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ORIGINAL CONTRIBUTION

Poly(methyl methacrylate)-kaolinite nanocomposites prepared by interfacial polymerization with redox initiator system

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Abstract Interfacial intercalative polymerization of methyl methacrylate (MMA) was developed to prepare PMMA-kaolinite nanocomposites using a redox initiator system, based on dodecylamine as reductant, immobilized into kaolinite by successive intercalation while the oxidant component of the redox system ($K_2S_2O_8$) was applied from aqueous phase. The X-ray diffraction (XRD) was used to prove the functionalization of the clay with the amine before starting the polymerization reaction. The progress of the polymerization reaction through the involvement of the amine in the initiation process was confirmed not only by successfully performing the reaction at 50 °C, a temperature at which the $K_2S_2O_8$ cannot start the polymerization alone, but also by the enhancement of polymerization rate and drop in activation energy required to start the polymerization. The produced PMMA/kaolinite nanocomposites were examined by XRD and transmission electron microscope as well; both confirmed the defoliation of the kaolinite layers into homogeneously distributed platelets within the polymer phase which supports the effectiveness of the redox initiation in the intercalative polymerization. Furthermore, more explanation about the interfacial structure of the nanocomposites was given using Fourier transform infrared. The thermal gravimetric analysis revealed a very similar behavior above 300 °C with respect to the pure PMMA prepared under the same reaction conditions while in the range from 220 °C to 320 °C, the degradation was earlier in the case of the nanocomposites due to the presence of the dodecylamine; on the other hand, the glass transition temperatures were increased remarkably as assigned by differential scanning calorimetry in comparison with the pure PMMA.

Keywords PMMA · Kaolinite · Nanocomposites

Introduction

The surface of clays and inorganic mineral fillers is hydrophilic, and this impedes their dispersion (wetting) by organic phases. The compatibility of the mineral with the organic phase, in terms of wetting and dispersion, may be substantially increased by the prior adsorption of a monolayer of a suitable organic substance over the particle surfaces or by the covalent addition of some simple organic compounds to the reactive surface groups of the mineral [1]. Several attempts to hydrophobize the clay surface by mixing with organic compounds [2] or absorption of these compounds on the surface itself [3] were reported. Unfortunately, these systems suffer from easy leaching of the organic component, which is very weakly fixed on the inorganic surface, by solvents or during compounding [4, 5], leading finally to macrocomposites which are characterized by weak interfacial adhesion as experienced by Bhattacharya et al. [4] who polymerized methyl methacrylate in the presence of montmorillonite and also by Kojima and coworkers when intercalated ε-caprolactam into montmorillonite followed by polymerization to give a nylon-6-clay macrocomposites [5]. For that reason, nanocomposites were developed based on a stable hydrophobic clay that can be prepared by replacing part or all of the exchangeable cations present in swellable clays such as montmorillonite with small organic cations or polycations [1, 6, 7]. Lagaly and Dekany [6–9] studied the resulting

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hydrophobic layer silicates intensively in organic liquids; accordingly, the structure and behavior of these silicates became well known from X-ray diffraction, adsorption, and microcalorimetric measurements.

It was found that the improved dispersibility of the inorganic phase with the polymer matrix in addition to the remarkable interfacial adhesion imparted excellent properties to these nanocomposites that could not be obtained with conventional composites. On other hand, kaolinite, which is a non swellable 1:1 phyllosilicate containing a gibbsite octahedral layer and a silicon oxide tetrahedral sheet with two distinct interlayer surface, has strong hydrogen bonds between the aluminol and Si-O groups, holding adjacent lamella to each other, and consequently makes the intercalation process inside the basal space difficult, in particular, because of the absence of any exchangeable cations inside the basal space [10]. Accordingly, all the nanocomposites prepared with kaolinite were of the intercalated type, where the clay disperses in the polymer matrix while keeping its lamella in completely ordered state [11, 12]. This differs dramatically from the exfoliated nanocomposite type, where the clay layers delaminate into individual platelets dispersed in the polymer phase, which may lead to composites with enhanced properties [8, 9].

Recently, Essawy et al. [13] attempted to conduct a typical emulsion polymerization of vinyl acetate in presence of a virgin kaolinite as well as pre-intercalated kaolinites with Dimethyl sulfoxide (DMSO) or *N*-methyl formamide (NMF), prepared according to the methods mentioned in the literature [14–19]. Unfortunately, polymer intercalation into the basal space was unsuccessful by this method; on the contrary, the pre-intercalated NMF or DMSO species deintercalated back into the reaction medium. As a result, collapse of the interlamellar space was observed. However, it was noticed that these pre-intercalated species may speed up the polymerization reaction as compared to the corresponding reaction in the presence of untreated Kaolinite.

In the last decade, many researchers [20–22] used two-component redox initiator systems comprising a hydrophobic oxidant component together with a hydrophilic reductant component to carry out interfacial polymerization. Here, we introduce the polymerization of methyl methacrylate using two-component initiator system. The hydrophobic reductant (dodecylamine) was immobilized inside the basal space of Kaolinite, according to the description of Dekany [23–27] and Cabedo [28], while the hydrophilic oxidant (potassium persulfate) was charged to the aqueous medium. We hope that interfacial polymerization of methyl methacrylate (MMA) takes place inside the basal space of the functionalized Kaolinite which may finally produce PMMA/Kaolinite nanocomposites of exfoliated type.

Experimental

Materials

MMA was purchased from Merck-Schuchardt, Germany; DMSO was supplied by Labscan Ltd. Unit Stillorgan Ind. Park, Co., Dublin. Methanol and dodecylamine were obtained from Sigma-Aldrich (Germany) at purity of at least 98% each. Potassium persulfate was obtained from El-Nasr Chemical Company, Egypt. Polyvinyl alcohol (PVA) of molecular weight 125,000 was purchased from S.D. Fine-Chem Ltd., India. Kaolinite was a gift from Sinai Manganese Company, Egypt.

Methods

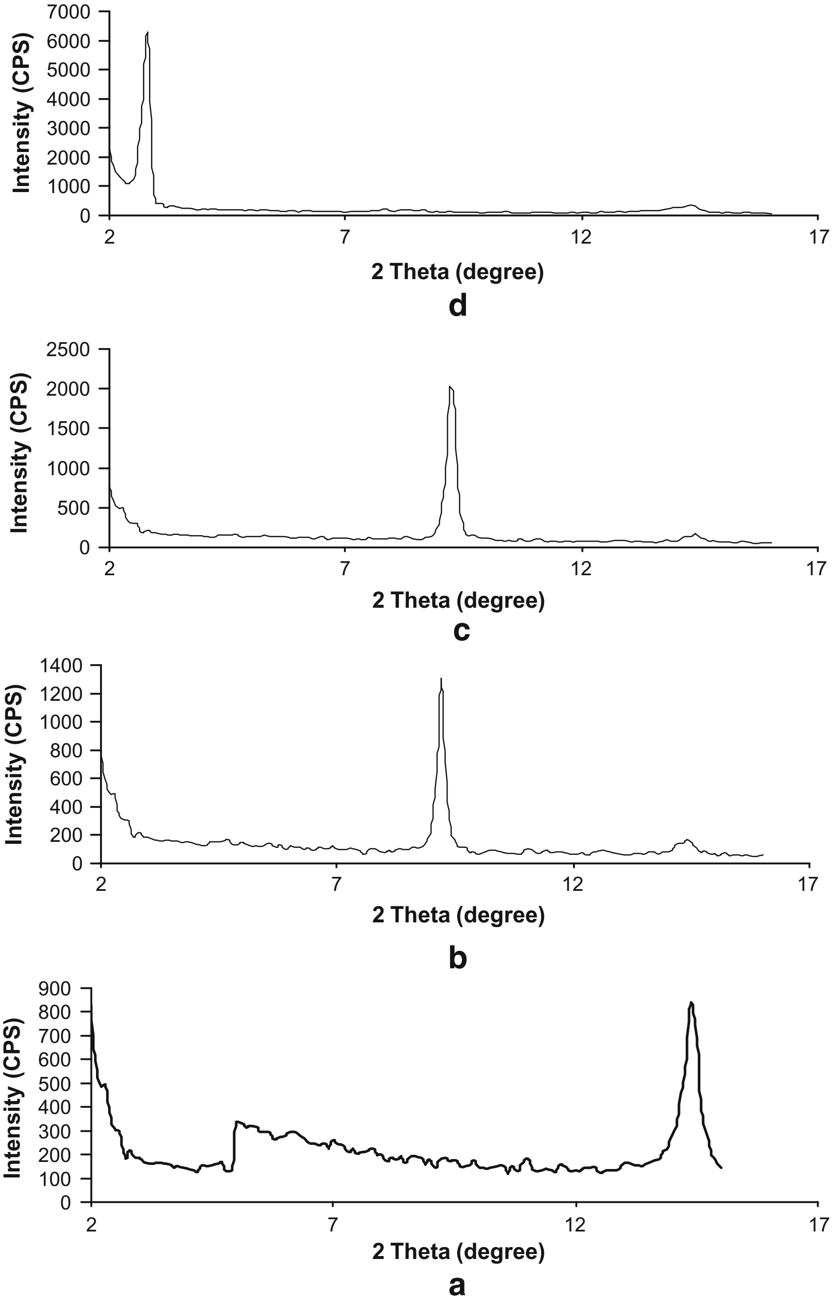
Kaolinite Treatment

Kaolinite was modified by dispersing 1 g in 10 ml of DMSO and kept under continuous stirring (500 rpm) for 3 days at room temperature. Finally, it was filtered off and washed with a reasonable amount of the same solvent before drying at 50 °C in electric oven. The kaolinite methanol intercalation compound was prepared using kaolinite-DMSO precursor immersed in excess methanol and kept under stirring for 10 days at room temperature; the methanol was exchanged frequently with a fresh methanol to displace the DMSO. Lastly, the product was centrifuged, and yellowish white powders were obtained and dried at 50 °C. Intercalation of dodecylamine into kaolinite was performed by using freshly prepared K-DMSO-MeOH as precursor. Five grams of K-DMSO-MeOH was dispersed in ~50 ml of dodecylamine in closed flasks for 24 h with continuous shaking. The dispersion was centrifuged, and the process was repeated with fresh amine for 2 days more. The final product was centrifuged and ground to a fine powder.

Emulsion polymerization of methyl methacrylate

In a 250-ml, two-neck flask equipped with a reflux condenser, 5 ml of methyl methacrylate monomer was added into 45 ml of distilled water followed by the addition of a predetermined amount of dodecylamine-functionalized kaolinite (0.5 g); the mixture was homogenized using mechanical stirring at 500 rpm. The emulsion was heated at the required temperature with an automatically controlled water bath. At once, polymerization started by addition of appropriate molar amounts of potassium persulfate as initiator and 7.5 ml of 15% PVA solution as emulsifier. In order to determine the conversion of monomer to polymer during polymerization process, it was necessary to withdraw the samples at different time intervals. These samples were relatively small so that the overall composition in this reaction vessel was not seriously affected. Once a sample was removed and put in a watch glass, the reaction was stopped with 7 ppm hydroquinone solution and the liquid content of the watch glass was evaporated at room temperature, and then dried in an electric oven at 60 °C until constant weight. However, this was done only during the polymerization of methyl methacrylate in the absence of clay. On the contrary, in the presence of the clay, many flasks were prepared and kept under stirring; each one was withdrawn at a given time and the reaction was stopped by the addition of the hydroquinone solution. In situ sampling was not possible to avoid any miscalculation in conversion due to the probable concurrent withdrawal of the clay with the monomer solution. The conversion percentage of monomer to polymer was easily calculated by weight difference. As well, the polymerization activation energies were determined following the procedure mentioned in our previous paper [13].

Fig. 1 XRD of **a** Kaolinite, **b** K-DMSO, **c** K-DMSO-MeOH, **d** K-DMSO-MeOH-dodecylamine



Techniques

The samples were examined in powder form using Diano X-ray diffractometer (XRD) using CoKα radiation source energized at 45 kV. The microstructure of the samples was examined for very dilute dispersions of the corresponding nanocomposites in toluene using JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of 80 kV. The microscopy probes of the nanocomposite samples were prepared by adding a small drop of the toluene dispersions onto a Lacey carbon-film-coated copper grid and allowed to dry in air. Perkin Elmer, thermogravimetric analyzer 7/dx (TGA) and differential scanning calorimeter (DSC) were used to determine the thermal degradation behavior in the range from 50 °C to 550 °C and glass transition temperatures of the samples, by heating about 10–20 mg of each sample with heating rate of 10 °C/min under nitrogen atmosphere. Fourier transform infrared spectra (FTIR) of the nanocomposite powders were collected from KBr disks using Nicolet, Nexus 821 spectrophotometer.

Results and discussion

The key for intercalation in kaolinite is the suitable selection of a guest precursor (intermediate) and a solvent. Based on this description, the mischance of either the guest intermediate or the solvent leads to abortive intercalation or even deintercalation of the guest species.

A method was described by some researchers [23–28] to modify Kaolinite by intercalation of alkylamines passing through two precursors, K-DMSO and K-DMSO-MeOH. The same procedure was followed in this study but dodecylamine was used instead of the other alkylamines. The treatment of kaolinite in this sequence is usually performed to increase the basal space so as to enhance the intercalation of the polymer chains within the inter-platelet gallery of the clay in a subsequent step or exfoliation of the clay platelet within the polymer matrix, furthermore, to compatibilize the surface of the clay platelets at the interface with the polymer chains, facilitating thus the dispersion of the clay within the polymer matrix [28]. The DMSO intercalation into kaolinite expanded the basal space from 0.72 to 1.12 nm (Fig. 1a,b). Subsequent intercalation of methanol into K-DMSO resulted in the formation of a new intercalate, K-DMSO-MeOH, with a basal space of 1.13 nm (Fig. 1c). The K-DMSO-MeOH was then used in the final step as a precursor to intercalate the dodecylamine, which enlarged the basal space to 3.7 nm (Fig. 1d). Therefore, the double aim of amine intercalation was verified according to the approach of Cabedo [28].

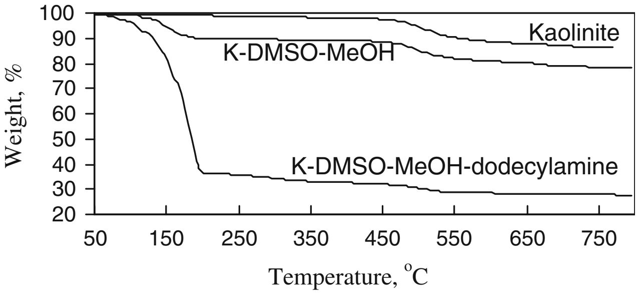


Fig. 2 TGA of *a* Kaolinite, *b* K-DMSO-MeOH, *c* K-DMSO-MeOH-dodecylamine

At the same time, four methods are known for the preparation of polymer-layered silicate nanocomposites: in situ polymerization, intercalation of the polymer from solution, direct intercalation of the molten polymer, and sol-gel technique. In situ polymerization is applied here in the presence of dodecylamine-functionalized kaolinite to polymerize methyl methacrylate from aqueous medium, as the intercalation of this amine into kaolinite increased the basal space; the hydrophobic nature of the hydrocarbon tail should also facilitate the MMA intercalation. Furthermore, it was expected that the amine can act as a reductant component if combined with potassium persulfate as oxidant component. Both components constitute together a redox initiator pair so the hydrophobic component is immobilized inside the basal space of kaolinite with its –NH_2 functionality protruded towards the aqueous medium [23, 28], while the other hydrophilic component dissolved in the aqueous phase.

Many interfacial polymerizations [20–22] were carried out using similar redox initiator systems; however, in this study, the initiator system was inversed. The immobilized hydrophobic component was acting as the reductant, whereas the oxidant was of hydrophilic nature and soluble in the aqueous phase. The first step to perform such interfacial polymerization was to estimate the amount of intercalated amine into kaolinite; this was achieved using TGA as displayed in Fig. 2. The kaolinite lost 11.38% of its initial weight in the temperature range of 450–700 °C, which is a characteristic feature of kaolinite, while the K-DMSO-MeOH started to degrade earlier at 100 °C and the weight loss attained was 10% by reaching 200 °C. On

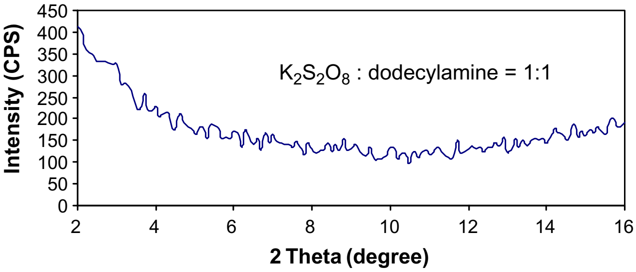


Fig. 3 XRD of PMMA/kaolinite nanocomposites prepared by in situ intercalative polymerization at 60 °C for 4 h using $K_2S_2O_8$/dodecylamine (1:1) as redox initiator system

going up with the temperature, additional 11% weight loss in the range of 475–700 °C was noticed. After the dodecylamine intercalation, the thermal stability of the K-DMSO-MeOH-dodecylamine was seriously affected; the degradation started at 70 °C and proceeded intensively up to 200 °C, where the total weight loss was about 62%, taking into account that at this temperature range, the forerunner precursor (K-DMSO-MeOH) lost only 10%. So by taking the difference, the amount of intercalated dodecylamine was estimated to 52% by weight. Based on this estimation, three molar ratios of potassium persulfate with respect to dodecylamine were calculated (1:1, 1:2, 2:1) and assigned to be used in the subsequent polymerization reaction as dissolved in the aqueous medium.

The polymerization was then started by raising the temperature to 60 °C; the obtained yield was exceeding

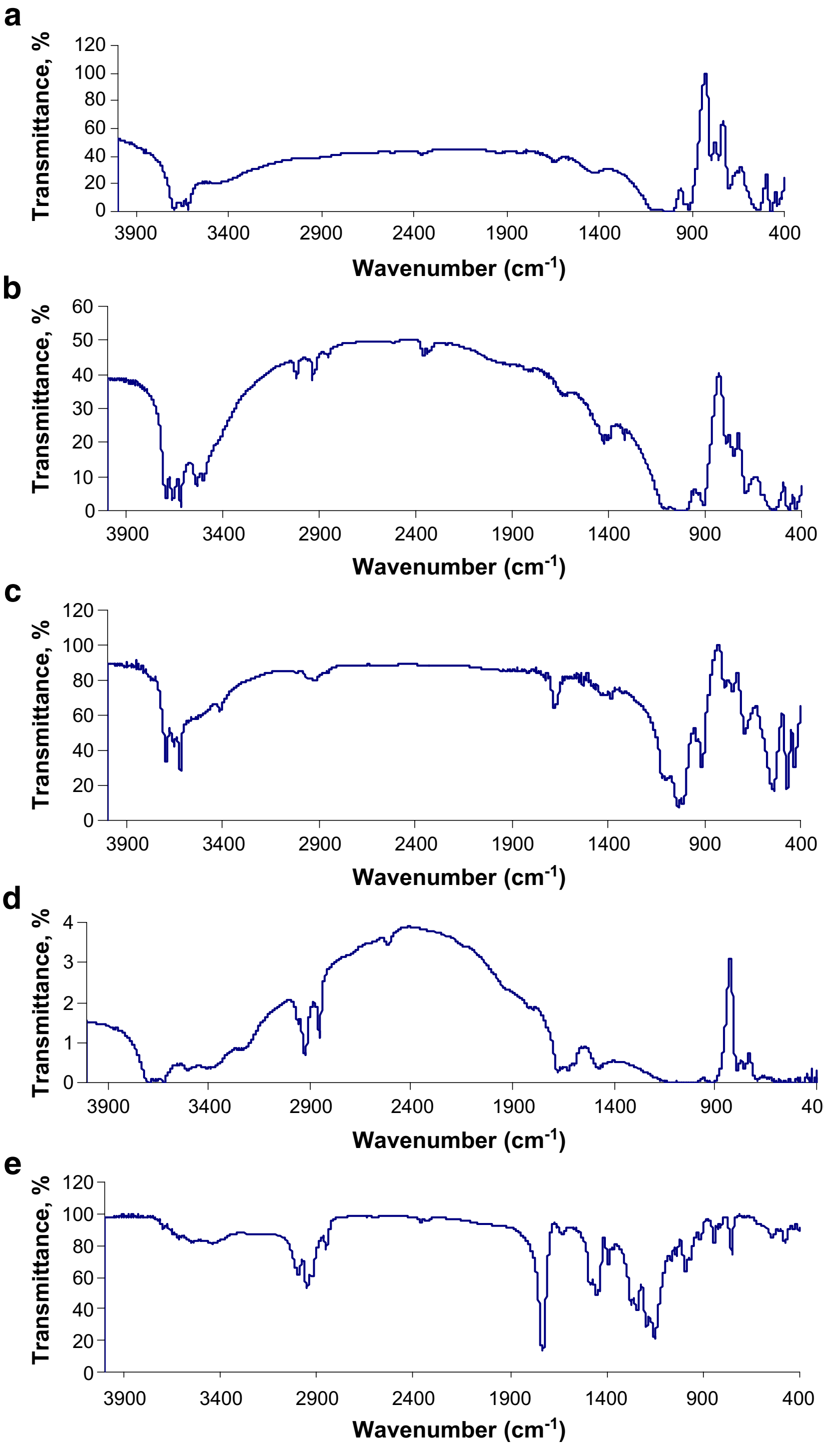


Fig. 4 FTIR spectra of **a** kaolinite, **b** K-DMSO, **c** K-DMSO-MeOH, **d** K-DMSO-MeOH-dodecylamine, **e** PMMA/K-DMSO-MeOH-dodecylamine nanocomposite

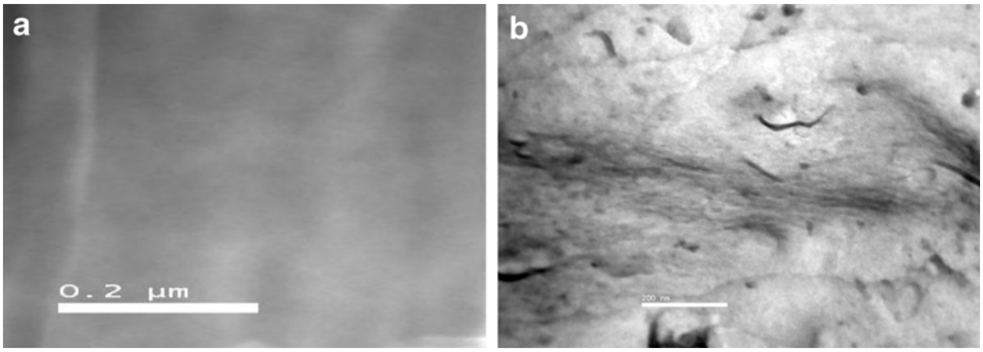


Fig. 5 TEM of PMMA/kaolinite nanocomposites prepared by in situ intercalative polymerization using redox initiator **a** $K_2S_2O_8$/dodecylamine (0.5:1) at 70 °C, **b** $K_2S_2O_8$/dodecylamine (1:1) at 60 °C (scale bar 200 nm)

60% after 4 h elapsed in the polymerization process. Surprisingly, this strategy of in situ intercalative polymerization proceeded effectively and led to exfoliation of the clay arrangements into individual platelets at all ratios as shown in the XRD taken for the nanocomposites (Fig. 3), which reveals the disappearance of any reflection referring to the ordering of the clay structure.

The viability of the proposed redox initiator system was further examined by carrying out the polymerization reaction at different temperatures; 50 °C was among them. It is well known that the minimum temperature required to break the potassium persulfate and liberate free radicals that can start the reaction is 60 °C, unless the redox initiator system is working effectively so the reaction proceeds at lower temperature which was the case, leading to conversion of over 80% and exfoliated nanocomposites at all temperatures in the range of 50–70 °C, which ensures the efficiency of this redox system, while the use of potassium persulfate alone with untreated kaolinite did not lead even to any intercalation. At the same time, using kaolinite treated to the extent of methanol (K-DMSO-MeOH) afforded deintercalation. This finding is in accordance with our previous work [13] when these precursors were employed during the in situ polymerization of vinyl acetate. Hence, this is a sign of the significant role of the $-NH_2$ groups in the initiation process and the eventual obtaining of exfoliated structure. It is thought that the presence of the redox initiator system accelerates the polymerization and guarantees fast growing of polymer chains so they can go through the basal space quickly before the extraction of the pre-intercalated species back to the reaction medium, leading finally to exfoliated nanocomposites. This was supported by the conversion rate determination of the monomer at 50 °C in the presence of different forms of kaolinite where it was found 1.9×10^{-4} mol. l^{-1} sec^{-1} for the amine-modified form, 1.23×10^{-4} mol. l^{-1} sec^{-1} in the presence of unmodified kaolinite as compared to 1.45×10^{-4} mol. l^{-1} sec^{-1} for the MMA polymerization in absence of any kaolinite form so the role of the unmodified kaolinite as radical scavenger might be assumed to be responsible for the decline of the initial rate of polymerization. Nevertheless, the presence of the intercalated amine served up to compensate this drop and assisted to elevate the rate of polymerization even higher (1.9×10^{-4} mol. l^{-1} sec^{-1}). On the other hand, the relevant activation energies of polymerization were 2.7×10^4, 9.55×10^4, and 15.6×10^4 J/mol., respectively, which emphasize the catalytic role of kaolinite, especially the modified one in accelerating the polymerization due to its active surface particularly after the modification; accordingly, the activation energy required for starting the polymerization reaction was reduced. This partial contradiction was discussed in detail in a previous work that belongs to us [13] and explained out by the opposition of this enhancement by the ability of the kaolinite to scavenge the radicals.

The FTIR spectra of kaolinite collectively with its modified forms in addition to a PMMA nanocomposite based on the amine-modified kaolinite were recorded and shown in Fig. 4. Kaolinite shows four OH-stretching bands at 3,697, 3,663, 3,650, and 3,620 cm^{-1} together with bands at 941 and 913 cm^{-1} ascribed to Al–OH vibration (Fig. 4a); a perturbation was observed for the OH bands to 3,695, 3,664, 3,646, and 3,621 cm^{-1} after the DMSO intercalation (Fig. 4b) [29] associated with a marked decrease in intensity of the Al–OH vibration bands. The successive intercalation of methanol caused a distinctive change in the

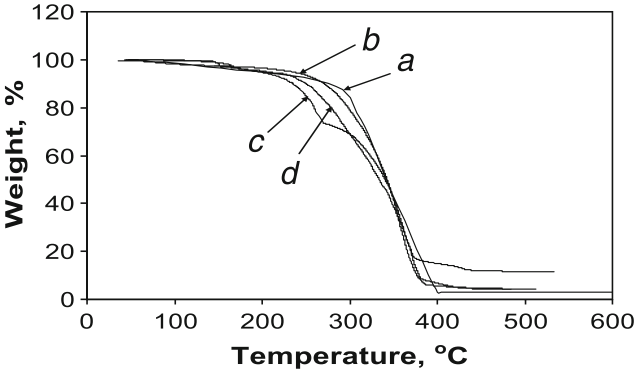


Fig. 6 TGA of *a* pure poly methyl methacrylate prepared by emulsion polymerization at 60 °C for 4 h using $K_2S_2O_8/NaHSO_3$ as well as nanocomposites based on kaolinite, prepared by in situ intercalative polymerization of methyl methacrylate using $K_2S_2O_8$/dodecylamine (1:1) as redox initiator, *b* at 50 °C for 6 h, *c* at 60 °C for 4 h, *d* at 70 °C for 4 h

OH-stretching region and also in the region of the Al–OH vibration, which confirms that hydrogen bondings are the major forces that hold the methanol molecules within the basal space of kaolinite (Fig. 4c). Furthermore, the two peaks at 3,021 and 2,936 cm^{-1} which refer to the (CH) aliphatic became extremely weak in K-DMSO-MeOH form; however, these peaks shifted to lower values, 2,922 and 2,852 cm^{-1}, with more sharpness in case of K-DMSO-MeOH-dodecylamine. The peak at 1,678 cm^{-1} which appeared in K-DMSO-MeOH-dodecylamine refers to CH_2 groups (Fig. 4d). It can be easily seen that the contribution of the amino groups in the hydrogen bonding led to additional change in the region of the OH stretching (3,580–3,700 cm^{-1}). The PMMA was characterized by some new peaks such as the carbonyl group (1,727 cm^{-1}) and C–O stretching at 1150 cm^{-1}, while the coexistence of

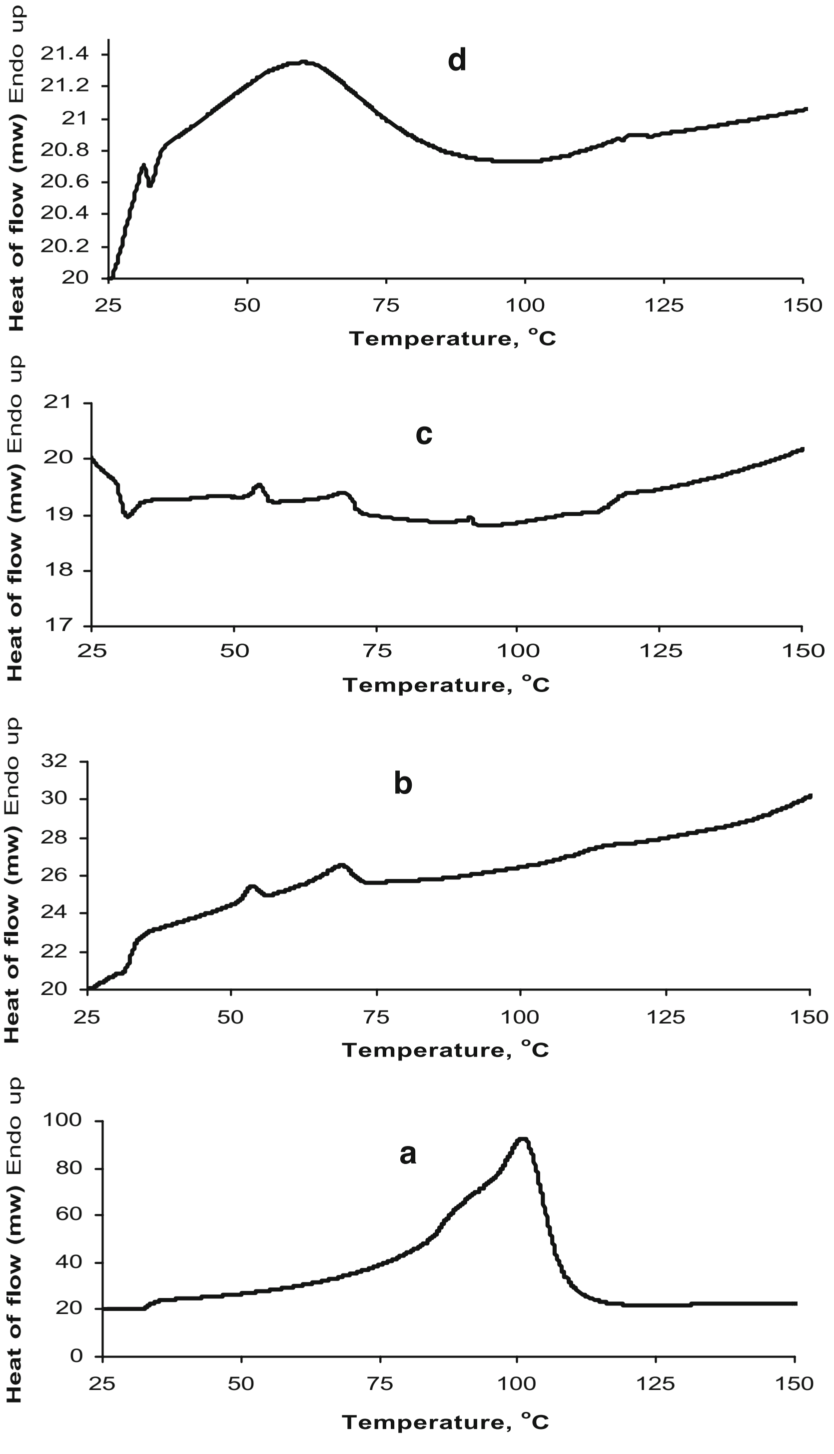


Fig. 7 DSC of **a** pure poly methyl methacrylate prepared by emulsion polymerization at 60 °C for 4 h using $K_2S_2O_8$/$NaHSO_3$ as well as nanocomposites based on kaolinite, prepared by in situ intercalative polymerization of methyl methacrylate using $K_2S_2O_8$/dodecylamine (1:1) as redox initiator, **b** at 50 °C for 6 h, **c** at 60 °C for 4 h, **d** at 70 °C for 4 h

CH stretching bands at 2,900; 3,000 cm^{-1} belong to PMMA and the ancestor (K-DMSO-MeOH-dodecylamine) led to a little shift with de-intensification of the bands. It can be noticed that the kaolinite did not retrieve its hydroxyl stretching bands after the nanocomposite formation which further proved the change in its nature (exfoliation of the clay into individual platelets) and involvement of the platelets hydroxyl groups in interaction with the PMMA (Fig. 4e); what is more, the dodecylamine molecules are no longer anchored to a platelet surface but to a greater extent embedded in the PMMA phase (compare spectra d with e).

The resulting nanocomposites were also characterized by TEM as displayed in Fig. 5. It is obvious from the figure that the kaolinite layers defoliated into separate laminates with uniform distribution within the polymer phase (Fig. 5a), and in some cases, exfoliation was detected jointly with very trivial intercalation (expanded phase; Fig. 5b); as a consequence, no ordering was observed in the XRD pattern, so a conclusion can be made that neither the temperature nor the ratio of the redox components have effect on the microstructure of the resulting composites.

To the best of our knowledge, no reports were found in the literature pertaining to similar approach for performing intercalative polymerization inside the basal space of kaolinite using a redox initiator pair, with one of its components immobilized in this basal space. Most of the work reported in the literature was focusing on the intercalation of monomers such as acrylonitrile or vinylpyrrolidone; afterward, the in situ intercalative polymerization was begun by γ-radiation or thermal treatment [30–32] leading to intercalated nanocomposites at most.

The TGA was used to investigate the thermal stability of the nanocomposites; the corresponding TG traces of the samples are revealed in Fig. 6 in addition to that of pure PMMA prepared under very similar conditions. It is obvious that the nanocomposites were slightly affected by the presence of the dodecylamine as a treating agent for the kaolinite and behaved less well in the temperature range of 220–320 °C; the temperature needed to cause a given weight loss as compared with the pure PMMA in this range decreased by about 11–28 °C. Nevertheless, the stability did not change noticeably to any further extent.

This may be rationalized on the basis that the exfoliation of the kaolinite platelets leads to appropriate dispersion through the polymer matrix; therefore, much higher surface area became accessible for the polymer - filler interaction. In the case of swellable clays, such as montmorillonite, where the cation exchange possibility provided a good way to convert the hydrophilic nature of the clay into hydrophobic by replacing the inorganic cation by organic one with long hydrocarbon tail, this leads eventually to improved interfacial adhesion between the hydrophobic polymer phase and the hydrophobized clay platelets. However, it is not the case on using kaolinite as the possibility of cation exchange is lacking. So after the exfoliation, the clay platelets with their higher surface area and consequently more polar sites, mainly hydroxyl groups, became exposed toward the nonpolar polymer phase. Hence, the thermal stability could not be enhanced anymore, owing to the amplified interfacial tension.

The glass transition temperatures (*Tg*) were determined using differential scanning calorimeter for the same samples as, displayed in Fig. 7. The pure polymer exhibited an endotherm at approximately 100 °C corresponding to the *Tg* of PMMA, which elevated by 16–23 °C in case of the nanocomposites. It is tentatively ascribed to the confinement of the polymer chains in the presence of the silicate platelets which hinder the segmental motion of the chains; it can hold for efficient and homogeneous distribution of the platelets within the polymer matrix which happens mainly upon exfoliation of the silicate galleries so the distribution of the clay layers within the polymer did not elevate the glass transition temperatures to the level that complicate the thermal processing of these nanocomposites as found by Huang and Brittain [33], where the *Tg* of PMMA nanocomposites based on montmorillonite were up to 62 °C higher with respect to pure PMMA. There are other minor endotherms between 50 °C and 85 °C (Fig. 7b–d) that can be attributed to water vapor adsorbed by the PMMA or even kaolinite.

Conclusions In situ intercalative polymerization of methyl methacrylate can be performed inside the basal space of kaolinite functionalized with dodecylamine, as a reducing part of dodecylamine–potassium persulfate redox initiator system. The polymerization can be started at a temperature lower than the usual employed one using such type of initiator system which proved to be efficient and could result delamination of the clay layers into individual platelets, homogeneously dispersed in the polymer matrix. The thermal degradation of the PMMA - kaolinite nanocomposites in the range of 220–320 °C enhances by following this approach as the temperature needed to cause a given weight loss decreases by 11–28 °C due to the presence of the dodecylamine. The glass transition temperatures of the samples slightly increased by 16–23 °C as compared with pure PMMA thus complication during the thermal processing of these nanocomposites is not expected.

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