

Full Length Research Paper

Categorization of exfoliated nano-composite of polyvinyl acetate and montmorillonite

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To improve the chemical, physical, and mechanical properties of polyvinyl acetate (PVAc), montmorillonite (MMT) was added in the synthesis of PVAc in conventional lab conditions. The final product was studied mainly by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), static tensile, and the rheology was also investigated by the power-law function equation and the Cross-Williamson model viscous equation. The exfoliated nano-composite of PVAc-MMT was obtained. Linear macromolecular chains of PVAc were formed in MMT layers. MMT was exfoliated into layers or sheets of nano-particles, and randomly dispersed in PVAc matrix. The particle diameter of MMT ranged from 50 to 100 nm, while PVAc's ranged from 250 to 500 nm, the smaller MMT particles were adsorbed around the larger PVAc particles to form the "Strawberry" structure. In addition, PVAc and PVAc-MMT were pseudo-plastic Non-Newtonian fluids, they all possessed the normal stress effect (or Weissenberg effect), that was the pole-climbing phenomenon.

Key words: Polyvinyl acetate (PVAc), montmorillonite (MMT), chemical structure, dispersion, particles, rheology, static tensile.

INTRODUCTION

Generally, polyvinyl acetate (PVAc) is synthesized by the monomer of vinyl acetate (VAc) in the mixture of polyvinyl alcohol (PVA) as protective colloid, non-ion emulsifier, initiator, and water. It has many characteristics, being non-poisonous, non-harmful, easily produced, low price, convenient in application, economizing resources, etc.. Because of these reasons, PVAc is widely applied in bonding of many porous materials, such as wood processing, furniture packaging, building decoration, texture bonding, and print bonding. Montmorillonite (MMT) is a natural nano-mineral. Its crystal structure is a 2:1 type layered silicate formed by a layer of aluminum (or magnesium) octahedral inserted in the middle of two layers of silicon oxygen tetrahedron. The structural units are joined by the molecular strength between layers, so it is very loose. Water or other organic molecules can enter into the layers which can lead to expansion through absorbing water, high dispersion and absorption, and can

also cause it to easily make mud, be activated, organized and modified.

Now, MMT has been applied in many polymers for many years, such as polyacrylate ester (Ray and Bhowmick, 2001; Ye et al., 2004), poly(methyl methacrylate) (Essawy et al., 2004; Metin and Yelda, 2007), polyurethane (Deng et al., 2007; Esposito et al., 2008), epoxy (Kommann et al., 2001; Cui et al., 2007), polyethylene (Zhao et al., 2004; 2005), and polypropylene (Qin et al., 2005; Chen et al., 2006), etc.. Ding et al. (2002, 2004a, 2004b, 2005) also reported the application in PVAc, but they mainly focused on the preparation of PVAc-MMT initiated by γ -ray radiation intercalation polymerization and the co-blending of PVAc-MMT with high density polyethylene. In the paper, based on our previous work (Cui and Du, 2011), and under the conventional conditions in the lab, with no ultrasonic dispersion and no radiation, PVAc-MMT was prepared by VAc and MMT. The obtained product was investigated mainly by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and static tensile. Its rheology was also investigated by the power-law function equation

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and the Cross-Williamson model viscous equation.

MATERIALS AND METHODS

Samples

1.00 g of MMT was immersed into 25.00 g of VAc for 24 h. It was then mixed with 70.00 g of 10% PVA solution, 0.50 g of alkylphenol polyoxyethylene (10) ether, 3.75 g of 10% ammonium persulfate solution, 6.25 g of sodium lauryl sulfate and 250 g of water whilst stirring vigorously for 8 h. When the mixture became a homogeneous emulsion, the temperature rose to 70°C. Whilst stirring vigorously, 3.75 g of 10% ammonium persulfate solution and 25.00 g of VAc were gradually added into the homogeneous emulsion in 6 h for polymerization.

Subsequently, the temperature rose from 85 to 90°C the emulsion further polymerized for 0.5 to 1 h. After polymerization, the temperature dropped to below 50°C, 4.00 g of ethanol, 3.00 g of water, 0.30 g of sodium benzoate, 0.18 g of sodium bicarbonate, and 6.00 g of Di-n-butyl phthalate were added into the emulsion. Finally, PVAc-MMT was obtained. PVAc was also prepared by the same process but without MMT.

Apparent viscosity

The samples were tested by NDJ-1 rotary viscometer; the shear rate ($\dot{\gamma}$) was 0.63, 1.26, 3.14 and 6.28 s^{-1} respectively. The apparent viscosity (η , mPa·s) under different shear rate was obtained.

Solid content

The solid content (O, %) is calculated by:

$$O = \frac{M - M_1}{M_1} \times 100\%$$

Where m_1 (g) is the original weight of samples, and m_2 (g) is the weight of samples dried for 1 h at 105°C.

XRD

The samples were tested by DX-2000 of XRD under Cu $K\alpha$ of radiating, 40 kV of tube voltage, 30 mA of tube current, scanning from 0.5 to 15° at a rate of 0.02°·s⁻¹, and $\lambda=1.54184$ Å of wavelength. The large value of $d_{(001)}$ for MMT is calculated by Bragg law of $\lambda=2d\sin\theta$, where λ is the wavelength representing the intensity of X-ray, d is the distance between layers of MMT, and θ is the diffraction angle.

FTIR

The samples mixed with kalium bromatum powder were pressed into plates, and then tested by the NICOLET 380 of FTIR.

TEM

The samples were observed by JEM-3100F TEM, the amplification was 20000 times.

Dispersion

3 to 5 drops of PVAc or PVAc-MMT were added to 20 ml of water in a glass dish (diameter 90 mm). When they became homogeneous, the dispersion was observed with water as reference.

Static tensile

PVAc and PVAc-MMT were made into films of 50×10×0.5 mm. After drying them to constant weight at room temperature, they were tested by SANS CMT 5000 computer-controlled electronic universal testing machine under a tension rate of 10 mm·min⁻¹ and a test temperature of 25°C. The test should be finished in 10 min.

Storage time

The glue was stored away from light at room temperature till it appeared as gel and/or delamination. The cycle was the storage time (S, days).

RESULTS AND DISCUSSION

Chemical structure

The diffraction peak representing $d_{(001)}$ of layers for MMT appeared in XRD patterns (Figure 1), its 2θ was 7.00°, its $d_{(001)}$ was 1.263 nm (Cui and Du, 2009). However, there was no diffraction peak from 1 to 12° of 2θ for PVAc-MMT. This phenomenon showed that the linear macromolecular chains of PVAc were formed in MMT layers, and MMT was greatly exfoliated into layers or sheets of nano-particles, randomly dispersing in PVAc matrix. The exfoliated nano-composite of PVAc-MMT was obtained. PVAc and PVAc-MMT were also tested by FTIR (Figure 2). No chemical bond was found between MMT and PVAc, but physical effect. The absorption bands of PVAc-MMT were stacked by those of MMT and PVAc. Neither new absorption bands formed, nor did existing absorption bands disappear. They also showed that MMT was greatly exfoliated into layers or sheets of nano-particles, and randomly dispersed in the matrix of PVAc. The results coincided with XRD results.

Dispersion and particles

From the visual, PVAc and PVAc-MMT were the same. They were viscous, milk-white, homogeneous, fine emulsions. All had no coarse particles, no foreign bodies and no delamination. However, when some dropped in water, their dispersion was a little different (Figure 3). Some coarse particles were found out in the dispersion of PVAc referred with water, but not PVAc-MMT. The dispersion of PVAc-MMT was much better.

PVAc and PVAc-MMT were further observed by TEM to investigate their particles (Figure 4). From the TEM comparison between PVAc and PVAc-MMT, the

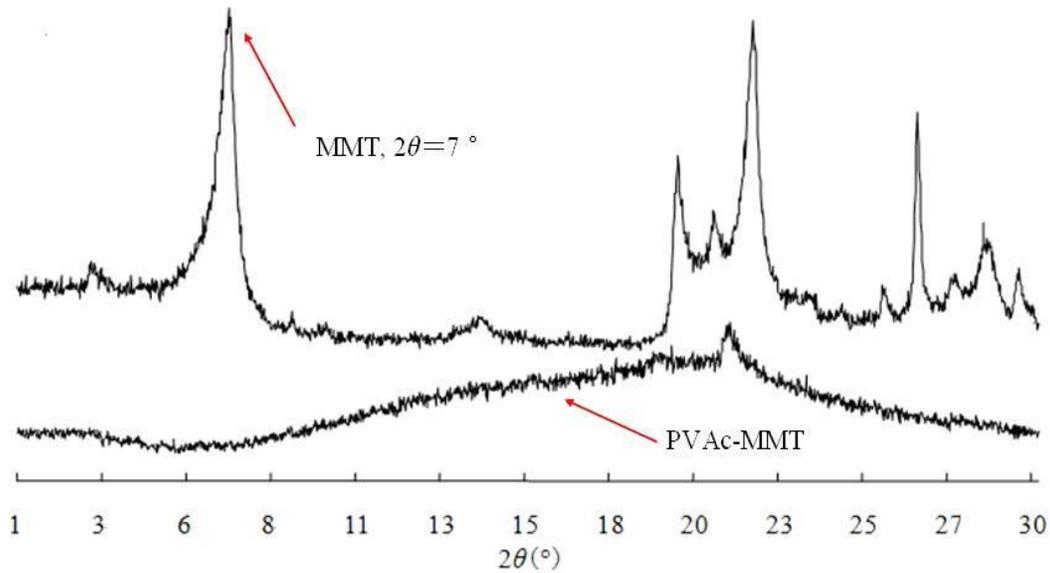


Figure 1. XRD patterns.

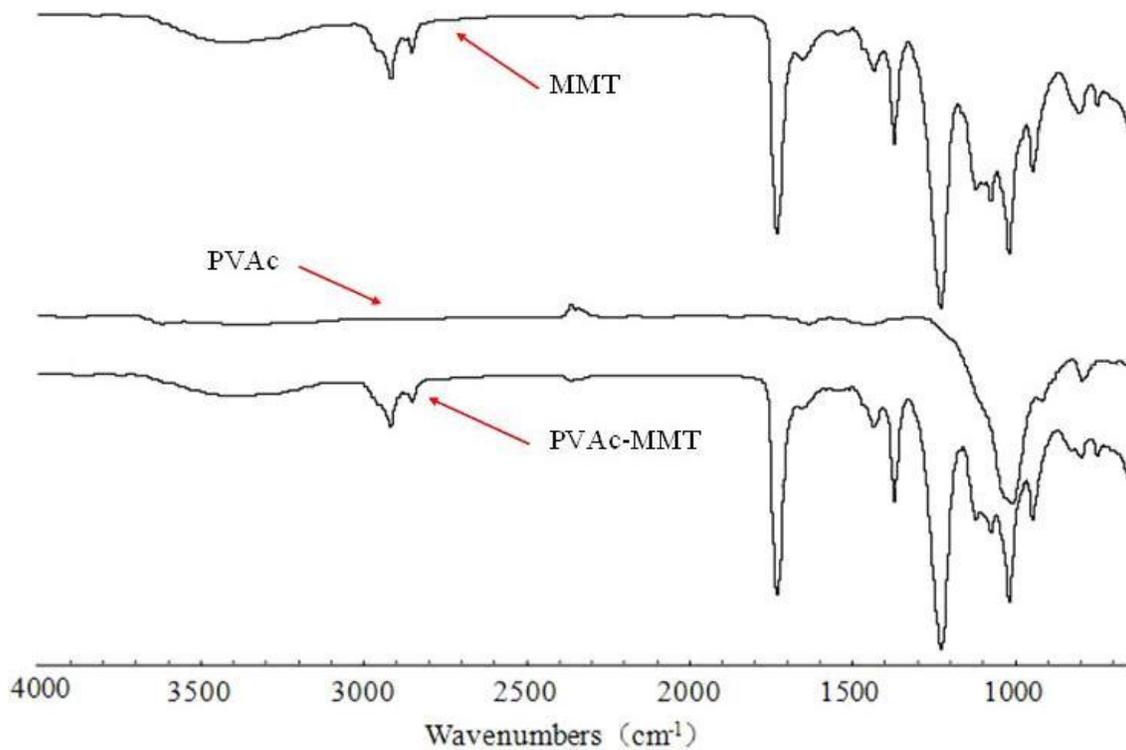
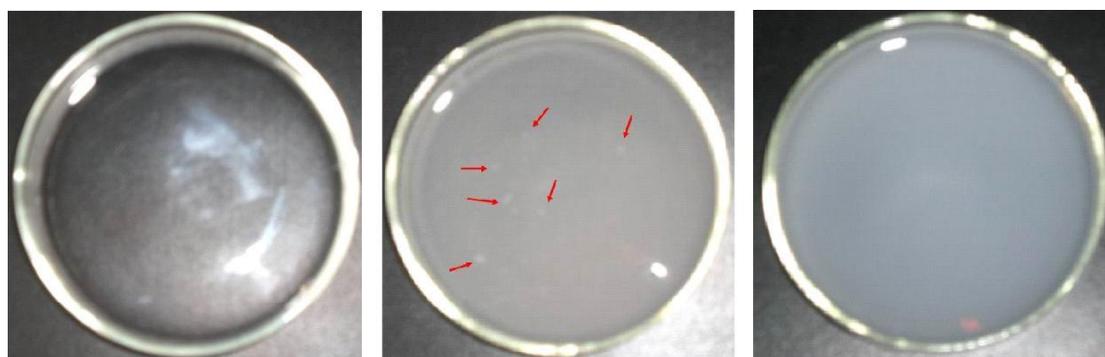


Figure 2. FTIR spectra.

differences were clearly apparent. The larger particles were PVAc, their diameter was from 250 to 500 nm, and the smaller particles were MMT, their diameter was from 50 to 100 nm. TEM also showed that MMT particles randomly dispersed with PVAc particles, this phenomenon coincided with the results of XRD and FTIR.

In addition, a “strawberry” structure was also found in the dispersion. This structure was only mentioned by Suprakas and Mosto (2005). As observed by TEM, the smaller MMT particles were adsorbed around the larger PVAc particles, and they formed the “strawberry” structure.

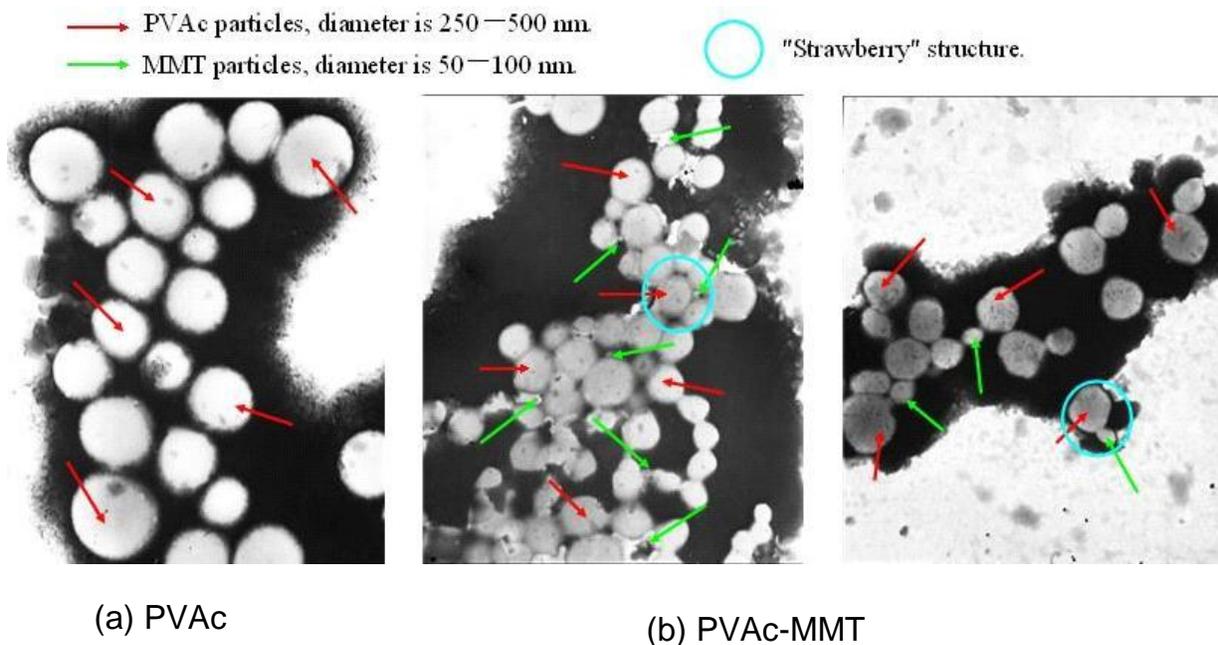


(a) Water

(b) PVAc

(c) PVAc-MMT

Figure 3. Dispersion.



(a) PVAc

(b) PVAc-MMT

Figure 4. TEM images.

Table 1. Apparent viscosity.

η (mPa·s)	$\dot{\gamma}$ (s ⁻¹)			
	0.63	1.26	3.14	6.28
PVAc	15	14	13	13
PVAc-MMT	14	13	13	12

Rheology

The apparent viscosity (Table 1) under different shear rate decreased with the increase of the shear rate. This

phenomenon indicated that both PVAc and PVAc-MMT were pseudo-plastic Non-Newtonian fluids. As we know, a pseudo-plastic fluid is one of the most common Non-Newtonian fluids. Rubber, most polymers, and their plastic melt and concentrated solution all are pseudo-plastic fluids. Their characteristic is that the apparent viscosity decreases with the increase of the shear rate. The orientation of the slender molecular chains of polymer in the flow direction causes the decrease of viscosity, so it is often called as the shear thinning fluid. The rheology of pseudo-plastic Non-Newtonian fluid is always described by power-law function equation:

Table 2. Rheological results.

	<i>i</i>	$\dot{\gamma}$ (mPa·s)	ζ (s)	η_0 (mPa·s)	η_∞ (mPa·s)	M_w	M_n
PVAc	0.93	14	4.6×10^{12}	1.2×10^2	0	1.0×10^2	1.0×10^2
PVAc-MMT	0.93	14	4.8×10^3	1.4×10^2	0	1.1×10^2	1.1×10^2

$$\tau = \dot{\gamma}^i$$

Where τ is the shear stress, $\dot{\gamma}$ (Pa·s) is the fluid consistency, $\dot{\gamma}$ (s^{-1}) is the shear rate, and *i* is the flow index, also called as the Non-Newtonian index.

The bigger $\dot{\gamma}$ is, the more viscous the fluid is. *i* is used to judge the difference between fluid and Newtonian fluid. If *i* is farther away from 1, the Non-Newtonian behavior is more obvious. For the Newtonian fluid *i*=1, then $\dot{\gamma}$ is equivalent to Newtonian viscosity (μ); for the pseudo plastic fluid, *i*<1.

Compare the power-law function equation with the Newtonian fluid flow equation:

$$\tau = \mu \dot{\gamma}$$

Combine them into the equation:

$$\tau = (\dot{\gamma}^{i-1}) \mu$$

And make:

$$\eta = \dot{\gamma}^{i-1}$$

The power-law function equation can be written as:

$$\tau = \eta \dot{\gamma}$$

Where η is the apparent viscosity of Non-Newtonian fluid that is the tested viscosity (Pa·s or mPa·s).

For Newtonian fluid and pseudo-plastic fluid, the relationship among their zero shear viscosity (η_0), η , and limit viscosity (η_∞) under lower $\dot{\gamma}$ is $\eta_0 > \eta > \eta_\infty$, and $\eta_\infty = 0$. According to the Cross-Williamson model viscous equation:

$$\eta = \frac{\eta_0}{1 + |\zeta \dot{\gamma}|^{1-i}}$$

η_0 is:

$$\eta_0 = \eta (1 + |\zeta \dot{\gamma}|^{1-i})$$

Where ζ (s) is the characteristic time of materials.

The polymer has a critical molecular weight (M_c), when the weight average molecular weight (M_w) < M_c , η_0 is

proportional to M_w ; when $M_w > M_c$, η_0 has a 3.4 exponential relationship with the increase of M_w . They illustrate that a large number of entanglement zones are formed among polymer chains. The substantial increase in viscosity is due to the contribution of the number of entangled points in entanglement zones and the maximum molecular weight. That is related to M_w . Their relationship can be expressed as:

$$\eta_0 = \mathcal{K}_1 M_w \quad (M_w < M_c)$$

$$\eta_0 = \mathcal{K}_2 M_w^{3.4} \quad (M_w > M_c)$$

Where \mathcal{K}_1 and \mathcal{K}_2 are the empirical constants, \mathcal{K}_1 is about 1 to 1.6, and \mathcal{K}_2 is about 2.5 to 5.0. For the linear and narrow width molecular weight polymer, the relationship between M_w and number average molecular weight (M_n) is $M_w \approx M_n$ when $M_w < M_c$; the relationship is $M_w/M_n < 2$ when $M_w > M_c$.

From the above calculations, the rheological results of PVAc-MMT were obtained (Table 2). *i* was all the same regardless of the addition of MMT, it was 0.93 and less than 1, so PVAc and PVAc-MMT were pseudo-plastic Non-Newtonian fluids. PVAc-MMT's $\dot{\gamma}$, ζ , η_0 , M_w , and M_n respectively were 14 mPa·s, 1.4×10^2 mPa·s, 1.1×10^2 , and 1.1×10^2 . ζ is a characteristics constant of materials, it is always expressed by time, usually measured in seconds. PVAc's ζ was 4.6×10^{12} s, and PVAc-MMT's ζ was 4.8×10^3 s. As previously set, η_∞ was 0 mPa·s all the time whether for PVAc or PVAc-MMT. In other words, MMT could improve the rheology of PVAc. As with other polymers, both PVAc and PVAc-MMT also possessed the normal stress effect that was the pole-climbing phenomenon, it is also called as the Weissenberg effect.

Static tensile

In the static tensile test, the obtained results only were the maximum break force of PVAc and PVAc-MMT films. Many other static tensile data would be calculated from the maximum break force through equations.

The static tensile strength (or static tensile stress) represented by σ (MPa = N·mm⁻²) is calculated by:

$$\sigma = F/S$$

Where *F* (N) is the maximum break force and *S* (mm²) is

Table 3. Static tensile.

	σ (MPa)	ϵ (ϵ_x) (mm·mm ⁻¹)	ϵ_y (mm·mm ⁻¹)	ϵt (%)	E' (MPa)	i	O (%)	S (days)
PVAc	2.07	1.92	0.30	192	1.08	0.16	13.35	≥180
PVAc-MMT	3.49	2.03	0.20	203	1.72	0.10	15.01	≥180

Note: Each data in this table was averaged from 20 sets of results.

the cross sectional area of samples.

The break elongation represented by ϵt (%) and the break strain represented by ϵ (mm·mm⁻¹) are calculated by:

$$\epsilon t = (l - l_0)/l_0 \times 100\%$$

$$\epsilon = (l - l_0)/l_0$$

Where l_0 (mm) is the original length of samples and l (mm) is the break length of samples.

The elastic modulus is represented by E' (MPa). It is calculated by Hooke's law :

$$E' = \sigma/\epsilon$$

Where σ (N·mm⁻²) is the stress and ϵ (mm·mm⁻¹) is the strain.

When a material is under tensile or compression, it experiences not only the vertical deformation along longitudinal direction, but also simultaneously the horizontal deformation as it is reduced or increased along a transverse direction. In the elastic deformation range, the horizontal strain (ϵ_y) is proportional to the vertical strain (ϵ_x), the ratio is known as Poisson's ratio (i) of material. It is generally calculated by the following equation:

$$i = \left| \frac{\epsilon_y}{\epsilon_x} \right|$$

Where $\epsilon_x = \epsilon$, $\epsilon_y = (b - b_0)/b_0$, b_0 (mm) is the original width of samples, and b (mm) is the break width of samples.

The results of static tensile were calculated (Table 3). σ of PVAc-MMT was 3.49 MPa, 1.69 times that of PVAc's 2.07 MPa, and its ϵ was 2.03 mm·mm⁻¹, 1.06 times that of PVAc's 1.92 mm·mm⁻¹. Therefore, E' of PVAc-MMT was still higher, it was 1.72 MPa, 1.59 times that of PVAc's 1.08 MPa. ϵt of PVAc-MMT was 203%, 1.06 times that of PVAc's 192%. Their ϵ_x were different as well as ϵ , their ϵ_y was almost the same, one was 0.30 mm·mm⁻¹, and the other one was 0.20 mm·mm⁻¹, so their i must be greatly different. i of PVAc-MMT was 0.10, and PVAc's i was 0.16. All indicated that the static tensile properties of PVAc-MMT were much better than PVAc. This

is because:

- (1) MMT was greatly exfoliated into layers or sheets of nano particles, randomly dispersing in PVAc matrix,
- (2) The smaller MMT particles were adsorbed around the larger PVAc particles to form the "strawberry" structure,
- (3) MMT possessed the small size effect as a natural nano-mineral.

In a word, the static tensile properties of PVAc were greatly improved because of the addition of MMT in polymerization.

Moreover, the solid content of PVAc-MMT was 15.01% (Table 3), a little higher than PVAc. The storage time of PVAc and PVAc-MMT was good. They all were more than 180 days. This showed their storage stability was very great.

Conclusions

In the synthesis, MMT was added and polymerized with VAc. From the analysis of XRD, FTIR, TEM, and static tensile, and the rheology investigated by the power-law function equation and the Cross-Williamson model viscous equation, the following conclusions were obtained:

- (i) The exfoliated nano-composite of PVAc-MMT was obtained. The linear macromolecular chains of PVAc were formed in MMT layers. There was no chemical bond between MMT and PVAc, but physical effect. MMT was exfoliated into layers or sheets of nano-particles, randomly dispersing in PVAc matrix.
- (ii) The dispersion of PVAc-MMT was better than PVAc. The particle diameter of PVAc was from 250 to 500 nm and MMT's was from 50 to 100 nm. They randomly dispersed together, and the smaller MMT particles were adsorbed around the larger PVAc particles to form the "strawberry" structure.
- (iii) MMT could improve the rheology of PVAc. PVAc and PVAc-MMT were pseudo-plastic Non-Newtonian fluids, their i was 0.93, and their storage stability was very good. Both PVAc and PVAc-MMT possessed the normal stress effect (or Weissenberg effect) that was the pole-climbing phenomenon.
- (iv) The static tensile properties of PVAc-MMT were much better. Its E' was 1.69 times that of PVAc, its ϵt was 1.06 times that of PVAc, its i was 0.10, and PVAc's i was

0.16.

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