Preparation and Properties of Nano-Montmorillonite Paper–Plastic Laminating Adhesive

Lunxue Ye, Anyong Zhong, Deben Chen, Fei Yang

Department of Chemistry, Sichuan University,Chengdu,610064, China

Received 1 August 2003; accepted 16 April 2004
DOI 10.1002/app.20795

ABSTRACT: Emulsion paper–plastic nanometer laminating adhesive of 1.5% organic montmorillonite (OMMT) was prepared by OMMT intercalating polyacrylate-system materials. In this article, it was discovered that nanometer-laminating adhesive has better adhesion, smaller latex particles size, lower surface tension, and higher drying speed than general laminating adhesive. The rheologic behavior of the emulsion was discussed and it was shown that the value of n (the flow index of emulsion) was reduced and viscous flow activation energy (E_a) was increased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 872–877, 2005

Key words: organic montmorillonite nanocomposites; emulsion polymerization; paper–plastic laminating adhesive

INTRODUCTION

Montmorillonite is a sort of layered silicate with natural nanometer structure.[1] At present, polymer/layered silicate nanocomposites are broadly studied throughout the world. It was reported that polymer/layered silicate nanocomposites were used as novel plastic, rubber, and fiber. The novel materials have many advantages, such as thermal resistance, mechanical property, gas barrier property, machinability, conductivity, and luminescence property.[2–9] However, it was scarcely reported that montmorillonite was applied in the adhesive field. In this article, nanometer-laminating adhesive was prepared by montmorillonite intercalating polyacrylate system materials. This novel emulsion adhesive was applied in the paper–plastic field, and it can substitute for solvent adhesive. Moreover, it has many advantages, such as good adhesion, good application properties, and low pollution, so it can be broadly applied in the foreseen future.

EXPERIMENTAL

Materials

Montmorillonite (MMT) was supplied by Zhejiang Geologic Institute, and its size is ~ 100 mesh. Monomers are butyl acrylate (BA), methyl methacrylate (MMA), hexyl-(2-ethyl)-acrylate (α-HEA), vinyl acetate (VAC), acrylic acid (AA), and acrylonitrile (AN) (supplied by Beijing East Chemistry Plant); emulsifiers are polyoxyethylene dodecyl ether sulfate sodium (AES, supplied by Shanghai Assistant Co., Shanghai, China) and dodecyl phenoxy polyoxyethylene ether (OP-10, Henkel International, Germany), and ammonium persulfate (initiator) and cetyl trimethyl ammonium bromide (CTAB, supplied by Shandong Jining Chemical and Technological Institute, Jining, China).

Preparation of organic montmorillonite (OMMT)

Twenty grams of MMT and 600 g water were put into the reaction vessel, and sodium silicate (Na_2SiO_3) was added to adjust pH to 11–12. After stirring for 4 h, the remainder of the reaction vessel bottom was removed. Then, 6 g CTAB was added and heated to 90°C and stirred 2 h at 90°C. Last, the solution was washed by distilled water and filtrated under reduced pressure many times and then dried and ground into 300-mesh OMMT powder.

Preparation of OMMT nanometer laminating adhesive

Monomers are 72.7 mL BA, 11.6 mL MMA, 11 mL α-HEA, 5.0 mL AN, 5.4 mL VAC, and 4.8 mL AA. OMMT (1.5 g) was dipped in the monomers above 24 h. First, preemulsion was carried out in a 500-mL three-necked flask equipped with a stirrer, a condensation tube, and a centigrade thermometer; there were 92 mL water and emulsifiers of 3 g AES and 4 g OP-10 in the flask. When the temperature reached ~ 52°C, the mixture of MMT and monomers was added and then the mixture was preemulsified ~ 10 min. Second, one-eighth of the preemulsion was heated to 72°C in

Correspondence to: A. Y. Zhong (zhongany@sina.com.cn).

Journal of Applied Polymer Science, Vol. 97, 872–877 (2005)

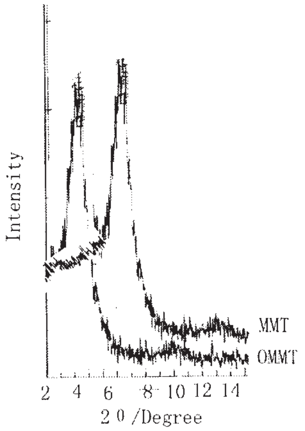


Figure 1 The XRD graph of MMT and OMMT.

the flask and then 2 g APS initiator was dropped; the polymerization was carried out ~ 30 min and the seed emulsion was obtained. Third, seven-eighths of the preemulsion was dropped into the seed emulsion in the flask and the mixture was finished in 2 h. In this polymerization process, 1.5 mL initiator solution containing 0.1 g APS was added every 0.5 h, finishing also in 2 h, and the polymerization temperature was kept at 75°C. After dropping, the temperature remained 2 h again, was then heated to 80°C, and remained for 1 h. At last, OMMT nanometer laminating adhesive was obtained. The preparation of laminating adhesive was similar, only without OMMT. They are the same solid content, ~ 42%. In the same method, the laminating adhesives with 1 and 2% OMMT were prepared, respectively.

Tests and instruments

X-ray diffraction (XRD)

XRD graph was performed on a D/max-rA X-ray diffractometer (Japan; tube voltage, 40 kV; tube current, 70 mA; CuKα, $\lambda = 0.154$ nm).

Transmission electron micrograph (TEM)

TEM was made by a TEM-100CX (Japan), and the latex particles were dyed by phosphotungstic acid solution and magnified ×36,000.

Peeling intensity

Peeling intensity was made by an electronic universal testing machine WD-5 (China; 180° peeling angle).

Surface tension

Surface tension was performed on a DO NOUY surface tension machine (Germany); the test temperature was at 25 ± 0.1°C.

Apparent viscosity

The viscosity was made by NXS-11 rotational viscometer (China); the test temperatures were 20, 25, 30, 35, and 40°C, respectively.

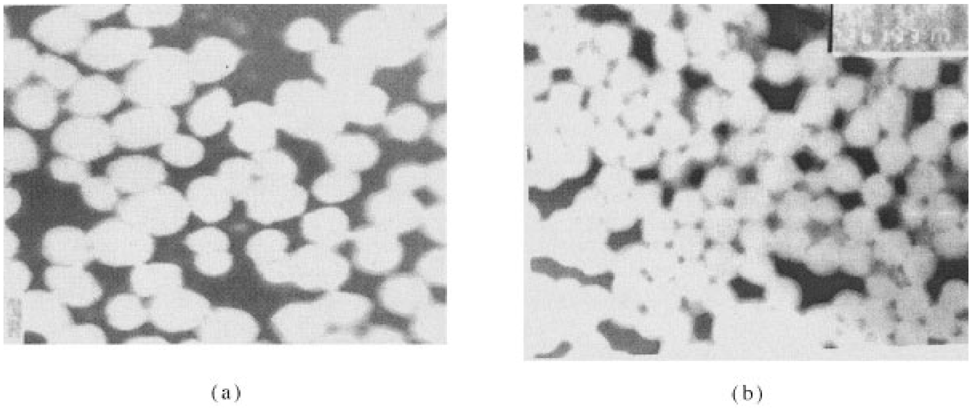
Drying speed

Drying speed was tested by electron balance at room temperature (25°C); the same mass of laminating adhesive and MMT laminating adhesive was coated on the same area substrates under the same test conditions.

RESULTS AND DISCUSSION

XRD tests of MMT and OMMT

Figure 1 is the X-ray diffraction spectra of MMT and OMMT; it shows that the diffracted peaks (2θ) of MMT and OMMT are at 7.68° and 4.46°, respectively. From Bragg law, $2d \sin\theta = n\lambda$, it can be obtained that the lamellar repeat distance of MMT increases from 1.150 nm (MMT) to 1.979 nm (OMMT). Therefore, the con-


(a)

(b)

Figure 2 (A) The TEM graph of laminating adhesive, magnified ×36,000. (B) The TEM graph of OMMT nanometer laminating adhesive, magnified ×36,000.

TABLE I
(A) Peeling Intensity Experiments

	Peeling intensity (N/2.5cm)									
(A) Peeling intensity of paper–plastic substrates										
Laminating adhesive	6.08	6.22	6.04	6.12	6.32	5.94	6.16	6.26	5.84	6.20
1% OMMT laminating adhesive	8.96	9.02	8.72	8.86	9.06	9.00	8.90	8.84	8.78	8.88
1.5% OMMT laminating adhesive	10.36	10.46	10.52	10.04	10.38	10.44	10.26	10.54	10.12	10.48
2% OMMT laminating adhesive	9.92	10.16	10.58	9.86	10.44	10.42	10.52	10.46	9.98	10.50
(B) Peeling intensity of cloth–cloth substrates										
Laminating adhesive	22.34	24.64	21.32	27.36	26.64	25.58	24.54	22.44	28.74	26.66
1.5% OMMT laminating adhesive	46.68	45.54	47.78	46.46	48.88	47.76	44.66	45.46	48.28	47.66

clusion is drawn that organic CTAB has intercalated into MMT layers.

TEM experiments

Figure 2(A, B) shows the TEM diagrams of laminating adhesive and OMMT laminating adhesive, respectively. They show that the particle size of the former is bigger, and that of the latter is smaller; furthermore, that of the latter has narrower distribution. OMMT layers are separated by the effect of the power of water and emulsifier under the stirred conditions.[10] Under the same polymerization conditions, because of the effect of OMMT layers, the total amount of the latex particles is increased. Therefore, the size of latex particles containing OMMT becomes smaller and the distribution is narrower.

Table I(A) shows that the values of peeling intensity of 1% OMMT laminating adhesive are ~ 40% higher than laminating adhesive in paper–plastic substrates, and those of 1.5 and 2.0% OMMT are higher by ~ 60%. In cloth–cloth substrates, those of 1.5% OMMT laminating adhesive are higher by ~ 100% in Table I(B). Because the size of latex particles containing OMMT is smaller, it results in the finding that the effect of power among latex particles is stronger; the amount of latex particles contacting the same area substrates is greater, and it can pervade into substrates more easily. Therefore, the value of peeling intensity of OMMT laminating adhesive is higher. In paper–plastic substrates, the two sorts of 1.5 and 2.0% OMMT laminating adhesive both are of good adhesion, but the storage stability of the latter is disadvantageous because of too much OMMT content; then, 1.5% OMMT laminating adhesive is more advantageous in the application. Therefore, in this article, we only discuss 1.5% OMMT laminating adhesive.

TABLE II
Surface Tension of Laminating Adhesive and OMMT Laminating Adhesive

	Surface tension ($10^{-5}N$)				
Laminating adhesive	28.1	28.2	27.9	28.0	28.1
OMMT laminating adhesive	25.6	25.5	25.3	25.4	25.5

Surface tension tests

Table II shows that the values of surface tension of OMMT laminating adhesive are lower than those of laminating adhesive. Low surface tension causes contact angle (θ) of liquid–solid interface to become small, so it is an advantage that adhesive outspreads on substrates. Low surface tension is in favor of adhesive and other materials mix; it can cause the drying velocity to speed up, so it is advantageous in the application.

Drying speed tests

Figure 3 shows that the drying speed of OMMT laminating adhesive is higher than laminating adhesive in 1 h. Because the surface tension of OMMT

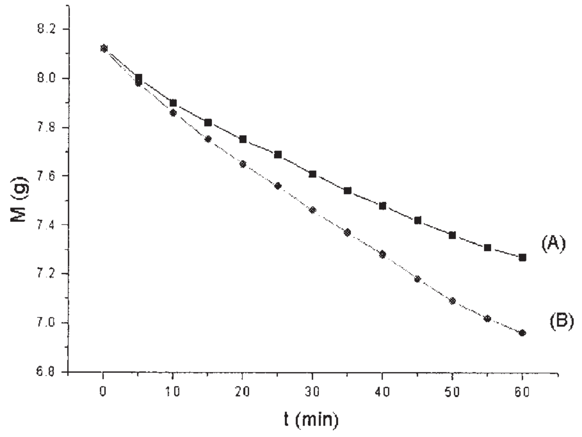
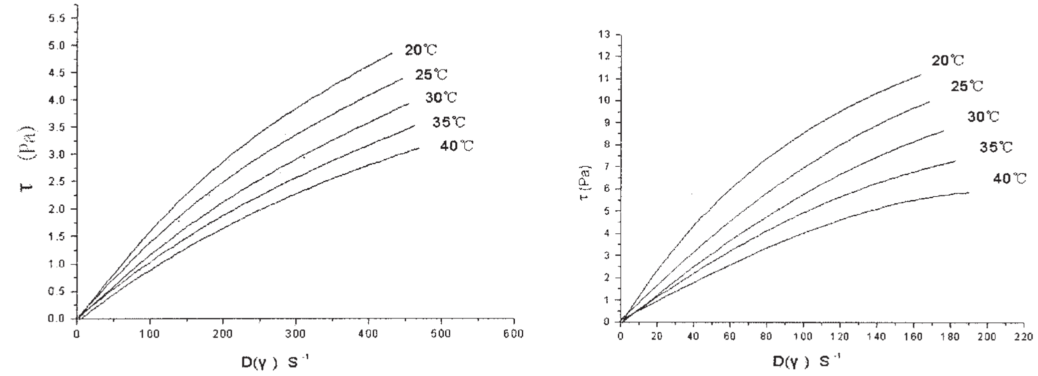
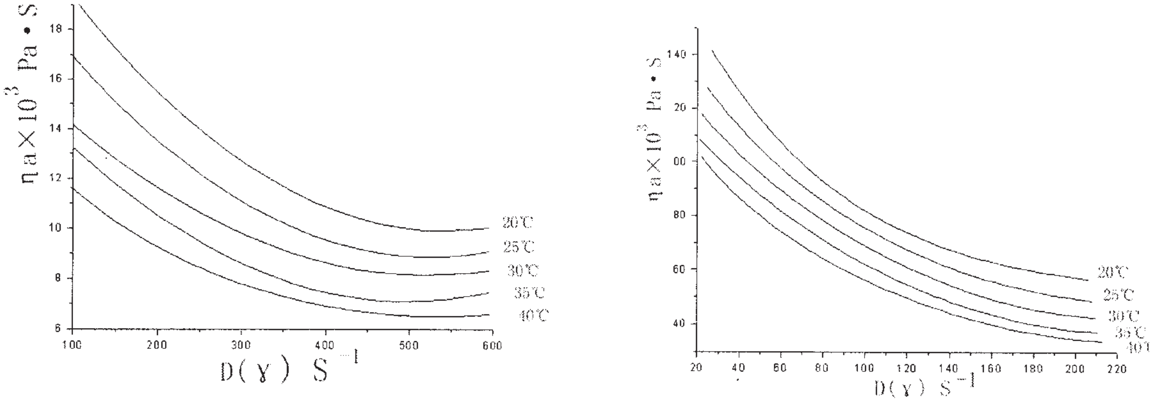


Figure 3 The mass (g) of laminating adhesive (A) and OMMT laminating adhesive (B) versus drying time (min).



(a) (b)

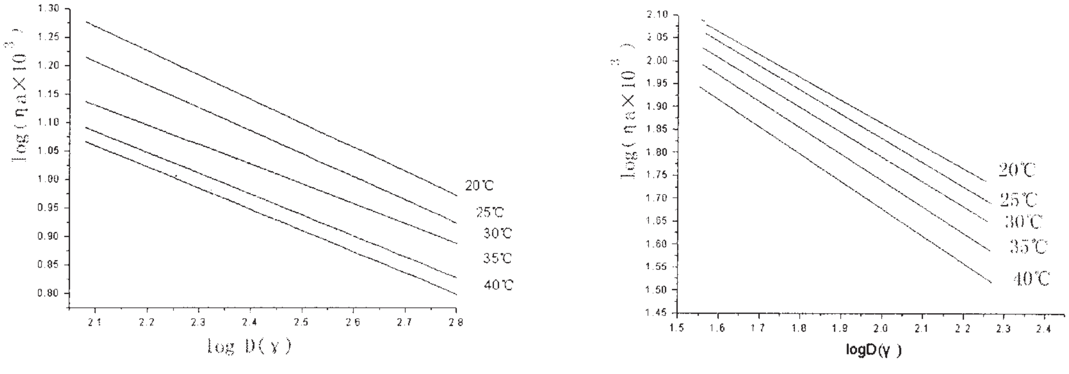
Figure 4 (A) Laminating adhesive shear stress (τ) versus shear rate, *D*(γ). (B) OMMT laminating adhesive shear (τ) versus shear rate, *D*(γ).



(a) (b)

Figure 5 (A) Laminating adhesive apparent viscosity (η_a) versus shear rate, *D*(γ). (B) OMMM laminating adhesive apparent viscosity (η_a) versus shear rate, *D*(γ).

laminating adhesive is lower, the volatilization speed of surface molecules is higher and then dries more quickly. Because the size of the OMMT latex particles is smaller, it more easily pervades into substrates, and the surface area become larger; then, the volatilization speed of surface molecules is also higher, so it can be dried more quickly. However, 48 h later, their weight remaining after drying was identical. Higher drying speed is more advantageous in the application.



(a) (b)

Figure 6 (A) Laminating adhesive log η_α versus log γ. (B) OMMM laminating adhesive log η_α versus log γ.

TABLE III
The Values of *K* and *n*

	20°C	25°C	30°C	35°C	40°C
	(A) Laminating adhesive				
K	0.1442	0.1096	0.07193	0.07120	0.06246
n	0.611	0.6023	0.6538	0.6337	0.6474
	(B) OMMT laminating adhesive				
K	1.1623	0.7261	0.6109	0.5715	0.3581
n	0.4981	0.4712	0.4521	0.4330	0.4090

TABLE IV
Zero Shear Viscosity ($\eta_0 \times 10^3$Pa S) of Laminating Adhesive and OMMT Laminating Adhesive

	40°C	35°C	30°C	25°C	20°C
Laminating adhesive	73.04	28.57	20.83	19.61	18.52
OMMT laminating adhesive	420.17	317.46	212.77	172.41	142.86

Rheologic behavior experiments

Rheologic behavior is very important for emulsion adhesive; Figures 4 and 5 are rheologic behavior curves of laminating adhesive and OMMT laminating adhesive.

Figures 4 and 5 show that the values of shear stress and apparent viscosity of OMMT laminating adhesive are higher than those of laminating adhesive. Because the size of latex particles containing OMMT is smaller, the specific surface area is bigger, the free volume of emulsion is smaller, and the effect among latex particles is stronger. Therefore, shear stress and apparent viscosity are increased.

The equation, $\eta_a = K\gamma^{n-1}$, induces $\log \eta_a = \log K + (n - 1)\log \gamma$, and the values of K and n from relationships between $\log \eta_a$ and $\log \gamma$ can be obtained as shown in Figure 6.

According to Figure 6(A, B), the values of K and n can be obtained as in Table III.

The values of parameter K of OMMT laminating adhesive are very much higher than those of laminating adhesive in Table III(A) and (B). Because the size of latex particles containing OMMT is smaller, the interaction effect among the latex particles is stronger, and the parameter K values are higher. The K values of laminating adhesive and OMMT laminating adhesive decrease with the temperature increase. In terms of n values, the n values of OMMT laminating adhesive are lower, and they reduce with temperature increase, but the n values of laminating adhesive change at random with temperature increase.

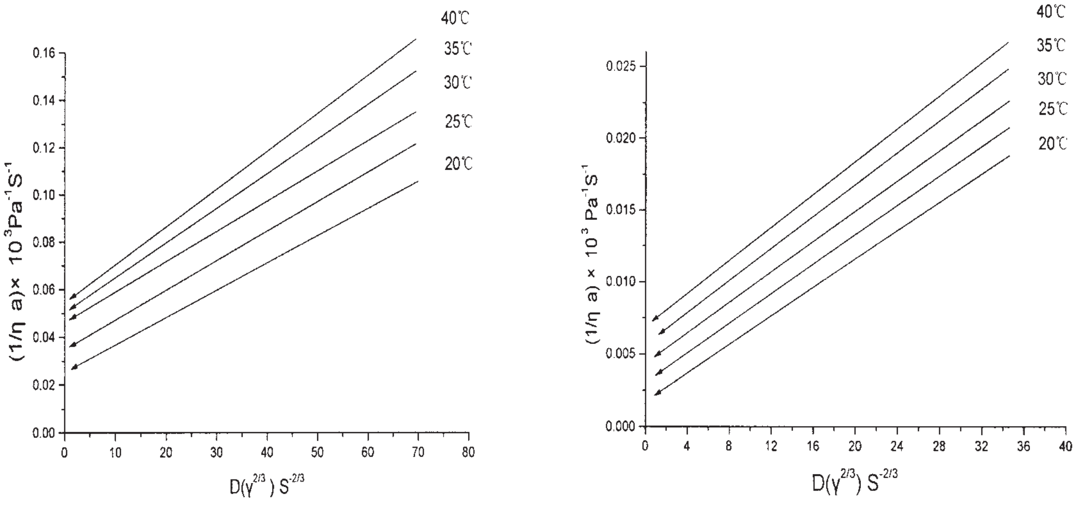
When shear rate (γ) is zero, zero shear viscosity (η_0) can be obtained from the Cross equation[11]:

$$1/\eta = 1/\eta_0 + \alpha/\eta_0\gamma^{2/3}$$

As follows from Figure 7(A, B), zero shear viscosity can be obtained in the Table IV.

From the equation, $\ln \eta_0 = \ln A + (E_a/R)/T$, it can be induced from the Arrhenius equation that $\eta_0 = A \exp(E_a/RT)$. Viscous flow activation energy (E_a) can be obtained from Figure 8.

The E_a/R value of laminating adhesive is the slope value of curve (1); it can be obtained that $E_{a1} = 26.74$ KJ/mol. The same calculation, OMMT laminating adhesive, $E_{a2} = 41.80$ KJ/mol. The flow behavior is more sensitive to the temperature when the value of viscous flow activation energy (E_a) is higher. The flow behav-



(a) (b)

Figure 7 (A) Laminating adhesive $1/\eta$ versus $D(\gamma^{2/3})$. (B) OMMT laminating adhesive $1/\eta$ versus $D(\gamma^{2/3})$.

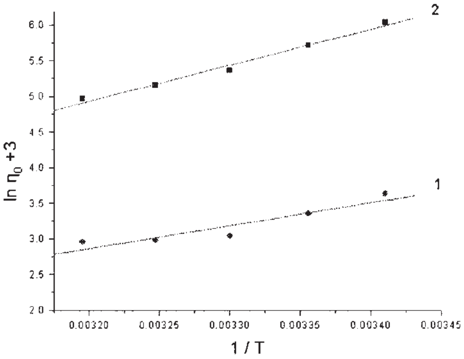


Figure 8 ln η_0 versus $1/T$. (1) Laminating adhesive; (2) OMMT laminating.

ior of OMMT laminating adhesive is more sensitive to the temperature, so it is more advantageous in the application.

CONCLUSION

In this article, emulsion paper–plastic nanometer laminating adhesive of 1.5% OMMT was prepared by OMMT intercalating polyacrylate system materials. The novel OMMT laminating adhesive is of the following advantages and characteristics: better adhesion, smaller size of latex particles, lower surface tension, higher drying speed, and higher value of viscous flow activation energy. Therefore, it can be broadly applied in the adhesive field in the future.

References

1. Calvert, P. Nature 1996, 383, 300–301.
2. Ke, Y.; Wu, Z.; Zhu, C. J Appl Polym Sci 2002, 85, 2677.
3. Tseng, C.; Wu, J.; Lee, H. J Appl Polym Sci 2002, 85, 1370.
4. Oriakhi, C. O.; Zhang, X.; Lerner, M. M. Appl Clay Sci 1999, 15, 109–118.
5. Pinnavaia, T. J.; Lan T.; Wang Muh, S. J Eng Appl Sci 1994, 346 (Better Ceramics Through Chemistry VI), 81–88.
6. Akelah, A.; Moet, A. J Mater Sci 1996, 31, 3589–3596.
7. Mohamed, N. Polymers 2002, 47, 326–331.
8. Huimin, W.; Minghua, M.; Yongcai, J.; Qingshan, L. Polym Int 2002, 51, 7–11.
9. Zeng. Q. H.; Wang, D. Z.; Yu, A. B.; Lu, G. Q. Nanotechnology 2002, 13, 549–553.
10. Tongnian, L. I.; Zhou, C. China Plast 2001, 15, 35.
11. Wang, W.; Xu, D. Acta Polym Sinica 1995, 3, 291.