

# Properties of Water-Soluble Acrylic Copolymer/Montmorillonite Nanocomposites for Warp Sizing

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**ABSTRACT:** Acrylic copolymer/montmorillonite (MMT) nanocomposites for warp sizing were prepared in the presence of Na<sup>+</sup>-MMT by the *in situ* intercalative polymerization of acrylic acid, acrylamide, and methyl acrylate in water solution. The properties of the solution and cast film were tested according to an application in sizing process of the nanocomposite size with various MMT contents. The results indicate that, for an exfoliated structure corresponding to the MMT content increasing to 7 wt %, the performance parameters of solution viscosity, glass-transition temperature, and tensile strength of the film increased and the moisture sorption, abrasion loss, and elongation at break of the film decreased. When the intercalated struc-

ture of MMT was 9 wt %, the gathered MMT layers acted as a common inorganic filler in the copolymer matrix, with limited contribution to the properties of the composite. The adhesion work of the nanocomposite solution was calculated by use of the Young–Dupre relation, which showed maximum values at an MMT content of 3 wt % on the surfaces of both the polyester and cellulose films. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2958–2964, 2010

**Key words:** adhesion; clay; mechanical properties; nanocomposites; water-soluble polymers

## INTRODUCTION

In recent years, much attention has been paid to polymer/clay nanocomposites as advanced plastic materials because of the dramatic improvement in their thermal and mechanical properties at low clay loadings over the polymer matrix.<sup>1–4</sup> The clay commonly used is montmorillonite (MMT), which belongs to the general family of layered silicates composed of the regular stacking of two-dimensional platelike layers bound together with weak dipolar, ionic, and van der Waals interactions. In the crystal structure, the isomorphic substitution of metals with lower atomic values for those with higher atomic values always generates negative charges on the layer surface, and hydrated alkali or alkaline

earth cations are then introduced between the galleries of the pristine clay units to counterbalance the charges.<sup>1</sup> In the case of alkali cations such as Na<sup>+</sup>-MMT, the layered silicates are readily intercalated by hydrophilic polymers via aqueous solution intercalation,<sup>5</sup> melt intercalation,<sup>6</sup> and *in situ* intercalative polymerization,<sup>7</sup> alternatively. There is some compatibility between the Na<sup>+</sup>-MMT layers and water-soluble polymers or their monomers so that the organized modification of MMT is not needed to prepare soluble nanocomposites. Chang et al.<sup>8</sup> researched a poly(vinyl alcohol) (PVA)/MMT system and found that Na<sup>+</sup>-MMT clay was more easily dispersed in a PVA matrix than was alkyl amine ion-exchanged clay and that the ultimate tensile strength and elongation at break of the Na<sup>+</sup>-exchanged clay hybrids were greater than those of the alkyl amine ion-exchanged clay hybrids. In other words, the miscibility of the polymer matrix with the clay in use determines the microstructures and properties of the resulting nanocomposite.

Water-soluble polymers are preferred candidates for textile sizes because of their basic abilities to bond the fibers together, to protect the warp from abrasion during weaving, and to be soluble, which is in favor of sizing and desizing processes. There are three major kinds of sizes used for warp sizing, that is, starch, PVA, and acrylic copolymers, each with advantages

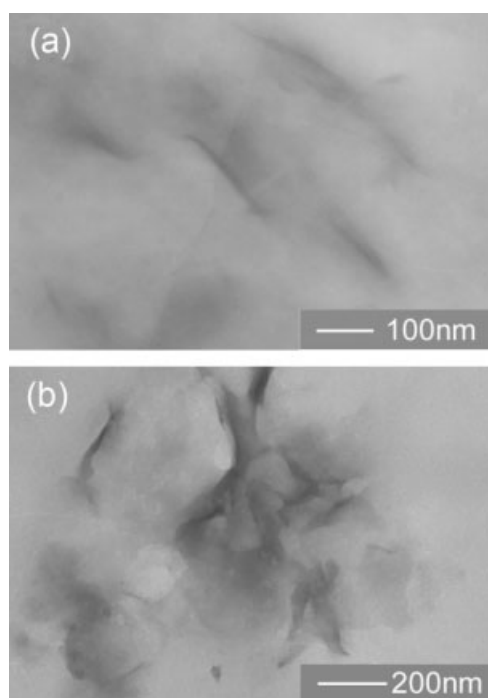
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**Figure 1** Transmission electron microscopy images of the acrylic copolymer/MMT nanocomposites with clay contents of (a) 7 and (b) 9%.

and disadvantages.<sup>9</sup> Different sizes are usually mixed together for different yarns to get the optimal technology target.<sup>10</sup> Modified starches are usually used for sizing cellulose yarns, whereas for synthetic yarns and synthetic fiber/cotton yarns, PVAs and acrylic copolymers are major ingredients in starch-based sizes for their good film-forming and sizing performances.<sup>9,10</sup> For this reason, water-soluble acrylic sizes<sup>11</sup> have been paid great attention with the hope of optimizing their sizing performance.

For this goal, in our previous study,<sup>12</sup> water-soluble acrylic copolymer/ $\text{Na}^+$ -MMT nanocomposites were synthesized with different contents of clay. The data of X-ray diffraction presented no diffraction peaks of clay single-crystal  $d_{001}$  for the acrylic copolymer/MMT nanocomposites with clay contents equal to or below 7 wt % (on a dry basis);<sup>12</sup> this implied an exfoliated microstructure of the MMT in the polymer matrices, as shown in Figure 1(a). When the clay loading was 9 wt %,  $d_{001}$  of the hybrid was 1.62 nm, in comparison with 1.29 nm for the pristine clay,<sup>12</sup> this indicated an intercalative structure on average, as shown in Figure 1(b).

In this study, we continued to investigate the water-soluble acrylic copolymer/ $\text{Na}^+$ -MMT nanocomposites on the basis of our previous study<sup>12</sup> and put an emphasis on performance parameters suitable for warp sizing. The properties of the solution and cast film were studied to evaluate effects of the MMT loading on the nanocomposites for sizing

applications. The adhesion of a size agent is a measure of the interaction between the size and the fibers sized, as reflected by interfiber cohesive forces,<sup>13</sup> which are necessary for the strand integrity of the fiber and directly affect the performance of the sized yarns.<sup>14</sup> Here, we analyzed the thermodynamic information by measuring the surface tension and contact angle of the size solutions on the size films and then calculating the adhesion work.

## EXPERIMENTAL

### Materials

$\text{Na}^+$ -MMT was supplied by Santai Mineral Clay Co., Ltd. (Mianyang, China) with a cation-exchange capacity of 128 mequiv/100 g. Ammonium persulfate, acrylic acid (AA), acrylamide (AM), and methyl acrylate (MA) were chemical reagents available from Kelong Chemical Reagent Co., Ltd. (Chengdu, China).  $\beta$ -Mercaptoethanol was from Sichuan Yongye Chemicals Co., Ltd. (Suining, China). Freshly redistilled water was used in all of the experiments.

### Preparation of the acrylic copolymer/ $\text{Na}^+$ -MMT nanocomposites

A certain amount of  $\text{Na}^+$ -MMT was dispersed in water by agitation, and after standing overnight to allow the MMT to swell adequately, it was sonicated with a KQ-250 sonicator (Kunshan Ultrasonic Instrument Co., Ltd., Jiangsu, China) for 30 min before use. The monomers, with an AA/MA/AM molar ratio of 1/3.1/7.2, along with  $\beta$ -mercaptoethanol (0.14 wt % on the basis of the monomers) as a chain-transfer agent, were then mixed with the clay slurry, and the system was sonicated again for 40 min at room temperature with the purpose of achieving the complete dispersion of MMT.

*In situ* intercalative solution polymerization was carried out in a 500-mL, three-necked flask fitted with a stirrer, a reflux condenser, two dropping funnels, and a thermostatic water bath. The intercalative dispersion, along with an initiator solution of ammonium persulfate, was added to the flask at 80°C under synchronous stirring at a feed speed at which explosive polymerization could be avoided. As the feeding finished, the system was kept stirring at 82°C for 3 h. Then, the whole system was cooled to 50°C, and some ammonia was added to neutralize the product under stirring for 40 min.

The product was a gray translucent viscous liquid, and the weight percentage of the synthesized nanocomposites was 25%, in which the MMT loadings were 1, 3, 5, 7, and 9% (w/w, on a dry basis of the copolymer).

## Solution properties

### Viscosity

The concentration of the composite solution was adjusted to 4 wt % by the addition of water, and then, the viscosity of the solution was tested with an NDJ-79 rotary viscometer (Shanghai Ande Instrument Equipment Co., Ltd., Shanghai, China) at 20°C.

### Surface tension measurements

The surface tensions of the resulting solutions were measured with the Wilhelmy plate technique with a Sigma 703 digital tensiometer (KSV Instrument, Ltd., Helsinki, Finland). The container, made of Teflon with a 70-mm inside diameter, for surface tension measurement was scrubbed with anhydrous ethanol three times, rinsed with redistilled water, and then dried in atmospheric conditions. After that, 50 mL of the composite solution with a 1 wt % concentration was slowly poured into the container. The surface tension in equilibrium was measured with error range  $\pm 0.01$  mN/m.

### Contact-angle measurements

The contact angle of the resulting solutions was measured in laboratory atmosphere at 20°C with the sessile drop method with a contact angle goniometer (OCAH200, Dataphysics, Filderstadt, Germany), where a polymer film was used to represent a fiber of the same polymer for convenience. A drop (4  $\mu$ L) of each 1 wt % composite solution was allowed to fall onto the polyester and cellulose films, and the static contact angles of the solutions relative to the polyester and cellulose films were evaluated separately with an error range of  $\pm 0.1^\circ$ .

### Adhesion work

The *adhesion work* is the work needed to dissociate a unit area of interface between two different phases and represents the intensity of interaction between the two phases. It can be deduced by way of the Young–Dupre relation as follows<sup>15</sup>:

$$W_a = \gamma(1 + \cos \theta) \quad (1)$$

where  $W_a$  is the adhesion work,  $\gamma$  is the static surface tension of the nanocomposite solution, and  $\theta$  is the contact angle of the solution on the polyester or cellulose film.

## Properties of the films

### Film formation

Each of the aqueous solutions of the acrylic copolymer/MMT nanocomposites was diluted with water

to a solid content of 6 wt %, under constant vigorous stirring at room temperature. The solution, with a volume of 60 mL, was spread out with a syringe onto a  $210 \times 150$  mm<sup>2</sup> glass dish paved with a polyester film of the same size, which rested on a leveled surface under ambient conditions until the casting film was dried. The film was then separated from the polyester film and further equilibrated in a desiccator at a controlled relative humidity (RH) of 65% and at 20°C for 1 week.

### Hygroscopicity

Bits of the film sample equilibrated at an RH of 65% and at 20°C were weighed accurately (weight  $W_1$ ) and then placed into a vacuum oven at 100°C for 5 h and weighed again (weight  $W_0$ ). The moisture sorption of the nanocomposite film was calculated as  $[(W_1 - W_0)/W_0] \times 100\%$ . Each film sample was tested 10 times, and the average moisture sorption and standard deviation were calculated.

### Solubility

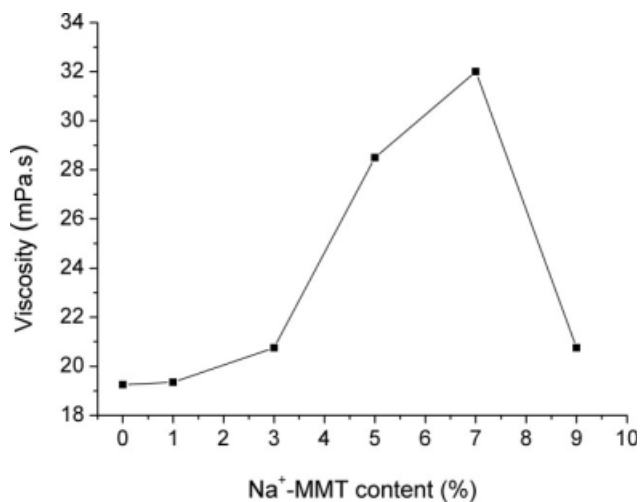
Cast film samples about 0.1 mm thick were cut in strips  $10 \times 20$  mm<sup>2</sup>, and then, each individual strip was immerse two-thirds of the strip into redistilled water at 50°C. At that moment, the time needed to break off the film by dissolution into the water was recorded with a stopwatch. For each sample, 10 data points were recorded, and the average time with standard deviation was taken to represent the solubility of the nanocomposite.

### Glass-transition temperature ( $T_g$ )

Differential scanning calorimetry was carried out to measure the glass transition of the samples under a nitrogen atmosphere at a heating rate of 10°C/min from 30 to 120°C with a 200PC/1/H differential scanning calorimeter (Beijing Beizhuo Sanyou Science and Technology Development Co., Ltd., Beijing, China).

### Abrasion resistance<sup>16</sup>

The film was tested for abrasion resistance on a Y571L fabric rubbing apparatus (Laizhou Electron Instrument Co., Ltd., Laizhou, China). After it was equilibrated at 20°C and 65% RH for 1 week, the film was abraded 400 times with a grinding head covered with 600-mesh sand paper. Then, the total abraded mass rubbed away from the surface of the film was weighed in the circle. Triple tests were run for each data point, and the average abraded mass, together with the standard deviation, was calculated.



**Figure 2** Viscosity of acrylic copolymer/Na<sup>+</sup>-MMT nanocomposite solutions (4 wt %) with different MMT contents at 20°C.

#### Strength and elongation measurement

The films were cut in strips (10 × 200 mm<sup>2</sup>) and conditioned at 20°C and 65% RH for 1 week. Before testing, the thickness of the strip was measured at 10 separate points for the strip with a CH-10-AT centesimal thickness testing instrument (Shanghai Liuling Instrument Co., Ltd., Shanghai, China), and the average thickness was taken.

The mechanical properties for each composite film were determined with a YG061 tensile testing instrument (Laizhou Electron Instrument Co., Ltd., Laizhou, China) with a clamping distance of 100 mm and a stretching speed of 100 mm/min. For each data point, 10 strips were tested, and the average values with corresponding standard deviations were taken.

## RESULTS AND DISCUSSION

Vinyl copolymers can be tailor made with the use of various comonomers to accommodate special uses. In this study, MA was used to increase the adhesion of the size to polyester fiber, together with a reduction in the  $T_g$  of the copolymer; AM and AA are soluble monomers that favor copolymer solubility and interaction with the surface oxygen of clay, promoting intercalative and exfoliative structures of MMT in the copolymers.<sup>17</sup> When the AA/MA/AM molar ratio was set to 1/3.1/7.2 here, we were interested in the effect of MMT content on the properties of the nanocomposites.

#### Viscosity

Figure 2 presents the viscosity of 4 wt % acrylic copolymer/Na<sup>+</sup>-MMT nanocomposites at different

contents of MMT. The solution viscosity increased with increasing MMT in the nanocomposite up to 7 wt %, at which point the nanocomposite solution achieved a maximum viscosity of 32 mPa s and then decreased as MMT increased to 9 wt %. This phenomenon could be explained by the fact that the MMT layers were exfoliated in the nanocomposites when the MMT content was less than or equal to 7 wt %, and intercalated when MMT was 9 wt %.<sup>12</sup> In the exfoliated case, the increase in viscosity was attributed to the formation of a percolation structure, in which there were interactions of the edge to edge and edge to face between the dispersed layers.<sup>1</sup> On the other hand, for the intercalated state, the percolation structure could not be formed yet, and the intercalated clay was similar to the crystalline domain in the polymer matrix,<sup>4</sup> with limited contribution to the solution viscosity.

#### Adhesion work

Good adhesion between a size polymer and the surface of the fibers is a major prerequisite for the sizing quality and loom efficiency. Loss of adhesion may lead to size shedding from warp yarns during dry splitting and weaving and may also compromise the mechanical protection of the yarns. The specific adhesion of the nanocomposite size in the roving test<sup>12</sup> is the macroscopic performance relative to the cohesive energy of the size itself, together with the adhesional energy between sizes and fibers. The precondition of adhesion is good wettability of the size liquid onto the fiber surface.<sup>18</sup> In this study, the thermodynamic adhesion work, including wettability, was emphasized according to eq. (1), that is, the adhesional energy.

Table I displays the results for the surface tension, contact angle, and corresponding adhesion work of the acrylic copolymer/MMT nanocomposites at 1 wt % concentration, along with specific adhesion, which was examined by the breaking force of lightly sized loosely twisted slubbing with a 1 wt % size paste,<sup>11,12,16</sup> the so-called roving method.

From the results in Table I, we determined that the adhesion work of the size solution to the films of polyester and cellulose were all in the range 60–80 mJ/m<sup>2</sup> and increased gradually with increasing MMT content up to 3% and then decreased with increasing MMT content. This, in principle, was similar to the specific adhesion, except the maximum specific adhesion value was at 5% MMT content.<sup>12</sup> The difference may have resulted from two complex factors in the roving method. One was the cohesive energy of the size itself, which could not be ignored because of the nonignorable thickness of the film between fibers in the method, and the other related to the difference in fiber strength for different



**TABLE I**  
**Adhesion Work and Specific Adhesion of the Acrylic Copolymer/Na<sup>+</sup>-MMT Nanocomposites**  
**(1 wt % Concentration) with Various MMT Contents**

MMT (%)	Specific adhesion (N) <sup>15</sup>		Contact angle (°)		Surface tension (mN/m)	Adhesion work (mJ/m <sup>2</sup> )	
	To polyester yarn	To cotton yarn	On polyester film	On cellulose film		To polyester film	To cellulose film
0	131.3	20.7	58.5	57.0	47.19	71.8	73.4
1	130.4	19.0	55.6	52.6	48.63	76.1	78.2
3	132.3	24.5	58.8	56.1	51.07	77.6	79.6
5	135.5	25.2	59.6	59.4	50.35	75.8	76.0
7	133.6	24.3	61.9	63.6	49.79	73.2	71.9
9	123.6	22.0	67.6	73.4	49.12	68.8	63.2

kinds.<sup>19</sup> Fibers are combined with each other as the roving is sized, so the fiber strength will obviously contribute to the breaking force of the roving. For this reason, the amount of soluble acrylic copolymer to polyester yarns was about six times as much the specific adhesion values of cotton yarns, as shown in Table I. Therefore, the adhesion work was more reliable for evaluating the real adhesion of a sizing agent to a yarn or fibers compared with the roving method, although there were similar variation tendencies in the two methods for the adhesion with changes in MMT content.

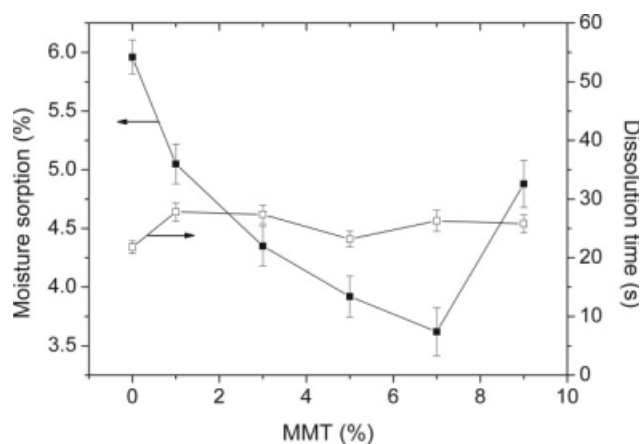
We also determined from Table I that the contact angles of the nanocomposite solutions were all lower than 90°; this indicated good wettability on both the polyester and cellulose surfaces. In addition, once the MMT was added to the acrylic copolymer, the contact angle decreased and then increased with increasing MMT content. This phenomenon may have resulted from interaction between the polymer and MMT, which was related to the aggregation state of MMT in the polymer matrix. This will need further studies for confirmation.

### Solubility and hygroscopicity of the films

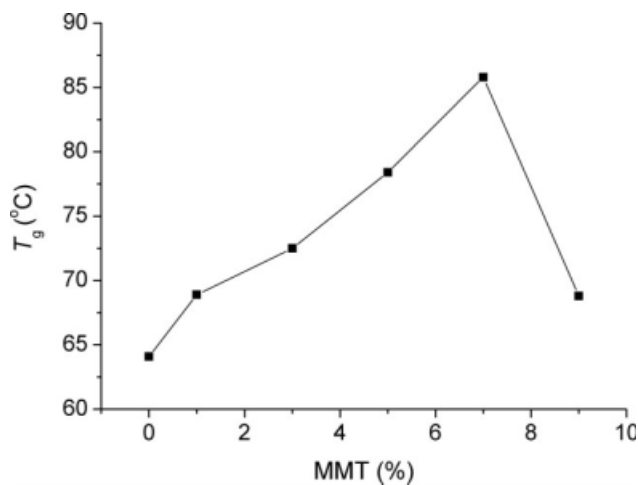
The weaving performance of sized yarns is considerably affected by the moisture content of the yarns, especially for cotton yarns sized with starch-based sizing agents.<sup>20</sup> Acrylic size has good moisture holding ability because of the ionized carboxyl lateral chain in its constitutional repeating unit, so it is always added in the starch sizing recipe.<sup>10</sup> However, the characteristic viscosity, or stickiness, of the acrylic size at higher humidity, commonly known as "stickiness caused by moisture," may result in severe problems corresponding to the mass transfer of the size to the sizing process machinery. So, appropriate hygroscopicity with good solubility is an essential requirement for acrylic sizes. Figure 3 shows the moisture sorption at 65% RH and 20°C and the dissolution time of the acrylic copolymer/Na<sup>+</sup>-MMT nanocomposites

with changes in the MMT content in 50°C water. All sizes with different contents of MMT had favorable solubility, and the addition of MMT had little influence on the solubility of the sizes. The moisture sorption first decreased to a minimum value as MMT increased up to 7% and then increased.

The mechanism of moisture sorption for the nanocomposites was related to the hydrophilic groups in the nanocomposite, including carboxyl, ammonium carboxylate, and amido in the polymer, and Na<sup>+</sup>-MMT. When the MMT content was in the range under or equal to 7 wt % range, corresponding to an exfoliated microstructure of the MMT in the polymer matrices,<sup>12</sup> the reduction in moisture sorption suggested a combination of hydrophilic groups in the polymer with silicate layers as a result of the gradual consumption of active sites that could attract water molecules.<sup>21</sup> When the MMT content increased further to 9%, the composite presented an intercalated microstructure on average,<sup>12</sup> in which the layered silicates were stacked and a majority of active sites in the polymer were free to adsorb water vapor, which would contribute the increase of the moisture sorption, although moisture sorption of the



**Figure 3** Moisture sorption and dissolution time of the nanocomposites with changes in the MMT content.



**Figure 4** Changes in  $T_g$  of the nanocomposites with the MMT content.

composite was still lower than that of the control sample.

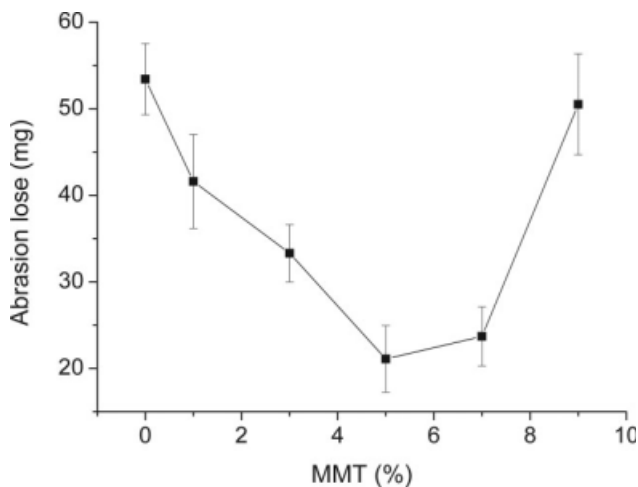
### $T_g$

$T_g$ , the critical temperature at which a material changes its behavior from being glassy to being rubbery, is an important thermal properties of polymers. In this study,  $T_g$  of the acrylic copolymers containing different amounts of MMT was tested by differential scanning calorimetry, as shown in Figure 4.  $T_g$  of the control in the absence of MMT was 64.1°C and approached the theoretical value 62.4°C calculated by the Fox equation.  $T_g$  of the nanocomposite increased gradually with increasing MMT in the case of exfoliated layers confirmed by X-ray diffraction.<sup>12</sup> The reason may have been that the movement of the polymer chains was strongly

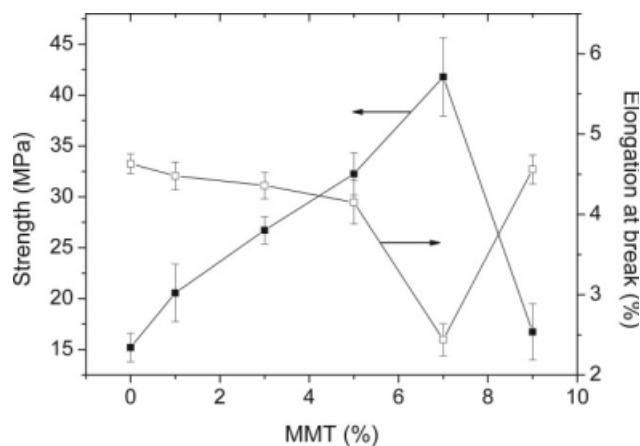
confined in polymer matrix when powerful interactions occurred between the silicate layers and polymer chains; this led to an increase in  $T_g$ . For the intercalated nanocomposite with 9 wt % MMT, however,  $T_g$  fell sharply, even close to that of the control; this indicated a small influence of the addition of MMT on  $T_g$ .

### Abrasive resistance

During the weaving process, sized yarns are under continuous abrasive actions from the loom parts and from frictions from the adjacent yarns themselves, especially in the case of high-speed shuttleless looms. Hence, for sizing agents, higher abrasion resistance is required. Abrasive resistance measurement is a customary test used for a size agent to simulate actual frictions occurred in weaving,<sup>22</sup> and the abrasion loss from a size film after 400 times of friction represents the extent of abrasive resistance of the size; that is, the more loss is abraded, the worse the abrasion grade is.<sup>16</sup> In Figure 5, the results of the abrasion loss with various MMT contents show that the addition of MMT improved the abrasion performance of the acrylic copolymer to a great extent when the MMT was exfoliated in the polymer matrix, here with MMT contents from 1 to 7 wt %. The probable reason was that the large specific area and great amount of active centers could make the MMT layers tightly coupled with the polymer chains and limit the mobility of the surrounding chains. In this case, the structure of the polymer/clay nanocomposites with strong interfacial interactions was analogous to that of semicrystalline polymers.<sup>4</sup> For the intercalated clay nanocomposite with 9 wt % MMT, however, the clay phase served as a crystalline phase<sup>4</sup> with limited interfacial interaction between the clay and polymer molecules; this led to



**Figure 5** Abrasion loss of the nanocomposite films with various  $\text{Na}^+$ -MMT contents.



**Figure 6** Tensile properties of the nanocomposite films with various  $\text{Na}^+$ -MMT contents.

much less additional resistance for the polymer to external forces.

### Strength and elongation at break

The tensile properties were tested for the nanocomposite films and the control sample without MMT, as shown in Figure 6. The break strength of the acrylic copolymer increased with increasing MMT contents up to 7 wt % and then dropped down greatly at 9 wt % MMT. The explanation of the phenomenon was similar to that of the abrasive resistance of the nanocomposites. On the other hand, the elongation at break of the composite films showed a slowly decrease as the MMT increased and came sharply down to a minimum at 7 wt % MMT; this was followed by a pronounced rising at 9% MMT, with an elongation value close to that of the control.

The strength performance shown in Figure 6 was consistent with the trend shown in Figure 4 for  $T_g$  of the nanocomposite. It was quite clear that the changes in  $T_g$  led to corresponding changes in the tensile properties, including break strength and elongation at break, for the nanocomposite in the glassy state, where the long-range polymer chain mobility through viscous movement was frozen. The exfoliated nanocomposite had some enhanced interactions between the layered silicates and the copolymer matrix to withstand external stress, as a result of an enhanced tensile strength and a reduced elongation at break. However, as the MMT loading increased to a higher quantity, such as 9 wt % in the study, the clay could not be exfoliated, and the less constrained polymer chains<sup>4</sup> contributed less to the tensile strength, but a higher elongation at break was found, which might have resulted from slippage between the pristine  $\text{Na}^+$ -MMT layers in the undispersed and intercalated silicates in the polymer matrix.

### CONCLUSIONS

The properties of the acrylic copolymer/ $\text{Na}^+$ -MMT nanocomposite changed with the MMT content, which depended on the dispersion state of MMT in the copolymer matrix. For the exfoliated microstructure of the water-soluble acrylic copolymer/MMT nanocomposites, which corresponded to an MMT content from 1 to 7 wt % in this study, such performances as the solution viscosity,  $T_g$ , and tensile strength of the film increased with increasing MMT content, and the moisture sorption, abrasion loss, and elongation at break of the film decreased with increasing MMT content. The results could be interpreted via interactions between the copolymer and the well-dispersed layered silicates. An increase in

the viscosity implied a higher apparent molecular weight as a result of the interactions; a decrease in the moisture sorption represented a masked effect of hydrophilic groups of the copolymer by their interaction with MMT layers; a higher  $T_g$  value could have originated from the restrained movement of the polymer chains by layered MMT; and the improvement in the mechanical properties was attributed to the strong interactions between the copolymer and dispersed layers.<sup>4</sup> On the other hand, for the intercalated state when MMT was 9 wt %, the gathered MMT layers could not be dispersed into nanosized layers, and MMT acted as a common inorganic filler in the copolymer matrix with limited contribution to the composite properties.

The adhesion work of the nanocomposite showed maximum values at an MMT content of 3 wt % for both the polyester and cellulose films. This was a more reliable measuring means, for ignoring cohesive energy of the size itself and the strength of the fiber sized, for evaluating the real adhesion of a sizing agent to a yarn or fibers compared with the roving method.

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