

Study on the Synthesis, Structure, and Properties of Polydimethylsiloxane-Acrylate/Organophilic Montmorillonite Nanocomposite Emulsions

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ABSTRACT: Polydimethylsiloxane-acrylate/organophilic montmorillonite (PDMS-ACR/OMMT) nanocomposite emulsions were prepared by the copolymerization between ACR and PDMS/OMMT seeding emulsion, which was prepared beforehand by ring-opening in situ polymerization of octamethyl cyclotetrasiloxane (D_4) intercalated into the interlayer of OMMT modified with dodecylbenzene sulfonate acid (DBSA). OMMT, PDMS/OMMT seeding emulsion, and PDMS-ACR/OMMT nanocomposite emulsions were characterized with X-ray diffraction, FTIR, laser particle size analysis, SEM, and TG; the physical properties of the PDMS-ACR/OMMT latex films were also characterized including adherence, impact property, bend property, hardness, and water resistance. The results showed that DBSA was intercalated into the

interlayer of montmorillonite, and ring-opening in situ polymerization of D_4 could be carried out favorably in OMMT interlayer. The onset weight-loss temperature of PDMS-ACR/OMMT latex films was higher than that of polyacrylate latex film by 44°C. When the addition of the amount of OMMT was 2 wt % in PDMS-ACR/OMMT emulsions, OMMT had been peeled into layered structure and dispersed in the continuous polymer phase, the shape of OMMT was regular and its size was uniform, the physical properties of the latex films were improved obviously. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 63–68, 2010

Key words: polydimethylsiloxane; acrylate; montmorillonite; nanocomposite emulsions

INTRODUCTION

In the past decades, silicone-acrylate emulsions have been widely used in textile coatings, leather finishes, architectural coatings, and pressure sensitive adhesives, because of its excellent properties such as anti-fouling property and resistance to weather, water, chemical, ultraviolet, high- and low-temperature, and so forth.^{1–3} However, some technical problems still need further effort to be solved, for example, the self-condensation of silicone monomers in the process of emulsion polymerization will result in the waste of silicone monomers and the decrease of reaction stability of emulsion polymerization. In addition, the resistance to weather, resistance to water, and antifouling of emulsion films will not

have obvious development.^{4,5} So the application of silicone-acrylate emulsions is limited at a certain degree.

In recent years, the polymer/layered silicate (PLS) nanocomposites have attracted much academic and industrial attention in the field of materials science. This is because that PLS has the characteristic of molecule-level dispersion between polymer chains and layered silicate by turns, which promise itself the superior properties in comparison with conventional polymers, including mechanical properties, heat resistance, gas permeability, low-cost, processability, and so forth.^{6–10} The layered silicate mainly includes montmorillonite (MMT),^{11–13} bentonite,¹⁴ calcium carbonate,¹⁵ and clay.¹⁶ Among the inorganic materials, MMT is the one used most widely. Chiu F C, et al.¹² reported that polyamide 6,6 (PA 6,6)/MMT nanocomposites were prepared with a twin-screw extruder, and characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy, and thermogravimetric analysis (TG). The results showed that organo-MMT was dispersed in PA 6,6 at nano-scale and the heat stability of PA 6,6 was enhanced remarkably. Chang J H, et al.¹³ reported that the tensile strength and elongation of poly (lactic acid) (PLA) nanocomposites with MMT or synthetic mica at

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low-nanofiller concentration (< 4 wt %) were higher than those of neat PLA. Jiang L, et al.¹⁵ compared the reinforcing effects and toughening mechanisms of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites. However, most research about PLS are related to plastics modification, and seldom related to emulsion, especially silicone-acrylate emulsion.

In this article, organophilic montmorillonite (OMMT) was first prepared with MMT and dodecylbenzene sulfonate acid (DBSA) for the insertion of organic silicone, and then with polydimethylsiloxane/organophilic montmorillonite (PDMS/OMMT) seeding emulsion and polydimethylsiloxane-acrylate/organophilic montmorillonite (PDMS-ACR/OMMT) nanocomposite emulsions were prepared with different amount of OMMT. The structure of OMMT, PDMS/OMMT seeding emulsion, and PDMS-ACR/OMMT nanocomposite emulsions were characterized by XRD, laser particle size analysis, SEM, and TG, the influence of the amount of OMMT on the physical properties of the PDMS-ACR/OMMT nanocomposite latex films were also investigated.

EXPERIMENTAL

Materials

Sodium montmorillonite (MMT) with ion-exchange ability of 100 mol/100 g was supplied by Guangdong Nanhai Nonmetal Mineral Company, Guangdong Province, China; Vinyltrimethoxysilane (A-171) was supplied by Foshan Daoning Chemicals Ltd., Guangdong Province, China; American Dow Corning Corporation; Octamethyl cyclotetrasiloxane (D_4) and hexamethyldisiloxane (HDS) were purchased from Jiangxi Xinghuo Chemical, Jiangxi Province, China; Methyl methacrylate (MMA), Butyl acrylate (BA); Acrylic acid (AA), Dodecylbenzene sulfonate (DBSA), Ammonia (28 wt %), Potassium persulfate (PPS), Polyoxyethylene octylphenol ether (OP-10), and Sodium dodecyl sulfate (SDS) were all purchased from Tianjin Fuchen Chemistry Reagent, Tianjin Municipality, China. All chemicals were used as received without further purification.

Synthesis of PDMS-ACR/OMMT nanocomposite emulsions

20 g of MMT and 180 g of distilled water were put into a four-necked flask, and heated to 80°C with stirring. 12 g of DBSA was added and stirred for 15 h at constant temperature. At last, the blend was washed using distilled water, dried at 80°C under vacuum oven, ground to 300 meshes and OMMT was obtained.

About 2.4 g of SDS, 1.2 g of OP-10, 120 g of distilled water, and required amount of OMMT were

added into four-necked flask with stirrer, air condenser tube and thermometer, and stirred to be homogenous system at room temperature. Then 1 g of D_4 , 5 g of DBSA, 2 g of A-171, and 0.3 g of HDS were added, heated to 75°C and kept for 6 h, ring-opening reaction of D_4 was occurred, meanwhile, A-171 was hydrolyzed and grafted to OMMT by means of condensation of OH groups. At last, the product was cooled to room temperature, adjusted to pH value at 7–8 with ammonia, and PDMS/OMMT seed emulsion was obtained. PDMS/OMMT nanocomposite seed emulsion was heated to 80°C. 10 mL water solution dissolved with 0.6 g of PPS, and monomers including 50 g of MMA, 50 g of BA, and 3 g of AA were added in 2 h, kept for 1 h, and was cooled to room temperature. Then the product was adjusted to pH value at 8.0 with ammonia, and PDMS-ACR/OMMT nanocomposite emulsion was obtained.

Preparation of latex films

Emulsions were coated on the tinplate to form 60-micron-thick films at room temperature and were heated in a vacuum oven at 100°C for 3 h.

Measurement and characterization

The samples were fully dried and then scanned continuously with a DMAX/III A power X-Ray diffractometer made by Japan Rigaku Corporation, using Cu target at the tube voltage of 30 KV and tube current of 30 mA. The scanning rate was 3° min⁻¹ from 1 to 20°.

The samples were mixed with KBr and pressed to a disc under vacuum. The FTIR spectra of the samples were recorded on a Vector33 FTIR spectrometer made by Germany Bruker Company.

Particle size of the emulsion analysis were carried out using N5 laser particle size analyzer made by American Beckman Coulter corporation, scattering angle was 90°, and the mass concentration of the samples were 0.015 wt %–0.020 wt %.

The SEM experiments were performed on fractured surfaces, formed with liquid nitrogen, of the samples with XL30 SEM, made by Holland Philips Corporation, and the accelerated voltage was 10 kV.

TG analysis was performed under nitrogen atmosphere at the heating rate of 10°C · min⁻¹ from 20 to 800°C with TG-209 thermogravimeter made by Germany Netzsch Company.

The adherence of film samples was measured with QFH film scribe made by Pushen Chemical Machinery (Shanghai, China), according to ISO 2409-72. The impact property of film samples was measured with CJQ-II impact tester made by Pushen Chemical Machinery (Shanghai, China), according to GB/T 1732–1993. The bend property of film samples

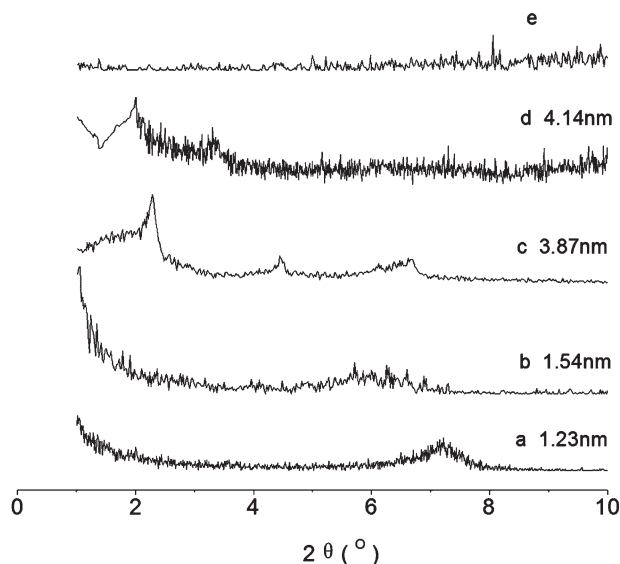


Figure 1 XRD spectra of (a) MMT, (b) OMMT, (c) PDMS-OMMT without extra DBSA, (d) PDMS-OMMT with extra DBSA, and (e) PDMS-ACR-OMMT.

was measured with QTY-32 column bend tester made by Tianjin Jingke Materials Machinery (Tianjin, China), according to ISO 1519-73. The hardness of film samples was measured with BY pencil hardness meter made by Pushen Chemical Machinery (Shanghai, China), according to GB/T 6739-1996. The water resistance of film samples was measured according to GB/T 1733-1993, the tinfoil samples coated with latex films were immersed in the distilled water at 23 ± 2 °C for 24 h.

RESULTS AND DISCUSSION

XRD analysis

XRD analysis is a powerful tool for examining the structure of polymer/MMT nanocomposites. The distances between MMT interlayer and OMMT interlayer, respectively, were calculated with Bragg law¹⁷:

$$2d\sin\theta = n\lambda$$

Where λ is the wavelength of the X-ray ($\lambda = 0.154$ nm), d is the interspaced distance, and Θ is the angle of incident radiation.

Usually, the peak that indicates the interlayer spacing of MMT shows in the range of $2\Theta = 2-15^\circ$, hence the interlayer spacing of MMT can be acquired from the place of diffraction peak in this range.^{18,19} The XRD patterns of MMT and OMMT are shown in Figure 1. The distance between MMT and OMMT layers is 1.23 and 1.54 nm, respectively, indicating that DBSA has been intercalated between MMT layer.²⁰

As shown in Figure 1, the distance between OMMT layers increased from 1.54 to 3.87 nm with the DBSA in the interlayers as catalyst. However, the peeled-off structure was not achieved, and there was a little crystal structure of MMT in OMMT interlayer, indicating that the peeled-off structure of nanocomposite materials were not obtained.²¹ When extra DBSA was added into the reaction system, the distance between OMMT layers increased from 1.54 to 4.14 nm, and the diffraction peaks changed to be flat. This is because that the van der Waals forces between OMMT interlayer was destroyed, the OMMT layers cast from the bondage force of other layers, and turned to be the state of peeling-off.

From the XRD spectra of PDMS-ACR/OMMT in Figure 1, it is clear that the diffraction peaks of OMMT were disappeared completely, indicating that the organic MMT modified by DBSA had better compatibility with D_4 , and the OMMT interlayer could supply larger space for the ring-open reaction of D_4 .²²

FTIR analysis

FTIR spectra of MMT, OMMT, OMMT/PDMS, and PDMS-ACR/OMMT emulsions were shown in Figure 2. In FTIR of MMT, the absorption peak at 3441 cm^{-1} is attributed to $-\text{OH}$ stretching vibration of silanol in OMMT interlayer, the peaks at 1034 cm^{-1} and 1089 cm^{-1} is attributed to the horizontal and vertical interlayer of $\text{Si}-\text{O}$ stretching vibration, respectively.²³

When MMT was turned into OMMT, the characteristic peaks of MMT were also existed but the intensity was decreased. Furthermore, the

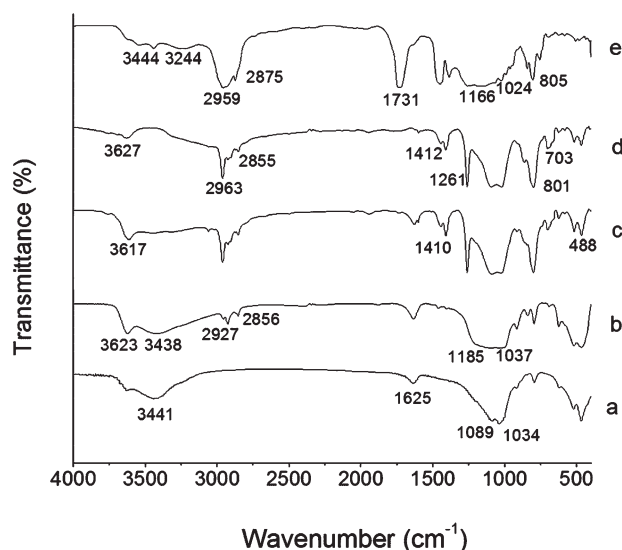


Figure 2 FTIR spectra of (a) MMT, (b) OMMT, (c) PDMS-OMMT without extra DBSA, (d) PDMS-OMMT with extra DBSA, and (e) PDMS-ACR-OMMT.

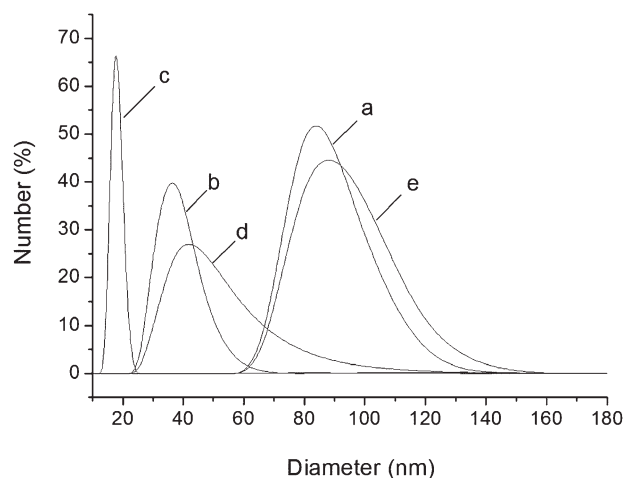


Figure 3 Diameter distribution curves of PDMS-ACROMMT with (a) 0 wt %, (b) 1 wt %, (c) 2 wt %, (d) 3 wt %, and (e) 5 wt % of OMMT.

appearance of the peaks at 2856 cm^{-1} and 2927 cm^{-1} assigned to symmetric stretching and asymmetric stretching of C—H in DBSA and the peaks at 1185 cm^{-1} and 1037 cm^{-1} assigned to stretching

vibration of S=O in sulfonic groups, indicated that DBSA had inserted into the OMMT layers. The peak about 1625 cm^{-1} in spectra of MMT and OMMT is attributed to the —OH bending mode of absorbed water.²⁴ As shown in spectra c and d, the absorption peak at 1089 cm^{-1} assigned to the vertical interlayer of Si—O stretching vibration is decreased and covered by the characteristic peaks of PDMS, indicating that the polymerization of D_4 in the interlayers of MMT widened the distance between the OMMT interlayers. It is accordance with the results of XRD analysis.

In the FTIR spectra of PDMS-ACR/OMMT, the peak at 805 cm^{-1} and 1024 cm^{-1} are assigned to asymmetric stretching vibration of Si—CH₃ and stretching vibration of Si—O—Si, respectively, indicating that siloxane chains had been grafted to the main chain of polyacrylate. Contrast to MMT and OMMT, the peak at 1089 cm^{-1} assigned to the vertical interlayer of Si—O stretching vibration is decreased, indicating that the graft reaction between siloxane and acrylate widened the distance between OMMT interlayer.

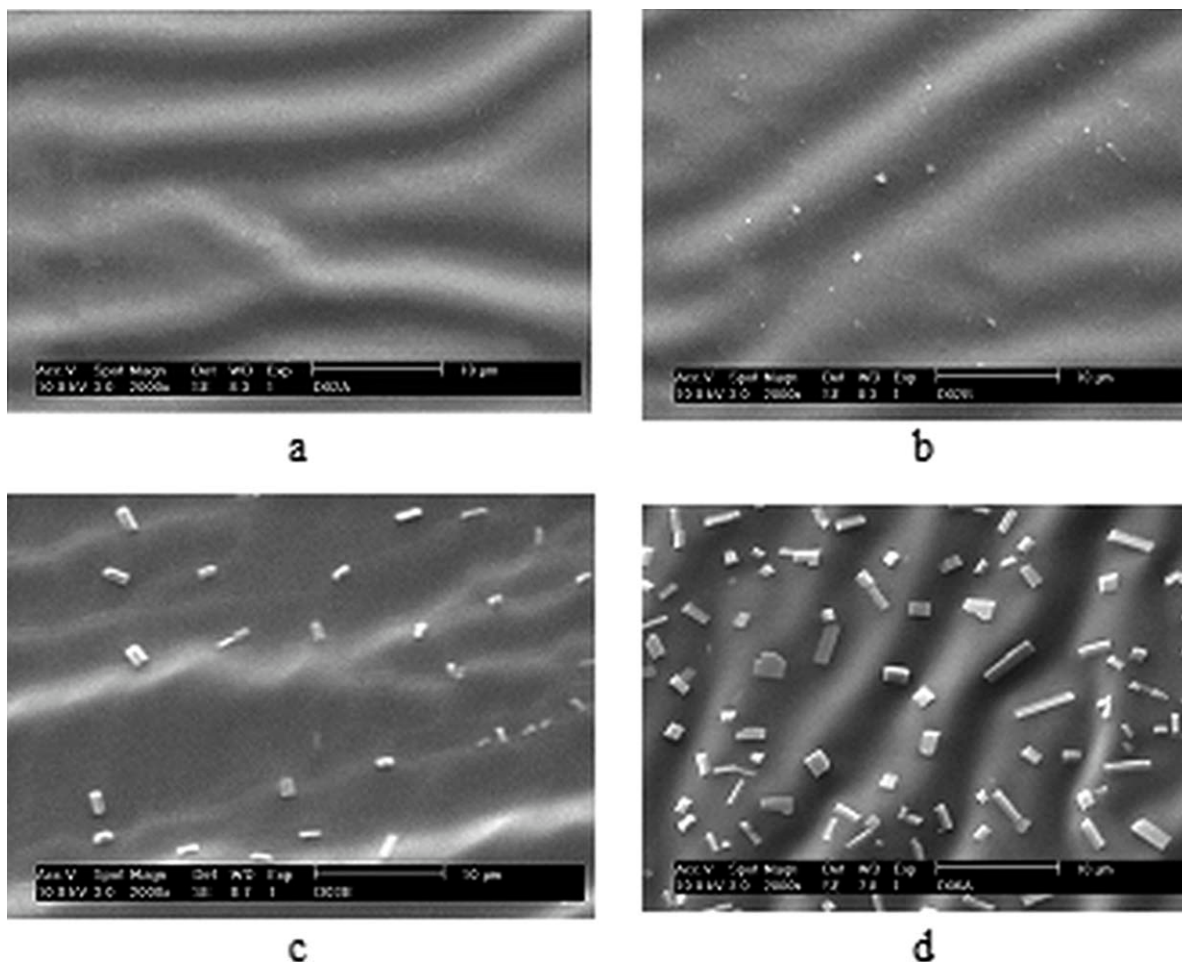


Figure 4 SEM photographs of PDMS-ACR-OMMT latex films with (a) 0 wt %, (b) 1 wt %, (c) 2 wt %, (d) 3 wt %, and (e) 5 wt % of OMMT ($\times 2000$).

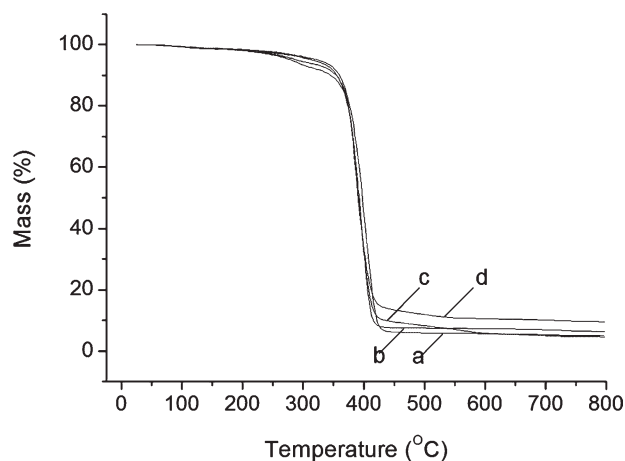


Figure 5 TG curves of (a) polyacrylate, (b) acrylaosilane, (c) ACROMMT, and (d) PDMS-ACROMMT.

Particle diameter and its distribution of latex particles

The particle diameter and its distribution of the latex particles is an important index of emulsion polymerization, which is correlated with the reaction rate, the physical property and performance of the emulsions, and the process of emulsion polymerization. Figure 3 showed the particle diameter distribution curves of PDMS/OMMT emulsion with different amount of OMMT.

As shown in Figure 3, the diameter of latex samples are all uniform and show the state of normal school. With the increase of the amount of OMMT, the diameter of latex particles decreased first, and increased latter. The reason is that with the existence of emulsifier and water, OMMT, and D_4 form insertion and in situ polymerization, and form composite structure of PDMS/OMMT. The OMMT was also probably peeled-off, form layered structure, and dispersed in PDMS latex particles randomly. When the amount of OMMT was appropriate, OMMT play the role of the carrier for catalyst and coemulsifier, and act as the polymerization center in the earlier reaction stage, which increase the number of latex particles and decrease the latex diameter. When the amount of OMMT was excess, some of OMMT could

not effectively integrate with PDMS, and just play as filler, which lead to the increase of average diameter of complex latex particles.

SEM analysis

The SEM photographs of PDMS-ACR/OMMT latex films modified by different amount of OMMT are showed in Figure 4. When the amount of OMMT was 1 wt % as shown in Figure 4(b), the disperse density of OMMT was uniform. However, as the amount of OMMT was low and the peeled structure were not formed. When the amount of OMMT increased to 2 wt % as shown in Figure 4(c), OMMT had been peeled to layered structure and dispersed in the continuous polymer phase. Furthermore, the shape of OMMT was regular and its size was also uniform. When the amount of OMMT increased to 5 wt %, although OMMT was peeled to layered structure and dispersed evenly in polymer phase, the size was non-uniform and part OMMT interlayer were larger. Moreover, most of OMMT appeared in the surface of polyacrylate and the organic and inorganic phases were clear, indicating that the high amount of OMMT caused agglomeration effect and some OMMT was simply dispersed physically in the polyacrylate phase without insertion and peeling-off, and phase separation was formed at a certain degree.

TG analysis

Figure 5 showed TG curves of polyacrylate, acrylaosilane, polyacrylate/OMMT, and PDMS-ACR/OMMT. In Figure 5, the onset weight-loss temperature of polyacrylate, acrylaosilane, ACR/OMMT, and PDMS-ACR/OMMT were 280, 290, 316, and 324°C, respectively. Contrasts to polyacrylate, the onset weight-loss temperature of polyacrylate/OMMT and PDMS-ACR/OMMT increased 36°C and 44°C, respectively, indicating that OMMT and organic silicone has superior effect to improve the heat resistance of polyacrylate. The increase of heat resistance of polyacrylate can be explained with the three reasons as follows: first, modified OMMT interlayer acted as physical cross-linking spots had stronger

TABLE I
Effect of Amount of OMMT on Physical Properties of PDMS-ACR/OMMT Latex Films

Physical properties	Amount of OMMT (wt %)				
	0	1	2	3	5
Adherence (degree)	1	0	0	0	2
Impact strength (cm)	40	50	50	40	30
Bend property	ok	ok	ok	ok	Partly fall-off
Hardness (H)	1	2	3	2	1
Water resistance	Partly fall-off	ok	ok	ok	Partly fall-off

action with polyacrylate polymers, and the activity of polyacrylate chains were limited.²⁵ Second, the insulation effect of organic OMMT interlayer restrained the transmission of the heat and the diffusion of the volatile decompositions. Third, the silicon element in the polysiloxane also prevented the transmission of heat and protected the polyacrylate chains from breaking at a certain degree.²⁶

Physical properties of the latex films

Table I shows the effects of the amount of OMMT on the mechanical properties of the latex films. As shown in Table I, the mechanical properties of parent polyacrylate latex film were poor. With the increase of the amount of OMMT, the adhesion, impact strength, bend property, hardness, and water resistance of the latex films were all increased first and decreased latter. When the amount of OMMT was 2 wt %, the over-all properties of the latex film were best. So it can be seen that the addition of OMMT was favorable to the improvement of mechanical properties of the latex films because of its inorganic property and particular structure. However, when the amount of OMMT increased to 5 wt % and was excessively high, the excessive OMMT would cause the phase separation between OMMT and polyacrylate polymers, and resulted in the obvious decrease of mechanical properties of the latex films.

CONCLUSIONS

PDMS-ACR/OMMT nanocomposite emulsions can be prepared with the addition of OMMT modified with DBSA as catalyst. DBSA can be intercalated into the interlayer of MMT and widen the distance between the layers from 1.23 to 1.53 nm. With extra DBSA, the distance between OMMT interlayer can be further increased from 1.54 to 4.14 nm. When the amount of OMMT was 2 wt %, OMMT had been peeled to layered structure and dispersed in the continuous polymer phase, the particle size of the PDMS-ACR/OMMT nanocomposite latex was decreased remarkably, and the physical properties of the latex films were as follows: adherence was 0°,

impact strength is 50 cm, hardness was 3 H, bend property, and water resistance was all good. In contrast to ordinary polyacrylate latex films, the heat resistance of PDMS-ACR/OMMT latex films was improved obviously.

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