# The Characterization of Organic Modified Clay and Clay-Filled PMMA Nanocomposite

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**ABSTRACT:** Recently, polymer–clay hybrid materials have received considerable attention from both a fundamental research and application point of view.[1–3] This organic–inorganic hybrid, which contains a nanoscale dispersion of the layered silicates, is a material with greatly improved physical and mechanical characteristics. These nanocomposites are synthesized through *in situ* polymerization or direct intercalation of the organically modified layered silicate (OLS) into the polymer matrix. Thus, understanding the relationship between the molecular structure and the thermal stability (decomposition temperature, rate, and the degradation products) of the OLS is critical. In this study, modern thermal analysis techniques combined with infrared spectroscopy and mass spectrometry (TGA-FTIR-MS) were used to obtain information on the thermal stability and degradation products of organic modified clay. Furthermore, the thermal and mechanical properties of clay-filled PMMA nanocomposites were determined by using TGA and DSC. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1702–1710, 2002

**Key words:** clay; nanocomposites

## INTRODUCTION

Nanocomposites are new class of composites derived from the ultrafine inorganic particles with dimensions typically in the range of 1 to 1000 nm that are dispersed in the polymer matrix homogeneously.[4] Recently, these kinds of materials are attracting the attention of government, academic, and industrial researchers because of their outstanding properties. These polymer layered silicate (PLS) nanocomposites can attain a certain degree of stiffness, strength, and barrier properties with far less ceramic content than comparable glass- or general inorganic-reinforced polymers. Furthermore, PLS nanocomposites exhibit a significant increase in thermal stability as well as self-extinguishing characteristics.[5] Although other solids can be used, the most common reinforcements currently used to make nanocomposites are natural silicates, such as mica, montmorillonite, saponite, and hectorite. What makes nanocomposites unique is the size and shape of the silicate particles dispersed through the polymer matrix. These particles are infinitesimally small, typically individual silicate platelets are only about 1 nanometer (1 nm = $10^{-9}$ m) thick and 1000 nm across the face, which is 1400 times smaller than the finest talc reinforcements in use today.

Pristine layered silicates has been known for more than 60 years.[6–11] They possess the same

structural characteristics as the well-known minerals talc and mica (2:1 phyllosilicate), and are comprised of hydrated aluminum silicate. They are generally classified as clay minerals, which are the most abundant minerals on the surface of the earth. Their crystal structure consists of two-dimensional layers (thickness = 0.95 nm) formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either alumina or magnesia.[12] Stacking of these layers leads to van der Waals gaps or galleries. The galleries (alternatively referred to as interlayers) are occupied by cations, typically $Na^+$ and/or $Ca^{2+}$, which balance the charge deficiency that is generated by isomorphous substitution within the layers (e.g., tetrahedral $Si^{4+}$ by $Al^{3+}$ or octahedral $Al^{3+}$ by $Mg^{2+}$). Because these cations are not structural, they can be easily replaced by other positively charged atoms or molecules, and are called exchangeable cations.[13] In contrast to pristine layered silicates containing alkali metal and alkali earth change balancing cations, organically modified layered silicates (OLS) contain alkyl ammonium or phosphonium cations.[14] The presence of these organic modifiers in the galleries renders the originally hydrophilic silicate surface, prganophilic. Depending on the functionality, packing density and length of the organic modifiers, the OLS may be engineered to optimize their compatibility with a given polymer. Montmorillonite, the most common of the smectite clays, can be neutralized and bonded either by substitutions within the lattice or, more commonly, by cations in the underlayer region. The degree of substitution depends on the structure of the montmorillonite. In the tetrahedral plane, substitution may proceed up to about 15%; but in the octahedral plane, it may extend to completion. Typical cation exchange capacities for montmorillonite clays 70–110 millequivlents per 100 gram.[14] In the case where organic cations are incorporated to modify the clay surface, they will significantly influence the thermal behavior of the clay materials.

When preparing polymer–clay nanocomposites via either *in situ* polymerization or direct intercalation, a very specific temperature is needed in the processing.[15,16] If the processing temperature to make the PLS is higher than that of the thermal stability of organic treatment on the OLS, some decomposition will take place. The onset temperature of decomposition of organic treatment, therefore, is meaningful in the process to make a clay/polymer nanocomposite. However, little work has been done on the thermal stability of organic modified clay used in nanocomposites. The relationship between the degradation and layered silicate–organic interface is critical in understanding the upper use temperature and processing environs.

The present article discusses the results obtained from the thermal analysis such as DSC, TGA, TG/FTIR, and pyrolysis-GC/MS. The possible degradation mechanism of organic-modified clay was concluded. According to its thermal stability, the clay-filled PMMA composite was prepared, and some of properties of PMMA–clay nanocomposite were obtained.

## EXPERIMENT

### Material

The purified sodium montmorillonite (CEC = 95 mEq/100 g) from Southern Clay Products Inc. was used for the synthesis of PMMA–clay nanocomposites. The swelling agent of stearyltrimethyl ammonium chloride (SAC) compound was obtained from Akzo Nobel Chemical Inc. Acetone received from Fluka Co. Ltd. were distilled before using. Poly(methyl methacrylate) (PMMA) was supplied by Aldrich Chemical Company, Inc. The molecular weight is 120,000.

### Preparation of Organophilic Clay

In 600 mL of solvent, 10 g of sodium montmorillonite was added to the solution of and concentrated orthophosphoric acid (0.5 mL). The mixture was stirred vigorously at 80°C for 24 h (when the solvent was acetone, the reaction temperature was 30°C). A white precipitate was isolated by filtration, then wash five times with the reaction solvent. The organophilic clay was collected after having dried on the vacuum for 8 h.

### Preparation of PMMA–Clay Nanocomposite

The PMMA was dissolved in the acetone and stirred vigorously at 40°C for 1 h. The organophilic clay was added into the polymer solution and continuously stirred for 5 h. The solution product was then filtered off and washed thoroughly with methanol. The product could be dried under the vacuum oven at 70°C for 8 h and the

PMMA–clay hybrid particles could be obtained from the crush machine.

### Instrument

The organic modified clay samples were examined using a TA Instruments TGA2950 Thermogravimetric analyzer in Ultra High Purity (UHP) nitrogen. The condition to compare weight loss of montmorillonite and organic modified montmorillonite was from room temperature to 500°C at 20°C/min. The X-ray diffraction (XRD) measurement was taken by using CuK$_\alpha$ (radiation, operating at 30 kV and 20 MA), and the FTIR spectra of samples were recorded on a Perkin-Elmer 1600 series Infrared Spectrophotometer. The samples were prepared by dispersing clay sample into KBr and pressing to a thin film. The FTIR detection range was 450 to 4500 cm$^{-1}$, with a resolution of 4 cm$^{-1}$. Pyrolysis-GC/TOFMS experiments were carried out on a Pegasus II GC/MS system (LECO), which includes a Time-of-Flight Mass Spectrometer and a High-Speed Gas Chromatograph. The samples were pyrolyzed using LECO ThermEx™ Inlet system.

The PMMA–clay samples were determined with TA Instruments DSC2920 and TGA2950 in Ultra High-Purity (UHP) nitrogen with a heating rate of 5°C/min. The storage modulus was obtained by dynamic mechanical analysis (DMA), TA Instruments 2980, with a 1-Hz frequency at a heating rate of 5°C/min to 200°C in the air. The transmission electron micrograph (TEM) was obtained from a JEM-100LX, JEOL, using an acceleration voltage of 120 kV.

## RESULTS AND DISCUSSION

### Organophilic Clay

The XRD results are revealed in the Figure 1. The distances of silicate layer can be calculated by Bragg's law ($n\lambda = 2d\sin\theta$, $d$ = layer distances). The wavelength ($\lambda$) of the X-ray is 1.5418 Å by using CuK$_\alpha$ radiation. The measure $d_{001}$-spacing of pristine montmorillonite is 1.40 nm ($2\theta = 6.25°$). After cation exchange with SAC, the $d_{001}$-spacing is 1.84 nm ($2\theta = 3.9°$).

The thermogravimetric analyzer (TGA) is the most powerful tool used to determine the thermal behavior of materials. Figure 2 is the overlay TGA and DTG (differential thermogravimetric) curves
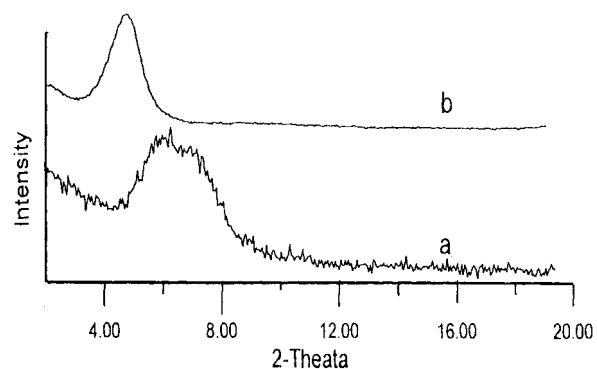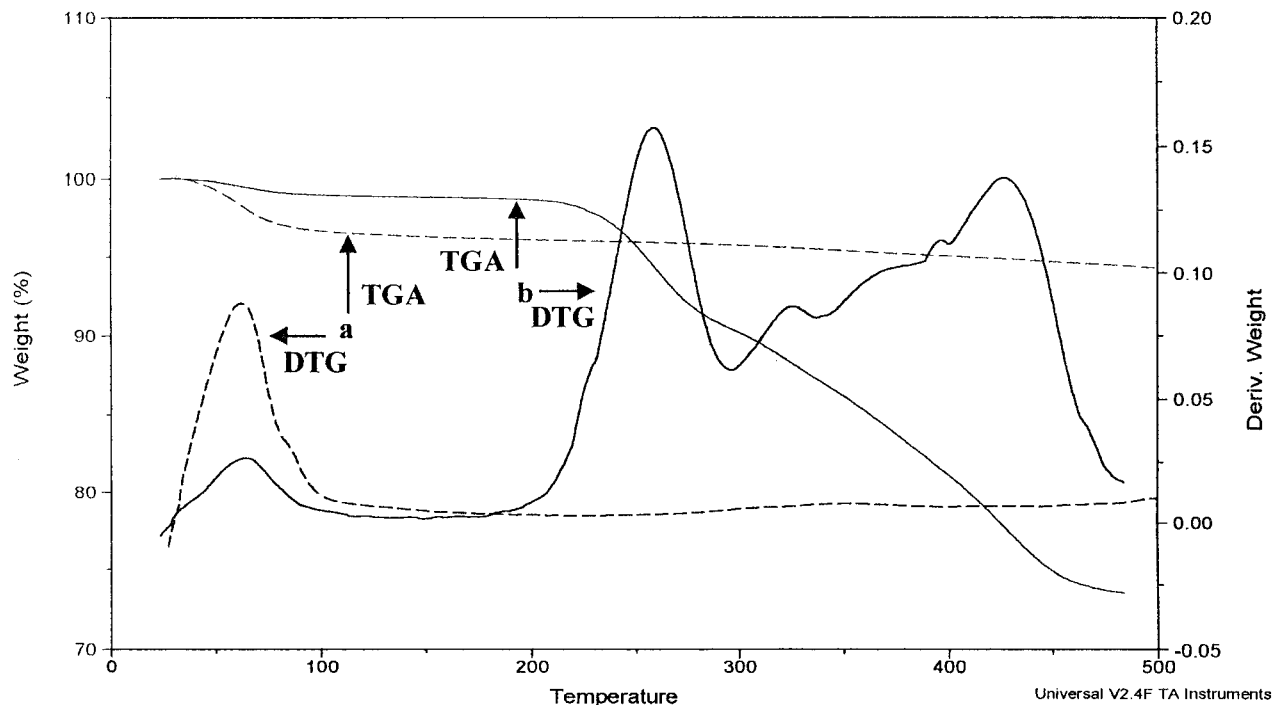


**Figure 1** The XRD curves of (1) montmorillonite and (b) organophilic clay.

of pure Na-montmorillonite and organically modified montmorillonite (SAC–clay). It is indicated that there is almost no weight loss for pure montmorillonite between 125 and 500°C, while two-step weight loss appeared for organic modified montmorillonite in the same temperature range. The difference between them is only organic modifiers (stearyltrimethyl ammonium chloride) in the SAC–clay sample. To determine the cause of the weight loss in this temperature range, Fourier transform infrared (FTIR) spectroscopy was employed to determine the organic group changes before and after heating to 500°C.

Figures 3 and 4 illustrate the FTIR results of original samples and their pyrolysis residues at the 500°C, respectively. In Figure 3, the absorbance of each wave number for pure montmorillonite sample shows no difference before and after heated to 500°C. However, the organic-modified montmorillonite samples (SAC–clay) seen in Figure 4 have obvious differences between the original samples and their pyrolysis residue at 500°C. Clearly, the organic C—H bond vibrations (wave number = 2629, 2853, 1478 cm$^{-1}$) disappear after samples were heated to 500°C. This indicates that the organic compounds are decomposed after the sample is heated to 500°C. It can be concluded that organic compound is decomposed in the range from 125 to 500°C. This result is in agreement with the TGA conclusion.

To clarify the degradation products over the temperature range of 150 to 500°C, ThermEx™ Inlet and GC/TOFMS technique was employed to examine the products evolved from the decomposition reaction (Table I). The organic modifier (SAC) was also used in this study as comparison. The decomposition products of two samples at

**Figure 2** The TGA and DTG curves of (a) montmorillonite and (b) organophilic clay.

different temperatures were identified against NIST library search.

From GC/TOFMS results, comparing the trapped evolved gases at different temperatures for SAC, it is indicated that before 160°C the small amount of water, solvent ($C_3H_8O$), 1-chloro-hexadecane and *N,N*-dimethyl-1-tridecanamine were evaporated from the pure organic compound. At higher temperatures, no water or solvent is observed, but there are still similar species such as 1-chloro-hexadecane and *N,N*-dimethyl-1-tridecanamine determined even at decomposition

temperature. This means that the pure organic compound is not stable even at lower temperatures, and when the temperature is above 200°C, the decomposition rate increases rapidly. About 60 wt % of organic compounds decomposed at this stage. The evolved gases of SAC contain mainly long carbon chains with chloro- or amine groups. For SAC–clay, GC/TOFMS results at different temperatures (listed in Table I) show that there is just absorbed water evolved from organic modified clay below 110°C. The evolved gases at 200
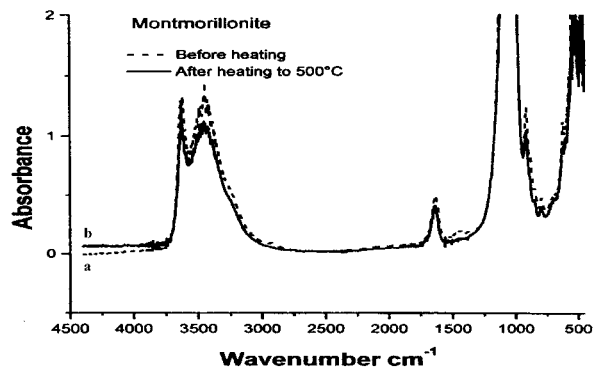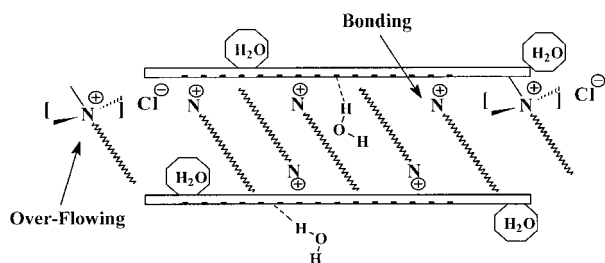


**Figure 3** The FTIR spectra of montmorillonite (a) before and (b) after heating to 500°C.
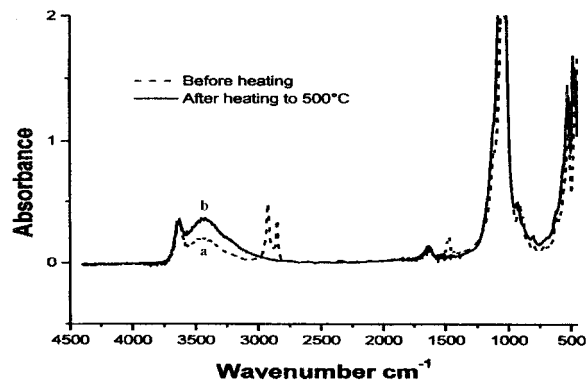


**Figure 4** The FTIR spectra of organophilic clay (a) before and (b) after heating to 500°C.

**Table I   The TOF/MS Results of SAC and SAC-Clay Trapped under Different Temperatures**

| Temperature | SAC Products | Temperature | SAC-Clay Products |
|---|---|---|---|
| 160°C | isopropyl alcohol, $C_3H_8O$<br>water, $H_2O$<br>hexadecane, $C_{16}H_{34}$<br>1-heptadecene, $C_{17}H_{34}$<br>**1-pentadecanamine, N,N-dimethyl-$C_{17}H_{37}N$**<br>hexadecane, 1-chloro-$C_{16}H_{33}Cl$<br>1-tridecanamine, N,N-dimethyl-$C_{15}H_{33}N$ | 200°C | water, $H_2O$<br>1-heptadecene, $C_{17}H_{34}$<br>**1-pentadecanamine, N,N-dimethyl-$C_{17}H_{37}N$**<br>hexadecane, 1-chloro-$C_{16}H_{33}Cl$<br>1-tridecanamine, N,N-dimethyl-$C_{15}H_{33}N$ |
| 175°C | 1-tridecanamine, N,N-dimethyl-$C_{15}H_{33}N$<br>1-undecanamine, N,N-dimethyl-$C_{13}H_{29}N$<br>hexadecane, 1-chloro-$C_{16}H_{33}Cl$<br>**1-pentadecanamine, N,N-dimethyl-$C_{17}H_{37}N$**<br>1-decanol, 2-hexyl-$C_{16}H_{34}O$<br>1-nonadecanamine, N,N-dimethyl-$C_{21}H_{45}N$ | 220°C | 1-heptadecene, $C_{17}H_{34}$<br>**1-pentadecanamine, N,N-dimethyl-$C_{17}H_{37}N$** |
| 210°C | hexane, 1-chloro-$C_6H_{13}Cl$<br>1-heptadecanamine, N,N-dimethyl-$C_9H_{21}H$<br>1-tridecanamine, N,N-dimethyl-$C_{15}H_{33}N$<br>1-pentadecanamine, N,N-dimethyl-$C_{17}H_{37}N$<br>hexadecane, 1-chloro-$C_{16}H_{33}Cl$ | 300°C | water, $H_2O$<br>trans-2-methyl-3-octene, $C_9H_{18}$<br>1-decene, $C_{10}H_{20}$<br>4-dodecene, $C_{12}H_{24}$<br>**1-pentadecanamine, N,N-dimethyl-$C_{17}H_{37}N$**<br>1-hexadecene, $C_{16}H_{32}$<br>1-heptadecene, $C_{17}H_{34}$<br>hexadecanal, $C_{16}H_{32}O$<br>9-octadecene, (E)-$C_{18}H_{36}$ |
| 260°C | dodecane, 1-chloro-$C_{12}H_{25}Cl$<br>1-undecanamine, N,N-dimethyl-$C_{13}H_{29}N$<br>hexadecane, 1-chloro-$C_{16}H_{33}Cl$<br>**1-pentadecanamine, N,N-dimethyl-$C_{17}H_{37}N$**<br>octadecane, 1-chloro-$C_{18}H_{37}Cl$ | 400°C | water, $H_2O$<br>trans-7-methyl-3-octene, $C_9H_{18}$<br>3-undecene, (Z)-$C_{11}H_{22}$<br>9-octadecene, (E)-$C_{18}H_{36}$ |

**Figure 5** The structure of montmorillonite that has been exchanged with SAC.

and 220°C are the same as that of SAC. However, the determined species at 300 and 400°C are different from that of SAC. Most of determined species at this temperature are both short and long carbon alkene chains without the chloro group. It is concluded that the intercalated organic compounds decomposed at higher temperatures, and the decomposition reaction are more complete than that of outside organic compounds. The reason may be due to the interference between organic compounds and clay sheets. This result provides strong support to the conclusion from TGA analysis for a two-step decomposition stage of SAC–clay.

The probable structure of organic modified montmorillonite is shown in Figure 5. According to the experimental results, there should be absorbed water in the clay sheet surface, and also the water structure should exist in the clay sheets with a hydrogen bond. Besides water, the intercalated and outside organic compounds are present in montmorillonite structure.

The detected water at 110°C may be due to the absorbed water. At higher temperatures, the water comes from the reaction of the hydroxyl group in the clay sheets and organic compounds. The first bond breakage in the organic compound may occur outside the clay sheets, between N and C bonds, at around 200°C. Because there is less hindrance in the clay sheets, they can evolve quickly without further degradation. At higher temperatures, the organic treatments decompose in clay sheets. Because of the hindrance in the clay sheets and the force between them, they evolve slowly and further decomposition occurs mainly between C and C bonds. The estimated decomposition mechanism is shown in Figure 6.

## PMMA–Clay Nanocomposite

The poly(methyl methacrylate)–clay nanocomposite was synthesized by the direct dissolved
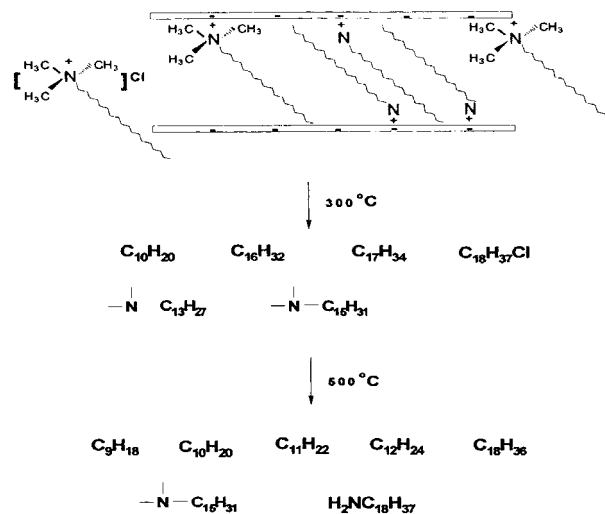


**Figure 6** The probable decomposition mechanism of SAC–clay.

solution method with acetone. A TEM micrograph of PMMA–clay nanocomposite containing 5.0 wt % organophilic clay is shown in Figure 7. The dark lines are intersection of silicate sheets. The silicate sheets of clay are dispersed in the PMMA matrix homogeneously because of swelling by SAC and further intercalation with PMMA chain. DSC traces of the pure PMMA and PMMA–clay nanocomposite are shown in Figure 8. The pure
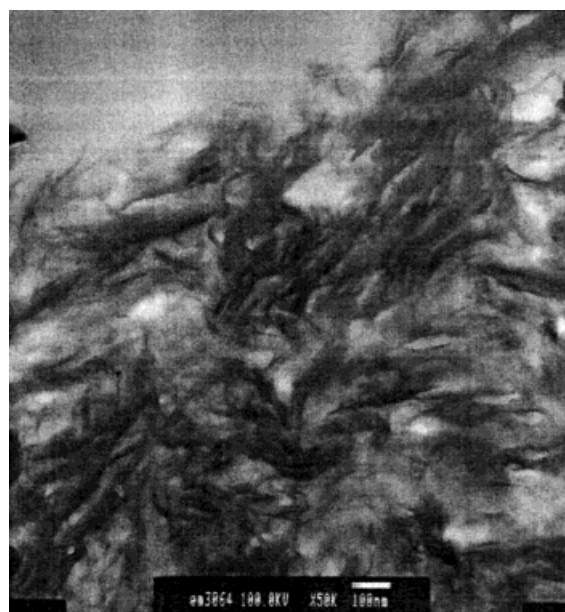


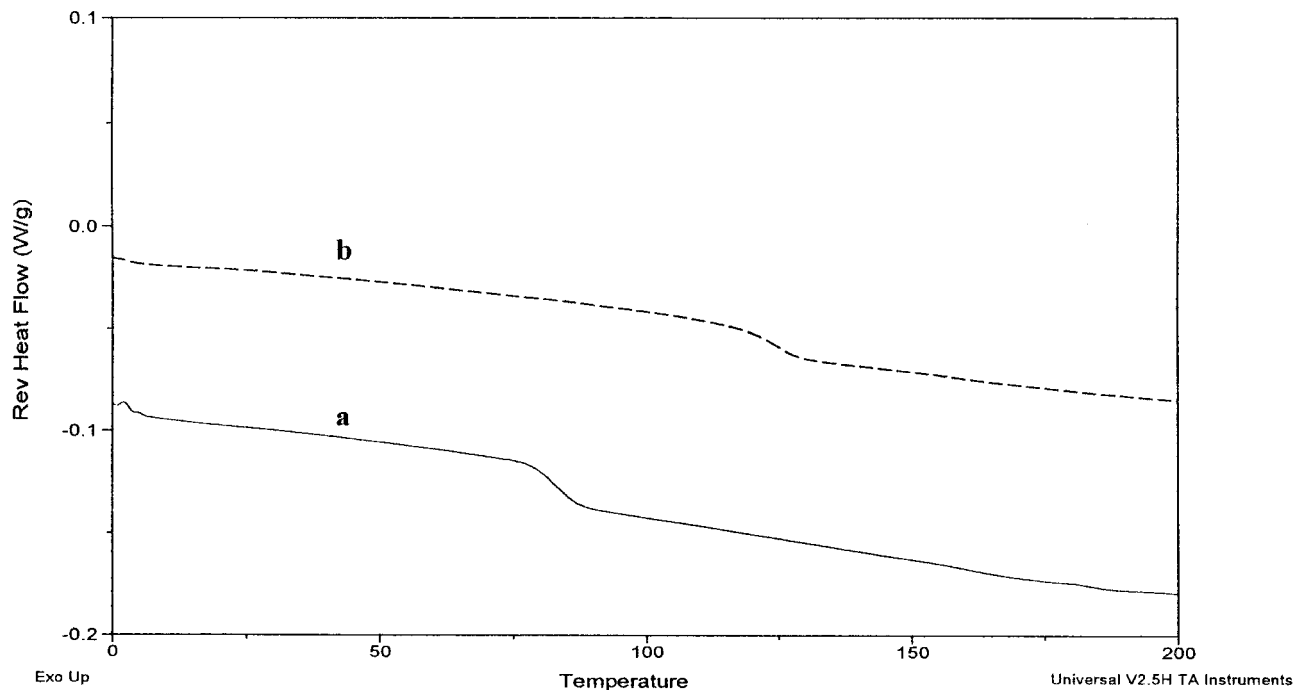**Figure 7** The TEM photograph of PMMA–clay (clay contents = 5 wt %).

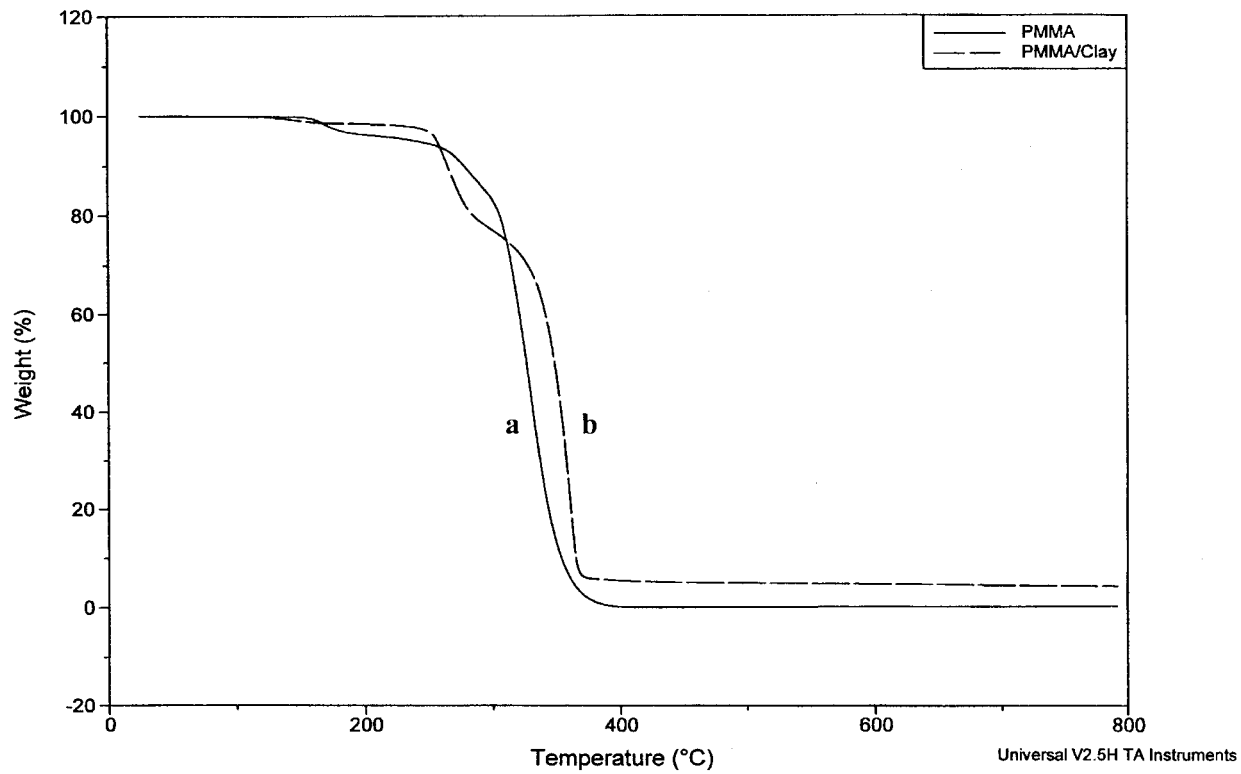**Figure 8**  The DSC curves of (a) PMMA and (b) PMMA–clay.



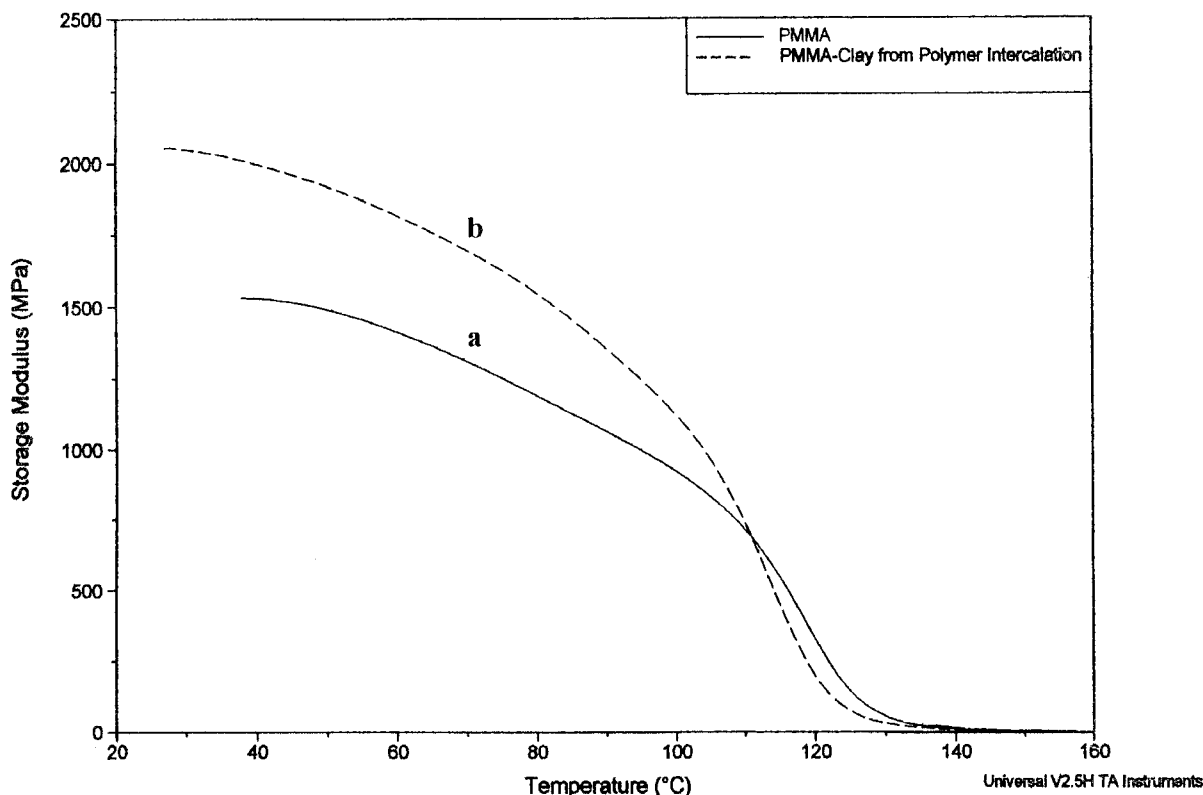**Figure 9**  The TGA curves of (a) PMMA and (b) PMMA–clay.

**Figure 10**    The storage modulus of (a) PMMA and (b) PMMA–clay.

PMMA exhibits a heat flow change at approximately 82 °C, corresponding to the glass transition temperature ($T_g$) of PMMA. Nevertheless, the clay intercalated PMMA shows the higher $T_g$ at about 124°C. This is ascribed to the confinement of intercalated PMMA chains within the silicate galleries that prevents the segmental motions of the polymer chains.

Figure 9 shows the TGA curves of the pure PMMA and the PMMA–clay nanocomposite. Thermal degradation of pure PMMA has three distinctive steps. The first is due to decomposition of relatively week head-to-head linkage, impurities, and solvent in the lattices. The second is the chain-end of PMMA, and the third is the PMMA main chains decomposition. The three steps of pure PMMA are at 167, 278, and 329°C. The PMMA–clay nanocomposite also appears to be a three-step decomposition reaction. The second step is mainly due to the swelling agent decomposition at 266°C. The main chains decomposition of the nanocomposite is higher than pure PMMA about about 40°C. It demonstrates that the PMMA–clay nanocomposite has better thermal stability than that of pure PMMA.

The mechanical properties are obtained from dymanic mechanical analysis. Figure 10 shows the storage modulus results of PMMA and PMMA–clay nanocomposite. The storage modulus of PMMA–clay is higher than pure PMMA. It is illustrated that the organophilic clay can increase the mechanical properties of polymer materials.

## CONCLUSIONS

According to this study, the organic modifiers in clay decompose between 150 and 500°C. A two-step decomposition process in this range is caused by different states of organic modifier in clay. A small part of modifier exists outside clay sheets while others stay in the clay sheet with stronger force and higher decomposition temperature. When the clay fills into the PMMA matrix, the thermal stability, glass transition temperature, and storage modulus increase.

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