

Synthesis and Properties of Poly(methyl methacrylate)/Clay Nanocomposites Prepared Via In Situ Polymerization with Ni(acac)₂ Catalyst

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ABSTRACT: Poly(methyl methacrylate)(PMMA)/clay nanocomposites were successfully prepared by a new method, *in situ* polymerization initiated with a nickel(II) acetylacetonate [Ni(acac)₂] catalyst in combination with methylalumoxane (MAO). The synthesized PMMA/clay nanocomposites materials were subsequently investigated through a series of characterization techniques. A partially-exfoliated and partially intercalated structure was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). PMMA/clay nanocomposites having low clay contents less than five weight percent (5 wt %) were found to retain over 90% of transparency

of pure PMMA in the visible light region, which is important for optical applications. Compared to pure PMMA, the thermal stability, glass transition temperature of the PMMA/clay nanocomposites were significantly improved by the presence of nanometric silicate layers. The unique properties of the nanocomposites resulted from the strong interactions between the silicate layers and the PMMA chains. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 784–790, 2008

Key words: clay; *in situ* polymerization; nanocomposites; poly(methyl methacrylate)

INTRODUCTION

In recent years, polymer/clay nanocomposites have generated substantial interest in many research fields due to their excellent properties.^{1–3} When the clay is well dispersed throughout a polymer matrix, significant improvements are seen in physical and mechanical properties. Among these are higher heat distortion temperatures, an enhanced flame resistance, an increased modulus, better barrier properties, a reduced thermal expansion coefficient, and altered electronic and optical properties.^{1–5} After the successful synthesis of the nylon-6/clay nanocomposite, an intercalation method for synthesizing polymer/clay nanocomposites has drawn a great deal of attention.^{6–9} There are two distinct nanostructures identified in these nanocomposites: intercalated and exfoliated (or delaminated). Polymer chains penetrate into the host layers while the ordered silicate registry remains (intercalated structure), or the exfoliated individual silicate layers are homogeneously

dispersed in the polymer matrix (exfoliated structure).¹⁰

The most widely used clay is montmorillonite (MMT), which belongs to a 2 : 1 layered silicate. Its crystalline structure consists of a two dimensional layer obtained by blending two tetrahedral silica laminae to form a corresponding octahedral metal oxide lamina.¹¹ It contains negatively charged layered silicates ionically bonded with metal cations such as Na⁺, K⁺, Ca²⁺, or Mg²⁺. Before the preparation of the intercalation catalyst, modification is generally required through a cation exchange reaction to render hydrophilic MMT more hydrophobic and to increase its interlayer basal spacing.

PMMA is an important material with several desirable properties, such as exceptional optical clarity, high strength and excellent dimensional stability. The main disadvantage is its poor heat resistance. PMMA/clay nanocomposites offer the potential for reduced gas permeability, improved physical performance, and increased heat resistance without significant reduction in optical clarity.¹² Recently, radical initiating MMA polymerization has been applied to *in situ* polymerization because it is insensitive to water, air, and other impurities.^{13–29} For example, MMA polymerization with benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN)

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initiator in the presence of organo-clay is one of the most common methods. However, coordination polymerization of MMA monomer is effective to obtain highly oriented polymers with good thermal properties although its sensitivity to moisture and minute impurities inhibits its wide application. Therefore, how to solve the sensitivity problem in coordination polymerization is a challenging topic.

Ni(acac)₂/MAO is an effective catalyst for the polymerization of MMA,^{30,31} but the preparation of PMMA/clay nanocomposites with Ni(acac)₂ has not yet been reported. In this article, we present a new method for the preparation PMMA/clay nanocomposites by *in situ* polymerization with coordination catalyst. This approach consists of anchoring the polymerization catalyst to the surface and into the interlayer of the silicate, and polymerizing the MMA *in situ*. The structure and properties of synthesized PMMA/clay nanocomposites were investigated. The optical clarity, thermal stability, and mechanical properties of the PMMA/clay nanocomposites were also discussed.

EXPERIMENTAL

Material

Sodium montmorillonite (Kunipia F, Cation Exchange Capacity (CEC) 119 meq/100 g, surface area: 750 m²/g) supplied by Kunimine was used as received. Methyl methacrylate (MMA) was purchased from Aldrich and was distilled from CaH₂ under a vacuum. The 1-tetradecylamine (95%), anhydrous *n*-heptane and MAO was purchased from Aldrich and used as received. Toluene (from J. T. Baker Chem) of extra pure grade was purified by refluxing over sodium metal/benzophenone in a nitrogen atmosphere. Nickel(II) acetylacetonate (Ni(acac)₂, 95%) purchased from Aldrich, was used after sublimation at 140°C.

Preparation of organophilic montmorillonite

The organophilic montmorillonite was prepared by a cation exchange method, which facilitated the exchange reaction between the sodium cations of the MMT and the alkyl ammonium ions used as an intercalation agent.^{32,33} Typically, 2.25 g (10 mmol) 1-tetradecylamine was dissolved in a 1 : 1 mixture of ethanol and deionized H₂O at 60°C, and an equivalent amount of HCl was also added to the solution. The 1% (by weight) of an aqueous suspension of the MMT (Kunipia F, 5 g) was added to the alkylammonium solution and the mixture was stirred for 5–6 h at 60°C. The cation-exchange silicates were collected by filtration and subsequently washed with a mixture of hot ethanol and deionized H₂O at least five

times to remove any excess ammonium ions. The product was then vacuum-dried and ground into a fine powder to obtain the organophilic-montmorillonite (organo-MMT).

Modification of organo-MMT

About 2.0 g of organo-MMT was suspended in 50 mL anhydrous *n*-heptane under an anaerobic atmosphere. Then, 5 mL of the MAO solution (2.0 μM in toluene) was added to the clay suspension using a dropper and the mixture was allowed to react for 5 h at 50°C. The suspension was then washed several times with dried *n*-heptane (5 × 30 mL) to eliminate the excess unbound MAO. After drying under a vacuum for 24 h at room temperature, modified clay with MAO was obtained.

Preparation of the PMMA/clay nanocomposites

Modified MMT was heated for 12 h under vacuum at 80–100°C and was dispersed in 40 mL of dried toluene at room temperature for 30 min to obtain a stable suspension, and the Ni(acac)₂ catalyst was added to the suspension and the mixture was allowed to react for 4 h at room temperature. MMA and the cocatalyst MAO were sequentially introduced and polymerization was carried out with continuous stirring for 20 h at room temperature under a N₂ atmosphere. The reaction was terminated by the addition of an acidified methanol solution. The polymer was precipitated and was dried under a vacuum at 60°C for 24 h to obtain the PMMA/clay nanocomposites.

Characterization

X-ray diffraction was carried out using a Rigaku X-ray generator (Cu Kα radiation with λ = 0.15406 nm) at room temperature. The diffractograms were scanned in 2θ ranges from 1.2° to 10° with a scan rate of 1°/min. A Fourier transform infrared (FTIR) analysis was obtained at a resolution of 4.0 cm⁻¹ using a MAGNA-IR 560 at room temperature. The KBr pellet method was used. UV–vis transmission spectra were obtained with a Hitachi U-2000 UV–vis spectrometer. Scanning electron microscopy (SEM) observations was performed with a LEO 1455 VP microscope with powder samples being mounted on aluminum stubs using an adhesive carbon tape, then gold coated in a sputter coater. A transmission electron microscope (TEM), Phillips CM20, was used to observe the dispersibility of the clay in the hybrids using an acceleration voltage of 120 kV. An ultrathin section (70 nm in thickness) was prepared by an ultramicrotome Leica EM FCS. The glass transition temperature (*T*_g) was determined using a TA2000

TABLE I
Polymerization Results for MMA Using Ni(acac)₂/MAO Catalyst System in the Presence of the Modified-MMT

Sample	Initial clay loading (g)	Yield (g)	Conversion (%)	Activity ^a	Clay contents in PMMA matrix (wt %)
PMMA0 ^b	0	7.65	81.1	3.83	0
PMMA1	0.05	8.02	84.5	3.99	0.62
PMMA2	0.15	6.40	66.3	3.13	2.33
PMMA3	0.18	4.36	44.3	2.09	4.13
PMMA4	0.20	1.92	18.2	0.86	10.4

Polymerization conditions: MMA 10 mL, Ni(acac)₂ 0.1 mmol; cocatalyst MAO, [Al]/[Ni] = 200 (molar ratio); toluene 40 mL as solvent; room temperature; polymerization time 20 h.

^a Kg_{PMMA}/mol Ni h.

^b Synthesized by Ni(acac)₂/MAO.

differential scanning calorimeter at a heating rate of 10°C/min from 30 to 200°C, for two continuous scanning cycles, and the data obtained from the second heating phase of the cycle were accepted. *T_g* was determined from the mid-point of the step transition in the heat capacity versus temperature thermogram. The thermal decomposition temperature was determined by TGA under N₂ flow from 40 to 700°C at the rate of 10°C/min.

RESULTS AND DISCUSSION

Coordination polymerization is very sensitive to the environment of the silicate layers of the clay. It is essential to modify the clay in order for the intercalated catalyst to retain its high activity. Alkylammonium ions were used as intercalating reagents to exchange the sodium ions of the clay. Hydrophilic Na⁺-type MMT was modified to form organo-MMT. MAO which is an oligomeric compound consisting of an -Al (Me)-O- unit, and acts as a very strong Lewis acid, was used to treat organo-MMT and react with the hydroxyl group and coordinated and physically adsorbed water of the MMT. Thus, a large amount of MAO was attached to the organo-MMT to obtain the active polymerization catalyst.³⁴ Following this, Ni(acac)₂ was intercalated into the layer of the modified MMT and a series of PMMA/clay composites were prepared. The experimental results are listed in Table I.

PMMA was synthesized in the absence of the clay to obtain pure PMMA. About 10 mL of MMA was polymerized with 0.1 mM of Ni(acac)₂ and MAO (Al/Ni molar ratio = 200) in toluene at room temperature for 20 h to obtain a 81.1% conversion. When the initial clay loading is low (samples PMMA1 and PMMA2), the catalyst Ni(acac)₂-MAO retains its good activity; however, with the increase in the initial clay loading, the activity is decreased. This indicates that a large amount of modified clay can cause the Ni(acac)₂ catalyst to become partially

deactivated due to the exposure to the few residual coordinated water from the MMT during exfoliation.³⁵

Figure 1 shows IR spectra of the pristine MMT (a), organo-MMT (MMT/C₁₄H₂₉N⁺H₃) (b), MMT/C₁₄H₂₉N⁺H₃/MAO (c), and extracted PMMA (from sample PMMA2) (d) which was extracted with hot tetrahydrofuran (THF) for 48 h to remove non-bonded PMMA. In the IR spectrum of MMT, characteristic absorptions were observed: —OH stretching at 3632 cm⁻¹, coordination and absorbed water molecule peak at 3430 and 1640 cm⁻¹, Si—O stretching at 1010 cm⁻¹, and Al—O stretching at 550 cm⁻¹.³⁵ In the spectra of MMT/C₁₄H₂₉N⁺H₃ and MMT/C₁₄H₂₉N⁺H₃/MAO, there are more intense absorption bands of C—H stretching at 2855 and 2950 cm⁻¹, which confirm the presence of alkylammonium ions in the layers of the clay. Additionally, a weak —OH stretching band and a weak peak from water molecule in the spectrum of the MAO modified organo-MMT indicates that MAO reacted with

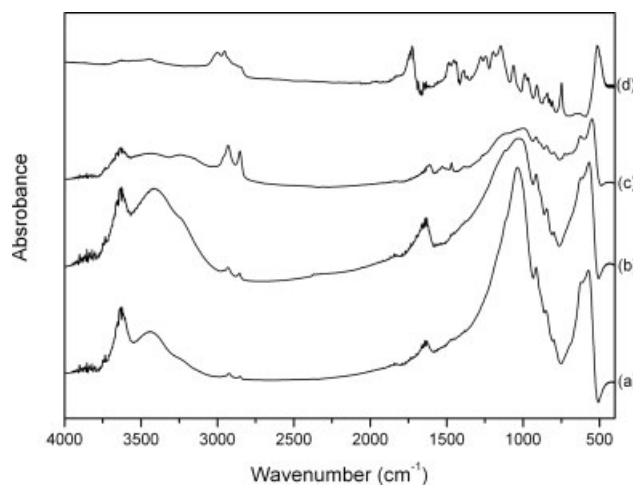


Figure 1 FTIR spectra of (a) pristine MMT, (b) MMT/C₁₄H₂₉N⁺H₃, (c) MMT/C₁₄H₂₉N⁺H₃/MAO, and (d) extracted PMMA/clay composites (Table I, sample PMMA2).

partial hydroxyl group of layers as well as the water on the clay surface. IR spectrum of extracted PMMA/clay composites shows an instinct absorption at 1730 cm^{-1} (C=O stretching) and $1300\text{--}1100\text{ cm}^{-1}$ (C—O stretching), which are the characteristic frequencies of PMMA. These results show that only part of the PMMA could be extracted from the nanocomposites, and part of the PMMA chains stayed immobilized inside and/or on the layered silicates. This confirms that there exist strong interactions between the nanometric silicate layers and the PMMA segments. However, the exact nature of bonding could not be studied due to broad and non-resolved peak pattern of the IR spectrum. Moreover, it is suggested from previous studies that there may be some supramolecular interactions between PMMA chains and the silicate layer.^{13,14}

Figure 2 displays a series of XRD patterns obtained from pristine MMT (a), organo-MMT (b), and PMMA/clay composites with different clay contents (c–f). The corresponding patterns in the range of the diffraction angle $2\theta = 1.2^\circ\text{--}10^\circ$ were recorded. The $d_{(001)}$ peak of the pristine MMT was at 1.16 nm ($2\theta = 7.62^\circ$). After the cation exchange, the $d_{(001)}$ spacing increased to 1.64 nm ($2\theta = 5.37^\circ$), as shown in the organo-MMT (MMT/C₁₄H₂₉N⁺H₃). This implies that the alkylammonium ion intercalated into the layer of the clay. Also, diffraction peaks for clay loading less than 4.13 wt % were not observed in the XRD patterns of PMMA/clay composites. The absence of diffraction peaks suggests that the $d_{(001)}$ spacing between the layered silicates were either intercalated to a spacing greater than the measurable range, or they exfoliated completely in the PMMA matrix. When the amount of modified clay increases to 10.4 wt %, a broad weak peak might be probably

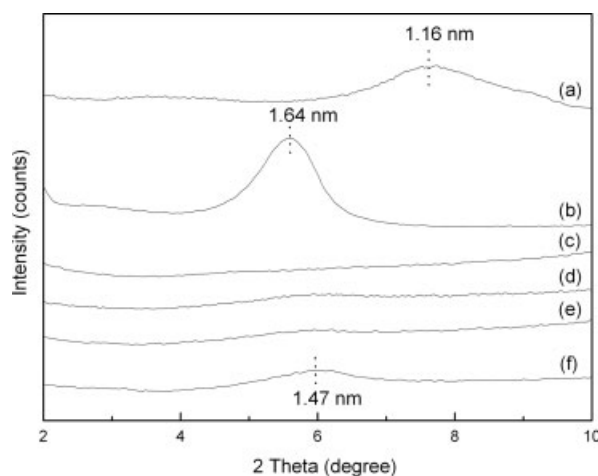


Figure 2 Wide-angle X-ray diffraction patterns of pristine MMT (a), organo-MMT (b), and PMMA/clay composites with different clay contents [(c) 0.62 wt %, (d) 2.33 wt %, (e) 4.13 wt %, and (f) 10.4 wt %].

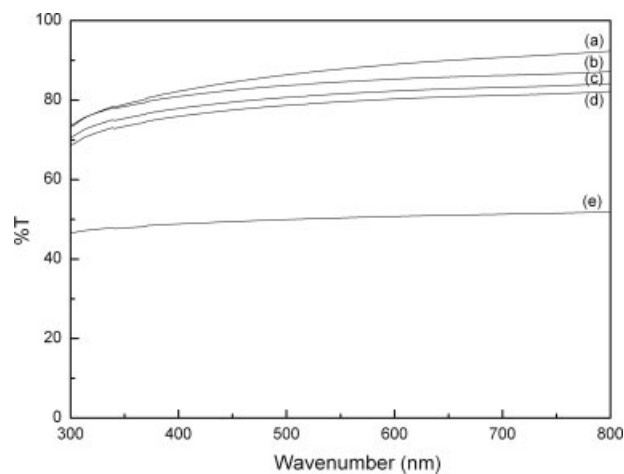


Figure 3 UV-vis spectra of (a) pure PMMA and (b–e) PMMA/clay nanocomposites with different clay contents [(b) 0.62 wt %, (c) 2.33 wt %, (d) 4.13 wt %, and (e) 10.4 wt %].

resulting from partially exfoliated or intercalated structures with d -spacings of 1.47 nm. When high clay content in PMMA matrix (Table I, sample PMMA4) is prepared, the catalyst intercalated into galleries of clay may not be uniform. Some modified agents can exchange into solvent, thus there might be relatively more attractive forces between the clay layers which lead to some intercalated tactoids that cannot be fully exfoliated in the PMMA, and it exists in the form of an intercalated layer structure.³⁶

The optical clarity of the PMMA/clay nanocomposites with different clay amounts in a membrane with a thickness of 100 μm can be compared via UV-vis transmission spectroscopy studies, as shown in Figure 3. The PMMA/clay nanocomposites with low clay contents (<5 wt %) show transmission somewhat lower than that of the pure PMMA, which retains more than 90% of transparency of pure PMMA in the visible light region. However, when the clay content is increased to 10.4 wt % in PMMA matrix, the transmission is lowered. It could be associated with different dispersion degrees and abilities of the nanoclay layers in the polymer framework. Better dispersion of clay platelets in PMMA matrix minimally affects the transparency of these nanocomposites. Therefore, it indicated that PMMA/clay nanocomposites with low clay contents had a better dispersion of clay platelets than that with high clay contents. However, the optical clarity of PMMA nanocomposites produced by such coordination catalyst is quite similar to that produced by emulsion polymerization and the advantage is the high T_g and T_d for this nanocomposite compared with the emulsion polymerization.³⁷

Microscopic differences between pristine MMT and the PMMA/clay composites (sample PMMA2) are obvious from comparisons of the morphological

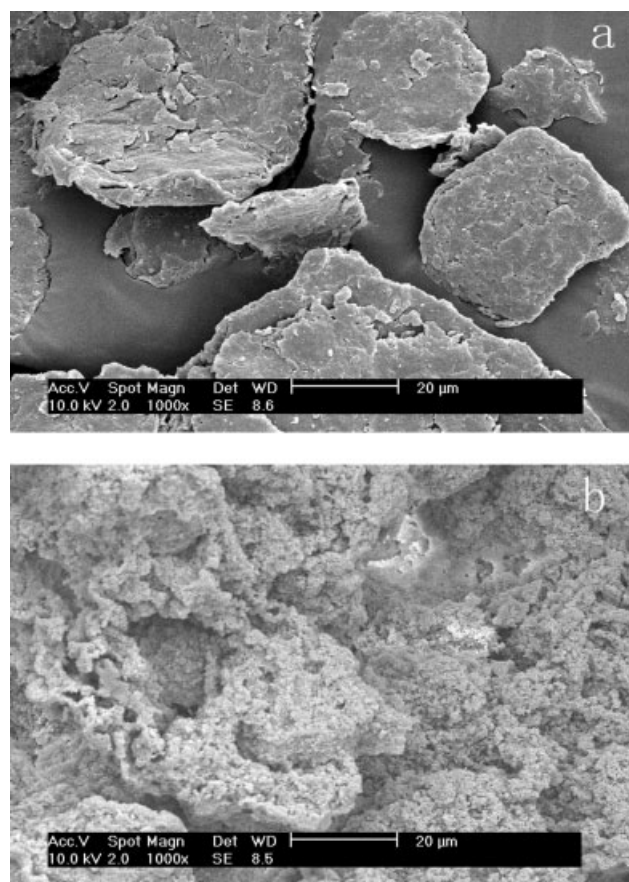


Figure 4 SEM images of (a) pristine MMT, (b) PMMA/clay nanocomposites (Table I, sample PMMA2).

details by means of SEM, as illustrated in Figure 4. MMT [Fig. 4(a)] has stacked aggregates with a polygonal structure, with a size that ranges between ~ 20 and $50 \mu\text{m}$. However, PMMA/clay nanocomposites [Fig. 4(b)] are composed of finely dispersed particles. The aggregated clay platelets are exfoliated and well dispersed in PMMA matrix. Reports by Tabtiang et al.³⁸ showed that the alkylammonium ions can lower the attractive forces between the clay layers and enable the polymer or monomer to intercalate into the clay layers more easily thereby aiding the dispersion of the clay.

The dispersion of clay in the polymer matrix can be directly observed by TEM. TEM is complementary to XRD, especially when peaks are not observed in XRD. Figure 5 shows a TEM micrograph of the PMMA/clay nanocomposites having 4.13 wt % organoclay. The thread-like dark lines represent intersections of the clay layers and the bright areas represent the PMMA matrix. The individual silicate layers, along with two and three layer stacks were observed. The silicate layers are disordered state and dispersed in the PMMA matrix. The delaminated structures are composed of only an individual layer and in stacks of a few layers. There exist exfoliated

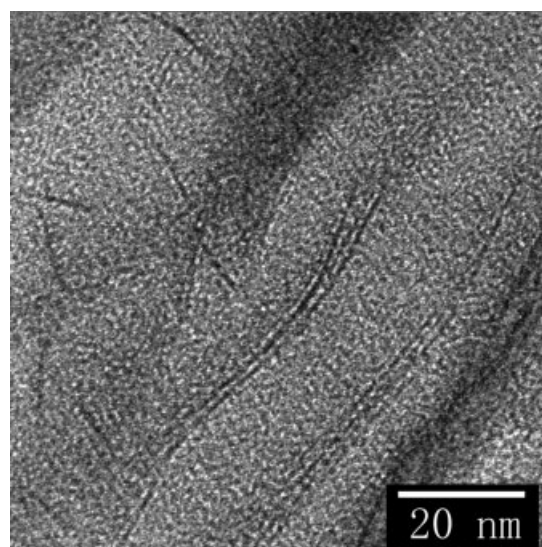


Figure 5 TEM images of PMMA/clay nanocomposites containing 4.13 wt % clay.

clay layers; meanwhile some aggregates of clay platelets are still present in the PMMA matrix. Therefore, the obtained PMMA/clay composites are partially exfoliated and partially intercalated nanocomposites, which are corresponding to what is obtained by XRD analysis.

DSC thermograms of the pure PMMA and a series of PMMA/clay composites are shown in Figure 6. Pure PMMA exhibits T_g of PMMA at $\sim 124.2^\circ\text{C}$, which is higher than that synthesized by radical polymerization.¹⁶ In contrast, the PMMA/clay nanocomposites exhibit an increasing endothermic trend at ~ 127.0 – 133.1°C as an increasing amount of the clay is added. The increase in T_g is due to the interactions between the clay layers and the PMMA

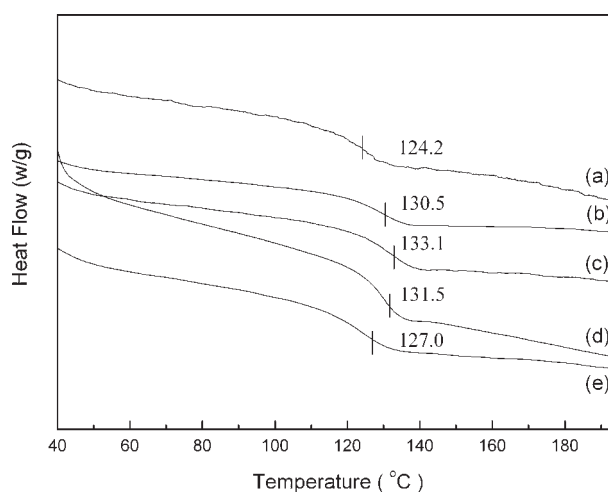


Figure 6 DSC thermograms of (a) pure PMMA and (b–e) PMMA/clay nanocomposites with different clay contents [(b) 0.62 wt %, (c) 2.33 wt %, (d) 4.13 wt %, and (e) 10.4 wt %].

chains. The interactions are strengthened to the point that major chain motions of the PMMA are greatly restricted. However, when the clay amount reaches ~ 10.4 wt % in the PMMA matrix, the T_g of the polymer is 127.0°C , which is lower than the other PMMA/clay nanocomposites. This may be related to the dispersed degree of the clay layers in addition to the interaction of the sheets with the chains of the PMMA. Additionally, a large amount of intercalating reagents in the organo-clay may act as a plasticizer or as a lubricants; the glass transition temperature is lower than that with a low amount of clay.³⁹

The TGA results in the PMMA and its nanocomposites, as shown in Table II and Figure 7, reveal that the onset temperature of the thermal decomposition increased by about $30\text{--}50^\circ\text{C}$, as measured at a weight loss of 5 wt %, by the nano-dispersion of the clay layers to the polymer matrix. This indicates that the introduction of MMT can improve the decomposition temperature of the PMMA matrix. This is most likely due to physicochemical adsorption of the volatile degradation products on the silicates.⁴⁰ The silicates delay the volatilization of the products that originate from carbon-carbon bond cleavage in the polymer matrix. In contrast, the origin of the evident increase in the thermal decomposition temperatures is likely due to the unique ability of the nanometer silicate layers to prevent heat from transmitting quickly, thus limiting the continuous decomposition of the nanocomposites.

CONCLUSIONS

PMMA/clay nanocomposites were successfully prepared via an *in situ* polymerization of MMA using $\text{Ni}(\text{acac})_2$ catalyst in the presence of MAO modified organo-MMT. This novel approach represents a new route toward high-performance PMMA materials. The occurrence of a partially exfoliation and partially intercalation structure of the clay layers in the PMMA/clay composites were confirmed. FTIR spectrum of the extracted PMMA/clay nanocomposites indicated that parts of the PMMA chains stayed immobilized inside and/or on the layered silicates, and

TABLE II
Onset of Thermal Decomposition (5 wt %) of PMMA and PMMA/Clay Composites

Sample	Clay contents in PMMA matrix (wt %)	Onset of thermal decomposition ($^\circ\text{C}$)
PMMA0	0	312
PMMA1	0.62	345
PMMA2	2.33	351
PMMA3	4.13	355
PMMA4	10.4	367

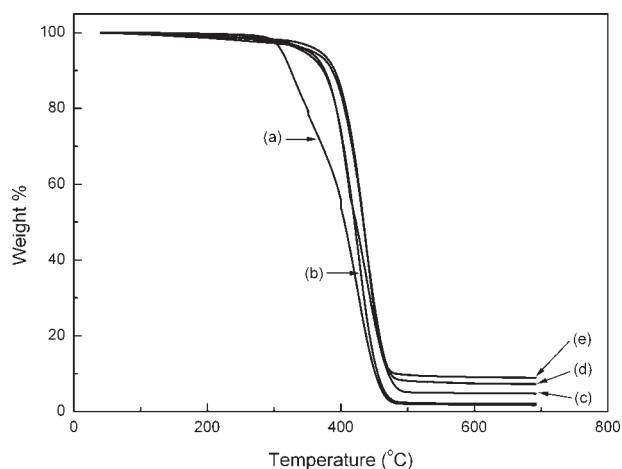


Figure 7 TGA thermogram of the weight loss as a function of temperature for (a) pure PMMA and (b–e) PMMA/clay nanocomposites with different clay contents [(b) 0.62 wt %, (c) 2.33 wt %, (d) 4.13 wt %, and (e) 10.4 wt %].

that the interactions between the nanometric silicate layers and the polymer segments are strong. The well-dispersed PMMA/clay nanocomposites retained good optical clarity. The thermal properties of the PMMA/clay nanocomposites significantly improved when the clay was exfoliated and dispersed into the PMMA matrix.

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