

THE CHARACTERIZATION OF ORGANIC MODIFIED MONTMORILLONITE AND ITS FILLED PMMA NANOCOMPOSITE

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Abstract

Thermogravimetric analysis (TG) and Fourier transform infrared (FTIR) results of commercial montmorillonite were compared to that exchanged with trimethyloctadecyl quaternary ammonium chloride (SCPX2048), both were treated up to 500°C. The time-of-flight mass spectrometer (TOF/MS) results of SCPX2048 trapped under 300 and 500°C were compared with that of N,N,N-trimethyl-1-dodecanammonium chloride (A 18-50) trapped under 200 and 300°C. The degradation mechanism of organic modified montmorillonite was proposed. PMMA-clay nanocomposite was synthesized through intercalation method and its properties were examined by both TG and DSC techniques. The thermal stability and glass transition temperature of montmorillonite filled PMMA increase comparing with that of the pure PMMA.

Keywords: DSC, FTIR, nanocomposite, organic modified montmorillonite, PMMA, TG

Introduction

Nanocomposites are a 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 [1]. Recently, these kinds of materials have attracted the attention of governments, academic and industrial researchers [2–4] 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

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nanometer ($1\text{ nm}=10^{-9}\text{ m}$) thick and 1000 nm across the face, which is 1400 times smaller than the finest talc reinforcements in use today.

When preparing clay/polymer nanocomposites via either in-situ polymerization or direct intercalation, a very specific temperature is needed in the processing [6–7]. 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. Organically modified layered silicates have been known for more than 60 years [8–17]. They possess the same structural characteristics as the well-known minerals talc and mica (2:1 phyllosilicate) and are comprised of hydrated aluminum silicate. 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.

This paper discusses the results of both organic modified montmorillonite and its filled PMMA nanocomposite obtained from the thermal analysis such as DSC, TG, TG/FTIR, pyrolysis-GC/MS. The possible degradation mechanism of organic modified clay was proposed. The properties of the synthesized montmorillonite filled PMMA nanocomposite were then compared with the pure PMMA materials.

Experimental

Material selection

Pristine montmorillonite is Na^+ exchanged. SCPX2048 is a montmorillonite exchanged with trimethyloctadecyl quaternary ammonium chloride. These samples were provided by Southern Clay Products Inc., and used without further treatment. A18-50 (Arquad 18-50) is N,N,N-trimethyl-1-dodecanammonium chloride from Akzo Nobel Chemicals Inc., which was used without further treatment. Poly(methyl methacrylate) (PMMA) was supplied by Aldrich Chemical Company, Inc. The molecular mass is 120 000.

PMMA-montmorillonite nanocomposites were synthesized through intercalation method. PMMA was dissolved in the toluene solvent, then the organic modified montmorillonite (SCPX2048). The reaction time is 24 h. After the reaction was completed, *n*-hexane solvent was used to precipitate the PMMA-montmorillonite hybrids. Then the products were dried and examined using TG and DSC.

Characterization

The organic modified montmorillonite was examined using a TA TGA2950. The experiments were conducted under nitrogen atmosphere with a heating rate of $20^\circ\text{C min}^{-1}$ from room temperature to 500°C . 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 pellet. The IR detec-

tion range was 450 to 4500 cm^{-1} with a resolution of 4 cm^{-1} . Pyrolysis-GC/TOFMS experiments were carried out on a LECO Pegasus II GC/MS system, which includes a time-of-flight mass spectrometer (TOF/MS) and a high speed gas chromatograph. The samples were pyrolyzed using LECO ThermExTM Inlet system, the evolved products were trapped and then analyzed by GC/MS. The montmorillonite/PMMA samples were examined using TA Instruments DSC2920 & TGA2950 in ultra high purity (UHP) nitrogen with a heating rate of 5 $^{\circ}\text{C min}^{-1}$.

Results and discussions

Figure 1 is the overlay TG and DTG curves of pure Na-montmorillonite and organically modified montmorillonite (SCPX2048). It is indicated that there is almost no mass loss for pure montmorillonite between 125 and 500 $^{\circ}\text{C}$, while two-step mass loss appeared for organic modified montmorillonite in the same temperature range. The difference between them is only organic modifiers (trimethyloctadecyl quaternary ammonium) in SCPX2048 sample. To determine the cause of the mass loss in this temperature range, Fourier transform infrared (FTIR) spectroscopy was employed to determine the organic group changes before and after heating to 500 $^{\circ}\text{C}$.

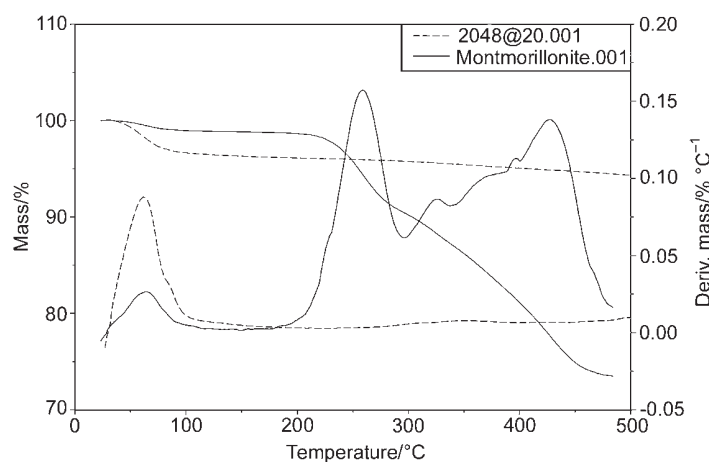


Fig. 1 The TG results of Na^+ montmorillonite and organic modified montmorillonite

Figures 2 and 3 illustrate the FTIR results of original samples and their pyrolysis residues at the 500 $^{\circ}\text{C}$, respectively. In Fig. 2, the absorbance of each wavenumber for pure montmorillonite sample shows no difference before and after heated to 500 $^{\circ}\text{C}$. However, the organic modified montmorillonite samples (SCPX2048) seen in Fig. 3 have obvious differences between the original samples and their pyrolysis residue at 500 $^{\circ}\text{C}$. Clearly, the organic C–H bond vibrations (wavenumber=2629, 2853, 1478 cm^{-1}) disappear after samples were heated to 500 $^{\circ}\text{C}$. This indicates that the organic compounds are decomposed after the sample is heated to 500 $^{\circ}\text{C}$. It can be con-

cluded that the organic compound is decomposed in the range from 125 to 500°C. This result is in agreement with the TG conclusion.

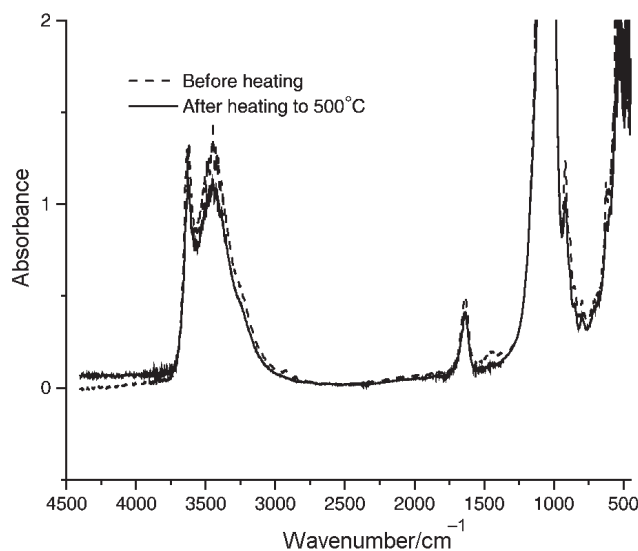


Fig. 2 FTIR spectra of Na⁺ montmorillonite before and after heating to 500°C

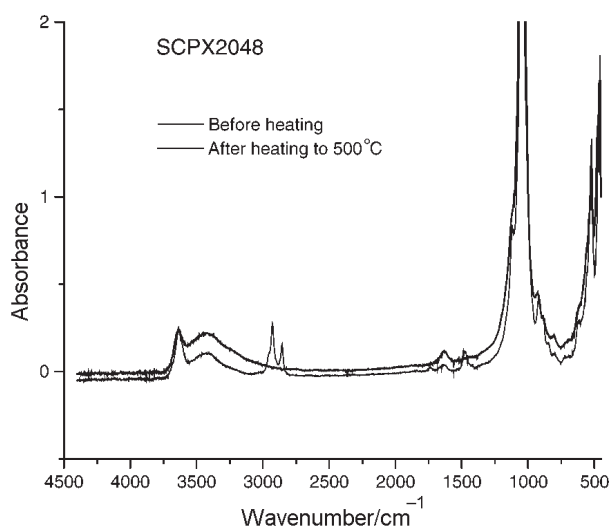


Fig. 3 FTIR spectra of organic modified montmorillonite before and after heating to 500°C

In order to clarify the degradation products over the temperature range 150 to 500°C, ThermExTM Inlet and GC/TOFMS technique was employed to examine the products evolved from the decomposition reaction. The organic modifier (A18-50)

was also used in this study as comparison. The decomposition products of two samples at different temperatures were identified against NIST library search. GC/TOFMS results, comparing the trapped evolved gases at different temperatures for A18-50, indicate that before 160°C the small amount of water, solvent (C₃H₈O), 1-chloro-hexadecane and N, N-dimethyl-1-tridecanamine were evaporated from the pure organic compound. At higher temperatures, no water or solvent was 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 mass% of organic compounds decomposed at this stage. The evolved gases of A18-50 contain mainly long carbon chains with chloro- or amine groups. For SCPX2048, GC/TOFMS results at different temperatures (listed in Table 1) show that there is just absorbed water evolved from organic modified clay below 110°C.

Table 1 The TOF/MS results of trimethyloctadecyl quaternary ammonium chloride trapped under 200 and 300°C, and organic modified montmorillonite (SCPX2048) trapped under 300 and 500°C

A18-50		SCPX2048	
200°C	300°C	300°C	500°C
water, H ₂ O	water, H ₂ O	water, H ₂ O	water, H ₂ O
1-propanol C ₃ H ₈ O	1-decene C ₁₀ H ₂₀	1-decene C ₁₀ H ₂₀	1-nonene C ₉ H ₁₈
dodecane	1-dodecene	1-hexadecene	1-decene
1-chloro-C ₁₂ H ₂₅ Cl	C ₁₂ H ₂₄	C ₁₆ H ₃₂	C ₁₀ H ₂₀
1-heptadecene C ₁₇ H ₃₄	octadecane 1-chloro-C ₁₈ H ₃₇ Cl	1-heptadecene C ₁₇ H ₃₄	4-nonene 2-methyl-C ₁₀ H ₂₀
1-undecanamine N,N-dimethyl- C ₁₃ H ₂₉ N	1-tridecanamine N,N-dimethyl- C ₁₅ H ₃₃ N	1-tridecanamine N,N-dimethyl- C ₁₅ H ₃₃ N	1-pentadecanamine N,N-dimethyl- C ₁₇ H ₃₇ N
undecanal 2-methyl-C ₁₂ H ₂₄ O	1-nonadecanamine N,N-dimethyl- C ₂₁ H ₄₅ N	octadecane 1-chloro-C ₁₈ H ₃₇ Cl	3-undecene (E)-C ₁₁ H ₂₂
hexadecane C ₁₆ H ₃₄	N,N-dimethyltetradecan- amine, C ₁₆ H ₃₅ N	tetradecanal C ₁₄ H ₂₈ O	5-dodecene (Z)-C ₁₂ H ₂₄
tetramethyl ammonium chloride C ₄ H ₁₂ ClN	1-pentadecanamine N,N-dimethyl- C ₁₇ H ₃₇ N	1-pentadecanamine N,N-dimethyl- C ₁₇ H ₃₇ N	5-octadecene (E)-C ₁₈ H ₃₆
1-tridecanamine N,N-dimethyl- C ₁₅ H ₃₃ N		pyrrolidine N-(4-pentenyl)- C ₉ H ₁₇ N	E-15-heptadecenal C ₁₇ H ₃₂ O
			1-octadecanamine C ₁₈ H ₃₉ N

The evolved gases at 200 and 220°C are the same as that of A18-50. However, the determined species at 300 and 400°C are different from that of A18-50. Most of the determined species at this temperature are both short and long 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 TG analysis for a two-step decomposition stage of SCPX2048.

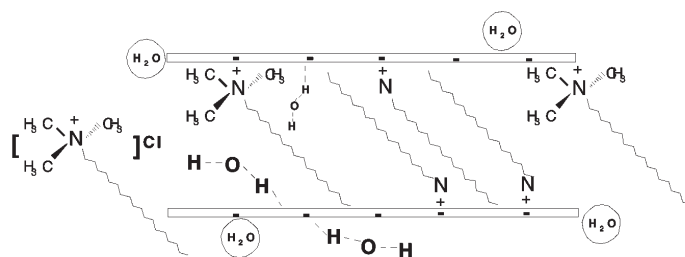


Fig. 4 The general structure of montmorillonite that has been exchanged with organic modifiers

The probable structure of organic modified montmorillonite is shown in Fig. 4. According to the experimental results, absorbed water should be in the clay sheet sur-

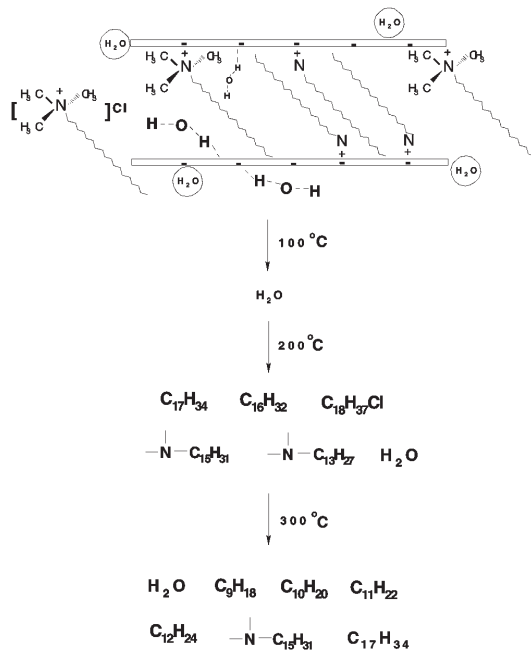


Fig. 5 The proposed decomposition mechanism of organic modified montmorillonite (SCPX2048)

face, 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 the 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 Fig. 5.

The poly(methyl methacrylate) (PMMA)/montmorillonite nanocomposite was synthesized by the direct dissolved solution method with acetone. DSC curves of the pure PMMA and PMMA/montmorillonite nanocomposite are shown in Fig. 6. The pure 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 a much 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.

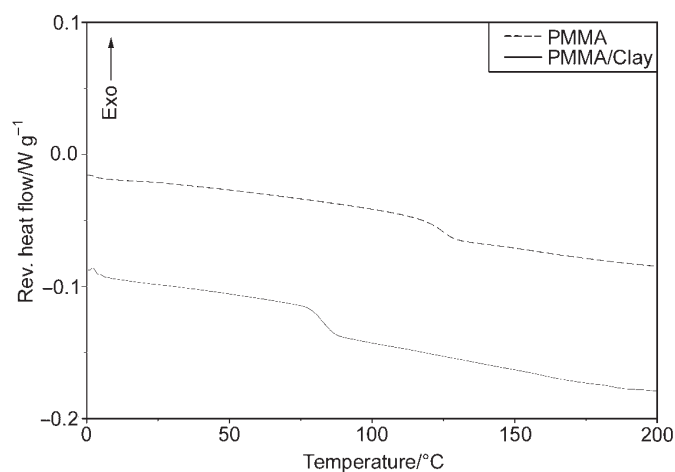


Fig. 6 The DSC overlay curves of pure PMMA and montmorillonite/PMMA nanocomposite

Figure 7 shows the TG curves of the pure PMMA and the montmorillonite/PMMA nanocomposite. Thermal degradation of pure PMMA has three distinctive steps. The first is due to decomposition of relatively weak 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 montmorillonite/clay nanocomposite also appears to be a

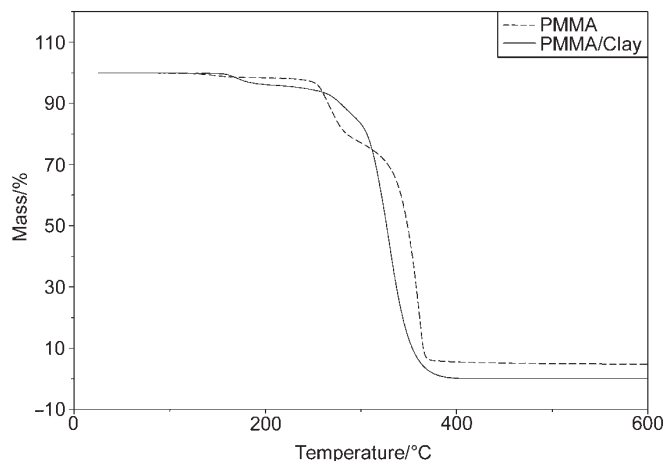


Fig. 7 The TG overlay curves of pure PMMA and montmorillonite/PMMA nanocomposite

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 40°C. It demonstrates that the PMMA/montmorillonite nanocomposite has better thermal stability than that of pure PMMA.

Conclusions

Generally, the organic modifiers presented inside organic modified montmorillonite system decompose at the temperature range between 150 and 500°C. A two-step decomposition process at this temperature range is due to, at least in part, the different states of organic modifier inside organic modified montmorillonite system. A small part of modifier exists outside clay sheets and while the others stay inside the clay sheet with stronger force and higher decomposition temperature. When the clay fills into the PMMA matrix, the thermal stability and glass transition temperature of montmorillonite filled PMMA show an increase when comparing with the pure PMMA.

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