Evaluation of Spectroscopic and Morphological Properties of PMMA Modified with ILs

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Summary: In recent years, an important class of new compounds, ionic liquids (ILs), has been investigated as additives for polymers. In this work, we carried out the synthesis of 4 different ILs: 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM.BF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIM.PF_6$), and the chiral ILs acetyl-(−)menthol-1-buthylimidazole tetrafluoroborate ([amebim]BF_4) and acetyl-(−)menthol-1-buthylimidazole hexafluorophosphate ([amebim]PF_6). These ILs were added to poly(methyl methacrylate) (PMMA) in 10, 20 and 30% ratios by weight and the ILs, PMMA and the obtained materials (PMMA:ILs) were characterized by infrared, visible spectroscopy and atomic force microscope. The ILs added to PMMA did not provide significant changes in the infrared spectra, compared to pure PMMA. However, the absorption spectra in the visible region of the PMMA:ILs materials showed differences, compared to the spectrum of pure PMMA.

Keywords: infrared spectroscopy; ionic liquids; morphology; poly(methyl methacrylate)

Introduction

Poly(methyl methacrylate) (PMMA) is used mainly on billboards, signs and in the manufacture of lenses due to its similarity to glass and its optical characteristics. In order to further improve its characteristics, research has been performed with the addition of different substances to this polymer.[1,2] Recently, ionic liquids (ILs) have been studied as additives for polymers. Studies report, among other applications, the performance of ILs as solvents for polymerization, modifiers of spectroscopic properties and their addition to provide conductivity to polymers.[3–6]

Thus, the objective of this study is to investigate the influence of the ILs 1-butil-3-methylimidazolium tetrafluoroborate ($BMIM.BF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIM.PF_6$) (Figure 1a), acetyl-(−)-menthol-1-butylimidazolium tetrafluoroborate ([amebim]BF_4) and acetyl-(−)menthol-1-buthylimidazole hexafluorophosphate ([amembim]PF_6) (Figure 1b) on the spectroscopic properties of PMMA. $BMIM.BF_4$ and $BMIM.PF_6$ were chosen for being commercially available and widely used as a reaction media and the menthol-based chiral ILs were chosen in view of our earlier studies about their properties as polymeric additives.[2]

Experimental Part

Synthesis of ILs

$BMIM.BF_4$ and $BMIM.PF_6$ were synthesized in two steps. The first involved to the alkylation of *N*-methylimidazolium with 10 equivalents of butyl iodide, producing 1-butyl-3-methylimidazolium (BMIM.I),

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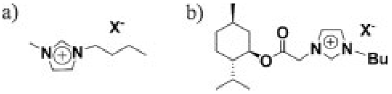


Figure 1.
ILs structures, where $X = BF_4$ or PF_6.

as a viscous reddish liquid (Scheme 1). This step occurred in a CEM Discover microwave reactor, CEM Co, at 150 °C, for 30 min. $BMIM.BF_4$ and $BMIM.PF_6$ were obtained by ion exchange with KBF_4 and KPF_6, respectively, according to the second part of Scheme 1.

The ILs [amebim]BF_4 and [amebim]PF_6 were obtained in three steps (Scheme 2).[6]

The first step was the reaction of (−)-menthol with chloroacetic acid to produce the acetylmenthol chloride. The second step involved the reaction of the chloride with 1- buthylimidazol, producing [amebim]Cl. An ion exchange reaction of [amebim]Cl with either KBF_4 or KPF_6 produced [amebim]BF_4 and [amebim]PF_6, respectively.

The formation of BMIM and [amebim] ILs was confirmed by ^{1}H Nuclear Magnetic Resonance (^{1}H NMR), ^{13}C NMR and Fourier transform infrared (FT-IR), giving data cosistent with those published.[6]

Preparation of PMMA:IL Materials

The synthesized ILs were used in the preparation of PMMA:IL materials in accordance to Scheme 3.

Characterization of Materials

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were obtained in a Bomem Michelson FT-IR spectrometer Hartmann & Braun, Series B (model BM 100) in the spectral region of 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

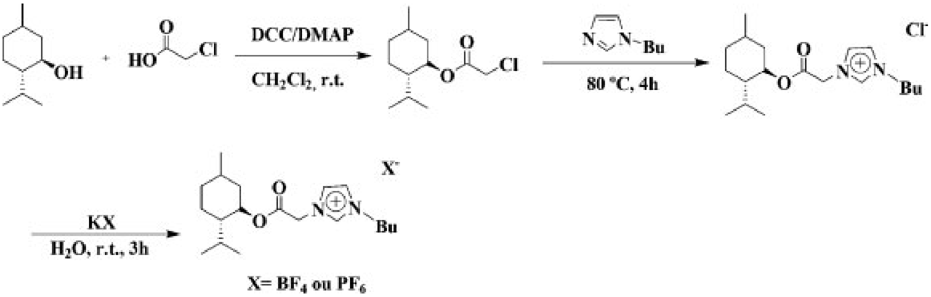
UV-Vis Spectroscopy

Analyses by UV-vis spectroscopy were monitored by a Beckman model DU-600 equipment in the range of 400–900 nm.

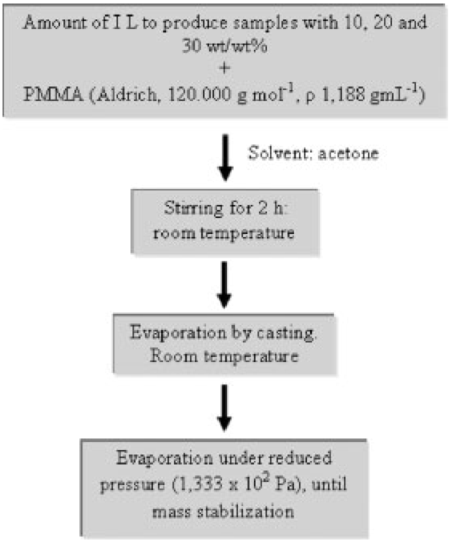
Atomic Force Microscope (AFM)

Tapping mode AFM was performed in a Veeco Innova (Instruments) scanning probe microscope. Topographic (height) images were recorded at ambient conditions. Commercial antimony (n) doped silicon cantilever probes with spring con-

Scheme 1.
Synthesis of BMIM.I, $BMIM.BF_4$ and $BMIM.PF_6$.[5]



Scheme 2.
Synthesis of [amebim]BF_4 and [amebim]PF_6.[6]



Scheme 3.
Schematic representation of the preparation of PMMA:IL materials.

stant in the range of 1–5 N/m were oscillated at their fundamental resonance frequencies, which ranged between 60 and 100 kHz.

Results and Discussion

FT-IR spectra of PMMA:BMIM.BF$_4$ and PMMA:BMIM.PF$_6$ (Figure 2) showed characteristic absorptions of their components: IL and PMMA. For BMIM.BF$_4$ materials, IL stretches can be highlighted at approximately 1500 cm^{-1} (C=C) and around 3100 cm^{-1} (aromatic CH). For PMMA:BMIM.PF$_6$ materials, IL stretches near 836 cm^{-1} and between 3100 and 3000 cm^{-1} (aromatic CH) are evident. At 1725 cm^{-1} a band corresponding to C=O stretching of saturated aliphatic ester, PMMA feature, was observed.

The menthol-based ILs provided more changes in the FT-IR spectrum of PMMA (Figure 3) compared to the normal BMIM ILs. FT-IR spectra of PMMA:[amebim]BF$_4$ (Figure 3a) showed absorption features of the [amebim]BF$_4$, while the FT-IR spectra of PMMA:[amebim]PF$_6$ (Figure 3b) indicated absorption of the ILs present in these materials, between 3100 and 3000 cm^{-1}. The changes promoted by [amebim]PF$_6$ in PMMA can be seen, also, in the absorptions between 1600 and 1500 cm^{-1}. The broad band at 3500 cm^{-1} was attributed to the presence of water in the samples.

The optical properties of the materials were analyzed by absorption spectroscopy in the visible region. It was observed that BMIM.BF$_4$ and BMIM.PF$_6$ materials presented a different concentration dependence (Figure 4).

The emergence of new absorption bands suggests that an interaction between the ILs

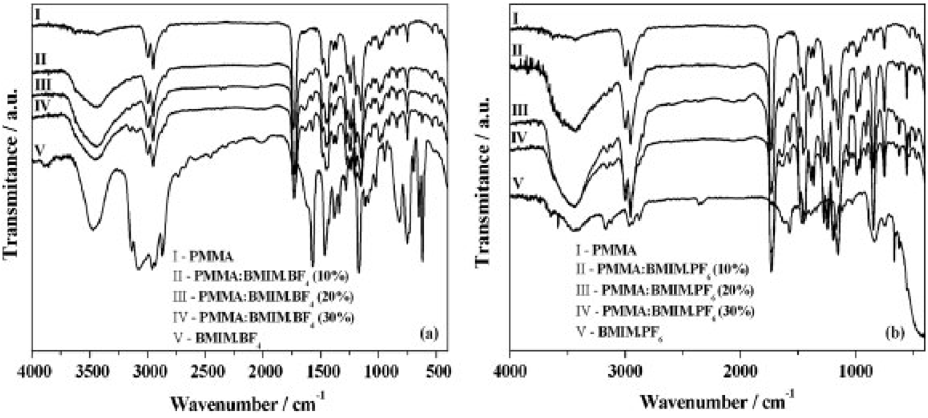


Figure 2.
FT-IR spectra of: (a) PMMA, PMMA:BMIM.BF$_4$ (10%), PMMA:BMIM.BF$_4$ (20%), PMMA:BMIM.BF$_4$ (30%) and BMIM.BF$_4$; (b) PMMA, PMMA:BMIM.PF$_6$ (10%), PMMA:BMIM.PF$_6$ (20%), PMMA:BMIM.PF$_6$ (30%) and BMIM.PF$_6$.

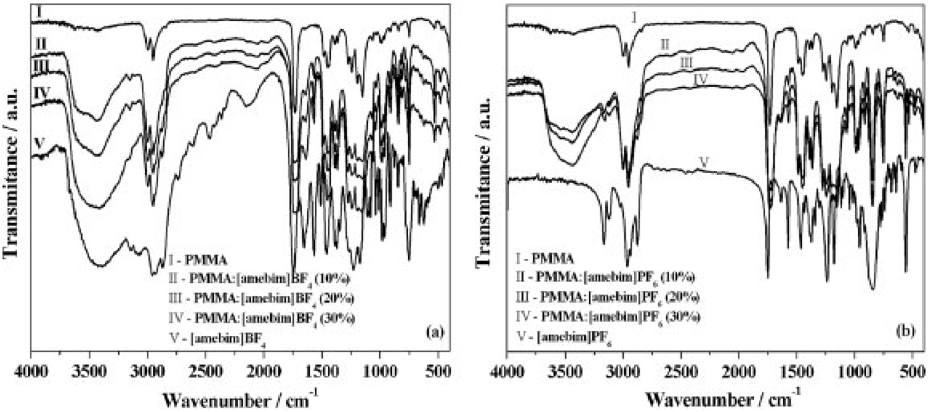


Figure 3.

FT-IR spectra of: (a) PMMA, PMMA:[amebim]BF_4 (10%), PMMA:[amebim]BF_4 (20%), PMMA:[amebim]BF_4 (30%) and [amebim]BF_4; (b) PMMA, PMMA:[amebim]PF_6 (10%), PMMA:[amebim]PF_6 (20%), PMMA:[amebim]PF_6 (30%) and [amebim]PF_6.

and the polymeric matrix has occurred, probably of the van der Walls type. Literature data shows that pure BMIM.BF_4 possesses an absorption band at 225 nm.[7] However, the materials prepared with achiral and chiral ILs presented absorptions bands in the visible spectrum range. The attribution of the excitation valence is not easy. Although calculations have not been carried out, we believe from the position of the absorption bands that the transitions in these materials are of the n-π^* and/or π-π^* type, because these transitions occur, experimentally, at 200-700 nm.

The material with 10 wt/wt% of BMIM.BF_4 presented a maximum absorption at 583 nm, corresponding to the yellow visible light region of the spectrum (Figure 4a). The material with 30% of BMIM.BF_4 showed three absorption regions with maximum at 439 nm (violet), 565 nm (green) and 756 nm (red), respectively (Figure 4a).

The polymer with 10% of BMIM.PF_6 presented three absorption bands (Figure 4b). The first band, with a λ_{max} at 439 nm, can be attributed to the violet region of the visible spectrum; the second

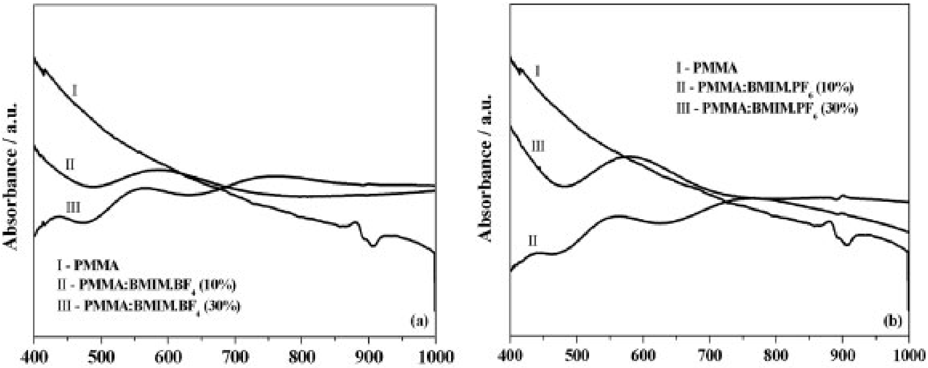


Figure 4.

Absorption spectra in the visible region of: (a) PMMA, PMMA:BMIM.BF_4 (10%) and PMMA:BMIM.BF_4 (30%); (b) PMMA, PMMA:BMIM.PF_6 (10%) and PMMA:BMIM.PF_6 (30%).

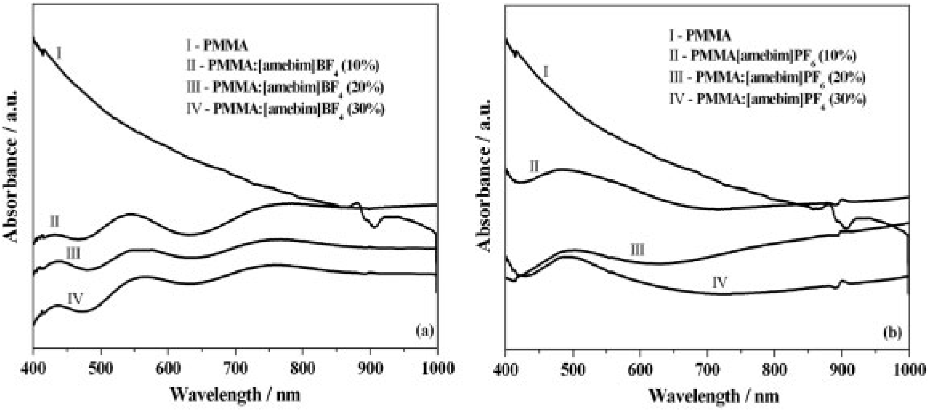


Figure 5.
Absorption spectra in the visible region of: (a) PMMA, PMMA:[amebim].BF_4 (10%), PMMA:[amebim].BF_4 (20%) and PMMA:[amebim].BF_4 (30%); (b) PMMA, PMMA:[amebim].PF_6 (10%), PMMA:[amebim].PF_6 (20%) and PMMA:[amebim].PF_6 (30%).

absorption band occurred at 557 nm, the region of the spectra relative to the absorption of green light; and the last absorption band appeared in the red region with λ_{max} at 760 nm. The material with 30% of BMIM.PF_6 showed a λ_{max} at 578 nm, which corresponds to an absorption in the yellow region of the visible spectrum.The materials produced with the menthol-beased ILs showed uniformity in the behavior of absorption in the visible region for the three concentrations used.

[amebim]BF_4 materials showed three absorption regions (Figure 5a): the first absorption near 436 nm (λ_{max}), violet region; the second band in the green region at approximately 560 nm (λ_{max}) and the third absorption was observed at approximately 770 nm (λ_{max}), red region.

Absorption spectra in the visible region for [amebim]PF_6 materials (Figure 5b) showed only one absorption. The polymer with 10% of IL presented absorption in a wider band of the spectrum, compared to other materials. This band, with λ_{max} at 482 nm, starts in the blue region and extends until the orange region. The sample with 20% of IL had a λ_{max} at 501 nm (green), while the polymer with 30% of IL showed a λ_{max} at 492 nm which corresponds to the cyan region.

The materials prepared with achiral ILs as well as the materials produced with chiral ILs showed one and three absorption bands. The samples that revealed three absorption bands seem to suggest better interactions with the polymeric chains. This idea can be suported by AFM images, which indicated that ILs changed the morphology of the PMMA (Figures 6 and 7). Lower concentration (10 wt/wt%, Figure 6b and 6e) of BMIM.BF_4 caused a disappearance of the PMMA cavities, while high concentration (30 wt/wt%) of BMIM.BF_4 promoted the destruction of cavities and the appearance of globules, with remaining structures of high relief. However, BMIM.PF_6 in the concentration of 30 wt/wt% did not change significantly the morphology of the polymeric chains.

[amebim].BF_4 promoted total destruction of the cavities of PMMA, producing materials with a homogeneous surface (7a, 7b and 7c), while [amebim].BF_6 modified substantially the surface in the concentrations of 10 and 20 wt/wt% (Figure 7d and 7e). It is possible to observe that the samples with homogeneous surface, as detected from the morphology analysis presented three absorption bands, except for the BMIM.PF_4 materials. This surface homogeneity may indicate a better inter-

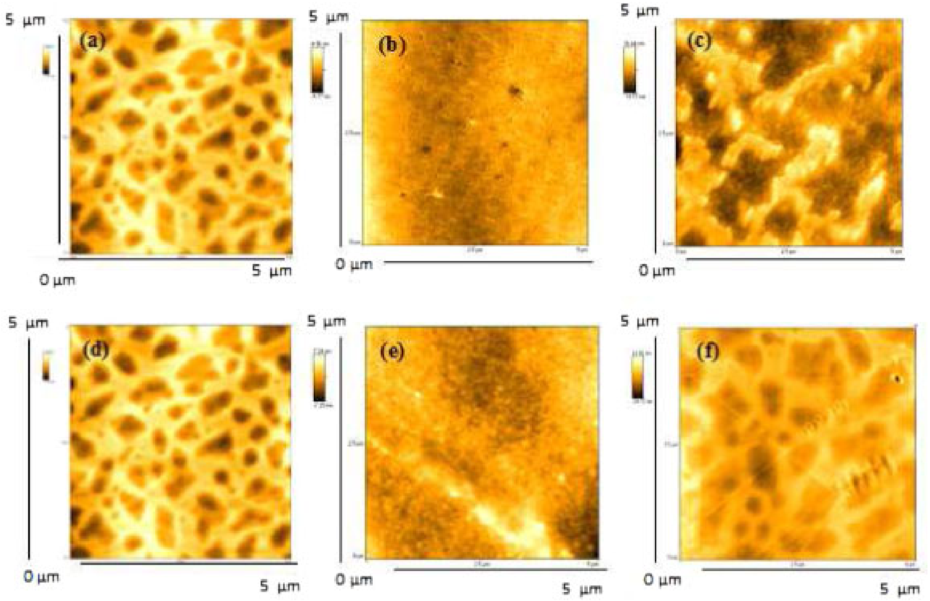


Figure 6.
AFM images (height) of (a) PMMA; PMMA:BMIM.BF$_4$ (b) 10 wt/wt% and (c) 30 wt/wt%; (d) PMMA (again), PMMA:BMIM.PF$_6$ (e) 10 wt/wt% and (f) 30 wt/wt%.

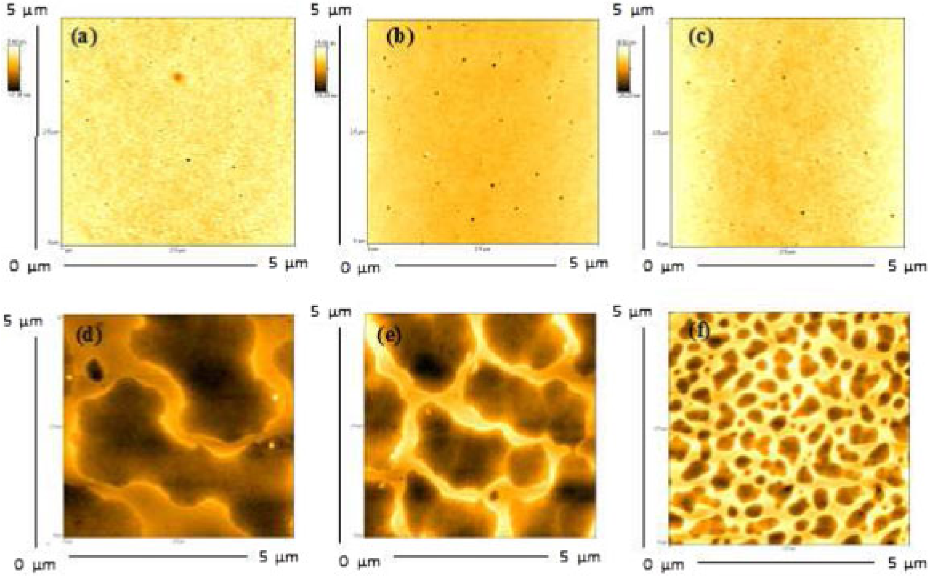


Figure 7.
AFM images (height) of PMMA:[amebim].BF$_4$ (a) 10 wt/wt%, (b) 20 wt/wt% and (c) 30 wt/wt%; PMMA:[amebim].PF$_6$ (d) 10 wt/wt%, (e) 20 wt/wt% and (f) 30 wt/wt%.

action between the polymeric matrix and the ILs, allowing and/or facilitating charge transfer processes with several eletronic transitions and consequentely absorption bands at different wavelengths.

Conclusion

FT-IR spectra of PMMA modified with ILs showed absorption bands corresponding to pure PMMA and ILs. Furthermore, these bands were intensified in the spectra of PMMA:ILs materials, suggesting interactions between the ILs and the polymer. The addition of the ILs to PMMA, which does not absorb in the visible region, provided changes in its optical properties. The materials gained capacity of absorption in different regions of the visible spectrum, depending on the type and concentration of the IL used. This suggests another application of the ILs studied, i.e., change of the capacity of absorption of the materials in the visible region. AFM images showed that the ILs changed the morphology of the PMMA matrix. In some case, the ILs promoted homogeneity in the PMMA surface. This homogeneity in the sample surface can help to understand the optical properties of the new materials prepared at different concentrations of achiral and chiral ILs.

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