

Effect of Intercalation Agent on the Structure and Properties of OMMT and RTV/OMMT Composites

Wang Jincheng, Yang Ke, Xu Nan

College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, 201620, People's Republic of China

Received 17 January 2010; accepted 30 March 2011

DOI 10.1002/app.34628

Published online 15 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Novel room-temperature vulcanized silicone rubber (RTV)/organic montmorillonite (OMMT) composites have been prepared. Di(2-oxyethyl)-12 alkane-3 methyl-amine chloride and hydrogen silicone oil were used as intercalation agents to treat Na⁺-montmorillonite and form two kinds of OMMTs. The structure and properties of OMMT were characterized by Fourier transform infrared spectroscopy and X-ray diffraction (XRD). The intercalation mechanism of different types of intercalation agents was proposed. RTV/OMMT composites were pre-

pared using these OMMTs. Properties such as viscosity, hardness, tensile strength, elongation at break, and thermal stability were researched and compared. A combination of swelling test, XRD and transmission electronic microscopy studies was used to characterize the structure and reinforcing mechanism of these OMMTs. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1293–1301, 2012

Key words: intercalation agent; OMMT; RTV; structure; properties

INTRODUCTION

Room-temperature vulcanized silicone rubber (RTV) is one of the most important multifunctional synthetic rubbers with excellent waterproof, moisture-proof, electrical insulation resistance, impact resistance, physical inertia, and permeability properties. It is mainly used in seal, instruments, electronic appliances, marine, metallurgy, and automobile, as well as in rubber molds and so on.^{1,2}

To meet the rising demands of applications, hybrids of inorganic "functional fillers" and polymeric materials are being continuously developed to combine their constituents' beneficial properties or to induce new ones.³ Montmorillonite (MMT), one of the layered clay minerals, is a hydrated alumina-silicate clay composed of units of two silicate tetrahedral sheets with a certain alumina octahedral sheet.

The silicate layers of MMT are planar, stiff and about 10 Å in thickness, 1000–2000 Å in length and width, and do not occur as isolated individual units but aggregate to form crystalline structures.⁴

The efficiency of MMT in improving the properties of polymer materials is primarily determined by the degree of its dispersion in the polymer matrix, which in turn depends on the compatibility of the MMT and the matrix. However, the hydrophilic nature of the MMT surface impedes its homogeneous dispersion in the organic polymer phase. To overcome this problem, it is often necessary to make the surface organophilic before use.⁵ Some researchers have prepared different intercalated silicate layers using different intercalation agents and examined their physical properties.^{6–10}

The reinforcement of rubbers is expressed by enhancement of tensile strength, modulus, and abrasion resistance. The main aim for the addition of fillers such as organic montmorillonite (OMMT) is to improve certain properties or cheapen the compounds.^{11–13}

In this article, two novel kinds of OMMT were prepared and applied to prepare RTV/OMMT composites. A combination of Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and transmission electronic microscopy (TEM) studies were used to characterize the structure and properties of OMMT and RTV/OMMT composites. Results showed that different intercalation agents had different effect on the structure and properties of OMMT, which led to different properties of RTV/OMMT composites.

Correspondence to: W. Jincheng (wjc406@126.com).

Contract grant sponsor: National Natural Science Funds; contract grant number: 50803034.

Contract grant sponsor: Shanghai Municipal Education Commission and Shanghai Education Development Foundation (Shu Guang' project); contract grant number: 10SG53.

Contract grant sponsor: Shanghai Nano-project Funds; contract grant number: 0952nm02600.

Contract grant sponsor: Shanghai Universities Knowledge Innovation Engineering Project; contract grant number: JZ0904.

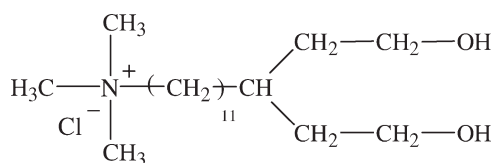
TABLE I
Formulation of RTV Vulcanizates

Components	Weight %
Part A, ethylene-terminated polysiloxane	35
Part A, aerosilica	15
Part B, hydrogenous silicane	49.8
Part B, Pt catalyst	0.2

EXPERIMENTAL

Materials

Na⁺-MMT, industrial grade, was obtained from Zhejiang Fenghong Clay Company (China). Di(2-oxyethyl)-12 alkane-3 methyl-amine chloride,



chemical pure, was received from Zhejiang Chemical Agent Company (China). Hydrogen silicone oil, industrial grade, was supplied by Bluestar Silicones Shanghai Company (China). Anhydrous ethanol and glacial acetic acid were provided by Shanghai Guoyao Chemical Agent Company (China). The formulation, shown in Table I, is used for the application of OMMT into RTV composites.

Preparation of OMMT

A 500-mL round-bottomed, three-necked flask with a mechanical stirrer, thermometer, and condenser with drying tube was used as a reactor. MMT (10 g) was gradually added to a prior prepared solution of dihydroxyethyl-12 alkane-3 methyl-amine chloride (3.52 g), which was dissolved of 120 mL ethanol and water mixture (weight ratio, 1 : 1), and the resultant suspension was vigorously stirred for 2 h. The treated MMT was repeatedly washed by deionized water. The filtrate was titrated with 0.1N AgNO₃ until no precipitate of AgCl was formed to ensure the complete removal of chloride ions. The filter cake was then placed in a vacuum oven at 80°C for 12 h for drying. The dried cake was ground to obtain OMMT-1.

Anhydrous ethanol (100 mL) was added with 10 mL glacial acetic acid. The pH value was adjusted to 5. Then, 2 g hydrogen silicone oil was added into 98 g above solution. The mixture was placed for 10 min to allow it to dissolve. MMT (10 g) was added into this liquid mixture, and was then stirred and reacted for 30 min. Finally, the product was washed by anhydrous ethanol and dried at 70°C. The dried cake was ground to obtain OMMT-2.

Preparation of RTV/OMMT composites

Different amounts of OMMT-1,2 (1, 3, 5, 7, 9 wt %) were mixed with 10 g of Part B, ethylene-termi-

nated polysiloxane, one component of RTV. After vigorous stirring at room temperature for 3 h, the mixture was blended with 10 g of Part A, hydrogenous silicane, the other component of RTV, and was stirred for 30 s. Then, the mixture was molded in a Teflon mould. Curing was conducted at room temperature 20°C for 24 h or at 80°C in a vacuum oven for 1 h, after which an elastic film was obtained.

Characterization

Infrared transmission spectra of MMT and OMMT were obtained using a FTIR spectrometer, model Avatar 370 from Nicolet Corporation. The scan range was from 4000 to 700 cm⁻¹ with a resolution of 2 cm⁻¹. To measure the change of gallery distance of OMMT and RTV/OMMT before and after intercalation, XRD was performed at room temperature with a Rigaku D-Max/400 (Japan) X-ray diffractometer. The X-ray beam was nickel-filtrated CuKα (λ = 0.154 nm) radiation operated at 50 kV and 150 mA. XRD data were obtained from 1° to 10° (2θ) at a rate of 2° min⁻¹. The samples for TEM were first prepared by microtoming the composites into 80–100-nm thick slices at -100°C. The graphs were obtained with JEM-2010 instrument using an acceleration voltage of 200 kV.

Viscosity of RTV/OMMT composites was measured by NDJ-1 apparatus. About 100 mL RTV (Part A: Part B = 1 : 1, weight ratio, uncured) or RTV/OMMT solution (Part A: Part B = 1 : 1, weight ratio, uncured, together with different amounts of OMMT-1 or 2) was used in the measurements. The measurements were carried out at 25°C in the rotational mode using concentric cylinder, type Z3 (according to the viscosity of the system).

Hardness test was conducted using a XY-1 rubber hardness instrument. Tensile test was carried out using a TCR-2000 instrument at room temperature with a crosshead speed of 500 mm min⁻¹. The samples were manufactured in a standard dumbbell-shape, and all measurements were repeated five times and a medium data was got. TGA of RTV/OMMT composites was carried out at 10°C min⁻¹ under air (flow rate 5 × 10⁻⁷ m³ s⁻¹, air liquid grade) using a Linseis equipment. In each case, the mass of the sample used was fixed at 10 mg and the samples (powder mixtures) were positioned in open vitreous silica pans. The precision of the temperature measurements was 1°C over the whole range of temperatures. Swelling test was conducted by using vulcanized 5.0 × 2.5 × 0.2 cm³ samples. They were weighed and allowed to swell in an excess of toluene at room temperature, in the dark, until equilibrium was achieved. The swollen samples were then weighed, and the solvent was removed under vacuum, and was then weighed again.

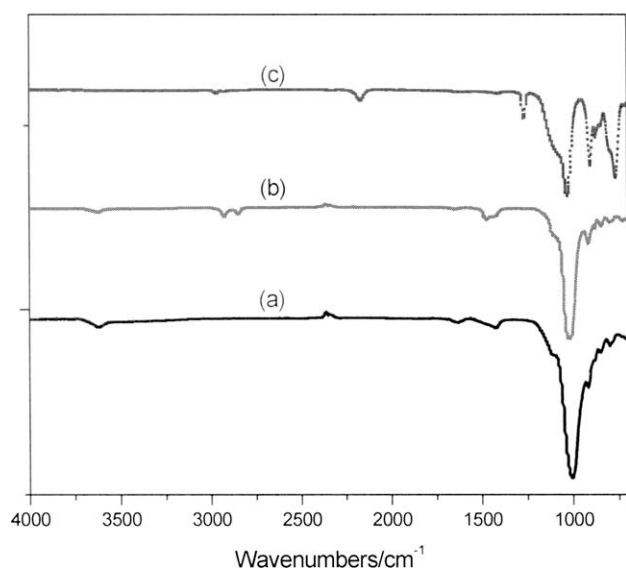


Figure 1 FTIR spectra of (a) MMT, (b) OMMT-1, and (c) OMMT-2.

RESULTS AND DISCUSSION

Analysis of OMMT

FTIR

The FTIR spectra of original MMT and OMMT are shown in Figure 1. The $3620\text{--}3650\text{ cm}^{-1}$ peak was caused by the stretching of —OH , which was due to the physical and chemical water existed in the Na^+ -MMT. The peaks at 1030 and 700 cm^{-1} resulted from the stretching vibration of Si—O and Al—O bonds in the MMT structure. In the spectrum of OMMT-1, except for the peaks existed in the MMT, there showed the presence of new peaks at $2800\text{--}3000\text{ cm}^{-1}$ and 1469 cm^{-1} , which were caused by C—H stretching and bending absorptions in the

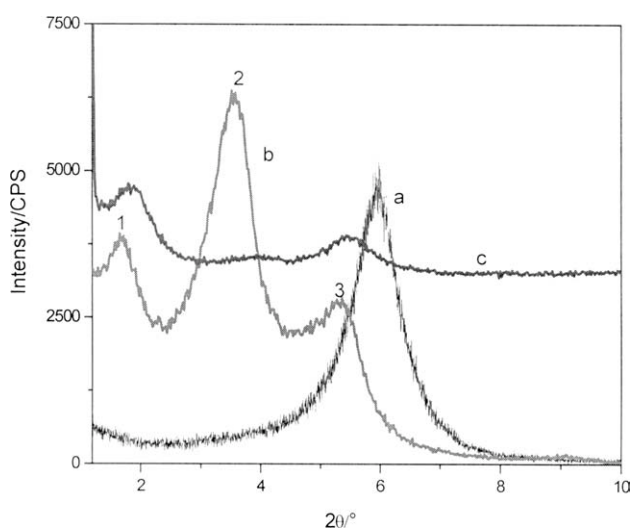


Figure 2 XRD spectra of (a) MMT, (b) OMMT-1, and (c) OMMT-2.

TABLE II
XRD Data of MMT and OMMT

Serial number	λ (Å)	2θ (°)	d (nm)
A	1.54056	6.036	1.46303
b-1	1.54056	1.680	5.25419
b-2	1.54056	3.172	2.78303
b-3	1.54056	4.540	1.94473
C	1.54056	1.890	4.92544

organic intercalation agent. The disappearance of peaks at 1640 cm^{-1} illustrated the exchanging of Na^+ cations in the MMT and N^+ cations in the intercalation agents.^{14,15} In the spectrum of OMMT-2, in addition to the peaks that existed in the MMT spectra, new peaks also appeared at 2250 and 1300 cm^{-1} . The shape changes of peaks at 1030 cm^{-1} were due to stretching and bending absorptions of C—H , Si—O in the organic intercalation agent.

XRD

The XRD patterns of original MMT and OMMT are shown in Figure 2. Curve a, XRD of original MMT, showed a characteristic peak at 6° of 2θ , which was assigned to the 001 basal reflection. In curve b, there were three peaks in the XRD spectrum of OMMT-1. This indicated the different expansion degree of organic silicate layers. This trimodal distribution in d -spacing was due to the special structure of the intercalation agent. In curve c, XRD of OMMT-2, the shifting of peaks from 6° to 5.4° and 1.9° resulted from the expansion of basal spacing of silicate layers by hydrogen silicone oil.^{16,17} The intensity of these peaks was very unobvious, which was ascribed to the small ratio of intercalated OMMT in the whole powder. That is, most part of OMMT-2 was exfoliated due to the active hydrogen existed in the intercalation agent.¹⁸

The data of MMT and OMMT calculated by Bragg formula: $2d \sin \theta = n\lambda$ are summarized in Table II.

Intercalation mechanism

The MMT clay is a phyllosilicate mineral. Cations such as Na^+ , K^+ , and Ca^{2+} compensate the negative charge that exists in the crystal lattice of each silicate layer in MMT. Polar molecules such as dihydroxyethyl-12 alkane-3 methyl-amine chloride and hydrogen silicone oil, which can make MMT more organophilic, can penetrate between the layers and swell.^{19,20}

The schematic depicting of the intercalation process between original MMT and the intercalation agents are illustrated in Figure 3. The underlying mechanism of intercalation process of OMMT-1, as shown in Figure 3(a), may be related to the branching chains of dihydroxyethyl, the strong polarity of

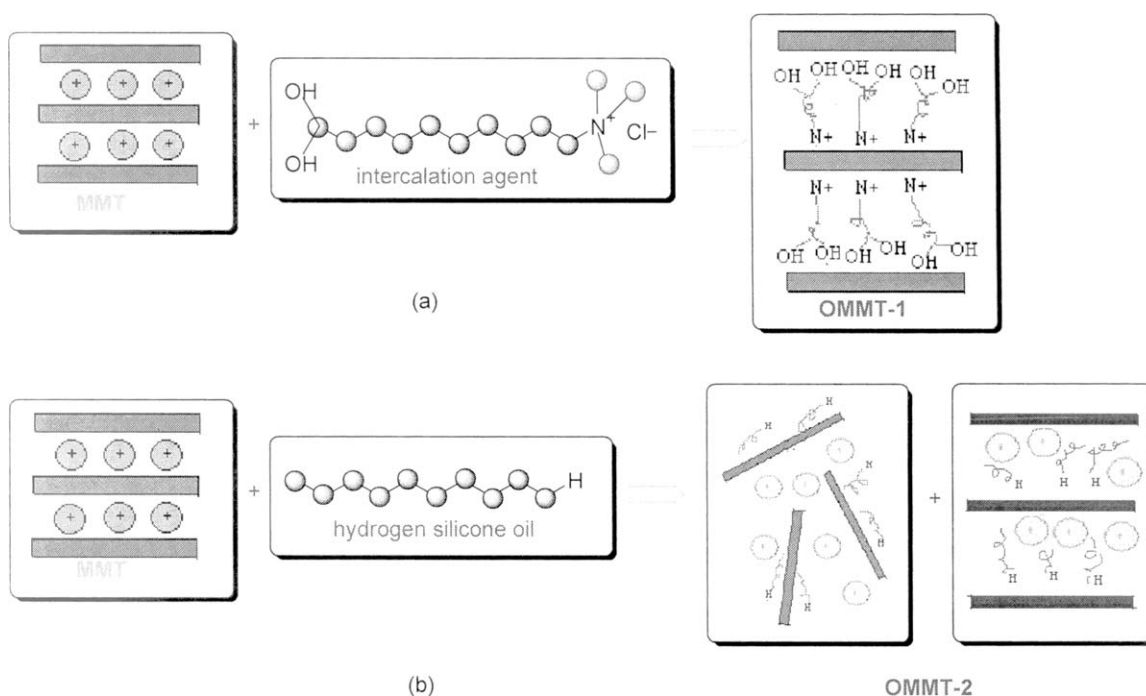


Figure 3 Scheme of intercalation process of (a) OMMT-1 and (b) OMMT-2.

—OH, and space distributing morphology of the whole molecular chains of this intercalation agent. As shown in Figure 3(b), OMMT-2 is mixed with exfoliated and intercalated silicate layers. The intercalation mechanism of OMMT-2 is ascribed to the reaction activity of —H bond. It may react with —OH in the silicate layers, and the heat produced by this reaction may have great effect on the exfoliation of silicate layers.²¹

Properties analysis of RTV/OMMT composites

Viscosity

Viscosity of silicone rubber is very important for its application in different fields. It was shown in Figure 4 that the addition of OMMT in RTV had obvious influence on its viscosity. With the increase of OMMT content, the viscosity of RTV was increased from 42,000 to 100,000 cps. The relationship between filler content and the viscosity can be deduced from following formula.

$$\ln \eta = \ln \eta_c + \frac{K_E V_i}{1 - \frac{V_i}{\Phi}}$$

where η_c , viscosity of RTV; K_E , shape parameters of OMMT; V_i , volume ratio of fillers; Φ , accumulation coefficient. In this experiment, Φ is about 0.5–1.0. The increase of OMMT content can increase V_i and thus may increase η .

Different intercalation agents led to different interactions and thus led to different viscosity. In the OMMT-

1 filled RTV, there were some reactions between the intercalation agent and the RTV molecules. The hydrogenous silicane not only can react with ethylene-terminated polysiloxane but also can react with —OH in the intercalation agent in OMMT-1. These reactions may have an important effect on the tangles between intercalation agents and silicone molecules. This may increase the viscosity of this composite. While in the OMMT-2-filled RTV, although there were some interactions between silicate layers and silicone molecules, silicone oil had some lubricating effect, and this may lead to lower viscosity of this composite.

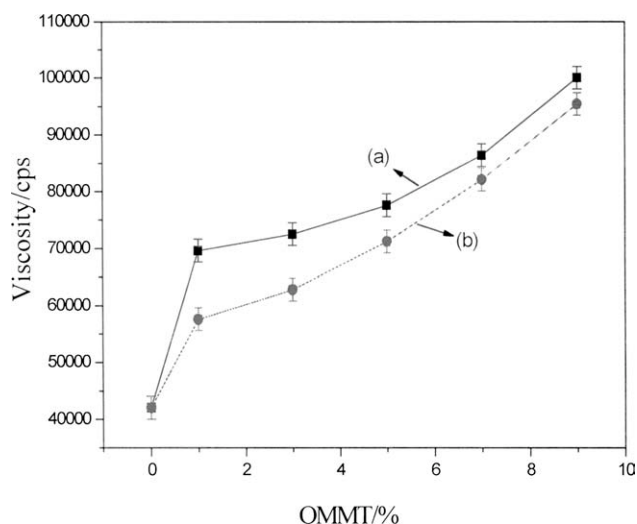


Figure 4 Viscosity of (a) RTV/OMMT-1 and (b) RTV/OMMT-2.

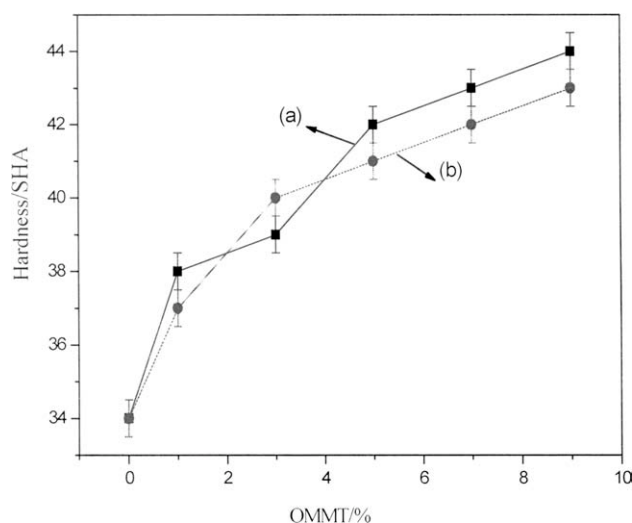


Figure 5 Hardness of (a) RTV/OMMT-1 and (b) RTV/OMMT-2.

Hardness test

Figure 5 shows the hardness of RTV/OMMT composites. It can be seen that with the increasing amount of OMMT, the hardness was increased. This may be beneficial for the application of these composites in some fields that need this property.

The hardness of OMMT-1-filled system was higher compared to OMMT-2 filled system. The reason may be resulted from the different initial interactions existed between RTV matrix and the different intercalation agents, such as hydrogen silicone oil and the ammonium salt. In addition, the hydrogen silicone oil was a kind of oil and had some lubricating effect, and this may decrease the hardness of this composite.

However, the hardness of OMMT-2-filled matrix was higher compared to OMMT-1 for 3% loading. This may be due to the stronger chemical bonds developed from initial interactions in this composite.

Tensile properties

The tensile properties of RTV/OMMT are illustrated in Figure 6. The tensile strength and elongation at break of RTV/OMMT composites showed different trend compared with that of original RTV. In conclusion, the OMMT-2 reinforced RTV showed relatively better properties than that of OMMT-1 filled composites.

These two kinds of composites all showed the highest tensile strength with the addition of 3% OMMT. The tensile strength of RTV addition of 3% OMMT-2 was improved about 22%. When the amount of OMMT was increased continuously to 5, 7, and 9%, the tensile strength was decreased. This, in some extent, was probably due to the aggregates of OMMT in the composites.²² The elongation at break changed irregularly indicating the addition of OMMT had no

obvious effect on the toughness of these composites. However, different reinforcing effects were found in our previous article that 1% OMMT was effective in improving the tensile strength and elongation at break of liquid silicone rubber. This may be due to the different interaction effect between aerosilica and OMMT in the silicone rubber matrix.²³

Thermal stability

The addition of 3% OMMT has two aspects on the thermal stability of RTV. This is shown in Figure 7. Some improvement can be seen between 250 and 450°C in TGA curves. This was beneficial for the application of this composite in special fields. In the temperature range 450–800°C, the thermal stability showed some decrease. The residue mass was decreased from 65 to 55%. As can be deduced from differential thermogravimetric analysis (DTG) curves, the centre temperature of thermal degradation was slightly improved from about 490 to 505°C. In addition, the degradation degree of RTV added

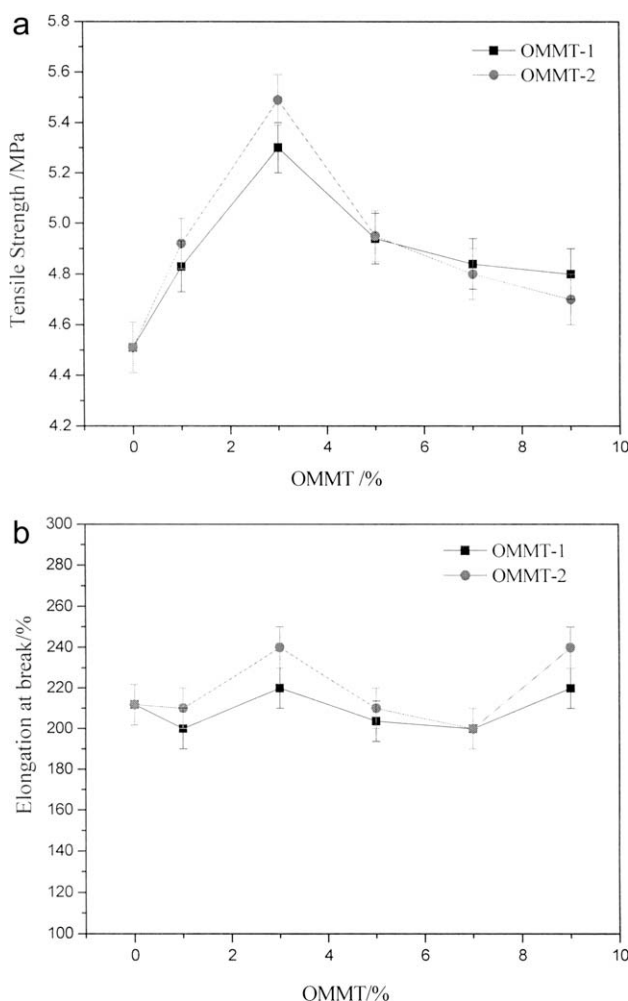


Figure 6 Tensile properties of RTV/OMMT (a) tensile strength and (b) elongation at break.

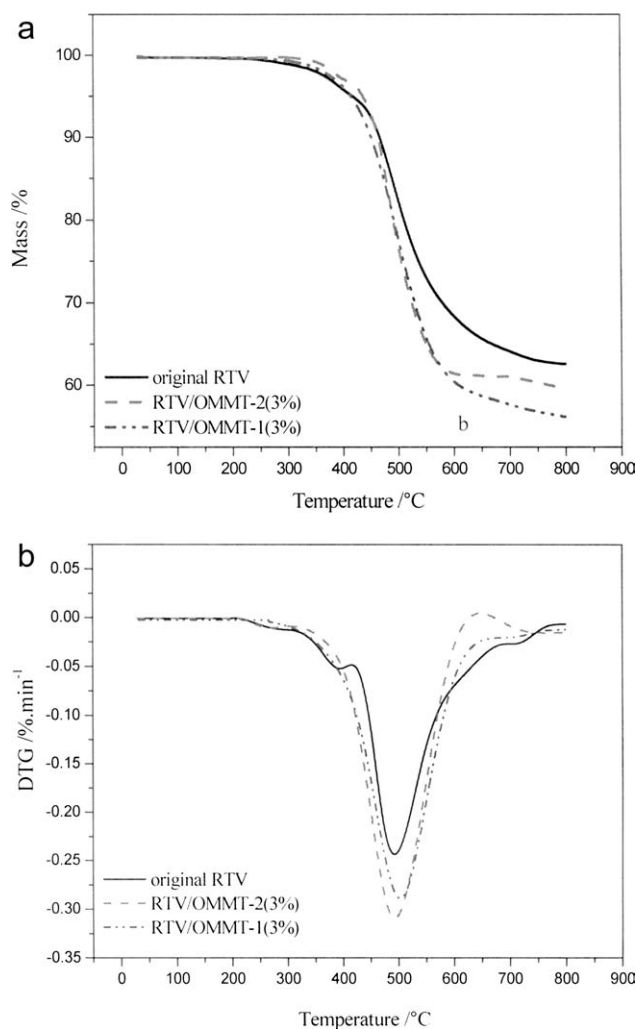


Figure 7 Thermal stability of RTV/OMMT(3%) (a) TGA and (b) DTG.

with OMMT showed some improvement in the temperature range 450–550°C.

It is noted from above that the thermal stability of the composites decreased and seemed to have something to do with the OMMT types. In these hybrid systems, thermal stability could be affected at least by following three factors. First, there could be the nanoreinforcement effect of OMMT layers together with the intercalation agent, which were dispersed in the continuous RTV matrix and restricted the motion of polymer chains and thus gave rise to the increase of thermal stability. Second, the dispersed silicate layers in the matrix might serve as nucleation seeds that might induce some additional crystallinity. The thickness of these crystalline could be improved by the silicate layers, which can make thermal stability improved. Third, the thermal stability could be affected by the crosslinking density of RTV composites. In RTV/OMMT-1 composites, hydrogenous silicane, one component of RTV, can react not only with ethylene-terminated polysiloxane, the

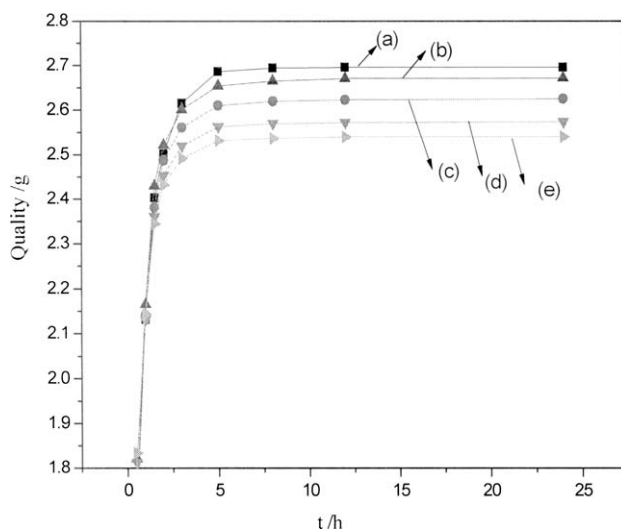


Figure 8 Swelling test curves of RTV/OMMT (a) original RTV, (b) RTV/OMMT-1(3%), (c) RTV/OMMT-2(3%), (d) RTV/OMMT-1(9%), and (e) RTV/OMMT-2(9%).

other component of RTV, but also with the intercalation agent, dihydroxyethyl-12 alkane-3 methyl-amine chloride. While in RTV/OMMT-2 composites, the intercalation agent of OMMT-2, hydrogen silicone oil, can react with ethylene-terminated polysiloxane. These could lead to the incomplete curing of the whole system, and thus introduce free volume and decrease thermal stability of above two types of composites. In the present case, the decrease of thermal stability together with the residual mass by the addition of different amounts and types of OMMT can be related to the integrated effect of above three factors. Furthermore, the relative increase of thermal stability of RTV/OMMT-2, may be caused by the higher thermal stability of hydrogen silicone oil.^{24,25}

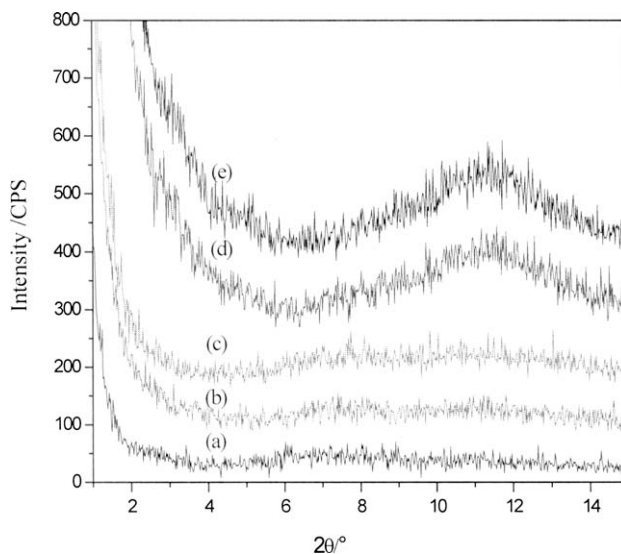


Figure 9 XRD of RTV/OMMT (a) original RTV, (b) RTV/OMMT-1(3%), (c) RTV/OMMT-2(3%), (d) RTV/OMMT-1(9%), and (e) RTV/OMMT-2(9%).

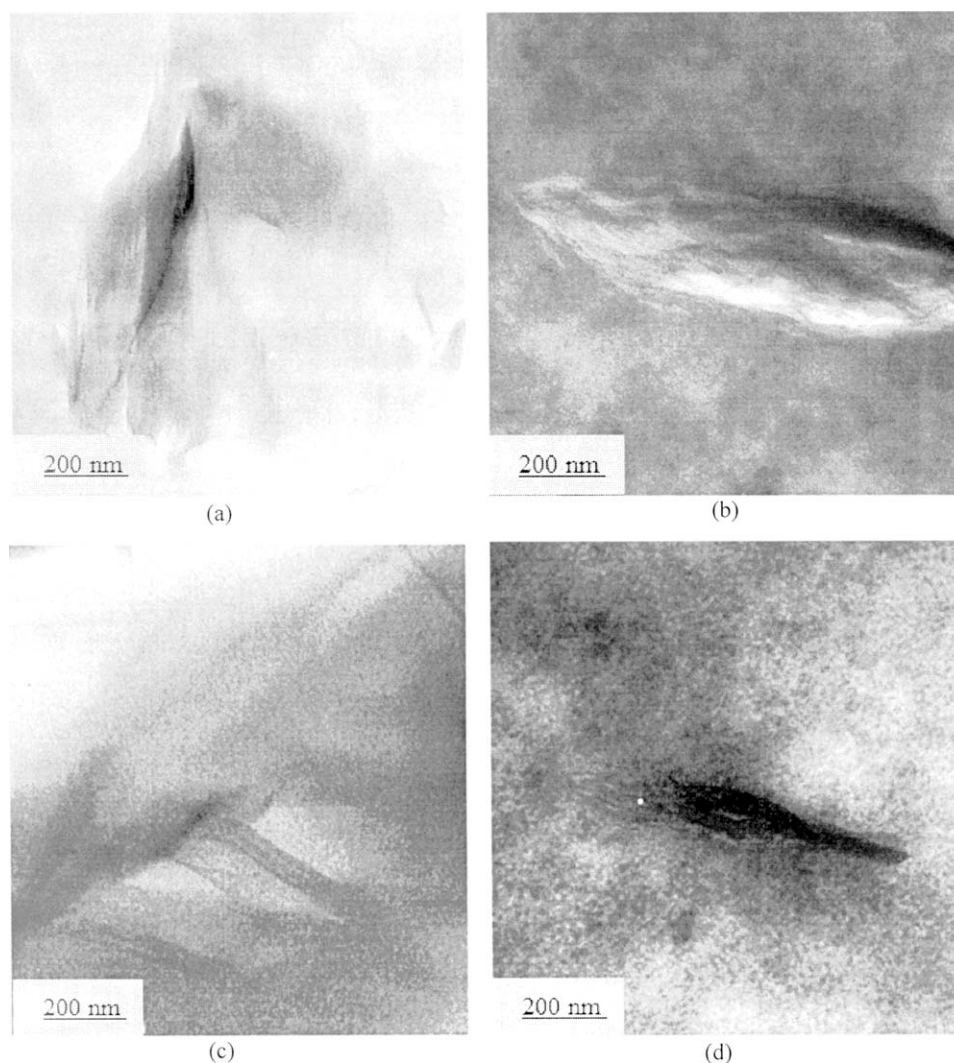


Figure 10 TEM of RTV/OMMT (a) RTV/OMMT-1(3%), (b) RTV/OMMT-1(9%), (c) RTV/OMMT-2(3%), and (d) RTV/OMMT-2(9%).

Microstructure analysis of RTV/OMMT composites

Swelling test

The swelling test, as shown in Figure 8, has some relationship with the tensile properties of RTV composites. The original RTV and RTV/OMMT-1,2 (3%) had the obvious solvent absorption behavior, while RTV/OMMT-1,2(9%) had lowest. The more were the networks, the more was the absorption capacity of the composites.²⁶ The original RTV and RTV/OMMT-1,2 (3%) composites had absorbed more solvent. This can also illustrate that the existence of more networks in these composites. However, RTV/OMMT-1,2 (9%) composites absorbed less. This may be due to the damage of crosslinking networks by the aggregated OMMT fillers.²⁷

Above phenomenon can be deduced from following formula.²⁸ M_c here can represent the crosslinking degree of the composites. Increasing ρ_2 can increase

Q , and thus increase M_c . The addition of more OMMT in RTV, for example, 9%, can lead to aggregated fillers and damaged networks in RTV and thus decrease the density ρ_2 , Q and corresponding M_c of composites. That is why the RTV/OMMT-1,2 (9%) had the lowest swelling quality.

$$M_c = Q^{\frac{5}{3}} \left(\frac{1}{2} - \chi_1 \right)^{-1} \rho_2 V_1$$

$$Q = \frac{v_1 + v_2}{v_2} = \frac{\left(\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \right)}{\frac{w_2}{\rho_2}} = 1 + \frac{w_1 \rho_2}{w_2 \rho_1}$$

In the above formula, M_c , average relative molecule mass; χ_1 , interaction parameter; ρ_2 , density of RTV/OMMT composite before swelling; V_1 , molar volume of toluene; w_1 , mass of toluene in swelling composite; w_2 , mass of RTV/OMMT composite; ρ_1 , density of toluene.

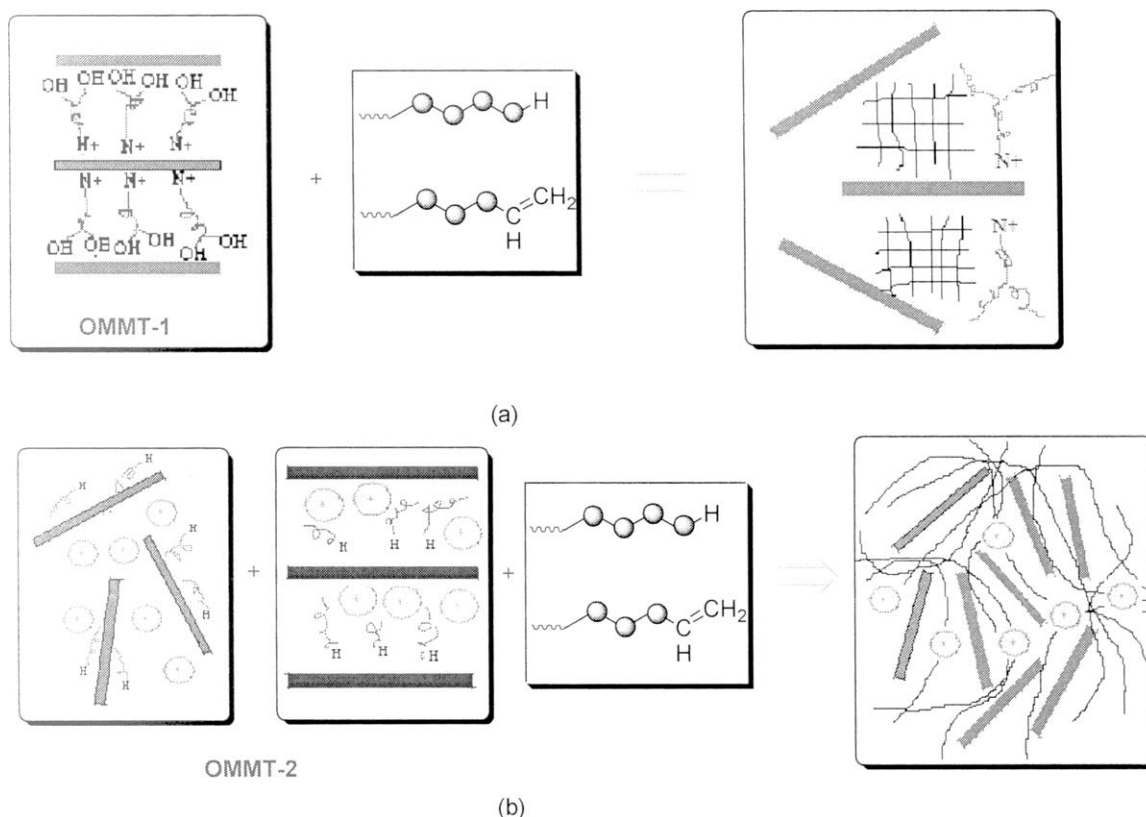


Figure 11 Scheme of intercalation process between OMMT-1,2 and monomers of RTV.

XRD test

An important measure of the degree of silicate intercalation and exfoliation can be obtained by XRD measurements. A series of XRD patterns of composites containing different amounts of OMMT are shown in Figure 9. Nearly no peaks were observed in Figure 9(a), which was a result of the original microstructure of RTV. When a small amount of OMMT1,2 was incorporated [RTV/OMMT-1,2(3%)], only very slight peaks appeared. These peaks corresponded to the expansion of gallery space by insertion of RTV polymer chains. The diffraction peaks were almost absent in the scattering curve besides the original peaks of RTV matrix. This was probably ascribed to the loss of structure registry, indicating the possibility of having exfoliated silicate layers dispersed in the polymer matrix. When 9% OMMT-1,2 was incorporated, The peaks at $2\theta = 11.4^\circ$ became more obvious [shown in Fig. 9(d,e)]. However, the peak at 11.4° was different from the characteristic peak of OMMT-1,2 [shown in Fig. 2(b,c)]. These peaks were broadened and shifted from 1.68, 3.17, 4.54, or 1.89 to 11.4° compared with the peaks of OMMT-1,2. This phenomenon indicated that some OMMT failed to form nanostructure in RTV matrix and illustrated the existence of stacked and repressed OMMT in the composites. Another possible reason may be obtained from what Yoon et al.²³

had demonstrated. Deduced from their similar phenomenon, it may be explained that the peaks at 1.68, 3.17, 4.54, or 1.89° (OMMT-1, 2) corresponded to the basal spacing for the bilayer arrangement of molecular chains of intercalation agents, while the peak at 11.4° might correspond to their monolayer arrangement. This was also resulted from the aggregation of OMMT in these composites.

TEM test

Further evidence of nanometer-scale dispersion of silicate layers in the case of different RTV/OMMT composites was supported by TEM photomicrographs. Representatively shown in Figure 10 are the TEM micrographs of the composite containing 3 and 9% OMMT-1, 2. Figure 10(a,c) showed that the OMMT layers did not fill the full volume, suggesting that the platelet tactoids of MMT were dispersed in RTV matrix at sub-microsized scale. A close observation of an area of platelet tactoid of 3% OMMT-2 filled composite revealed the individual platelets of OMMT clearly separated by polymer matrix, that is, some polymer had diffused between some of the platelets. This was an evidence that these organoclays were mostly exfoliated in the RTV matrix.²⁹ It had been reported that the formation of intercalated or exfoliated clay composites was dependent on the

nature of the intercalation agents, and the ammonium with long chains could allow more organic species to diffuse into the layered silicates.³⁰ The subsequent polymerization could be a driving force between the negatively charged silicate layers and the gallery cations. From Figure 10(b,d), it can be deduced that OMMT-1,2 were becoming agglomerated in the composites as the amount was increased to 9%.

Mechanism analysis of RTV/OMMT composites

The speculation of schematic development process of intercalated or exfoliated RTV/OMMT-1,2 composites is shown in Figure 11. During the drying process of RTV/OMMT-1 composite, hydrogenous silicane probably not only can react with ethylene-terminated polysiloxane but also can react with —OH in the intercalation agent in OMMT-1. This has an important effect on the intercalation and exfoliation of the organoclay. During the drying process of RTV/OMMT-2 composite, the intercalation agent of OMMT-2, hydrogenous silicone oil, not only may react with —OH existed in MMT but also may react with ethylene-terminated polysiloxane. This gives an important attribution on the exfoliation of OMMT-2 in RTV matrix and is beneficial for the improvement of crosslinking degree of these composites.²³ Moreover, RTV is an important low polar polymer and the MMT environment may be not compatible with them. With the modification of low polar intercalation agent such as hydrogen silicone oil, the compatibility between OMMT and RTV matrix may be improved. This is attributed to the improvement of tensile properties for these composites.³¹

CONCLUSIONS

Organically modified MMT was successfully prepared by two kinds of intercalation agents, dihydroxyethyl-12 alkane-3 methyl-amine chloride and hydrogen silicone oil. FTIR and XRD analysis demonstrated that different intercalation agents had different effect on the intercalation or exfoliation of OMMT.

Results of viscosity, hardness, tensile, and thermal stability test verified the incorporation of OMMT into RTV composites. The enhanced mechanical and physical properties demonstrated the efficiently reinforcing ability of these OMMTs. Results showed that hydrogen silicone oil-modified MMT had better

properties than that of dihydroxyethyl-12 alkane-3 methyl-amine chloride modified ones. Swelling test, XRD, and TEM revealed that the degree of basal-spacing expansion was largely increased and an intercalated or exfoliated structure was formed in these two kinds of composites.

References

1. Mark, W. S.; Keith, T. S.; Duan, L. O. *J Inorg Organomet Polym* 2008, 18, 364.
2. Celine, L.; Fabien, M.; Michael, A.; Philippe, D. *J Nanosci Nanotechnol* 2009, 9, 2731.
3. Maged, A. O.; Vikas, M.; Massimo, M. *Macromolecules* 2003, 36, 9851.
4. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
5. Usuki, A.; Tukigase, A.; Kato, M. *Polymer* 2002, 43, 2185.
6. Bujdak, J.; Hachett, E. P.; Giannelis, E. P. *Chem Mater* 2000, 12, 2168.
7. Fu, X.; Qutubuddin, S. *Polymer* 2001, 42, 807.
8. Gatos, K. G.; Sawanis, N.; Apostolov, A. A.; Thomann, R.; Karger-Kocsis, J. *Macromol Mater Eng* 2004, 289, 1081.
9. Usuki, A.; Tukigase, A.; Kato, M. *Polymer* 2002, 43, 2185.
10. Wang, J. C.; Chen, Y. H.; Jin, Q. Q. *High Perform Polym* 2006, 18, 325.
11. Arroyo, M.; Lopez-Manchado, M. A.; Herrero, B. *Polymer* 2003, 44, 2447.
12. Zhou, N. L.; Xia, X. X.; Wang, Y. R. *Acta Polym Sinica* 2002, 2, 253.
13. Wang, S. J.; Long, C. F.; Wang, X. Y. *J Appl Polym Sci* 1998, 69, 1557.
14. Han, B. H.; Cheng, A. M.; Ji, G. D. *J Appl Polym Sci* 2004, 91, 2537.
15. Wei, F.; Abdellatif, A. K.; Bernard, R. *Macromol Rapid Commun* 2002, 23, 705.
16. Xu, R. J.; Manias, E.; Alan, J. S.; Runt, J. *Macromolecules* 2001, 34, 338.
17. Yao, K. J.; Song, M.; Hourston, D. J. *Polymer* 2002, 43, 1018.
18. Yang, K.; Wang, J. C. *Chin. Pat. CN200910052859.6* (2009).
19. Ma, J.; Xu, J.; Ren, J. H. *Polymer* 2003, 44, 4619.
20. Rodlert, M.; Christopher, G. P.; Garamszegi, L. *Polymer* 2004, 45, 952.
21. Tsutomu, T.; Yong, G. *J Appl Polym Sci* 2003, 90, 4075.
22. Jin-tae, K.; Taeg-su, O.; Dong-ho, L. *Polym Int* 2003, 52, 1058.
23. Wang, J. C.; Chen, Y. H.; Jin, Q. Q. *Macromol Chem Phys* 2005, 206, 2512.
24. Tortora, M.; Gorrasi, G. *Polymer* 2002, 43, 6147.
25. Celine, L.; Fabien, M.; Michael, A.; Philippe, D. *J Nanosci Nanotechnol* 2009, 9, 2731.
26. He, G.; Chen, Y.; Zhang, M. M.; Wang, D. X.; Cong, K.; Fan, H. B.; Zhou, F. J. *Polym Mater Sci Eng* 2011, 27, 150.
27. Liu, C. W. *Comprehensive Experiment of Polymeric Materials and Engineering*; Chemical Industry Press: Beijing, 2004.
28. Yoon, J. T.; Jo, W. H.; Lee, M. S. *Polymer* 2001, 42, 329.
29. Zhang, Z. J.; Zhang, L. N.; Yang, L. *Polymer* 2005, 46, 133.
30. Mousa, A.; Karger-Kocsis, J. *Macromol Mater Eng* 2001, 286, 260.
31. Zhu, J. D.; Liao, M. Y.; Li, Y.; Xu, H. D. *Chin J Polym Bull* 2003, 2, 29.