

PHOTO-OXIDATION OF POLYSTYRENE/MONTMORILLONITE NANOCOMPOSITES

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Polymer layered silicate nanocomposites (PLSN) are a new class of composites that have received considerable attention from both industry and academia. These materials exhibit, with respect to conventional mineral-filled composites or unfilled polymer, superior physical, mechanical and thermal properties at very low silicates contents. These improvements of performances depend greatly on the distribution of the layer of the silicates in the polymer matrix (intercalated or exfoliated) with better performance associated to higher degree of exfoliation. In the preparation of PLSN, the most commonly used clay is montmorillonite (MMT). In its pristine form, the excess of negative charge generated from isomorphous substitution within the layers (for example Al^{3+} replaced by Mg^{2+} or Fe^{2+}) is balanced by cations (Na^+ , Li^+ , Ca^{2+}). In order to achieve a higher exfoliation degree the inorganic cations present within the layers are exchanged with organic ones (o-MMT), rendering the silicate surface organophilic and so more compatible with the polymer matrix.

Photo-oxidative degradation in polymer materials caused by light and oxygen is an important issue concerning the use of these materials in outdoor applications. The very few studies concerning the photodegradation of PLSN converge on showing an important result: the presence of the silicate causes a higher instability of PLSNs to UV ageing with respect to the pristine polymers. Although several hypotheses has been proposed in order to explain this behaviour, it not yet clear the mechanism.

Since no study has been published on UV photodegradation of polystyrene/o-MMTs (PS/o-MMT) and in order to get new information to understand the photo-oxidation processes of PLSN, we carried out the study, reported in this communication, on the photo-oxidation of PS/Na/MMT and PS/o-MMTs obtained using C12, C16, C18/MMTs (Figure 1) and a o-MMT modified with the standard alkyl ammonium cation octadecyltrimethylammonium bromide (ODTA/MMT).

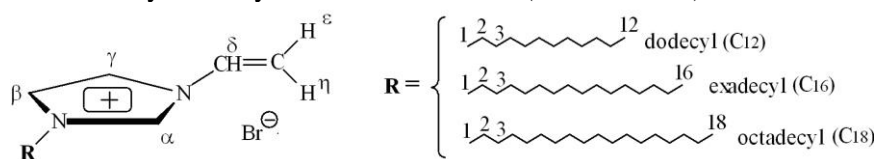


Figure 1 – Scheme of the used surfactants

The samples, containing 3% by weight of o-MMT and prepared via bulk polymerization, were characterized by X-Ray diffraction (XRD) and transmission electron microscopy (TEM). Their films were exposed to accelerate weathering in a Xenotest Alpha apparatus ($\lambda > 300\text{nm}$) and the chemical modification caused by photo-oxidation process were investigated by FTIR.

The XRD curves of PS/C12, C16, C18 3% nanocomposites reveal a possible exfoliation, as verified by the absence of any diffraction peak. TEM analysis revealed that while PS/C12/MMT 3% present an intercalated nanomorphology with very few exfoliated layers in the polymer matrix, the sample containing C16 surfactant is partially exfoliated and finally the PS/C18/MMT 3% present the highest degree of exfoliation.

FT-IR spectra, recorded for each sample in order to follow the progress of photo-oxidation, showed that, while the shape of oxidation bands of the nanocomposites is similar to that observed for neat PS films, the relative intensities of the carbonyl bands in the region between 1732 cm^{-1} and 1686 cm^{-1}

were different. In the MMT containing samples, the intensities of the bands associated to the monomeric and dimeric forms of benzoic acid (absorption maximum at 1731 cm^{-1} and 1698 cm^{-1} , respectively), and the ones relative to $\text{H}-(\text{C}=\text{O})-\text{Ph}$ and $\text{CH}_2-(\text{C}=\text{O})-\text{Ph}$ (absorption maxima at 1703 cm^{-1} , and 1692 cm^{-1} , respectively) are higher with respect to the corresponding intensities present in the UV photoaged PS. Besides these also the absorption maximum assigned to OH bending of carboxylic acids (at 1417 cm^{-1}) is more intense in the nanocomposites (Fig. 2).

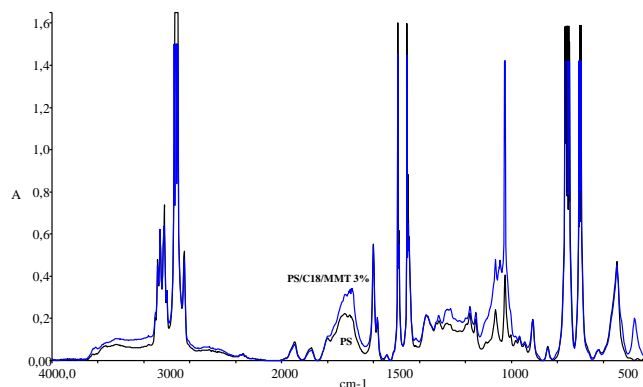


Figure 2 – FT-IR spectra of PS and PS/C18/MMT 3% after 334 h of UV irradiation

The rate of photo-oxidation of the nanocomposites and pristine PS were compared by measuring the variation in the areas of the carbonyl bands with the irradiation time as shown in fig.3

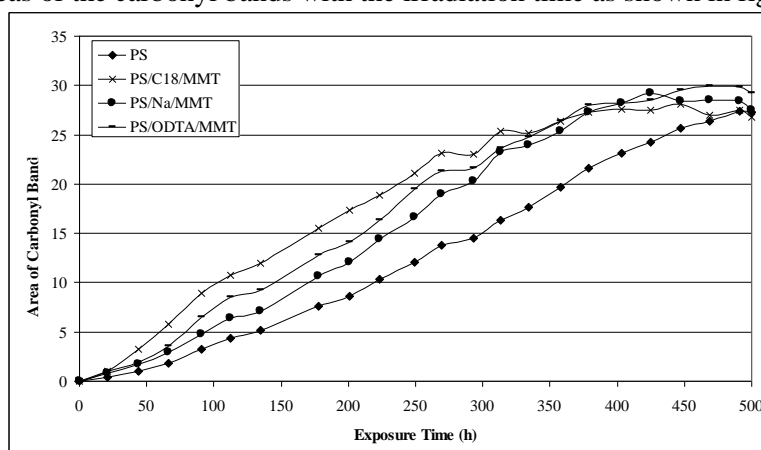


Figure 3 – Variation in the area of carbonyl bands areas as a function of UV irradiation time (h) for 100μ film of pure PS, PS/Na/MMT 3%, PS/ODTA/MMT 3%, PS/C18/MMT 3%

We found that the samples that presented the higher degree of exfoliation showed a shorter induction period and degraded more quickly than the less exfoliated one (PS/C18/MMT 3%). We suppose that in PS/o-MMT nanocomposites under UV exposure the catalytic active sites present in MMTs can accept single electrons from donor molecules of PS matrix forming free radicals in the polymer matrix that could accelerate the normal photo-oxidative process. This effect is more evident in the more exfoliated nanocomposites in which the catalytic active sites are more accessible than in the intercalated ones. Moreover, in PS/o-MMT this catalytic effect seems kinetically promote the formation of carbonyl and carboxylic species directly bonded to aromatic ring.

References

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