Preparation and Properties of Poly(silicone-*co*-acrylate)/ Montmorillonite Nanocomposite Emulsion

Xiaoping Feng, Anyong Zhong, Deben Chen

College of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China

Received 5 November 2004; accepted 4 September 2005
DOI 10.1002/app.22906

ABSTRACT: Poly (silicone-*co*-acrylate)/montmorillonite nanocomposite emulsion were prepared by *in situ* intercalative emulsion polymerization of acrylate and organosilicone, in the presence of organic modified montmorillonite (OMMT) with different OMMT contents (0, 0.5, 1, 1.5, and 2 wt %). The nanocomposite emulsions were characterized with X-ray diffraction (XRD), laser light scattering, fourier transform infrared (FTIR), rheological measurements, surface tension, drying speed, and water absorption property. Results showed that OMMT could improve the properties of emulsion, in other words, the properties of nanocomposite emulsion were better when compared with those of the silicone–acrylate emulsion. The properties of nanocomposite emulsion containing 1 wt % OMMT was the best one, and obtained the following advantages: smaller particle size, faster drying speed, shorter curing time, smaller surface tension, bigger apparent viscosity, and improved resistant water by the incorporation of OMMT. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3963–3970, 2006

Key words: montmorillonite; organosilicone; acrylate; intercalative polymerization; nanocomposite emulsion.

INTRODUCTION

Silicone–acrylate emulsion have been widely used as adhesives, architectural coatings, textile coatings, and hide finishes because of its various advantages, such as good film forming property; high adhesive strength; resistance to high and low temperature, chemicals, water, weather, ultraviolet; and anticontamination.[1–3] However, the application of silicone–acrylate emulsion was limited because the price of silicone was high.

The Polymer/Layered Silicate (PLS) nanocomposite have drawn much research attention because they effectuate in improving material properties by the presence of a small amount of layered silicate, and promise superior or unique properties in comparison with those of the conventional polymer composites, including increased modulus, decreased thermal expansion coefficient, increased heat distortion temperature, reduced gas permeability, better fire-retardant properties, enhanced ionic conductivity, low flammability, increased solvent resistance, lower material cost, and the ease of preparation and processing.[4–9] PLS nanocomposite can be prepared in four main ways: solution intercalation, *in situ* intercalative polymerization, melt interaction, and template synthesis.[10] Montmorillonite (MMT) was a kind of layered silicate, which was used usually. It has been particularly important in forming effective polymer nanocomposite. It belongs to a smectite group of clay minerals that has 2:1 type of layer structure, in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets.[11] Polyacrylate/OMMT nanocomposite being made by the *in situ* polymerization route have been reported, and the properties have been substantially enhanced.[12]

PLS nanocomposite was actively studied. However, there has been few studies on the PLS nanocomposite emulsion. In this article, we prepared the poly (silicone-*co*-acrylate)/montmorillonite nanocomposite emulsion with different OMMT contents (0, 0.5, 1, 1.5, and 2 wt %) and organosilicone (5, 10, and 15 wt %) via *in situ* intercalative polymerization, and investigated the properties of nanocomposite emulsion and the influence of different contents of OMMT and organosilicone on the nanocomposite emulsion.

EXPERIMENTAL

Materials

Sodium montmorillonite (MMT) is supplied by Zhejiang Geologic Institute. Monomers are butylacrylate (BA), methlmeacrylate (MMA), acrylic acid (AA; supplied by Beijing East Chemical Industry Factory), and Vinyl triethoxy saline (A-151, supplied by Chengdu Kelong Chemical Industry Regent Factory). Emulsifiers are MS-1 and OP-10 (supplied by Shanghai Ingredient Factory). Chengdu Kelong Chemical Industry

---

Correspondence to: A. Zhong (zhongany@sina.com.cn) or X. Feng (sharpen_f@163.com).

Journal of Applied Polymer Science, Vol. 101, 3963–3970 (2006)

TABLE I
Content of A-151 and OMMT of Emulsion

No.	A-151 (%)	OMMT (%)	No.	A-151 (%)	OMMT (%)	No.	A-151 (%)	OMMT (%)
1	5	0.0	6	10	0.0	11	15	0.0
2	5	0.5	7	10	0.5	12	15	0.5
3	5	1.0	8	10	1.0	13	15	1.0
4	5	1.5	9	10	1.5	14	15	1.5
5	5	2.0	10	10	2.0	15	15	2.0

Factory supplies ammonium persulfate (initiator), sodium hydrogen carbonate (buffer agent), and ethylene glycol (inhibitor). Cetyl trimethylammonium bromide (CTAB) is supplied by Shandong Jining Chemical and Technological Institute. Sodium silicate (Na_2SiO_3) is supplied by Beijing East Chemical Industry Factory. PVA1788 (protective colloid) is supplied by Sichuan Vinylon Factory.

Preparation of OMMT

The required weights of MMT and distilled water were put into a three-necked flask. Sodium silicate was added to adjust pH to 11. The mixture was allowed stand for 1 day after stirring for 4 h, at room temperature. The supernatant of the mixture was subsequently poured into another flask, and followed by addition of the required weights of CTAB. The blend was heated up to 90°C and stirred at the same temperature for 2 h. After that, the blend was washed using distilled water to make it free from bromide ions and filtrated with pump down. Finally, the resultant was dried in a vacuum oven and ground to 300 meshes.

Preparation of emulsion

The given weights of BA, MMA, AA, and OMMT were premixed for 1 day to get mixture I. Initiator was dissolved in distilled water to make 10% of solution. Two-thirds of the required weights of distilled water, emulsifier, and total protective colloid and buffer agent were put into a dried three-necked flask equipped with a stirrer, a thermometer, and a condenser. The mixture was heated to 52°C, then, the mixture I was added into the flask. The blend was stirred vigorously at 52–55°C for 10 min to obtain preemulsion. 1/8 of the preemulsion were taken into another flask and heated to 75°C. Then, 1/3 of given amounts of initiator solution, emulsifier, distilled water, and total inhibitor were added to the flask. The blend was reacted for 30 min and a seed emulsion was obtained. Two-thirds of initiator solution was added to remaining 7/8 of the preemulsion. The preemulsion with initiator and A-151 were, respectively, dropped into the seed emulsion at the same time in about 2 h, and kept at 75°C for another 2 h. Then, the system was heated up to (81 ± 1)°C and maintained at this temperature for 1.5 h. Finally, a kind of white fluid poly(silicone-*co*-acrylate)/montmorillonite nanocomposite emulsion was obtained. Table I shows the contents of A-151 and OMMT of emulsion.

Preparation of film

Emulsions were laid on the polytef mold and formed a film at room temperature for 3 days. Then, the films were further heated in a vacuum oven at 100°C for 3 h.

Characterizations

The X-ray diffraction(XRD) analysis were performed using a Japanese D/max-rA X-ray diffractometer (Cu-K_α radiation, $\lambda = 0.154$ nm, 40 kV, 70 mA).

Laser scattering was carried out using a Mastersizer-2000 of Malvern Instruments (Worcestershire, UK).

Fourier transform infrared (FTIR) spectra was carried out on a 16PC FT-IR (Perkin–Elmer Japan Co., Tokyo).

The surface tension was measured using German du Noüy surface tension equipment. The measured temperature was established at (25 ± 0.1)°C.

The drying speed was measured by weighing the emulsion on microscope slide, using an electronic balance, for 4 h at 25°C and 60% dampness. All of the samples were measured under the same condition.

The water absorption was tested by weighing the film, which was submerged in distilled water for 2 days at room temperature and dried with a paper towel before weighing. The water absorption was calculated from following equation.

$$Water\ absorption\ (\%) = [(w_1 - w_0)/w_0] \qquad (1)$$

where w_1 is the weight of dried film, w_0 is the weight of the film after absorbing water.

The solid content of emulsion was obtained by weighing the emulsion on an electronic balance before and after the emulsions were dried at 120°C for 20 min. The solid content T was calculated by the equation:

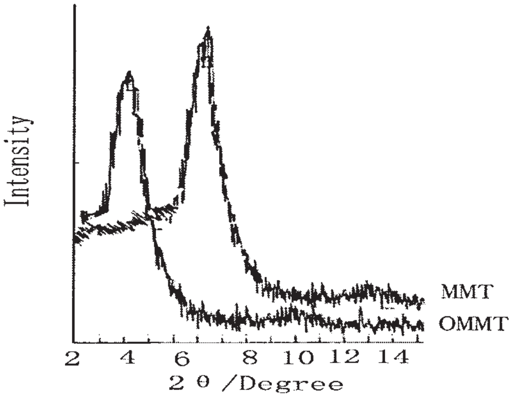


Figure 1 XRD patterns of MMT and OMMT.

$$T = (m_2 - m_0)/(m_1 - m_0) \tag{2}$$

where m_0 is the weight of the vessel; m_1 is the weight of the emulsion and the vessel; m_2 is the weight of the vessel and dried emulsion. The solid contents of emulsion came out to be (39.2 ± 0.2)%.

The viscosities of composite emulsion were measured with a NXS-11 rotational viscometer at 20, 25, 30, 35, and 40°C after the solid contents of emulsion were adjusted to equalize using distilled water.

RESULTS AND DISCUSSION

Distance of MMT and OMMT layers

The distances between MMT layers and OMMT layers, respectively, were calculated with Bragg law:[13]

$$2d \sin \theta = n\lambda \tag{3}$$

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 (Fig. 1). It can be obtained that the distance between MMT layers are 1.150 nm, and the distance between OMMT layers are 1.979 nm. The results showed that organic CTAB has been intercalated between MMT layers.

Particle size of the emulsion

The particle size and the distribution of particle size of the emulsions were measured by laser light scattering and is shown in Figure 2. The geometric mean diameter (d_g) was calculated according to eq. (4).[14]

$$d_g = \exp[\Sigma(n_i \ln d_i)/N] \tag{4}$$

where n_i is the number of particles in group i, with a midpoint of size d_i, and $N = \Sigma n_i$, means the total number of particles. According to Figure 2 and eq. (4), it can be obtained that the d_g were 583 nm, 444 nm, and 506 nm for the emulsions containing 0 wt %, 1 wt %, and 2 wt % of OMMT, respectively. It is obvious that the particle size of nanocomposite emulsion was smaller than the nonmodified emulsion, and the nanocomposite emulsion containing 1 wt % of OMMT has the smallest particle size.

In the polymerization process, a part of OMMT formed sheets under the effect of water and emulsifier. A part of monomers polymerized around the OMMT sheets and formed core-shell nanocomposite. This ren-

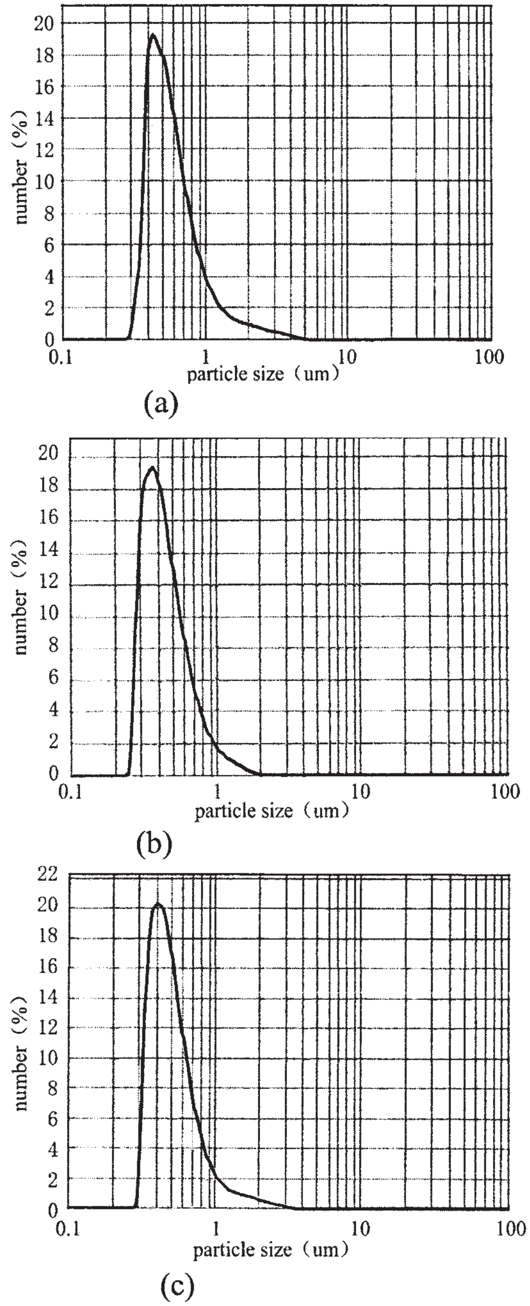


Figure 2 Laser light scattering graphs of the emulsion containing (a) 10 wt % A-151 and 0 wt % OMMT, (b) 10 wt % A-151 and 1 wt % OMMT, and (c) 10 wt % A-151 and 2 wt % OMMT.

TABLE II
Surface Tension of Emulsion (m N/m)

No.	σ	No.	σ	No.	σ
1	35.2	6	36.1	11	38.1
2	33.0	7	35.5	12	36.4
3	32.4	8	33.2	13	34.5
4	33.3	9	33.5	14	35.1
5	34.3	10	35.1	15	35.3

dered an increase in number of emulsoid particle. Therefore, the emulsoid particle size decreased. However, if the content of OMMT exceeds the intercalative capacity of monomer, emulsion will change into the blend of *in situ* composite and direct composite. The particle size was increased.

Particle size distribution breadth (B) was calculated according to eq. (5).[15]

$$B = (D_{90} - D_{10})/D_{50} \tag{5}$$

where D_{90}, D_{50}, and D_{10} are the particle diameters for the 90th, 50th, and 10th cumulative mass percentiles, respectively. The particle size distribution breadth of emulsions containing 0 wt %, 1 wt %, and 2 wt % OMMT were 1.27, 1.08, and 1.11, respectively. This shows that the particle size distribution of nanocomposite emulsion was narrower. This was because OMMT sheets are regular.

Surface tension of the emulsion

The surface tension (σ) was one of the important properties of the emulsion. The flow property and wetting property to base substrate were related to the surface tension.

Table II shows that the values of surface tension (25°C) of emulsion are enhanced with increase of A-151 content, and the value goes down to the smallest at 1 wt % of OMMT. Again, the surface tension of nanocomposite emulsion was lower in comparison with the silicone–acrylate emulsion. The surface tension of water is very big (72 m N/m), and far larger than wetting tension on substrates, therefore, one of the key elements for improving properties of emulsion was decreasing the surface tension. The equation describing surface tension was given by Young.[16]

$$\sigma_S = \sigma_{SL} + \sigma_L \cdot \cos\,\theta \tag{6}$$

where σ_S and σ_L are surface tension of solid and liquid, respectively, σ_{SL} is the interface tension of solid–liquid, θ is contact angle. The smaller the value of θ; the better is the wetting property. Lower surface tension causes θ to become smaller, so it is of advantage that emulsion wetting to base substrate, increasing the adhesion outspreads on substrates, enhancing flowing leveling. Thus, it can be seen that the nanocomposite emulsion was superior to the silicone–acrylate emulsion in the surface tension, and the nanocomposite emulsion containing 1 wt % OMMT was the best.

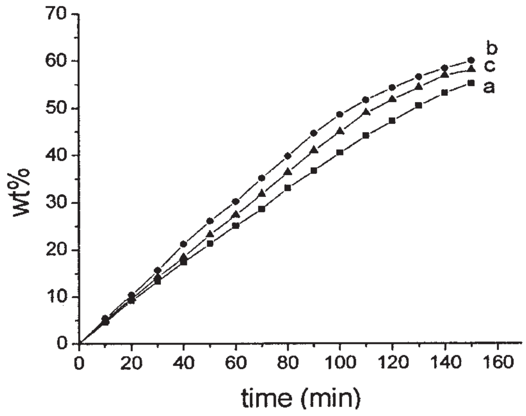


Figure 3 Drying speed graphs of emulsion containing 10 wt % A-151 and (a) 0 wt % OMMT, (b) 1 wt % OMMT, and (c) 2 wt % OMMT.

Drying speed of the emulsion

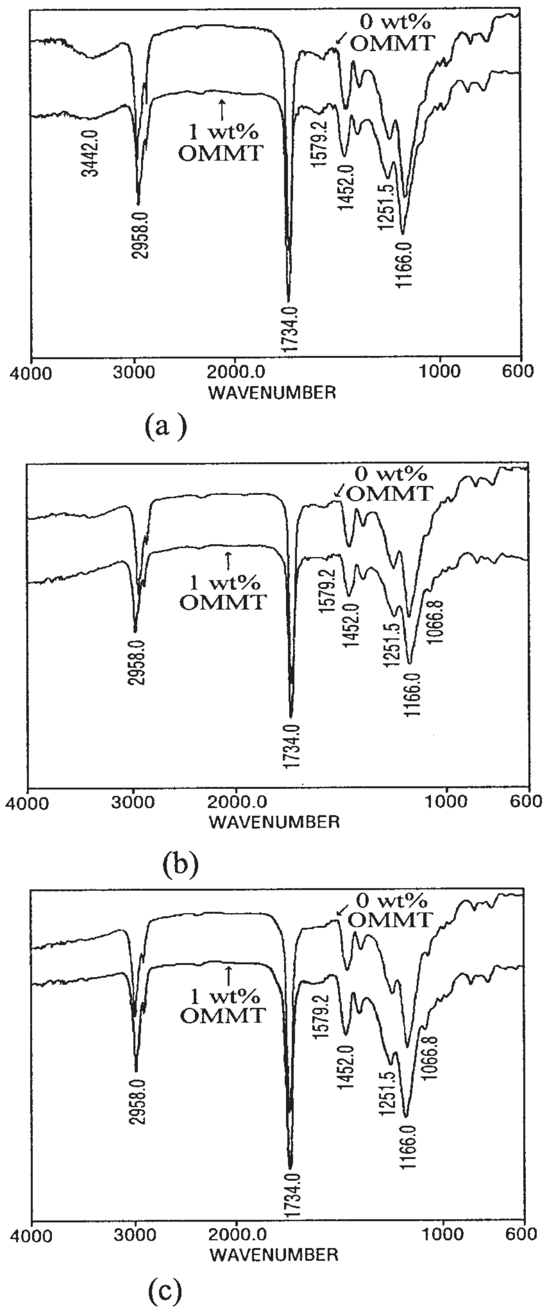
Figure 3 shows that the drying speed of the nanocomposite emulsion was faster than that of the silicone–acrylate emulsion, and the nanocomposite emulsion containing 1 wt % OMMT was the fastest one. Water volatilization was related to the free volume of material and surface tension. The particle size of the nanocomposite emulsion is smaller, the free volume is bigger, therefore, vapor volatilize easily. In addition, the surface tension of nanocomposite is lower, the volatilization speed of surface molecules is higher, and is dried more quickly. Higher drying speed is more advantageous in practice.

Water absorption of the emulsion

As shown in Table III, the film water absorption of the emulsion is far less than that of the uncomposite. In other words, the water resistance of the former is far

TABLE III
Water Absorption of The Emulsion Film

No.	Water absorption	No.	Water absorption	No.	Water absorption
1	0.2544	6	0.2056	11	0.2021
2	0.1711	7	0.1639	12	0.1596
3	0.1648	8	0.1545	13	0.1535
4	0.1773	9	0.1700	14	0.1621
5	0.1976	10	0.1725	15	0.1691



(a)

(b)

(c)

Figure 4 IR spectra of the composite emulsion after forming film for (a) 1 day, (b) 11 days, (c) 18 days.

better than that of the uncomposite. In addition, the water absorption can be decreased by increasing A-151 content, and also it can reach to the smallest when the content of OMMT is 1 wt %.

This can be explained on the basis of intercalation of poly (silicone–acrylate) into the OMMT layers, making less room for water molecules. The higher OMMT concentration suppresses the intercalation and makes the framework of nanocomposite loose, which results in the water absorption increase. In addition, organic groups of A-151 arrange outwardly on the emulsoid particle. This could also enhance the water resistance for the emulsion film.

FTIR of the emulsion

During the film curing, FTIR spectrometer was used for the investigation of the structural changes of the curing system. The FTIR spectra of the emulsion containing 10 wt % A-151 and 0 wt % OMMT or 1 wt % OMMT were shown in Figure 4.

When the crosslinking reaction takes place within the emulsion film, two Si—OH groups reacted and produced Si—O—Si bond. The asymmetric stretch of Si—O—Si bond occurs in the region of 1060 cm^{-1}. After 1 day of film having formed, the spectra of silicone–acrylate emulsion and nanocomposite emulsion films [Fig. 4(a)] were similitude. There were no absorption peaks in the region of 1060 cm^{-1}. This indicated that the crosslinking reaction did not take place. After 14 days [Fig. 4(b)], the absorption peak at 1066 cm^{-1} was found to be present in the nanocomposite emulsion film, and the absorption peak at 3442 cm^{-1} disappeared. This indicated that the curing reaction of the emulsion film containing 1 wt % OMMT has happened, and the degree of crosslinking reaction was deeper. There was no absorption peak in the region of 1060 cm^{-1} in the emulsion film containing 0 wt % OMMT, but the absorption peak at 3442 cm^{-1} was weakened. This suggested that the curing reaction of the emulsion film containing 0 wt % OMMT was weak after forming film 11 days. Figure 4(c) showed that the absorption peak at 1066 cm^{-1} was also found to be present in the emulsion film containing 0 wt % OMMT after 23 days of curing. All these clearly show that the curing speed for the nanocomposite emulsion was faster compared with that of the silicone–acrylate emulsion.

Rheological property of the emulsion

Rheological property is related to the nonreversible deformation of liquid under the stress. It is a key

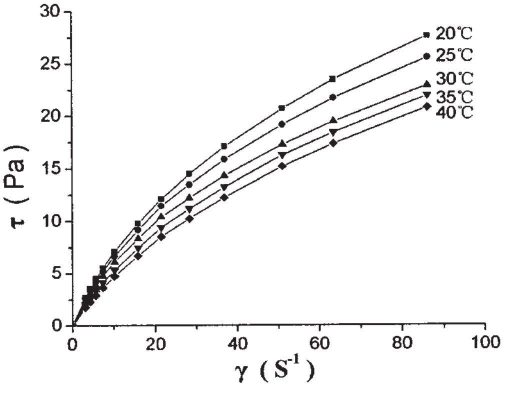


Figure 5 Flow curve of composite emulsion containing 10 wt % A-151 and 1 wt % OMMT.

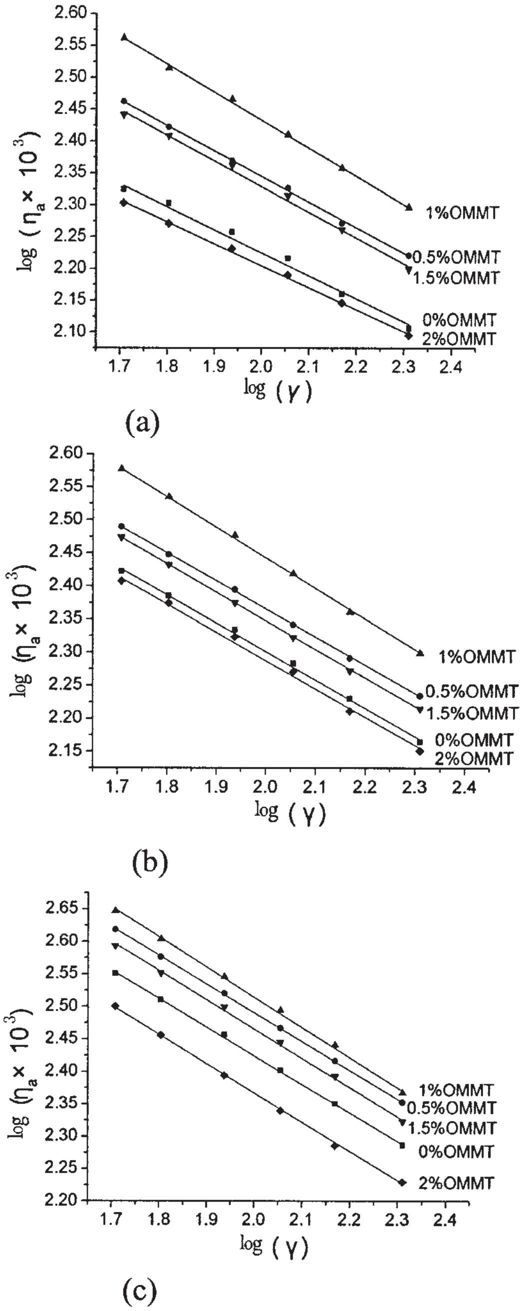


Figure 6 log η_a versus log γ of emulsion of (a) 5 wt % A-151, (b) 10 wt % A-151, and (c) 15 wt % A-151.

factor for the emulsion.[12] Figure 5 showed the relationship between shear stress (τ) and shear rate (γ) of the nanocomposite emulsion, which contains 10 wt % A-151 and 1 wt % OMMT.

From the curves in Figure 5, it is clear that the shear stresses of the nanocomposite emulsion increases with increasing of the shear rates. Therefore, the nanocomposite emulsion is pseudoplastic fluid. The rheological properties of emulsion can be characterized by the Ostwald De Waele power law $\eta_a = K\gamma^{n-1}$,[17] it can be obtained from the following equation.

$$\log \eta_a = \log K + (n - 1) \log \gamma \qquad (7)$$

where η_a is apparent viscosity; K is consistency factor, which is proportional to the apparent viscosity, n is flow index, (to non-Newtonian fluid, $n < 1$; to Newtonian fluid, $n = 1$).[13] The values of K and n can be obtained from the linear relationship between log η_a and log γ in Figure 6, and is listed in Table IV.

Data in Table IV revealed the following results. The values of K are increased with increasing the content of OMMT and reached the smallest when the content of OMMT was 1%, meanwhile, both of them are directly proportional to the contents of A-151. The values of n are inversely proportional to the content of A-151. All of n values were smaller than 1 and reached the smallest when the content of OMMT was 1%. Again, it can be seen that the nanocomposite emulsion is pseudoplastic fluid. On the other hand, apparent viscosity of the nanocomposite emulsion increased with the increasing of the content of A-151, and they were the biggest when the contents of OMMT changed to 1%.

When shear rate is zero, zero shear viscosity (η_a) can be obtained from Cross equation:[18]

$$1/\eta_a = 1/\eta_0 + (a/\eta_0)\cdot\gamma^{2/3} \qquad (8)$$

The relation of $1/\eta_a$ and $\gamma^{2/3}$ of the emulsions was shown in Figure 7.

According to Cross equation, the values of η_0 can be obtained from Figure 7, and are listed in Table V.

Figure 7 and Table V showed that the zero shear viscosity of emulsion were increased with the increasing of A-151, and the value ofη_0 went up to the biggest

TABLE IV
Values of Consistency Factor (*K*) and Flow Index (*n*) of Emulsion

Sample	*K*	*n*	Sample	*K*	*n*	Sample	*K*	*n*
1	0.889	0.638	6	1.434	0.572	11	2.080	0.561
2	1.399	0.599	7	1.640	0.575	12	2.364	0.558
3	2.063	0.559	8	2.331	0.538	13	2.819	0.532
4	1.361	0.597	9	1.617	0.569	14	2.315	0.550
5	0.789	0.654	10	1.374	0.574	15	1.748	0.562

when the OMMT content were 1%. This result could be explained with Mooney eq. (9).[19]

$$\ln \eta_a = \ln \eta_e + [K_e V_i/(1 - V_i/\Phi)] \qquad (9)$$

where K_e is form constant of particle,η_e is the viscosity of the continuous phase, V_i is volume fraction of dispersed phase, and Φ is packed coefficient. As the particle size distribution of the nanocomposite emulsion contenting 1 wt % OMMT was the smallest, the Φ value was the smallest and the viscosity was the biggest at the same shear rate. The K_e value decreased, and Φ value increased after the emulsion was sheared. The K_e and Φ value of emulsion containing 1 wt % OMMT change to the smallest, but the changing degree of Φ value was the biggest. This caused the viscosity of emulsion containing 1 wt % OMMT go up to biggest when the changed degree of sheer rate was equal. Therefore, pseudoplasticity of the nanocomposite containing 1 wt % OMMT was the most strong.

TABLE V
Zero Shear Viscosity (η_0) of Emulsion

No.	η_0	No.	η_0	No.	η_0
1	0.3720	6	0.5631	11	0.8499
2	0.5499	7	0.6341	12	0.9134
3	0.7950	8	0.9176	13	1.0173
4	0.5440	9	0.6225	14	0.9036
5	0.3341	10	0.5400	15	0.8163

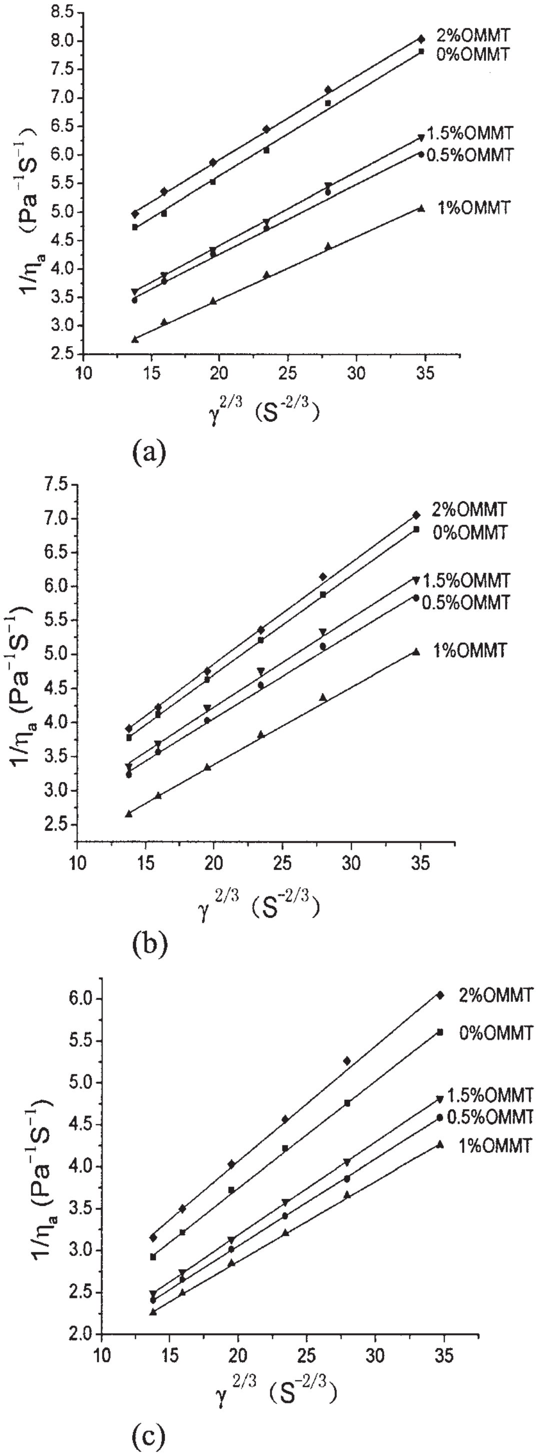


Figure 7 $1/\eta_a$ versus$\gamma^{2/3}$ emulsion of (a) 5 wt % A-151, (b) 10 wt % A-151, and (c) 15 wt % A-151.

The hydrolysis of a part of Si—OR group of emulsion produced Si—OH group. The action was strong between the Si—OH group and polar acrylate copolymer element. Therefore, the action of emulsoid particle increased with increasing of A-151 content. In other words, the viscosity of emulsion increased with increasing of A-151 content at same shear rate. The emulsoid particle occur deformation at shear action, and the action of Si—OH group and polar acrylate copolymer element decreased. The pseudoplasticity was enhanced with increasing A-151 content.

CONCLUSIONS

It is effective that the properties of silicone–acrylate emulsion were improved by the intercalative polymerization of acrylate and silicone in the presence of OMMT. And the modified effect was the best when the content of OMMT was 1%. Comparing with the common silicone–acrylate emulsion, the as-synthesized poly (silicone-*co*-acrylate)/montmorillonite nanocomposite emulsion has the following advantages: smaller particle size, lower surface tension, faster drying speed, better water absorption, and bigger apparent viscosity.

References

1. Huang, S. Q.; Peng, H.; Huang, H.; Li, S. B. New Chem Materials 1997, 9, 22.
2. Ma, W. S.; He, J. H.; Ou, Z. Y.; Pan, H. M. Paint Coating Ind 2003, 4, 1.
3. Wang, J.; Chu, F. X. China Adhesives 2003, 5, 52.

4. Le Bavon, P. C.; Wang, Z.; Pinnavaia, T. Appl Clay Sci 1999, 15, 11.
5. Okada, A.; Kawasami, M.; Usuki, A.; Kojima, Y.; Kamigaito, O. Mater Res Soc Proc 1990, 171, 45.
6. Shen, Z. Q.; Simon, G. P.; Cheng, Y. B. J Appl Polym Sci 2004, 94, 2101.
7. Messersmith, P. B.; Ciannelis, E. P. Chem Mater 1994, 6, 1719.
8. Huang, X.; Lewis, S.; Brittain, W. J. Macromolecules 2000, 33, 2000.
9. Kim, T. H.; Jang, L. W.; Lee, P. C.; Choi, H. J.; Jhon, M. S. Macromol Rapid Commun 2002, 23, 191.
10. Li, X.; Ha, C.-S. J Appl Polym Sci 2003, 87, 1901.
11. Chin, I.; Albrecht, T. T.; Kim, H.; Russell, T. P.; Wang, J. Polymer 2001, 42, 5947.
12. Liang, Y.; Jia, D.; Zhou, Y.; Du, M.; Huang, A. Paint Coating Ind 2004, 5, 11.
13. Sadhu, S.; Bhowmick, A. K. J Appl Polym Sci 2004, 92, 698.
14. Hinds, W. C. Aerosol Technology, 2nd ed.; Wiley: New York, 1999; Chapter 4.
15. Chinwanitcharoen, C.; Kanoh, S.; Yamada, T.; Hayashi, S.; Sugano, S. J Appl Polym Sci 2004, 91, 3455.
16. Adamson, A.; Physical Chemistry of Surfaces, 5th ed.; Wiley: New York, 1990; Chapter 10.
17. Han, C. D. Rheology in Polymer Processing; Academic: New York, 1976.
18. Wang, W.; Xu, D. Acta Polymerica Sinica 1995, 3, 291.
19. Mooney, M. J Colloid Sci 1951, 6, 162.