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PMMA/Nontronite nanocomposites thermal stability: experimental evidence of the e diffusion barrier and radical trapping effect

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Polymer-Clay nanocomposites present improved flame retardancy and thermal properties as compared to the pristine polymer matrix. The physical barrier induced by the clay and radical trapping assisted by the presence of selected 3d atoms in the inorganic phase are responsible for these properties. In this context, nanocomposites containing Poly(methyl methacrylate) (PMMA) and smectite clay such as nontronite (Non) (Fe loading: 5.6 wt.%) were prepared (XRD). Thermal stability of the samples was investigated by TGA, time-resolved XAS and Raman measurements during thermal decomposition of PMMA-clay. The diffusion barrier effect on the entrance of O_2 was proved by TGA and DTG where the curve of the PMMA-Non presents a shift towards higher temperatures in dynamic synthetic air compared to pristine PMMA. The contribution of the radical trapping on the thermal stability of nanocomposite was evidenced by the significant shift of the rising edge position by -5 eV experienced by Fe species upon heating under N_2 for PMMA-Non as soon as similar treatment of nontronite does not lead to rising edge shift. This shift at lower energy of the rising edge is indicative that reduction of Fe^{3+} species occurs by the sequestration of radicals formed by the PMMA depolymerization. The non-overlapping region between the energy position shift of the rising edge and the TGA curve measured under N_2 strongly indicates that the mechanism which delays the decomposition of PMMA for PMMA-Non is the redox transformation. Raman spectroscopy evidences the formation of char deposits (characterized by the D and G lines in the 1000-1600 cm-1 range) above 400°C. At this stage the formation of chars contributes to the stability of remaining PMMA up to 550°C though additional physical barrier to the mass transport.