J Therm Anal Calorim (2010) 99:539–543
DOI 10.1007/s10973-009-0203-4

Thermal study and evaluation of new menthol-based ionic liquids as polymeric additives

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Received: 19 February 2009 / Accepted: 5 June 2009

Abstract Thermal properties of new ionic liquids (ILs) were investigated by thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC). Chlorides, tetrafluoroborates and hexafluorophosphates of (−)mentholpyrrolidinium and (−)-mentholimidazolium cations revealed good thermal stability at air atmosphere. Morphological characteristics of poly(methyl methacrylate) (PMMA) matrices doped with 10% of these ILs were also investigated by DRX and water absorption test. Into the matrix, they exhibited a very satisfactory pattern concerning the polymer thermal stabilization. DSC results show that some of these ILs also present plasticizer features since they can lower the polymer glass transition temperature (T_g) up to 317.15 K.

Keywords Ionic liquids · Plasticizers · Polymer morphology · Poly(methyl methacrylate) · Thermal stabilizers

Introduction

Ionic liquids (ILs) have a widespread use in many areas of chemistry due to features of first-rate chemical and thermal stabilities, good electronic and ionic conductivities and ability to dissolve a great variety of organic, inorganic or organometallic compounds [1]. ILs tend not to crystallize easily, being liquid at temperatures below 273.15 K [1, 2]. Many ILs are also stable to air and water, due to the possibility of varying their structures by substituting the anion or by changing the alkyl substituents at the cation. The most studied ILs belong to the dialkylimidazolium or dialkylpyrrolidinium groups [1–3]. In the green chemistry scenario, the applications of ILs include, among others, solvents for reactions [3, 4] and for spectroscopic methods [5, 6], polymeric plasticizers and thermal stabilizers [7, 8]. In this respect, poly(methyl methacrylate), PMMA, has been largely investigated due to its industrial role [1] and compatibility with assorted IL systems [7, 8]. In addition, PMMA is an amorphous, colorless thermoplastic material of excellent optical transparency, and a luminous transmittance of about 92%. It has good abrasion resistance and dimensional stability, but is brittle and notch sensitive. Its water absorptivity is very low when compared to other polymer materials [9]. Recent studies showed that buriti oil acts as a plasticizer of PMMA [10].

The ILs reported herein are based on (−)-menthol and are grouped according to their pyrrolidine or imidazole moiety (Fig. 1). The preparation of these chiral ILs was straightforward and is published elsewhere [11]. They were called: acetyl-(−)menthol-1-buthylimidazole chloride ([amebim]Cl), acetyl-(−)menthol-1-buthylimidazole tetrafluoroborate ([amebim]BF_4), acetyl-(−)menthol-1-buthylimidazole hexafluorophosphate ([amebim]PF_6), acetyl-(−) menthol-1-methylpyrrolidine chloride ([amempyr]Cl), acetyl-(−)menthol-1-methylpyrrolidine tetrafluoroborate ([amempyr]BF_4) and acetyl-(−)menthol-1-methylpyrrolidine hexafluorophosphate ([amempyr]PF_6).

It is important to emphasize that there are several studies related to the application of chiral compounds like these on

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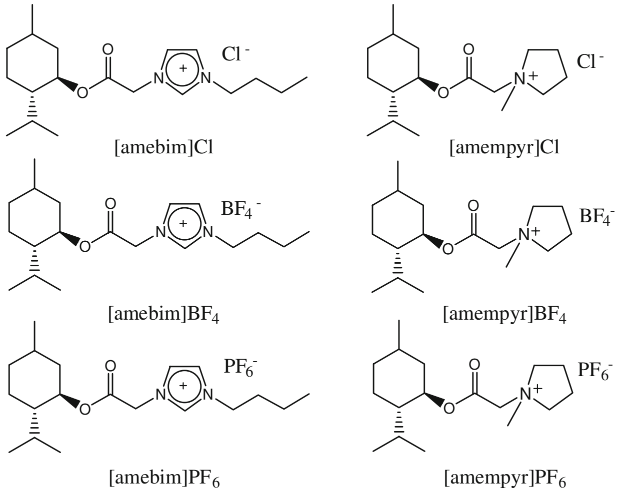

Fig. 1 Structures of the ionic liquids studied

organic synthesis and other areas [12–14]. Aiming to investigate the thermal properties of some chiral ILs as well as to evaluate their performance as polymeric additives, PMMA matrices were added to the different (−)-menthol-based ILs and further morphological, calorimetric and thermogravimetric analyses were realized.

Experimental

Samples preparation

Modified PMMA films were prepared using the solvent casting method. All IL:polymer samples were formulated using 10% IL and 90% PMMA (mass/mass) dissolved in acetone. Mixtures were placed in Petri dishes at atmospheric pressure to evaporate the solvent and afterwards the samples were kept in a vacuum chamber (~5 torr). Analyses were performed only when mass variation in the samples was not noticed anymore. By the same way, a pristine sample was prepared. It was employed low molecular mass PMMA purchased from Aldrich Co. ($\bar{M}_w = 120,000$; $\rho = 1.188$ g mL^{-1}; $T_g = 387.15$ K) and analytical reagent grade acetone (Proquimios) in all preparations. The ILs used were prepared following the route reported by Andrade and Matos [11].

DRX analysis

X-ray diffractograms of the samples were obtained on a Rigaku Diffractometer Mod. Geiger FlexD/Max-2/C, Cu-K$_\alpha$, operating at 40 kV, 20 mA and at a rate of 1° min^{-1}.

Water absorption test

The samples (2 cm^2) were submerged on water during 6 h; the water absorption was calculated as the difference in the sample's mass as a function of the time of exposure.

Calorimetric analysis (DSC)

Calorimetric measurements were performed on a DSC-50 Shimadzu calorimeter under helium flow (50 mL min^{-1}). The samples (6–8 mg) were heated in the range of −223.15–473.15 K at a heating rate of 10 K min^{-1}. The polymer analysis was carried out using aluminum sealed pans.

Thermogravimetric analysis (TG/DTG)

Small samples (6–8 mg) of the ILs, PMMA and ILs: PMMA films were placed into Pt crucibles and heated on a TGA-50 Shimadzu thermobalance, at a heating rate of 10 K min^{-1}, from 298.15 to 773.15 °C, under an air atmosphere. The decomposition temperatures (T_d) were determined through the TG curves derivative, i.e., DTG curves.

Results and discussion

According to the DRX results, which are shown in Fig. 2, it is possible to infer that the ILs incorporation into the matrix promoted minor changes in the polymer structure that is predominantly amorphous. Despite that no absorption peaks were registered along the investigated range, as a

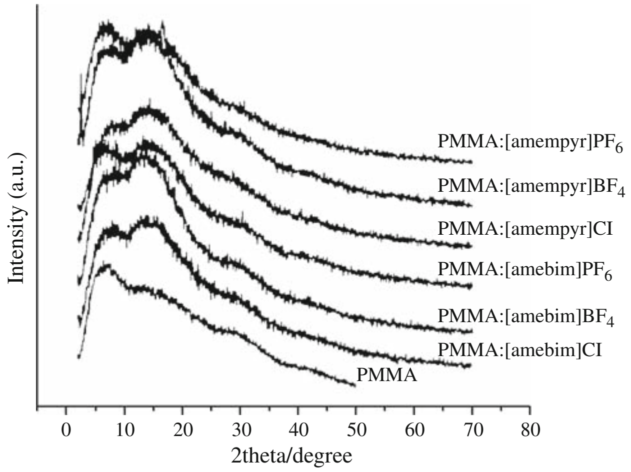

Fig. 2 DRX diffractograms of PMMA and PMMA doped with different ILs

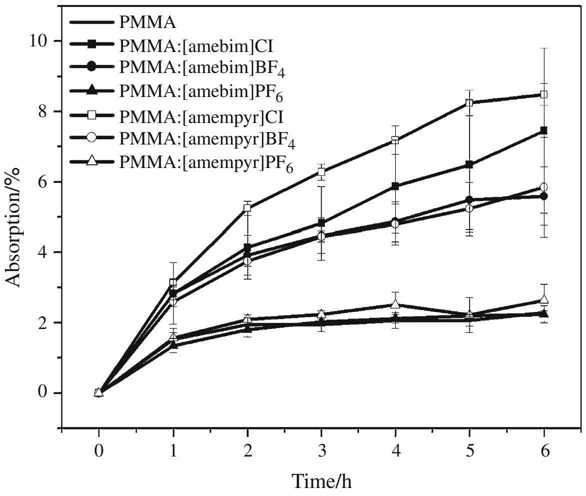

Fig. 3 Water absorption test

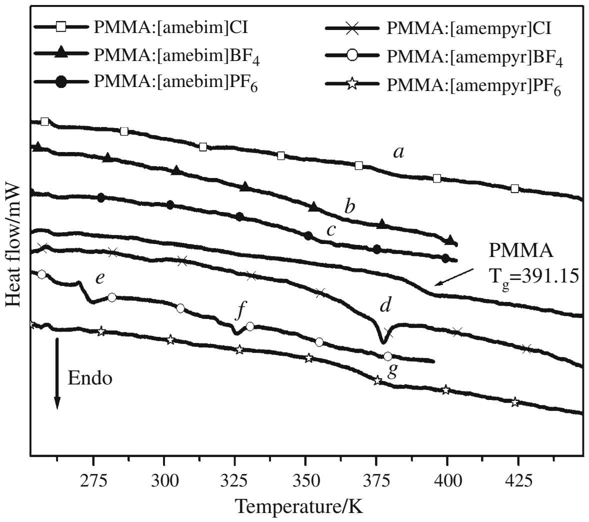

Fig. 4 DSC heating curves of PMMA:ILs acquired at a heating rate of 10 K min^{-1} under helium flow of 50 mL min^{-1}

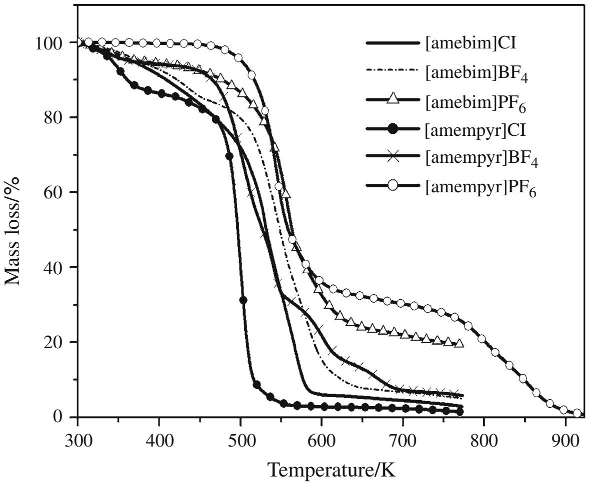

Fig. 5 TG curves of the ILs obtained at a heating rate of 10 K min^{-1} under atmospheric air

clear indication that only a few or no crystalline domains are present in the doped matrices, it can be observed an intensity gain at a broad band near 11°.

Furthermore, the water absorption test also suggests that the addition of the investigated ionic compounds does not favour the full polymer chains organization since all the doped matrices absorbed more water than the pure PMAM sample as is shown in Fig. 3. It is important to note that ILs with a pyrrolidine nucleus presented a slightly greater capability of water absorption than those with an imidazole one, as a consequence of the structures length. In the same way, Cl^- anions allow higher absorption than BF_4^- and PF_6^- anions which are bulkier.

Concerning the calorimetric data, DSC curves of PMMA matrix doped with the different ILs (Fig. 4) show that a good dopant-matrix compatibility was established since only PMMA:[amempyr]Cl and PMMA:[amempyr]BF_4 materials presented thermal transitions which are characteristic of the corresponding IL. Such transitions are marked at the thermogram (Fig. 4) as the dots *d* (melting at 377.15 K), *e* (glass transition at −271.86 K) and *f* (melting at 323.55 K). In the other cases, a single glass transition was registered: *a* at 347.65 K, *b* at 374.15 K, *c* at 364.85 K and *g* at 369.65 K. Thus, the (−)-menthol-based ILs investigated were able to decrease the glass transition temperature of the PMMA matrices. In certain cases, the difference reached more than 313.15 K. Taking into account that this is a requirement to classify a compound as a plasticizer, the most promising for this aim seems to be [amebim]Cl and [amebim]BF_4 which also promoted a widening at the glass temperature range, as is indicated in Fig. 4. On the other hand, the incorporation of PF_6^- ILs brought about more organization of the doped matrices polymeric chains since in the range of the temperature investigated no glass transition was registered. Such observations are in perfect accordance with DRX analysis and water absorption test.

TG/DTG results reveal that all the investigated ILs have good thermal stability, as is depicted in Fig. 5. All ILs presented temperature of 10% mass loss (T_{10}) above 433.15 K, according to Table 1. These (−)-menthol-based ILs are decomposed basically in two steps which are related to the anion hydrolysis and degradation of the organic portion. Another initial degradation below 393.15 K can be associated to some remaining solvent. It was clearly observed that the chlorides are less thermally stable than the other ILs, as a consequence of the high reactivity of the anion which accelerates the degradation process. Tetrafluoroborates exhibited higher trend to

Table 1 Temperature of 10% mass loss (T_{10}) of menthol-based ILs

Sample	T_{10} (K)	Sample	T_{10} (K)
[amebim]Cl	437.15	[amebim]Cl	447.15
[amebim]BF_4	453.15	[amebim]BF_4	480.15
[amebim]PF_6	508.15	[amebim]PF_6	532.15

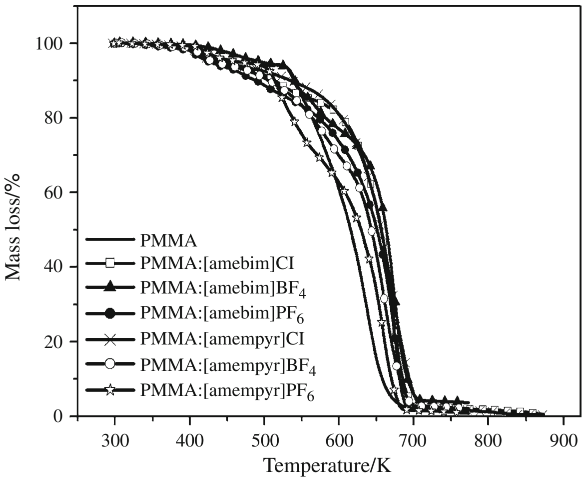

Fig. 6 TG curves of the PMMA:ILs obtained at a heating rate of 10 K min^{-1} under atmospheric air

undergo oxidative reactions during its degradation, although they began to lose mass only at temperatures over 423.15 K. Without influence of the imidazole or pyrrolidine nucleus, the PF_6^- ILs turned out to be the most stable systems. In this case, the great mass and the highest stability of the anion contributed to such observation.

Initially, a three-step mechanism was registered for the decomposition of pure PMMA. The first one is related to bond linkages of tail-to-tail bond, followed by radical decomposition of terminal double bond. The third step is due to random chain cleavage that takes place around 593.15–623.15 K, as is described in the literature [15]. The incorporation of the menthol-based ILs into the matrices promoted significant changes in their thermal degradation. The results, according to the ILs' chemical structure, menthol-pyrrolidinium or menthol-imidazolium, reveal a random behavior (Fig. 6). For instance, chloride ion, did not increase the initial temperature of the matrix decomposition, but the last degradation temperature of PMMA increased from 634.15 to 675.15 K.

The poor performance of [amebim]Cl as thermal stabilizer is due to the high reactivity of the anion, which undergoes hydrolysis at temperatures below 453.15 K (Fig. 5). Above this temperature, unzipping of the polymeric main chain goes faster; however, many of the formed radicals are trapped by the cationic portion of the salt and thus a little stabilization is reached at the last degradation step of the polymer. [amempyr]PF_6 and [amebim]PF_6 ILs promoted most notable thermal stabilization of the matrices since they are more thermally stable than their analogous. This is a result of the hexafluorophosphate cations influence whose hydrolysis takes place between 503.15 and 533.15 K (Fig. 6). Both salts promoted a considerable increase in the PMMA first stage temperature of degradation: 8.2 and 129.6 K, respectively. Another contribution to the good performance of [amebim]PF_6 in the thermal stabilization process of the matrix comes from its higher number of active sites for radicals trapping, in comparison to [amempyr]PF_6. In this way, it is possible to suggest an order for the stabilization of the PMMA first degradation step: $Cl^- < BF_4^- < PF_6^-$. The following stage, which will lead to depolimerization, was delayed/inhibited by the trapping action, which is more available in the imidazolium than in the pyrrolidinium ILs.

Conclusions

In this preliminary study, thermal and morphological properties of new menthol-based ILs used as polymer additives were discussed. The performed analyses indicated that the ILs are thermally stable and some of them present good features of polymer plasticizer. In these results, it was observed a great influence of the type of the anion as well as the cations length. Nevertheless, none of the investigated IL promoted significant change in the polymer morphology. In addition, due to the low volatility of the ILs, they may offer a green chemistry contribution by reducing emission during processing. Moreover, the electrical and optical properties provided by the chiral ILs to PMMA are being investigated.

Acknowledgements The authors are grateful to financial support from UnB, FINATEC, CNPq and CAPES.

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