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KINETIC STUDY OF THE THERMAL DEGRADATION OF PS/MMT NANOCOMPOSITES PREPARED WITH IMIDAZOLIUM SURFACTANTS

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Styrene and montmorillonite organically modified with imidazolium surfactants (MMT) at various alkyl chain lengths (C_{12}, C_{16} and C_{18}) were used to prepare the corresponding PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18} nanocomposites by *in situ* polymerization. XRD and TEM analyses evidenced the formation of both intercalated and exfoliated structures. The glass transition temperatures (T_g) of nanocomposites, as well as that of neat PS, were obtained by DSC measurements. The thermal degradations were carried out in the scanning mode, in both inert and oxidative environments, and the initial temperatures of decomposition (T_i) and the apparent activation energies of degradation (E_a) were determined. Due to an oxidative degradation mechanism, the T_i and E_a values in air atmosphere were lower than those under nitrogen.

The results indicated that nanocomposites are more thermally stable than polystyrene, and suggested an increasing degree of exfoliation as a function of alkyl chain length of surfactant, associated with enhancing thermal stability.

Keywords: *activation energy of degradation, nanocomposites, polystyrene, thermal stability*

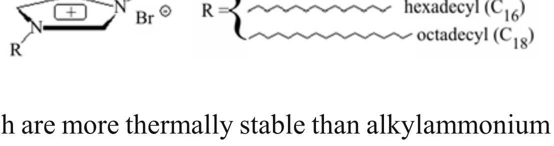
Introduction

Polymer layered silicate nanocomposites (PLSNs) are a novel class of materials formed through the dispersion at nanoscale level of a clay in a polymer. If clay is well dispersed, intercalated or delaminated (exfoliated) morphologies (nanocomposites) are obtained. Intercalated nanocomposites consist of well-ordered layers in which registry among clay layers is maintained, while this registry is lost in the delaminated ones. By contrast, if the clay is not well-dispersed, no nanocomposite is formed.

The major reason of the interest in introducing clays into polymers at nanoscale level is the enhancement in physical, mechanical, barrier and flammability properties as compared to virgin polymer and conventional filled polymer composites. In addition, nanocomposites exhibit a pronounced increase in thermal stability [1–3], which is very important because they can be subjected to high temperatures during processing or in service. A first indication of nanocomposites thermal stability improvement appeared in the work of Blumstein [4] and it has been confirmed in some more recent papers [5–7]. Moreover, in a very recent paper, it has been reported that the glass transition of cured epoxy nanocomposites is lower than that of the cured neat resins [8].

Montmorillonite (MMT) is the most used layered silicate to obtain PLSNs. Since it is hydrophilic, the exchangeable cations (Na^+, K^+, Ca^{2+}, Li^+ and Mg^{2+}) present in its interlayer region are substituted by organic cations, aiming to increase interlayer spacing and to make inorganic material more organophilic and more compatible with polymer. Long carbon-chain alkyl ammonium salts commonly used to this purpose present the drawback of a low thermal stability [9, 10], and then the use of more thermally stable phosphonium, piridinium and iminium cations has been considered [11, 12].

In this work we carried out a comparative study on the thermal degradation in dynamic heating conditions of some polystyrene (PS)-clay nanocomposites, prepared by using montmorillonite (MMT) organically modified with the following imidazolium salts as surfactants,



which are more thermally stable than alkylammonium and pyridinium cations [12–14].

The aim of this study was to draw useful information about the thermal stability of investigated

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nanocomposites, and about the influence of the alkyl chain length of surfactant on it. Since the comprehensive thermal stability of polymers is connected, in our opinion, to both the initial temperature and the rate of degradation, the determination of a kinetic parameter (E_a) associated with the degradation processes is considerably important, in particular when the initial temperatures of decomposition are close or the same.

Experimental

Materials

The chemicals used in this study were acquired from Aldrich Chemical Co. The MMT was a fine powder with a particle size of 10–15 μm in a dry state and a cation exchange capacity (CEC) of 100 mEq/100 g. Styrene monomer was purified using an Aldrich inhibitor removal column. AIBN was crystallized twice from dry ethanol out of direct light, at temperature lower than 40°C.

The synthesis and the characterization of imidazolium surfactants and organically modified MMT were described in our previous paper, as well as those of the PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18} nanocomposites prepared at the 3% by mass of organically modified MMT [15].

Methods

TEM analyses

TEM investigations were performed by a Jeol JEM 2010 operating at an acceleration voltage of 200 kV. Samples were prepared as follows: a small piece of nanocomposite in a PS support was cut by an ultratome and placed on a 100 mesh copper grid for analysis.

XRD experiments

XRD measurements were recorded on a Bruker-AXS D5005 θ–θ X-ray diffractometer, using CuK$_\alpha$ radiation, operating at 20 kV and 30 mA.

DSC measurements

The glass transition (T_g) temperatures were determined by a Mettler DSC 20 calorimeter coupled with a Mettler TC 10A processor as control and evaluation unit. Both heat flow and temperature calibrations of calorimeter were performed following the procedures suggested by the supplier and reported in the operating instructions of equipment [16].

Samples of about $6.0\cdot10^{-3}$ g, held in sealed aluminum crucibles, the scanning rate of 10°C min^{-1} and a static air atmosphere were used for determinations.

TG and DTG measurements

Thermal degradations were performed in a Mettler TA 3000 thermogravimetric analyser coupled with a Mettler TC 10A processor. The temperature calibration of thermobalance was made according to the procedure suggested by the supplier [16], based on the change of the magnetic properties of three metal samples (Isatherm, Nickel and Trafoperm) at their Curie points (142.5, 357.0 and 749.0°C, respectively). The temperature calibration was repeated every month.

Degradations were performed in dynamic heating conditions, from 35 up to 600°C, in both flowing nitrogen (0.02 L min^{-1}) and static air atmosphere, at various heating rates (Φ=2, 5, 7.5, 10, 12.5, 15, 17.5 and 20°C min^{-1}). Samples of $4\cdot10^{-3}$–$6\cdot10^{-3}$ g, held in alumina open crucibles, were used and their mass were measured as a function of temperature and stored in the list of data of the appropriate built-in program of processor. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were immediately printed at the end of each experiment and the mass of sample at various temperatures were then transferred to a PC. These data were later used to plot the percentage of undegraded sample (1–D)% as a function of temperature, where $D=(W_o-W)/W_o$, and W_o and W were the masses at the starting point and during scanning. The thermoanalytical data at various heating rates were used to calculate the apparent activation energy values of degradation (E_a) by the Kissinger method [17], which is based on the following equation

$$\ln(\Phi/T_m^2)=\ln(n\mathrm{RAW}_m^{n-1}/E_a)-E_a/\mathrm{R}T_m$$

where Φ is the heating rate, T_m is the temperature at the maximum rate of mass loss, n is the apparent reaction order, R is the universal gas constant, A is the pre-exponential factor and W_m is the mass of the sample at the maximum rate of mass loss. The degradation E_a values can be thus obtained by the slope of the linear relationships $\ln(\Phi/T_m^2)$ *vs.* $1/T_m$.

Results and discussion

XRD and TEM analyses were carried out in order to verify the formation of nanostructures.

The XRD patterns of the PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18} nanocomposites revealed a possible exfoliation, as verified by the absence of any diffraction peaks.

The TEM images showed, for all systems investigated, the formation of both intercalated and exfoliated morphologies, thus confirming the formation of nanostructures. But although TEM is an effective tool, it is limited because it only probes a small volume of sample. Then from these analyses it was not possible to draw reliable conclusions on the degree of intercalation and exfoliation. The TEM microphotographs of PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18} are reported as examples in Figs 1a, b and c, respectively.

Thermal degradation experiments were thus carried out in inert environment, at the various selected heating rates. PS degraded completely through a single stage, as well as PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18}. The TG curves at 10°C min^{-1} of PS and nanocomposites are reported as an example in Fig. 2. Since an aim of this work was to obtain information on the comprehensive thermal stability of the studied compounds, the characteristic parameters of decomposition were determined, i.e.: the initial temperature of decomposition (T_i) and the apparent activation energy of degradation (E_a), which is connected with the rate of decomposition.

The apparent activation energy values of degradation of various nanocomposites were determined by the slope of the linear relationships $\ln(\Phi/T_m^2)$ *vs.* $1/T_m$. To this aim several runs were carried out at every scanning rate used for the degradation experiments. We considered as T_m values the average temperatures of the DTG peaks (Table 1). The least square treatment of the data in Table 1 was then performed according to the Kissinger equation, giving rise to single linear relationships in all cases. The degradation E_a values of PS and various nanocomposites were calculated and reported in Table 2.

The T_i values were obtained by the TG curves, as the intersection between the starting mass line and the maximum gradient tangent to the TG curve. Since the experimental conditions largely influence both the shape and the position of TG curve, the T_i values of each sample at different scanning rates were different with each other, though the values of various samples at the same scanning rate showed in every case the same trend. For the sake of simplicity only the values at 10°C min^{-1} were considered. This heating rate was selected because it is a medium value among those employed for degradation experiments and, also, is

Fig. 1 TEM microphotographs of a – PS/MMT/C_{12}, b – PS/MMT/C_{16} and c – PS/MMT/C_{18}

Table 1 Temperatures at maximum rate of mass loss (T_m) for the degradation stage of PS and studied nanocomposites at the various heating rates (Φ) used under nitrogen flow

Polymer Φ/°C min^{-1}	PS T_m/K	PS-MMT-C_{12} T_m/K	PS-MMT-C_{16} T_m/K	PS-MMT-C_{18} T_m/K
2	662	682	687	689
5	681	696	700	705
7.5	688	704	708	710
10	693	709	714	712
12.5	697	712	716	717
15	701	715	718	718
17.5	704	718	720	721
20	706	721	723	724

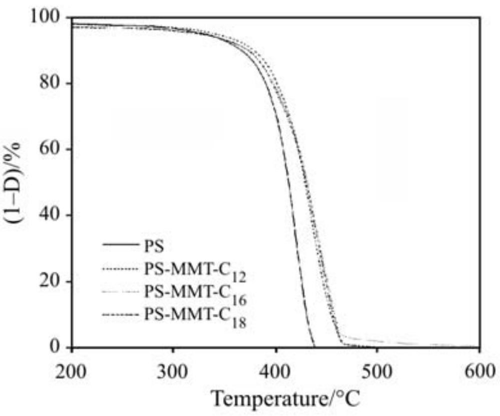

Fig. 2 TG curves under N_2 flow of PS and PS/MMT/C_{12}, PS/MMT/C_{16}, PS/MMT/C_{18} nanocomposites at the heating rate of 10°C min^{-1}

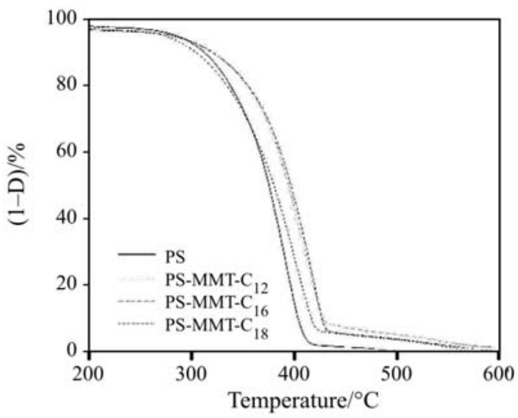

Fig. 3 TG curves in static air atmosphere of PS and PS/MMT/C_{12}, PS/MMT/C_{16}, PS/MMT/C_{18} nanocomposites at the heating rate of 10°C min^{-1}

the same than that used for T_g determinations. The considered T_i values were averaged from those of three runs, the maximum differences between the average and the experimental values being within ±1°C, and are reported in Table 2.

Degradation experiments were thus carried out in a static air atmosphere. The TG curves obtained were similar to those under nitrogen, though shifted to lower temperatures (Fig. 3). The average T_m values were determined (Table 3) and treated according to the Kissinger equation. Single linear relationships were obtained in all cases, and the degradation E_a values were calculated. The initial temperatures of decomposition in oxidative environment were also obtained by the TG curves, and the values at 10°C min^{-1} were selected.

The glass transition temperatures were also determined calorimetrically aiming to draw more information about the property – structure relations of the studied systems, and are reported in Table 2, together with the T_i and degradation E_a values.

The data in Table 2 indicate that PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18} have, under nitrogen, higher thermal stability than polystyrene, as

Table 2 Glass transition temperatures (T_g), initial decomposition temperatures (T_i) and apparent activation energies of degradation (E_a) of PS and studied nanocomposites

Polymer	Under N_2 flow		In static air atmosphere		
	T_i/K[a]	E_a/kJ mol^{-1}	T_g/K	T_i/K[a]	E_a/kJ mol^{-1}
PS	666	192±4	371	610	128±6
PS-MMT-C_{12}	675	229±5	372	616	138±6
PS-MMT-C_{16}	675	253±7	374	632	145±6
PS-MMT-C_{18}	675	266±11	375	639	189±7

[a] determined at 10°C min^{-1}

Table 3 Temperatures at maximum rate of mass loss (T_m) for the degradation stage of PS and studied nanocomposites at the various heating rates (Φ) used under static air atmosphere

Polymer	PS	PS-MMT-C_{12}	PS-MMT-C_{16}	PS-MMT-C_{18}
Φ/°C min^{-1}	T_m/K	T_m/K	T_m/K	T_m/K
2	626	642	638	658
5	644	665	660	673
7.5	653	670	666	683
10	663	678	672	688
12.5	672	687	677	694
15	676	692	683	696
17.5	679	696	689	697
20	680	697	693	702

supported by the higher T_i and E_a values, in agreement with the formation of nanostructures. The three systems show the same T_i values, and a very good linear increase of activation energy of degradation as a function of number of carbon atoms in the surfactant alkyl chain (n_c). The linear dependence of degradation E_a values on n_c is shown in Fig. 4. The uncertainties there reported were calculated by the least square treatment of the data of Table 1 according to the Kissinger equation.

Also in oxidative atmosphere our nanocomposites evidenced higher initial temperature of decomposition than polystyrene, but the trend observed was different from that in inert environment. The T_i values increased with the alkyl chain length of surfactant (from C_{12} to C_{18}). In addition, the activation energy values of degradation for PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18}, which were quite higher than polystyrene, increased as a function of n_c, although the same good linearity found under nitrogen was not observed (Fig. 4). The trend shown by the glass transition temperature, very slightly increasing from PS/MMT/C_{12} to PS/MMT/C_{18} (Table 2), was similar to those of the degradation E_a values in both investigated environments.

On considering the over reported findings and observations, only an interpretation on the basis of the thermoanalytical data obtained can be attempted.

The T_g, T_i and E_a values of our systems, higher than those of PS in both studied environments, appear consistent with the formation of nanostructures, as also supported by XRD and TEM analyses.

Concerning the results in flowing nitrogen, the initial decomposition temperatures of nanocomposites are higher than that of virgin polystyrene, but are not affected by the alkyl chain length of surfactant. This behaviour could be explained as follows: the clay incorporated into a polymer matrix acts as a mass transport barrier to the volatile products generated during decomposition [18]. Since a sample starts to decompose when the partial pressure of the gaseous products exceeds the ambient pressure, decomposition will be observed only when the produced gases can freely effuse from the sample. In the case of the formation of nanostructures, the free effusion is more difficult, so giving rise to higher T_i values than virgin PS. Our results are in agreement with those obtained by Doh and Cho on intercalated PS-based nanocomposites produced by *in situ* polymerization of styrene, for which the onset temperatures of decomposition under nitrogen were higher than that of PS, but substantially independent on surfactant alkyl chain length [6].

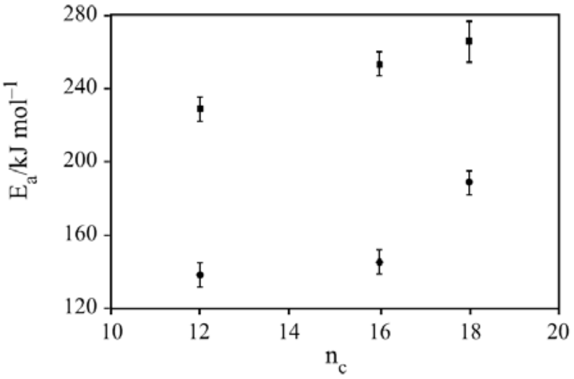

Fig. 4 Apparent activation energy of degradation (E_a) as a function of number of carbon atoms in the surfactant alkyl chain (n_c): ■ – under nitrogen flow, ● – in static air atmosphere

The trend observed for the apparent degradation E_a values, which are higher than that of PS and linearly rise from PS/MMT/C_{12} to PS/MMT/C_{16} and to PS/MMT/C_{18}, could be due, in our opinion, to the increasing degree of exfoliation when the number of carbon atoms of alkyl chain in the organically modified clay increase. On considering that the degradation E_a values were determined through mass loss measurements during decomposition, the lower mass loss rates at higher chain lengths of surfactant suggest an increasing degree of exfoliation in agreement with the lesser permeability usually observed in exfoliated structures [19].

This hypothesis is also in agreement with the trend observed for glass transition temperature, which is analogous to that of degradation E_a values. The glass transition temperature of a polymer can change for several reasons, including, for example, changes in tacticity or in molecular mass. Inorganic nanofiller does not contribute directly to the T_g of matrix, but the interactions of polymer chains with clay can alter the chain kinetics in the region near inorganic particles [20, 21]. Also, for some PS – based nanocomposites, the increase of glass transition temperature was explained in literature with enhanced clay – PS interactions [22]. In the case of the systems here studied, the T_g changes observed are in agreement with the enhancement of interactions between polymer and organically modified clay when the degree of exfoliation increases.

The results in static air atmosphere (Table 2) partially agree with those in flowing nitrogen. Both T_i and E_a values of our systems were considerably lower than the corresponding ones under nitrogen flow, thus indicating that a different degradation mechanism, probably oxidative in nature, occurs. This finding disagrees with a recent paper, where the Authors did not observe any difference in the TG data for reaction carried out in nitrogen *vs*. an air atmosphere, and assert that this is sometimes a criterion of nanocomposite formation [23].

Also in oxidative environment PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18} evidenced higher initial temperatures of decomposition than virgin polystyrene, but the trend, showing an increase of T_i with the number of alkyl chain carbon atoms of surfactant, was different if compared with that in flowing nitrogen. This different behaviour could be explained, in our opinion, as follows: the driving factor of the initial decomposition temperature is, in oxidative environment, the oxygen-polymer contact. The alkyl chain length of surfactant is thus significantly influent on the initial temperature of decomposition because it acts on the exfoliation degree. If the degree of exfoliation increases the diffusion of oxygen into the system is delayed, and higher initial temperatures of decomposition are found.

The trend exhibited by the E_a values was increasing as a function of the number of carbon atoms of surfactant alkyl chain, such as that in inert environment, even though the same linearity observed under nitrogen flow was not found (Fig. 4). A dramatic increase of the apparent activation energy of degradation was observed on going from PS/MMT/C_{12} to PS/MMT/C_{18}, which was, in percentage, much higher than under nitrogen. This finding could be explained, in our opinion, with a double effect of the increasing degree of exfoliation on the decomposition rate: in oxidative environment the lower permeability at higher degrees of exfoliation influences twice the decomposition rate, and then the calculated E_a values, by both a more difficult oxygen-polymer contact and a hindered out-effusion of the volatile decomposition products, so giving rise to the large degradation E_a increase observed.

Conclusions

The TEM analyses clearly indicated the presence of both intercalated and exfoliated nanostructures in the PS/MMT/C_{12}, PS/MMT/C_{16} and PS/MMT/C_{18} here studied, but did not allow to obtain any reliable information on the degree of exfoliation of various nanocomposites. Moreover, only hypotheses on the basis of the thermoanalytical data are possible.

All the investigated systems exhibit higher thermal stability than PS in both inert and oxidative environments, as evidenced by their higher initial decomposition temperatures and apparent activation energies of degradation. The comprehensive picture of the T_g, T_i and E_a values shows a rising thermal stability from PS/MMT/C_{12} to PS/MMT/C_{18}. The obtained results appear in agreement with decreasing permeability and increasing clay – polymer chains interactions when the chain length increases, thus suggesting an increasing degree of exfoliation.

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