of phosphonium ionic liquids at the interphase of PA6 nodules generates an opposite effect promoting coalescence of PA6 domains through ionic bonds.

In addition, we propose two different distributions of ILs in PP/PA6 blends when the amounts of ILs increase. A schematic

representation of the distribution of ILs in PP/PA blends is shown in Fig. 5.

Whatever the chemical nature of the ionic liquid, it is located at interphase of polyamide 6 phases. However, the ionic liquid combined with the phosphinate anion (IL-TMP) is preferentially located in the PA matrix when the amount of ILs increases. Conversely, the ionic liquid coupled with the bis(trifluoromethylsulfonyl)imide counter anion has a better affinity with PP matrix. To confirm these assumptions, the transmission electron microscopy and energy surface measurements were performed on the ternary blends PP/PA6/IL-TMP 20% and PP/PA6/IL-TFSI 10%, respectively. The ternary blend PP/PA6/IL-TMP is presented in Fig. 6.

For high content of ionic liquid (20 wt%), a contrast difference between the polyamide matrix 6 and the ionic liquid IL-TMP is observed. Thus, TEM images show very clearly an accumulation of ionic liquid inside PA6 phases. In contrast, it is difficult to detect the presence of IL-TFSI due to the low contrast density between IL and PP/PA6 blends.

3.1.2. Surface energies of ILs and polymer blends

The contact angles and surface energy determined by the sessile drop method on binary and ternary polymer blends are

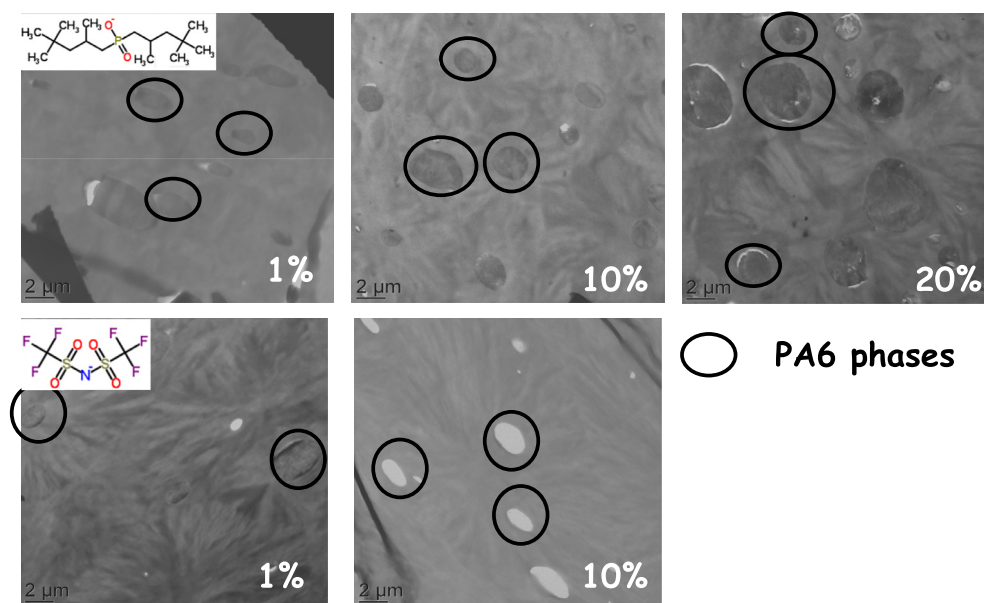


Fig. 3. TEM micrographs of the PP/PA blends with different amount of ILs (a) 1–10–20% for IL-TMP and (b) 1–10% of IL-TFSI.

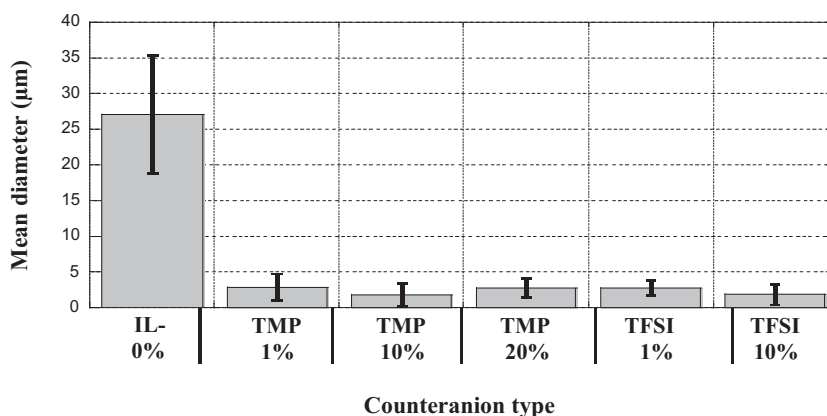


Fig. 4. Variation of mean diameter of PA6 nodules in PP/PA6/ILs blends as a function of type and concentration of ionic liquids used.

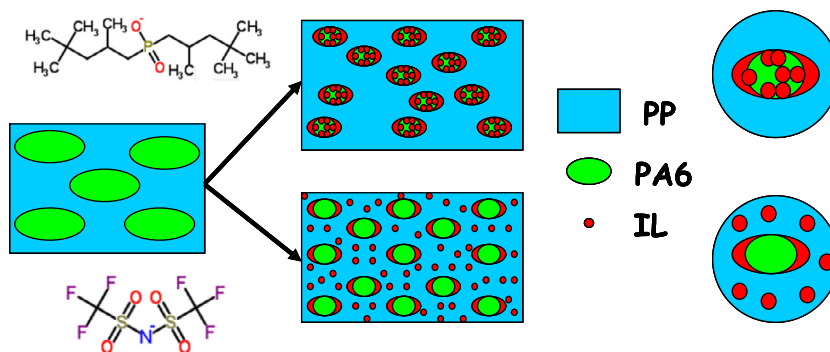


Fig. 5. Schematic representation of the effect of the ionic liquids on the morphology of polymer blends.

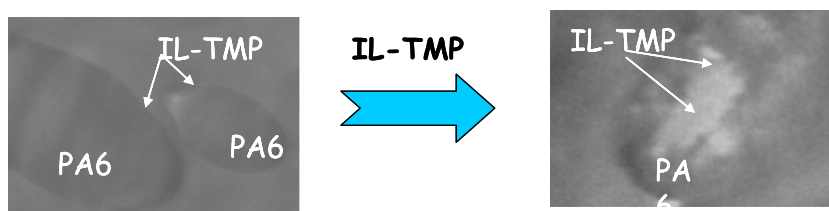


Fig. 6. TEM micrographs of PP/PA blends containing 20% of IL-TMP.

Table 3

Determination of total, polar, and dispersive components of the surface energy at 20 °C on PP, PA6, IL-TFSI, IL-TMP and contact angles values of ILs on polypropylene and polyamide 6.

Samples	Contact angle (°)	γ polar (mN/m)	γ dispersive (mN/m)	Surface energy (mN/m)
PP [34]	–	0.4	28.6	29
PA6 [35]	–	29.1	23.8	52.9
IL-TFSI	–	–	–	30.4
IL-TMP	–	–	–	30.7
PP with IL-TFSI drop	38 ± 5	–	–	–
PP with IL-TMP drop	54 ± 4	–	–	–

summarized in Table 3. To highlight the chemical affinity of ionic liquids with polymer matrices composing the mixture, IL-TFSI and IL-TMP drops were deposited on the neat polypropylene and polyamide 6.

In both cases, ionic liquids have a surface energy close to the polypropylene matrix with values in the range of 30.7–30.4 mN/m for IL-TMP and IL-TFSI, respectively. These values are consistent with the literature where for example, Coutinho et al. have also determined similar surface energies for these phosphonium salts [36,37]. However, significant differences were observed with the PP matrix. In fact, when a drop of ionic liquid denoted IL-TFSI is deposited on the polymer matrix, a contact angle of $38 \pm 5^\circ$ is obtained while for the ionic liquid named IL-TMP, a value of $54 \pm 4^\circ$ is observed. These results highlight the best affinity of IL-TFSI with polypropylene matrix and also show that the chemical nature of the counter anion plays a key role in the dispersion of the ionic liquid in the polymer mixtures.

3.1.3. Thermal stability of ILs and ternary blends

3.1.3.1. Thermal stability of ionic liquids. These phosphonium ionic liquids functionalized with long alkyl chains represented in Fig. 7 are used as new compatibilizing agents of polymer blends. By tuning the chemical nature of the counter anion, the intrinsic thermal stability of ionic liquids has been investigated.

According to the literature, the combination of the anion associated with the organic cation has a key role on the thermal stability of phosphonium salts [38–40]. In fact, the use of TFSI

anion combined with the phosphonium cation leads to an increase of degradation temperature of about 90 °C compared to the phosphonium salt coupled with phosphinate anion (IL-TMP) which is degraded at about 350 °C. Many authors have reported similar results in the use of ionic liquids associated with fluorinated anions such as hexafluorophosphate (PF_6^-) or tetrafluoroborate (BF_4^-) [16,41]. Recently, Livi et al. had highlighted that the replacement of halide anion (Br^- , I^-) with fluorinated anion on phosphonium cation increased the thermal stability of 140 °C [16].

3.1.3.2. Thermal behavior of polymer blends. Thermogravimetric measurements were carried out on the ternary polymer blends PP/PA6/IL-TMP and PP/PA6/IL-TFSI. The thermal decomposition of polymer mixtures is described in Fig. 8.

From TGA analysis, two organic species populations have been identified for PP/PA6 blends corresponding to the degradation of (i) neat polypropylene matrix at 360 °C and (ii) neat polyamide 6 at 460 °C. Whatever the amount of IL-TMP (1, 10, 20 wt%) introduced into the PP/PA6 blend, a significant increase in the thermal stability of polymer materials is observed (+35 °C). In fact, between the degradation temperatures of neat polymers (PP and PA6), an intermediate peak appears at a temperature of about 385 °C which also indicates a good compatibility thanks to the phosphonium ionic liquid combined with phosphinate anion. In the case of IL-TFSI, the use of only 1 wt% generates the same thermal behavior with an increase of 20 °C of the degradation temperature. Nevertheless, an increase in the amount of ionic liquid (10 wt%) leads

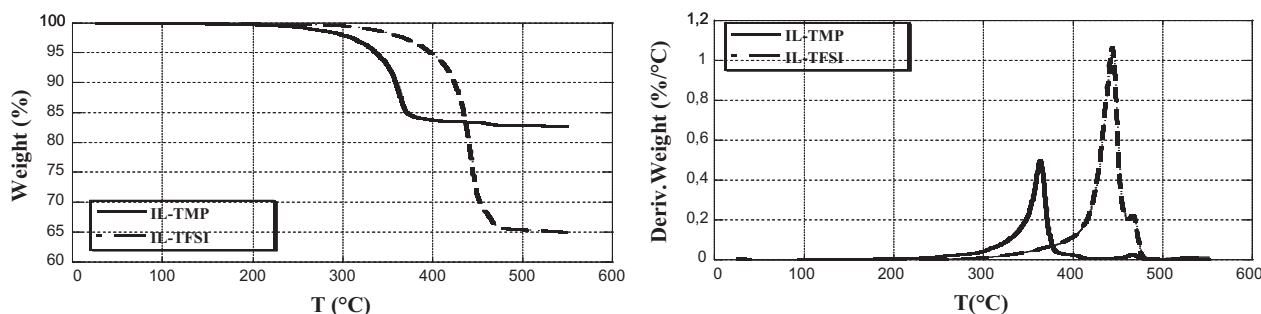


Fig. 7. Influence of the anion chemical nature associated to phosphonium ILs: Evolution of the weight loss as a function of temperature (TGA, DTG) of the (—) IL-TMP and (---) IL-TFSI (heating rate: 20 K min⁻¹, air atmosphere).

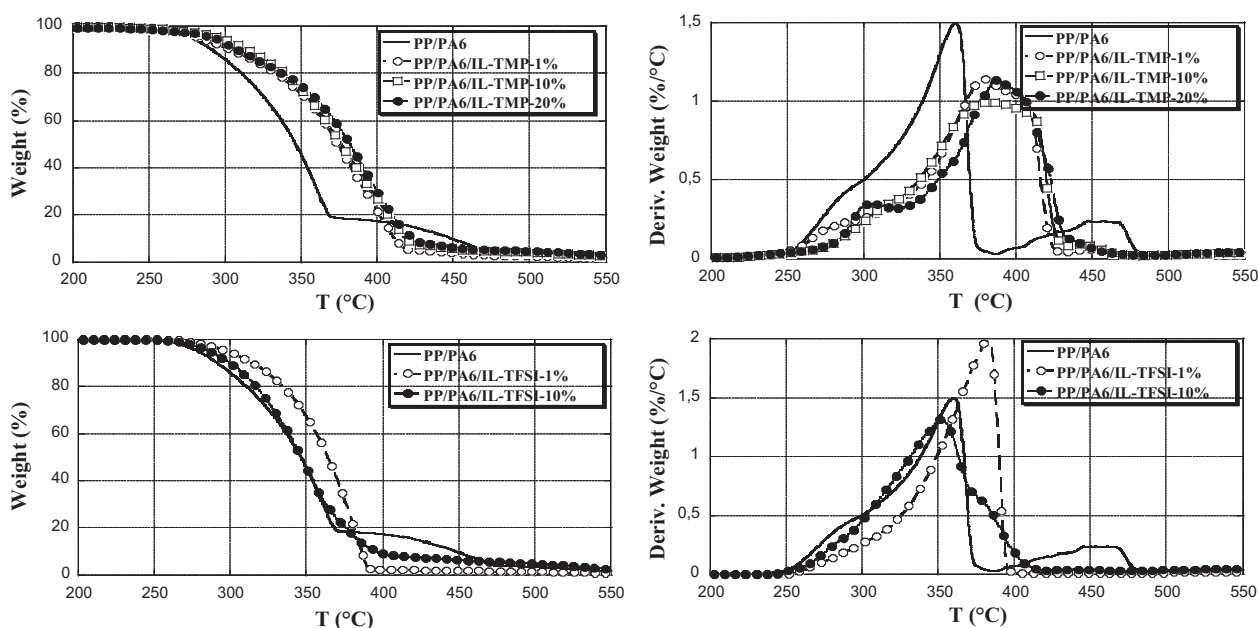


Fig. 8. Evolution of the weight loss as a function of temperature (TGA, DTG) of (a) neat PP/PA6 and PP/PA6/IL-TMP blends and (b) neat PP/PA6 and PP/PA6/IL-TFSI blends (heating rate: 20 K min⁻¹, air atmosphere).

to a decrease in thermal stability. Thus, the thermal behavior of the polymer mixture containing 10 wt% of IL-TFSI is the same compared to PP/PA6 blend without compatibilizer. In conclusion, these results show the effect of the chemical nature of the counter anion (TMP versus TFSI) and confirm our hypothesis on the distribution of the ionic liquid in the PP/PA6 blend. The higher affinity of the hydrophilic ionic liquid (IL-TMP) with polyamide 6 matrix enables better thermal stability of the blend while the preferred and excessive localization of IL-TFSI in polypropylene matrix induces a decrease in thermal properties.

3.1.4. Effect of ionic liquids on crystallisation behavior of the polymer blends

Table 4 summarizes the melting, crystallization temperatures and half crystallization time of virgin PP/PA6 binary blends and PP/PA6/ILs ternary blends. As previously mentioned in the experimental section of this manuscript, the melting temperature (T_m) and crystallization temperature (T_c) of PP and PA6 phases, are determined as the maximum of melting and crystallization peak from second heating and cooling DSC thermograms respectively. $t^{1/2}$ represents the time corresponding to 50% of the relative crystallinity.

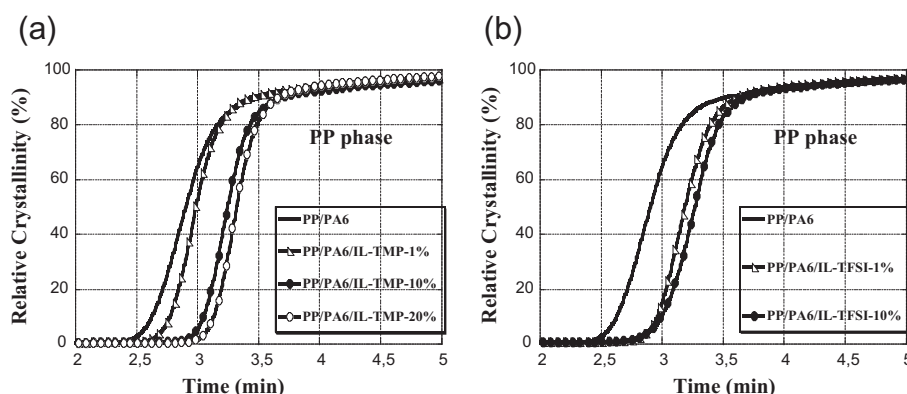
Fig. 9(a) and (b) shows the non-isothermal crystallization kinetics profile of PP component for IL-TMP and IL-TFSI-ionic liquids

filled blends respectively. With the increase of IL content in the polymer blends, it was observed that the curve reporting the relative crystallinity shifted towards the larger time region. On the other hand, the crystallization temperature (T_c) tends to shift to a lower temperature region with increasing the IL content in the blends. The crystallization temperature (T_c) of PP was 122.1 °C for neat PP/PA6 samples and decreased to 118.3 °C at a mass fraction of 10wt% of IL-TMP. In the presence of IL-TFSI, (T_c) was slightly lower (117.9 °C) since the TFSI anions are more compatibles with PP matrix compared to TMP ones. When the IL-TMP was added for about 20 wt%, the $t^{1/2}$ of PP component increased to 3.25 min and the $t^{1/2}$ increased of about 24 s when the amount of IL-TMP reached 20 wt% in the blend indicating a slow-down crystallization process of PP component. Yang et al. have demonstrated that the crystallization time of PP in PP/PA6 blends compatibilized with PP-g-MA was longer than that of uncompatibilized PP/PA6 samples [42]. According to the authors, PP-g-PA6 generated by the chemical reaction between the functional group of PP-g-MA and the terminal groups of PA6 restricted the crystallization of PP. Xue et al. found that the crystallization process shifted considerably to lower temperatures in the case of PP-g-MA compatibilized poly(trimethylene terephthalate)/polypropylene blends [43]. The crystallization temperatures (T_c) of PTT and PP shifted significantly to lower temperatures. The shift of PTT's (T_c) was larger than that of the

Table 4

The corresponding crystallization and melting parameters for virgin PP/PA6 and PP/PA6/ILs with different contents of ionic liquids.

Sample	T_c (PP) (°C)	T_c PA6 (°C)	$t^{1/2}$ (PP) (min)	$t^{1/2}$ (PA6) (min)	T_f (PP) (°C)	T_f (PA6) (°C)
PP/PA6	122.1	191.8	2.94	5.95	164.0	221.9
PP/PA6/IL-TMP-1%	120.9	184.8	3.03	6.65	163.5	219.9
PP/PA6/IL-TMP-10%	118.3	181.4	3.25	6.95	162.0	214.9
PP/PA6/IL-TMP-20%	117.6	177.9	3.34	7.29	161.2	212.3
PP/PA6/IL-TFSI-1%	119.7	185.9	3.19	6.53	163.9	218.5
PP/PA6/IL-TFSI-10%	117.9	– ¹ –	3.28	– ¹ –	162.3	– ¹ –

¹ No detection of the peak of PA6 in the DSC curve.**Fig. 9.** The relative crystallinity development with crystallization time of PP phase in virgin PP/PA6 and PP/PA6/ILs blends at different contents of ionic liquids. (a) TMP-anion; (b) TFSI-anion.

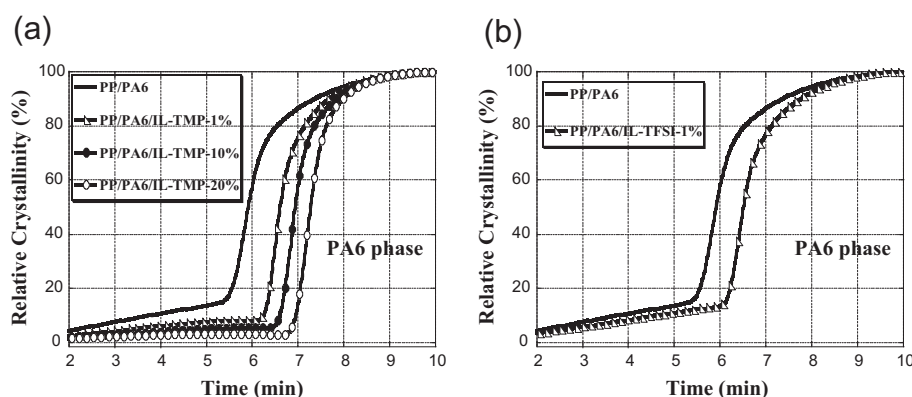
PP, suggesting that addition of the PP-g-MA had a larger effect on PTT's crystallization than on PP due to reaction between maleic anhydride and PTT.

It is interesting to note that in our case, the crystallization temperatures of both PP and PA6 phases decreased with increasing ionic liquid concentration in the blends. This indicates that the interfacial interaction marginally slowed down the crystallization rate of PP and PA6 phase.

Fig. 10(a) and (b) shows the non-isothermal crystallization rate of PA6 component for blends prepared in the presence of IL-TMP and IL-TFSI respectively. The crystallization process of PA6 was also retarded after the addition of ionic liquids. The (T_c) of PA6 phase decreases gradually with the increase of mass fraction of ILs and this decrease was more pronounced for the PA6 component compared to PP matrix. (T_c) of PA6 decreased to 177.9 °C (–10.4 °C) when the IL-TMP concentration in the blends increased to 10 wt% while the (T_c) of the PP phase shifted only to 117.6 °C (–3.8 °C). When the IL-TMP content increased to 20 wt%, the (T_c) of PA6 was depressed by 13.9 °C. These (T_c) shifts suggest that the compatibilization in PP/PA6 blends is accomplished by the addition

of the ILs, which promotes miscibility through intermolecular interactions between ionic liquids and PP/PA6 phases as already observed by TEM analysis. Psarski et al. explained the slowing of the kinetics of crystallization of PA6 phase in PP/PA6 blends by the reduction of size of PA6 dispersed particles, caused by the interactions between the functional groups of the compatibilizer (PE-AA copolymer) and the polar groups in polyamide chain [44]. By increasing the number of droplets per unit volume via decreasing the droplet size, the fraction of droplets that crystallizes at lower temperatures increases. But, the amount of shift cannot be explained solely by the size of the PA6 dispersion.

We noted that in the presence of 10 wt% of IL-TFSI, the signal of PA6 phase was almost not detectable in the DSC thermogramm. This result suggests probably a partial dissolution of PA6 chains by TFSI anions. Similar behavior was observed by Campoy et al. when they have prepared PP/PA blends with different amounts of PP-g-MA [45]. The increasing amount of compatibilizer caused a large decrease in the enthalpy associated with the crystallization of PA6 without change in the peak position. At 10 wt% of PP-g-MA, the peak of crystallization of PA6 phase disappears. On the

**Fig. 10.** The relative crystallinity development with crystallization time of PA6 phase in virgin PP/PA6 and PP/PA6/ILs blends at different contents of ionic liquids. (a) TMP-anion; (b) TFSI-anion.

other hand, the crystallization temperature of PP matrix shifted towards the lower temperatures when the mass fraction of PP-g-MA increased.

In PP/PA6 blends, two distinct melting peaks are observed at 164.0 and 221.9 °C, which correspond to that of pure PP component and PA6 component, respectively. The (T_m) of PP in PP/PA6/ILs blends show no significant shift compared with that of PP/PA6 blends. However, we note that the (T_m) of PA6 in ternary blends varies with the composition compared with the binary blend. When the IL-TMP was added for about 1 wt%, the (T_m) of PA6 was depressed by 2 °C, and the (T_m) of PP had no significant shifts (−0.5 °C). With increasing ILs concentration in the blends, the (T_m) of PA6 decreased much more and the shifts in 10 wt%IL-TMP and 20 wt% IL-TMP were 7.0 and 9.6 °C respectively.

Lahor et al. used sodium-neutralized poly(ethylene-co-methacrylic acid) ionomer to compatibilize PE-PA6 blends (80/20) at different concentrations [46]. They found that the blends exhibited different crystallization and melting behaviors due to different content of ionomer. Since the ionomer has the ability to form interactions with both blend components, the (T_c) and (T_m) of PE and PA6 decreased after addition of the ionomer. This decrease was more pronounced when the mass fraction of ionomer increased.

In our case, the (T_m) and (T_c) shifts suggest that the compatibilization in PP/PA6 blends is accomplished by the addition of ILs which promotes miscibility through intermolecular interaction between IL-TMP and IL-TFSI and PP/PA6 phases. Indeed, ILs could be localised at the interface of PP/PA6 and polar-polar interactions could be formed between sulfonate or imide groups of ILs, and amine groups of PA6. The level of these ionic interactions will depend on the level of the polarity of anion in ILs. In the case of TMP anions, these interactions will be more favorable compared to TFSI anions. Meanwhile, the strong interactions between nonpolar part (aliphatic chains in phosphonium cation of ILs) and nonpolar unit [−CH(CH₃)−] of PP increased the interfacial miscibility between PP and PA6 phases.

3.1.5. Influence of ionic liquids on the dynamical mechanical properties of polymer blends

As reported in Fig. 11, the dynamic mechanical spectrums of PP/PA6 and PP/PA6/IL blends display the storage and loss moduli E' , E'' and the main relaxation peaks ($\tan \delta$). In both cases, concerning the rubbery state, the storage modulus (E') of PP/PA6 mixtures decreased with the addition of ILs (Table 5). In addition, this decrease of (E') was more pronounced in the case of PP/PA6/

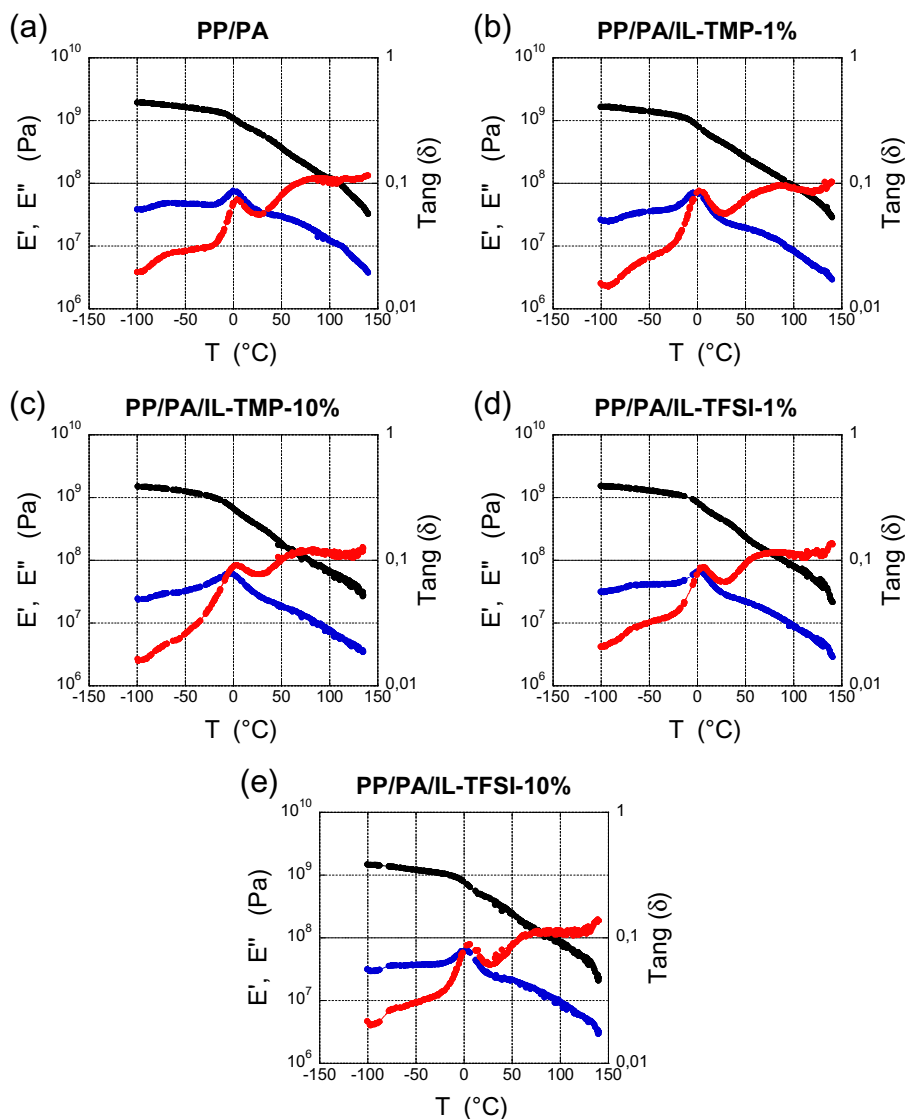


Fig. 11. Thermo-dynamic mechanical properties of neat PP/PA6 and PP/PA6/ILs blends as a function of temperature (T). (a) 0% IL, (b) 1 wt%-IL-TMP, (c) 1 wt%-IL-TMP, (d) 1 wt%-IL-TFSI, (e) 10 wt%-IL-TFSI. [Black curve (storage modulus E'), Blue curve (loss modulus E''), Red curve ($\tan \delta$)].

Table 5

Dynamic mechanical analysis of PP/PA and PP/PA/IL blends: storage moduli at glassy and rubbery states.

Sample	E' (MPa)			
	Glassy state	(T = −50 °C)	Rubbery state	(T = +80 °C)
PP/PA	1630		170	
PP/PA/IL-TMP-1%	1390	(−14.7%)	142	(−16.5%)
PP/PA/IL-TMP-10%	1250	(−23.3%)	96	(−43.5%)
PP/PA/IL-TFSI-1%	1290	(−20.9%)	121	(−28.8%)
PP/PA/IL-TFSI-10%	1210	(−25.7%)	124	(−27.0%)

IL-TMP blends. In fact, decreases of 17–44% are obtained in the case of PP/PA6/IL-TMP blends containing 1 and 10 wt% of IL-TMP, respectively. The same phenomenon is observed when IL-TFSI was used. However, the storage modulus remains stable regardless of the percentage of IL-TFSI introduced into the binary mixture.

In both cases, three relaxation peaks were observed at around −70, 1 and 80 °C, which referred to γ , β and α relaxation transitions of polypropylene, respectively. Thus, the relaxation peak corresponding to the glass transition of PA6 (around 45–60 °C) is included in the peak corresponding to the PP matrix. According to Schaefer et al. [47], the α relaxation peak of PP, which can usually be observed as a shoulder at highly temperature was assigned to the crystalline fraction. The authors demonstrated that the chain motion in crystalline phase can be described as a limited number of helical jumps about the chain helix beginning at 80 °C. The β relaxation peak was related to the amorphous phase, and generally was related to the glass transition of the polymer. However, the γ relaxation peak was attributed usually to the local mode relaxation in the amorphous phase [48,49]. In this work, no significant

temperature shift was seen in the presence of ILs. In the case of the γ relaxation peak, a broadening of the peak amplitude was observed particularly with a larger amount of IL-TMP. Concerning the β and α relaxations, the use of IL-TMP and IL-TFSI does not have influence on the shape of the shoulder.

3.1.6. Influence of ionic liquids on the rheological properties of polymer blends

Fig. 12 shows the evolution of complex viscosity (η^*) as a function of frequency (ω) for PP/PA6 and PP/PA6/IL blends. All samples exhibit pseudoplastic behavior with a shear thinning at high shear rate range. The thinning behavior is more pronounced when the concentration of ionic liquid increases. In the case of PP/PA6/IL-TMP samples, a progressive increase in the viscosity with the concentration of the ionic liquid can be observed over the entire frequency and this viscosity increase is much greater at low frequencies. However, in the presence of IL-TFSI ionic liquids, at high frequencies, the viscosity (η^*) slightly decreased indicating that the IL-TFSI ionic liquids have little effect on the short-range motion of polymer chains which can relax more easily compared to pure PP/PA6 blends. Furthermore, in the low frequency region, both ionic liquids induced an increase of the complex viscosity of blends compared with pure PP/PA6 blends. But, (η^*) values of IL-TMP filled samples increased more than that of PP/PA6/IL-TFSI compounds implied stronger ionic interactions with IL-TMP surfactants compared to IL-TFSI ones. This observed difference between the two phosphonium ionic liquids can be explained by the higher basicity of the phosphinate anion. Indeed, the phosphinate anion would better interaction with the terminal acid groups of PA6 while TFSI anion has a strong interaction with the NH_2 groups. Thus, the strong ionic interactions generated could significantly restrain the large-scale polymer relaxation motions in the blend. In such

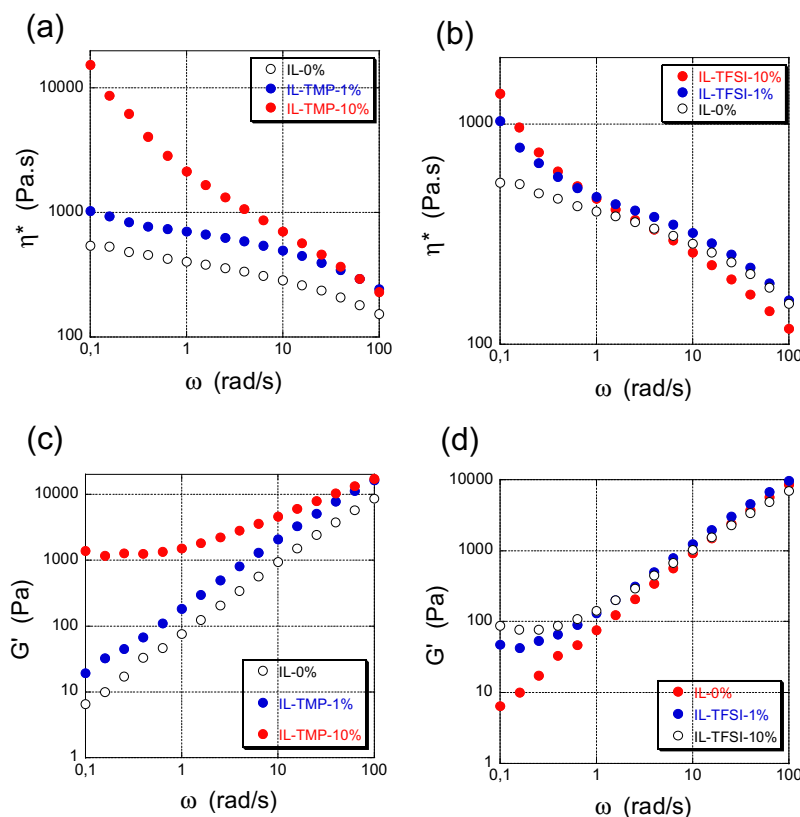


Fig. 12. Shear storage moduli and complex viscosity versus frequency for neat PP/PA6 and PP/PA6/ILs blends. (a) and (c): (G') and (η^*) for PP/PA6/IL-TMP samples respectively. (b) and (d): (G') and (η^*) for PP/PA6/IL-TFSI samples respectively.

Table 6Viscosity ratio at a shear rate of 40 (s^{-1}) of neat PP/PA6 and PP/PA6/ILs blends.

Sample	Viscosity ratio at 40 (s^{-1}) [$\eta(\text{PA6})/\eta(\text{blend})$]
PP/PA6	0.77
PP/PA6/IL-TMP-1%	0.47
PP/PA6/IL-TMP-10%	0.43
PP/PA6/IL-TFSI-1%	0.72
PP/PA6/IL-TFSI-10%	0.95

a situation, the rheological response exhibited more solid-like viscosity behavior instead of liquid-like probably due to the ionic liquid induced network structure [50].

Because the viscosity of ionic liquids is much lower (some mPa.s) than that of PP and PA6 phases, the significant enhancement in complex viscosity of the compatibilized blends cannot be attributed to the viscosity of ILs, as such, the effect that the presence of ILs should exert on the viscosity of the blend is the opposite (Table 6). The increase in complex viscosity can solely be attributed to the formation of stronger interactions provoked by the formation of new ionic bonding between ionic liquid functional groups and the terminal acid groups and amine of PA6. Thus, the significant enhancement in complex viscosity of the compatibilized blends depending on the nature of the counteranion used implies a possible influence of selective location of ionic liquid in the two phases on the changing of the viscosity ratio. According to the literature, the decrease in viscosity ratio was also observed in various compatibilized PP/PA6 blend systems [45,51].

Fig. 13 shows the dependence of the storage modulus (G') on frequency for PP/PA6 and PP/PA/ILs blends. It is observed that the effect of IL percentage on (G') for PP/PA6/IL blends is similar to that on complex viscosity. The storage moduli of PP/PA6/ILs blends were always higher than those of the unfilled PP/PA6

blends. The higher elastic moduli of PP/PA/ILs blends may attribute to the enhanced interaction between phases caused by compatibilization effect, which reduces the possibility of the interlayer slip, and increases formation of associative network formation between the interfaces [50]. However, a slight difference in the rheological behaviors between PP/PA/IL-TMP and PP/PA/IL-TFSI ternary blend systems could be explained by the different level of interaction between IL-TMP (hydrophilic) and IL-TFSI (more hydrophobic) with PA6 phase. It's useful to note that an increase of ionic liquid concentration promotes closer surfactant aggregates and hence the possibility of network formation. This could explain the increase of relaxation time at low frequency (presence of plateau). Thus, the cluster network is more protected against deformation. From this behavior, a formation of a three-dimensional network can be deduced and the lifetime of the cross-links can be estimated from the inverse of the angular frequency at which G' and G'' cross. For the PP/PA6 and PP/PA6/ILs blends with IL < 1 wt%, G'' exceeds G' over the entire frequency range accessible. For PP/PA6/ILs containing 10 wt% of phosphonium ILs, a cross-link relaxation times of 1.5 and 10 s was obtained for PP/PA/IL-TMP and PP/PA/IL-TFSI, respectively.

3.1.7. Influence of ionic liquids on the mechanical properties of polymer blends

The uniaxial tensile properties were determined to evaluate the impact of ionic liquids on the mechanical behavior of PP/PA blends. The moduli and the fracture properties are presented in Table 7.

Due to the different distribution of ionic liquids IL-TFSI and IL-TMP in the binary mixture, the mechanical performances are totally various. The addition of only 1 wt% of IL-TMP in the PP/PA blends leads to an increase of the strain at break of 1400% without reducing the Young modulus. In fact, for PP/PA6/IL-TMP, a Young's modulus of 1800 MPa and a strain at break of 254% are obtained

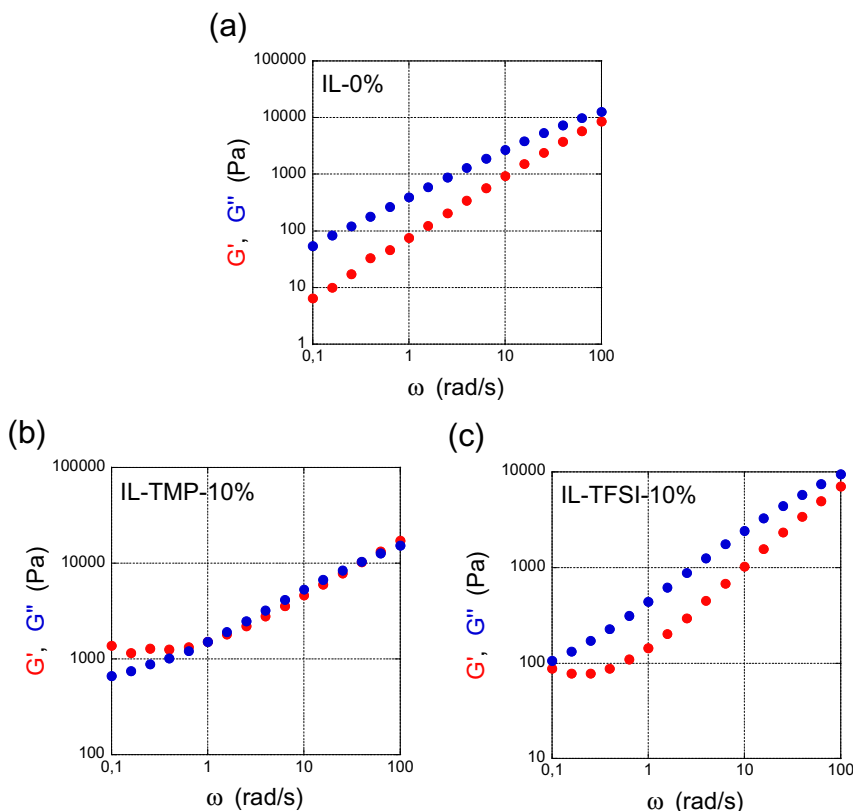


Fig. 13. Shear storage moduli (G') and shear loss moduli (G'') of neat PP/PA6 (a), PP/PA6/IL-TMP-10% (b) and (c) PP/PA6/IL-TFSI-10% blends.

Table 7

Mechanical data from tensile tests performed on virgin PP/PA6 and PP/PA6/ILs blends with different contents of ILs.

Sample	PP/PA6	PP/PA6/IL-TMP-1%	PP/PA6/IL-TMP-10%	PP/PA6/IL-TMP-20%	PP/PA6/IL-TFSI-1%	PP/PA6/IL-TFSI-10%
Young modulus (MPa)	1880	1757 (−6.5%)	1139 (−39.4%)	1026 (−45.4%)	1415 (−24.7%)	1420 (−24.5%)
Standard deviation	16	88	69	222	73	148
Elongation at break (%)	17.2	253.4	105.4	12.5	215.6	329.5
Standard deviation	6.6	48.6	99	0.5	32.8	135
Yield stress (MPa)	28.8	36.2	29.8	24.4	32.8	29.4
Standard deviation	1.2	0.6	0.8	2.5	1.2	1.0

compared to values of 1880 MPa and 17%, respectively for PP/PA6 blend. Contrariwise, an increase in the amount of ionic liquid IL-TMP (10% and 20%) in the polymer blend leads to a fall in the modulus (−39% and −46%) and a decrease in strain to failure (+520% and −30%). This phenomenon can be explained by the fact that IL-TMP acts as a plasticizer in the PA6 matrix which leads to poor mechanical properties. In comparison with the commonly used PPgMA in PP/PA6 blends, the results are promising, especially when one percent of IL-TMP was used as compatibilizer. In fact, similar polymer mixtures of PP/PA6 (70/30) have been studied by Chow et al. [52]. Thus, they demonstrated that the use of 5% and 10% of PPgMA leads to a slight increase in elongation at break (38% instead of 23% to 10% PPgMA) without reducing the Young's modulus. These results are confirmed by various studies which have highlighted the need to use a quantity of 20 wt% of PPgMA to obtain a significant improvement in mechanical properties [7].

In the case of IL-TFSI, the introduction of ionic liquid in the binary mixture produces a plasticizing effect of the PP/PA blend. Indeed, 1 and 10 wt% of IL leads to decreases in the Young's modulus of 23% and 30%, while a significant increase in elongation at break is observed: 1% of IL-TFSI leads to an increase of 1200%, while 10% generates an increase of 1800%. These results are similar to those described in the literature where authors have also shown that the use of 5 wt% of SEBSgMA in PP/PA6 (70/30) blends leads to a plasticizing effect with a decrease of Young Modulus (−20%) combined with an increase of the strain at break (+215%) [53,54]. In the case of nanoparticles such as layered silicates (MMT), the results are different. In most cases, the addition of 4–7% of modified-MMT generates increases of the rigidity coupled with a drastic drop in the elongation at break [54]. Recently, Li et al. [55] demonstrated that the addition of a small amount of imidazolium ionic liquid (0.6 wt%) to ultra-high molecular weight polyethylene (PE) leads to a significantly increase in the elongation at break without reducing the tensile strength (106% for neat PE and 338% for PE/IL blends). However, when the content of IL increases (3 wt%), the elongation at break dropped to 252% accompanied by a significant decrease in the tensile strength. This phenomenon is observed for 1 wt% of IL-TMP. According to the literature, the use of an excess of ILs suppress the formation of a crystallite region, leading to a less effective crystalline network [56].

In conclusion, these results highlighted the key role of the chemical nature of the phosphonium ionic liquids [56]. Thus, ionic liquids are excellent candidates to compatibilize the polymer blends and are a new alternative to conventional compatibilizing agents such as copolymers (PPgMA), ionomers (Surlin®) or the use of nanoparticles (layered silicates, carbon nanotubes, silica) [6–9,11,14,29,51,57,58]. In addition, due to their versatility, ionic liquids can be adapted to any types of polymers and their behavior is finally close to ionomers.

4. Conclusions

In this study, new specific compatibilizing agents based on phosphonium ionic liquids have been used in order to prepare high performance PP/PA6 polymer blends, in particular with excellent

thermal and mechanical properties. The incorporation of only 1 wt% of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide named as IL-TFSI and trihexyltetradecylphosphonium bis 2,4,4-(trimethylpentyl)phosphinate designated as IL-TMP in polypropylene/polyamide 6 (80/20 wt/wt) blends generated decrease in the size of the dispersed phase i.e. PA6. In fact, the size of the PA6 domains decreased from 27 to 1–2 μm . This reduction is attributed to the migration preferentially of ionic liquid at the interphase between PP and PA6 which creates a barrier around the PA6 drops, preventing their coalescence. In addition, the chemical nature of the counter anion has been demonstrated on the final properties of PP/PA6 blends. Thus, the use of ionic liquid combined with phosphinate anion (IL-TMP) results in a significant increase in strain at break of 1400% without reducing the Young's Modulus while the ionic liquid with the ionic fluorinated anion (IL-TFSI) has a plasticizer effect characterized by an increase in elongation at break and a drop of Young's modulus (−30%). Then, the addition of ionic liquid also causes an increase in the thermal stability of polymer blends: +20 °C for 1 wt% of IL-TFSI and +35 °C for IL-TMP. Nevertheless, an increase in the amount of ionic liquid leads to two different behaviors due to the distribution i.e. to the affinity of the counter anion with the polypropylene or polyamide 6 matrices. In fact, the more hydrophilic IL (IL-TMP) has a better affinity with the PA matrix while the hydrophobic salt (IL-TFSI) has a preference with the PP matrix which leads to a degradation of the final properties, especially for a large amount of IL used.

In conclusion, a small amount of ionic liquid may be used as new compatibilizers for thermoplastic blends and offers an alternative to the use of copolymers such as PPgMA or ionomers commonly used in the literature [48,53].

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