PMMA-ORGANO BENTONITE NANOCOMPOSITES FROM THE EXFOLIATION-ADSORPTION TECHNIQUE AND THEIR CHARACTERIZATION BY FTIR, XRD, TEM, TSDC AND DSC.

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This work is related to the preparation of polymer-clay nanocomposites (PCNs) by the exfoliation-adsorption technique, from atactic poly(methyl methacrylate) (PMMA) in solution, using Bentonite (B) as a layered-silicate natural clay. To optimize the intercalation of B with PMMA, it has been organically modified (OB) with a quaternary ammonium salt that helps the interchange of cations, and thus converting its hydrophilic surface to an organophilic one. An investigation of the morphology and molecular motions or dynamics of the net polymer film as well as the PCN final films was performed by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Infra-Red Spectroscopy (IR), Thermally Stimulated Depolarization Currents (TSDC), and Differential Scanning Calorimetry (DSC) techniques. One of our interests was to discuss the solvent influence on the polymeric matrix. Herein, comparative studies of the effects of different solvents on the thermal and dielectric properties of the net PMMA films are reported. Four solvents were used to prepare the films, toluene, dichlorometane, tetrahydrofuran and acetone.

Fig. 1 XRD diffraction pattern of B, OB, and PMMA /5%OB

In Figure 1, XRD diffraction patterns(using Cu Kα radiation), reports the spacing between ordered layers of clay via the presence of the d100 or basal spacing. The original B exhibits a peak associated with a spacing of 14.7 Å, whereas the expanded OB shows a value of 19.2 Å. The absence of this basal peak suggests a high dispersion of clay platelets (exfoliation) in the PMMA/OB with 5% OB. The broad peak at around 15°=20 is due to the amorphous hallow of the atactic PMMA nanocomposite. The efficiency of the intercalation can be also check by TEM microphotographs. Figure 2 clearly shows that the OB layers are mainly exfoliated in the PMMA/OB with 2% OB.

Fig. 3 FTIR curves of PMMA/OB PCNs and PMMA/B

The FTIR spectra of the Si-O stretching region are shown in Figure 3 for PMMA/OB with varying % OB concentration, and PMMA with 15% of natural B. The graph shows the presence of a peak with increasing intensity and slight shift of its maximum towards higher λ⁻¹ position as the OB content increases. The absence of this peak in the PMMA/B sample corroborates their previous assignation to Si-O groups interacting with polymer molecules. The significant changes of this peak with the OB content obviously reflect the variation in the distribution of environments of the Si-O bonds, providing also an indication of the increasing overall degree of intercalation/exfoliation.

Figure 4 shows the dielectric spectra of the PMMA films prepared with the different solvents and the compressed molded sample. It displays a series of well established intrinsic relaxation signals, i.e., γ (methyl groups), γ' (adsorbed polar water molecules), β (carboxymethyl side
groups flip, $\beta'$ (postulated as a main chain rearrangement accompanying the side group flip, characterized as a rotation around the local chain axis), and long-range conformational change of the polymer backbone. (A) displays the secondary relaxations whose intensity and profile vary with the selected solvent. The glass transition is shown at higher temperature (B) as a huge peak, with intensity and temperature position (Tg) variations among the different solvents. The whole spectra of the cast samples exhibit evident intensity attenuation as compared to the molded film. A lower value of Tg is also a common feature among the cast samples. Comparable Tg trends have been obtained by DSC technique. Traces of the different solvents are expected to reside in relatively strong binding sites [2], e.g., hydrogen bonded to C=O groups. The measured amount of the remnant acetone, dichloromethane, toluene, and tetrahydrofuran solvents, obtained by NMR, is 0.30, 0.40, 9.00, and 14.00% respectively. The samples with higher solvent contents exhibit lower Tg values. The retained solvent molecules, trapped inside the PMMA films, affect the dynamics of the segmental and localized dielectric relaxations. This effect differs in function of the nature and the amount of the solvent, and it could be partly explained by acid-base interactions between PMMA and the solvents [3].

Figure 5 (A) shows that, on increasing the OB content the intensity of the low temperature relaxations decreases in the sample with 0.5% OB, increases up to 5% OB, and then drops again at 15% OB. A positive high-temperature shift of the low temperature spectra is observed in the samples with 2, 5, and 15% OB. This shift, related with the enhancement of the $\beta'$ process, could be explained by the increased exfoliation, as it increases the rotational mobility of the PMMA chains [4]. Figure 5 (B) shows that the temperature position of the dielectric manifestation of the glass transition is a decreasing function of the OB content. Similar Tg decreasing trend was obtained by DSC. This behavior is consistent with previous results [4-5] and have been rationalized assuming that the layered silicates reduce the intermolecular (cooperative) domain size, which increases with the exfoliation. However, as the layered silicate/polymer interactions could restrict segmental mobility, the outcome should be a “tug-of-war”, where the influence of these opposite effects must be accounted for.

References: