

Tremolite-Reinforced Nylon 66 Composites: Mechanical and Rheological Properties

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ABSTRACT: The reinforcement effect of an acicular inorganic filler, tremolite, on nylon 66 was studied. The mechanical properties of tremolite-filled nylon 66 composites and the effect of the filler particle size on them were obtained. The dynamic mechanical properties and rheological properties of the composites were measured. Two treatments, silane and unsaturated polyester, were used to improve the interface between tremolite and the nylon matrix. The morphologies of the composites were investigated using SEM. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 589–598, 1998

Key words: tremolite; nylon 66; reinforcement; interface; property

INTRODUCTION

People early on knew that the using of some fibrous materials to fill polymers improved their mechanical properties. Continuous glass fiber and carbon fiber have been applied in many polymers including thermoplastics and thermoset resin.^{1,2} Short glass fiber and carbon fiber have been used in some polymers because of their lower cost and better processability.^{3,4} As well as synthetic fibers, all kinds of natural organic and inorganic fibers have also been used to reinforce polymer. Kuruvilla et al.^{5,6} reported the dynamic mechanical properties and tensile properties of short sisal fiber-reinforced low-density polyethylene composites. Maldas and Kokta^{7,8} investigated the effect of coating treatments on the mechanical behavior of wood fiber (aspen, spruce) and hybrid fiber-filled polystyrene composites. Garcia-Zetina and Martinz⁹ reported a numerical analysis of the experimental mechanical

properties in polyester resins reinforced with short natural fiber (palma samandoch-zacate). Shenoy and Saini¹⁰ studied the dynamic and steady-state melt-flow behavior of wollastonite-reinforced polypropylene. Jarvela et al.¹¹ reported the strength properties and their dependence on the humidity and temperature of polyamide 6/wollastonite composites. Luo et al.¹² studied the effects of coupling agents on the rheological behavior and physical/mechanical properties of filled nylon 6.

Tremolite is a naturally occurring, white, non-metallic mineral. Its chemical formula is $\text{Ca}_2\text{Mg}_5[(\text{OH})/\text{Si}_4\text{O}_{11}]_2$. The particle crystalline shape is acicular or fibrous according to different geologic conditions. Its theoretical length-to-diameter ratio (aspect ratio) is 24 : 1, which is similar to that of wollastonite (20 : 1),¹³ so that it should, in theory, improve the mechanical properties of a filled polymer composite.

In the present article, the mechanical and rheological properties of tremolite-reinforced nylon 66 composites were studied for various levels of filler content. The effects of several treatment agents on the surface of tremolite have been studied.

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Table I Typical Chemical Composition and Physical Properties of Tremolite

Chemical composition (%)	
SiO ₂	56
MgO	28
CaO	13
H ₂ O	2.5
Physical properties	
Specific gravity (g/cm ³)	2.6–2.8
Mohs' hardness	5.0–5.5
Melting point (°C)	1200–1300
Specific heat (J/g K)	0.8–1.1
pH	8
Coefficient of thermal expansion (L/°C)	6.5×10^{-6}
Refractive index	1.60–1.63

EXPERIMENTAL

Materials

The tremolite used in this study was supplied by Jilin Province Institute of Geology, China, with an average particle size of 10 and 35 microns and an aspect ratio of 5 : 1–24 : 1. The typical chemical composition, as well as other physical properties of tremolite, are given in Table I. Figure 1 is a typical SEM photograph of tremolite.

The nylon 66 resin used was commercially available and manufactured by the Heilongjiang Province Nylon Co. (Harbin, China). The silane coupling agent used was commercially available and manufactured by the Gai County Chemistry Co. (Yingkou, China). The unsaturated polyester and catalyst used was commercially available and manufactured by the Tianjin Synthetic Resin Co. (Tianjin, China).

Table II Conditions for Coating Tremolite with UP Resin

Condition	Temperature (°C)	Concentration of	
		UP Resin (wt %) ^a	Reaction Time (h)
C-1	80	4	1
C-2	80	2	5
C-3	80	4	5
C-4	80	6	5

^a UP resin/tremolite by weight.

Surface Modifications

The tremolite surface was separately treated with a silane coupling agent and unsaturated polyester (UP resin). The condition for treating tremolite with silane was mixing for 10 min at 80°C in a high-speed mixer. For tremolite coated with unsaturated polyester, at first, the filler was mixed with unsaturated polyester at room temperature in a high-speed mixer according to different UP resin concentrations and then put in an oven to react at 80°C for different times. Detailed coated conditions are shown in Table II.

Sample Preparation

Modified tremolite and nylon resin were blended and extruded on a twin-screw extruder with a screw diameter of 30 mm, maintaining the following conditions: barrel temperature, first zone 242–250°C, second zone 248–254°C, third zone 254–264°C, and die zone 260–265°C, and screw speed 100–150 rpm. The extrudate coming out in the form of a filament strand was chopped and granulated.

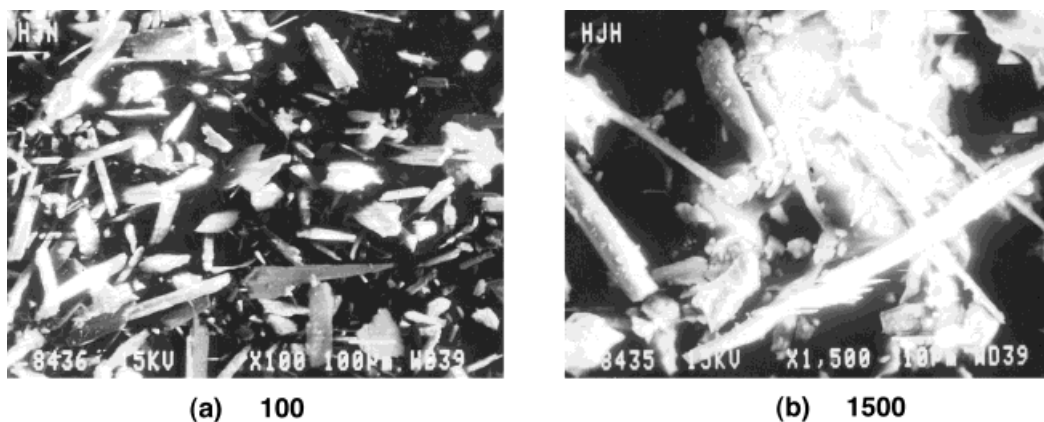


Figure 1 Typical SEM photographs of tremolite particle: (a) 100; (b) 1500.

Extruded samples were injection-molded on a screw injection-molding machine to prepare test standard specimens according to ASTM D638 and to D790. The injection pressure was maintained at 60 MPa; barrel temperature was first zone 250–255°C, second zone 255–265°C, and nozzle zone 260–270°C; injection time, 5–10 s; cooling time, 20 s; and screw speed, 100–150 rpm.

Testing

The tensile and flexural properties of the composites were measured with an Instron 1121-type tester according to ASTM D638 and D790, respectively. The crosshead speeds were 5 and 20 mm/min, respectively.

The Charpy impact test was carried out on a JJ-20 Model instrumented impact tester (made by Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, and the Intelligent Instrument and Apparatus Institute of Changchun) at room temperature. The span was 40 mm; the capacity, 20 J; and the striking velocity, 3.8 m/s.

A DuPont 9900 dynamic mechanical analyzer was used to study the thermal behavior at a heating rate of 3°C/min. The morphology of the composites was observed using a scanning electron microscope (Model JAX-840).

The rheological characteristics were measured using a cone and plate rheometer, Contraves CP-400 (Switzerland). The cone has an angle of 0.5° and diameters of 20 and 50 mm. The temperature scanning rate was 2°C/min from 250 to 300°C. The range of the shear rate adopted was 10^{-2} to 10^2 s⁻¹. All the measurements were carried out in a nitrogen atmosphere.

Data Treatment

The data of the mechanical properties measured were treated with a statistical method. The average value and deviation per point were calculated with formulas (1) and (2), respectively:

$$\bar{X} = \sum_{i=1}^n X_i/n \quad (1)$$

$$S = \sqrt{\sum_{i=1}^n (X_i - \bar{X})^2/(n - 1)} \quad (2)$$

where \bar{X} is the average value of the n time measurement per point; X_i , the measured value of the

i time; S , the standard deviation of the n time measurement per point; and n , the measured number per point. The detail number is shown in Table III.

RESULTS AND DISCUSSION

Effect of Tremolite Particle Size and Content on Mechanical Properties of Composites

The effect of the tremolite particle size and content on the mechanical properties of filled nylon 66 composites is shown in Figures 2–5. It is apparent that the tensile strength of the composites is improved with the addition of tremolite. Within the scope of the tremolite content of 10–50%, the tensile strength of the composites is always higher than that of the matrix. The particle size is very important to improve the properties of the composites. For a filler size of 35 microns, the tensile strength of the composites exhibits a maximum value at a filler content of 10% and then markedly decreases within the whole scope of testing: At a filler content of 50%, the tensile strength of the composites decreases to close to the strength of the matrix. For a filler size of 10 microns, the tensile strength of the composites is improved with increasing tremolite content and is maintained at the higher level. These results show that better adhesion exists in the tremolite–nylon interface. This interface interaction was considered to be associated with the crystallinity of the matrix on the filler surface.^{14–16} Thus, the acicular tremolite filler appears to function this way in its reinforcement effect. Although the maximum tensile strength of the composites is similar for the different particle sizes, the difference is larger and larger with increasing filler content. This may be because the larger-size particles more easily agglomerate with increasing filler content, resulting in voids, which should be the initial point of fracture for the composites, and therefore lowers the mechanical strength of the composites. Berlin et al.¹⁷ also considered that for large-size particles ($\cong 100 \mu\text{m}$) matrix dewetting will have a disastrous effect on the composite strength since the voids will immediately begin to grow.

The effect of tremolite on the flexural strength of the composites is similar to that on the tensile strength. For a particle size of 10 microns, the flexural strength is improved with increasing tremolite content and is maintained at higher levels. For a particle size of 35 microns, the flexural

Table III Measured Numbers per Test Point

	T_p	F_p	E_p	I_p	T_s	F_s	E_s	I_s	T_l	F_l	E_l	I_l	T_c	F_c	E_c	I_c	T_u	F_u	E_u	I_u	
PA	5	5	5	5																	
Filler content																					
10					5	5	5	5	5	5	4	4									
20					5	5	5	5	5	5	4	4									
30					5	5	5	5	5	5	5	5									
40					5	4	4	4	5	5	5	5									
50					4	4	4	4	5	5	5	5									
Silane concentration																					
0.50													5	4	5	5					
0.75													5	4	5	5					
1.00													5	4	4	5					
1.25													5	5	5	5					
1.50													5	5	4	4					
UP treatment																					
C1																	5	5	5	5	
C2																	5	4	5	5	
C3																	4	4	5	5	
C4																	5	5	5	5	

T , F , E , and I are tensile strength, flexural strength, flexural modulus, and impact strength of the materials, respectively. The subscripts p , s , l , c and u represent the nylon resin, 10-micron filler, 35-micron filler, silane treatment, and UP resin coating, respectively.

strength exhibits a maximum value at a filler content of 10% and then decreases. The flexural modulus of the composites is increased with increasing tremolite content. The effect of particle size on the modulus is insignificant compared to the effect on the strength.

The Charpy impact strength of the composites sharply decreases when there is tremolite filler in the composites. This is attributed to the stress

concentration in the matrix near the inorganic filler particles.¹⁷ The content and particle size of tremolite has a relatively weak effect on the impact strength.

Effect of Tremolite Surface Modification

To study the effect of surface modification of the filler particles on the interface adhesion between

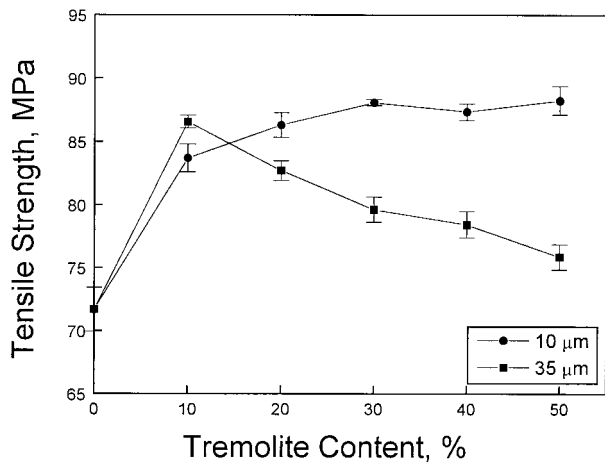


Figure 2 Tensile strength of tremolite–nylon composites as a function of tremolite content and particle size.

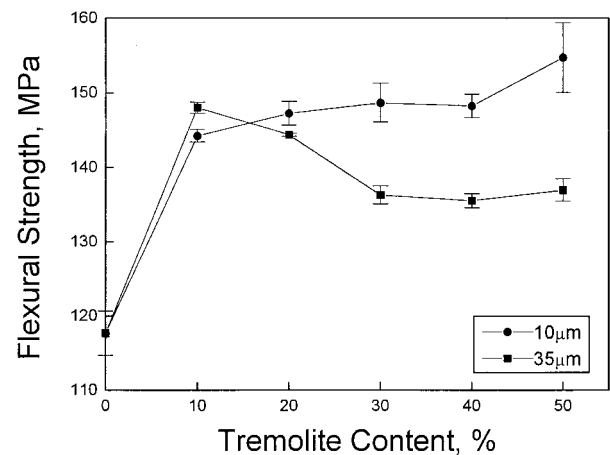


Figure 3 Flexural strength of tremolite–nylon composites as a function of tremolite content and particle size.

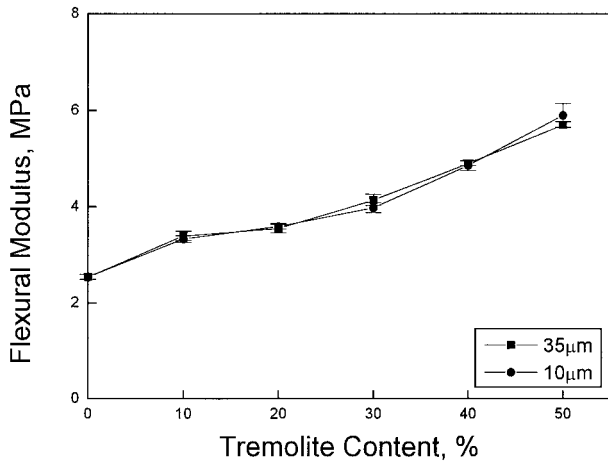


Figure 4 Flexural modulus of tremolite–nylon composites as function as tremolite content and particle size.

tremolite particles and the matrix, two kinds of surface-modified methods are used. One is the coupling agent treatment method and the other one is the particle surface coating method. The coupling agent used is silane, and the surface coating agent used is unsaturated polyester. In all treated composites, the tremolite used is of 10-micron particle size and the loading content is 40%. Figures 6–8 show the effect of the coupling agent concentration on the mechanical properties of the composite. We can see that the silane coupling agent has a marked effect on the Charpy impact strength of the composite. At a silane concentration of 1.25%, the impact strength of the composite is about double that of the untreated

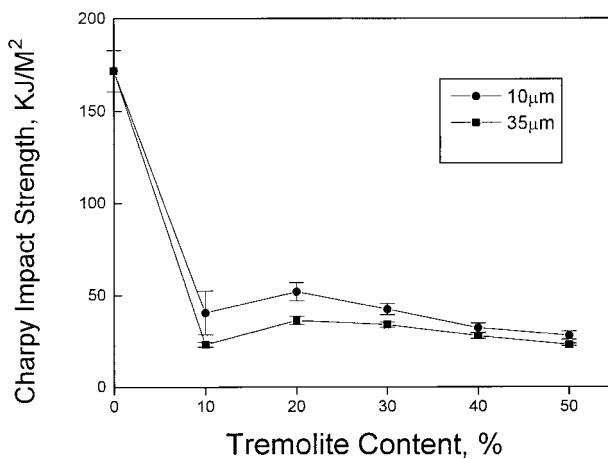


Figure 5 Charpy impact strength of tremolite–nylon composites as a function of tremolite content and particle size.

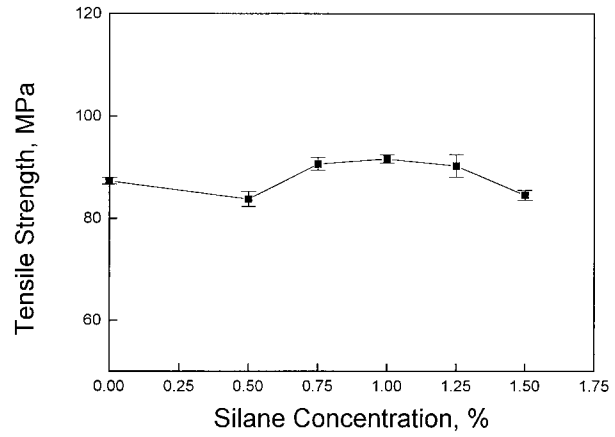


Figure 6 Tensile strength of tremolite–nylon composite as a function of silane concentration.

composite. This shows that the silane can improve the wetting between the matrix and the filler. However, there is a small effect of the silane on the tensile strength and flexural strength. Within the scope of the silane concentration from 0.75 to 1.25%, the tensile and flexural strength of the composite shows a slight increment. This indicates that the silane is helpful to improve the interface of both the filler and the matrix although the improvement effect is not very significant.

Table IV gives the properties of the tremolite coated with the unsaturated polyester-reinforced nylon 66 composite. From conditions 1–4, the time of reaction increases and the concentration of the UP resin increases. The mechanical properties of the composite are decreased with an increasing concentration of the UP resin and the time of the reaction and are always lower than those of the noncoated system. This indicates that the interface adhesion between tremolite coated with the UP resin and the nylon 66 matrix is poor because of the poor compatibility of both the UP resin and nylon 66. An SEM micrograph (Fig. 9) shows that the tremolite particle surface coated with the UP resin is smooth, which may protect the crystallization of the nylon on the filler particle surface. In this case, the effect of crystallization is somewhat similar to grafting and is favorable to improve the interface adhesion in the filler–matrix, therefore improving the mechanical properties of the composite. Although using unsaturated polyester alone is unfavorable to improve the interface adhesion between the tremolite particles and the nylon matrix, we think it is possible to add another component, having better compatibility with nylon 66, to the UP resin to

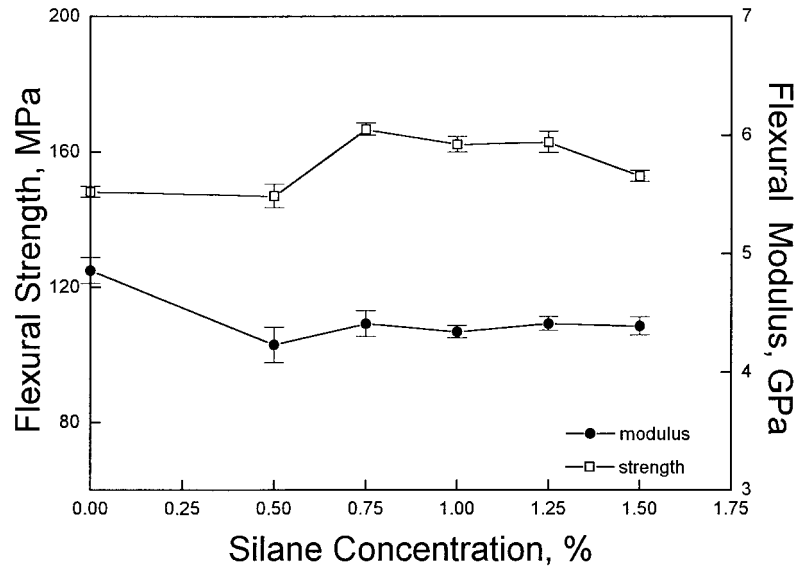


Figure 7 Flexural strength and modulus of composites as a function of silane concentration.

improve the interface adhesion between the filler and the matrix.⁷ Of course, this needs further work. Twardowski and Geil¹⁸ reported that an epoxy resin coating on the fiber improves the fiber-matrix interface.

Dynamic Mechanical Properties of the Composites

Figures 10 and 11 show the dynamic mechanical properties of tremolite-nylon 66 composites. In

all cases, the flexural modulus decreases with increasing temperature from 50 to 250°C; the flexural modulus of the filled composites is obviously higher than that of the nylon matrix within the whole range of the testing temperature. For example, at a temperature of 200°C, the modulus of the filled composites is about double that of nylon, that is, the filled composites can resist higher temperature at the same modulus value. Thus, the addition of the filler improves the useful tempera-

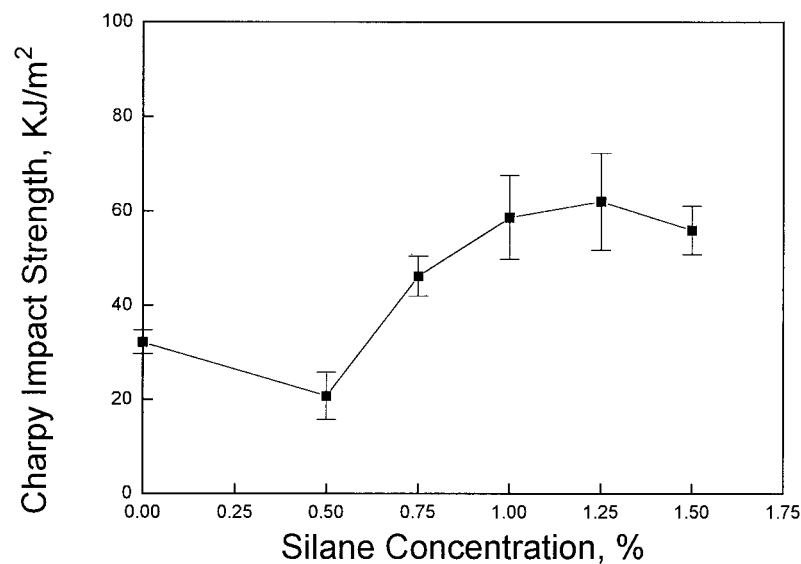


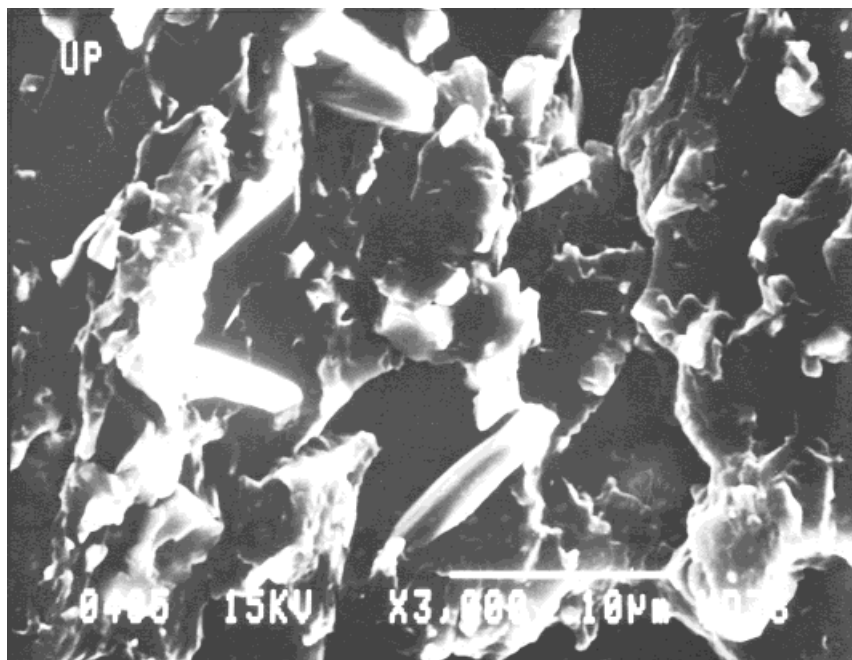
Figure 8 Charpy impact strength of the composites as a function of silane concentration.

Table IV Properties of UP Resin-Coated Tremolite-Filled Nylon 66 Composite

Condition	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Charpy Impact Strength (kJ/m ²)
C-1	81.99 ± 1.62	120.32 ± 2.87	3.40 ± 0.13	34.45 ± 2.54
C-2	70.45 ± 3.93	115.30 ± 2.84	3.70 ± 0.07	21.57 ± 2.41
C-3	62.97 ± 2.20	106.09 ± 3.15	4.02 ± 0.04	14.64 ± 2.38
C-4	62.44 ± 3.19	105.92 ± 0.97	3.65 ± 0.08	11.46 ± 3.12
Noncoated	87.36 ± 0.64	148.24 ± 1.57	4.86 ± 0.11	32.22 ± 2.54

ture range of the nylon resin. The improvement effect is somewhat different with different treatments. Generally, the silane is better in improving the flexural modulus of the composite. Although the modulus of the UP resin-coated composite is much improved over that of nylon, its effect is slightly less than that of the noncoated composite. This result, the same as the one above, can be explained by the poor compatibility of both the UP resin and the nylon. Figure 11 shows the mechanical loss factor of the composites as a function of temperature. The peak of the curve shows the glass transition temperature of the composites. The glass transition temperature is changed toward the high-temperature area with the addition of the fillers. The measured glass transition temperature of the nylon 66 resin is 61.11°C and increases to 78.47°C at a filler content of 40%. This may be due to that the addition of the filler in-

creases the interface interaction between the filler particles and the matrix. One interesting fact is that the glass transition temperature of the composites is different with different treatments. The T_g of the silane-treated composite is 84.03°C, which is higher than the T_g of the untreated one. The T_g of the UP resin-coated composite is 75.65°C, which is lower than the T_g of the untreated one. We consider that in the tremolite filler particle surface there might exist some tiny defects which should result in the initial crystallinity of the nylon macromolecule on it. The treatment affects the interface interaction through affecting the crystallization, resulting in the different T_g 's. In addition, the mechanical loss factor reflects the material's rigidity. In Figure 11, the lower trend from curve 1 to 4 reflects the lower of composites' rigidity. This is in accordance with the trend of the increment of the flexural storage modulus in Figure 10.

**Figure 9** SEM photograph of UP resin-coated composite.

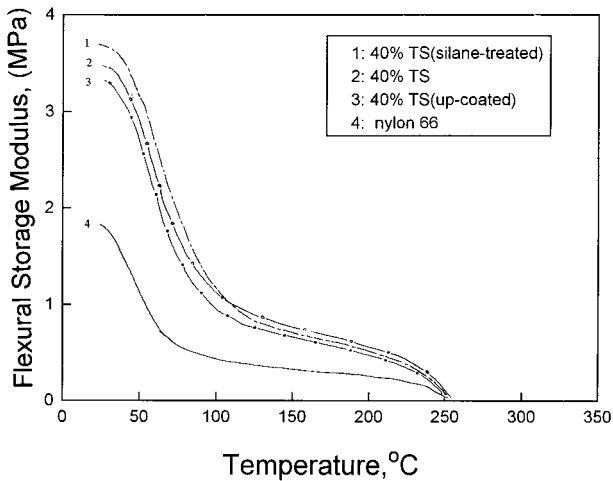


Figure 10 Flexural modulus as a function of temperature for tremolite–nylon composites.

Rheological Properties of the Composites

Figures 12–14 show the rheological properties of tremolite–nylon composites. The tremolite particle size used is 10 microns. The effect of the tremolite content on the melt viscosity of the composites is shown in Figure 12. From this, we can understand that the melt viscosity of the composites is decreased with an increasing shear rate and is enhanced with an increasing tremolite content. All the composites show a non-Newton fluid rheological behavior. This is similar to many filler-filled polymer composites. Figure 13 shows the melt viscosity of different treated composites. We find that, in the case of a higher shear rate ($>1 \text{ S}^{-1}$), the melt viscosity of the silane-treated composite is higher than that of the untreated

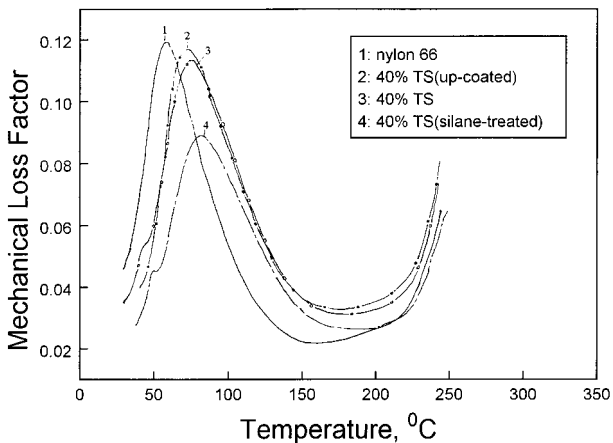


Figure 11 Mechanical loss factor as a function of temperature for tremolite–nylon composites.

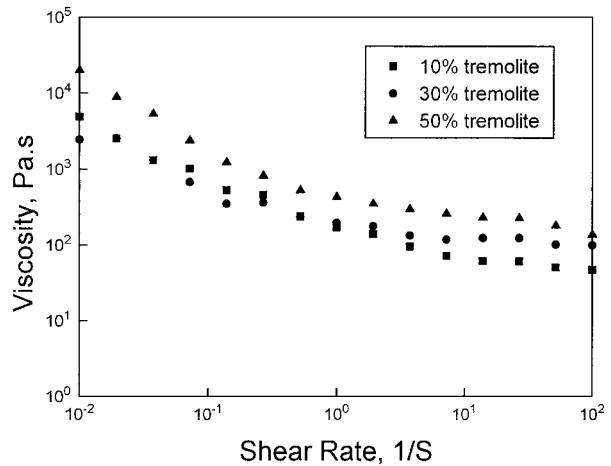


Figure 12 Viscosity of the composites as a function of tremolite content.

composite and the melt viscosity of the UP resin-coated composite is lower than that of the non-coated composite. This may be due to the different treatments, resulting in different interface interactions and exhibiting different viscosities. To indicate the sensitivity of the melt viscosity of the composite to the temperature, the melt viscosity of the composite was measured at different temperatures. According to the Arrenius’ equation,

$$\eta = A \exp(E_a/RT) \tag{1}$$

$$\lg \eta = \lg A + E_a/R \cdot 1/T \tag{2}$$

where η is the melt viscosity and E_a is the activation energy for the melt flow.

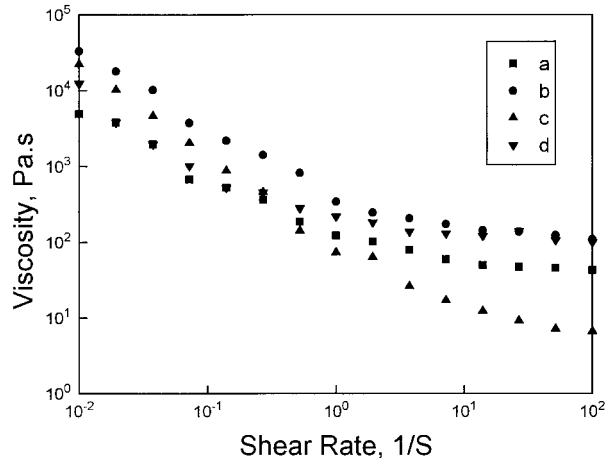


Figure 13 Effect of modification method on viscosity of the resin and composites: (a) nylon 66; (b) 40% tremolite (silane-treated); (c) 40% tremolite (up coated); (d) 40% tremolite.

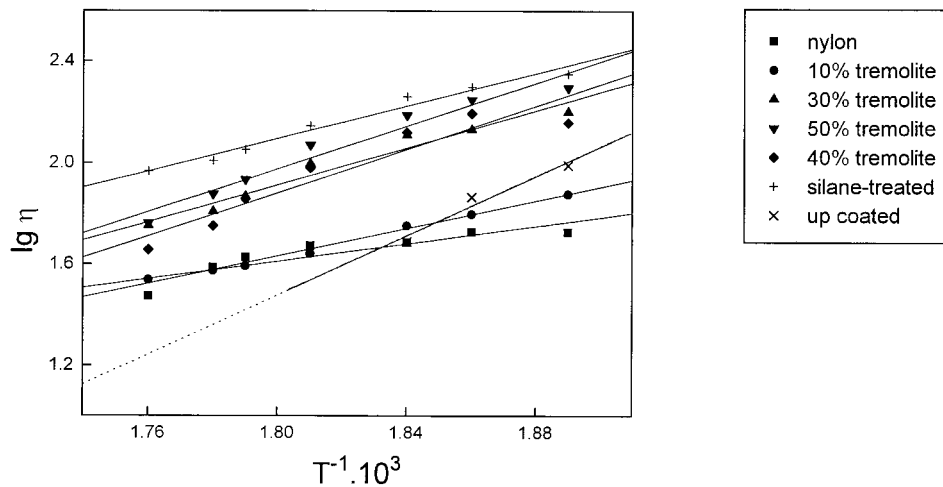


Figure 14 Activation energy for melt flow of tremolite–nylon composites.

We made a plot of $\lg \eta - 1/T$ (Fig. 14) and calculated the activation energy for the melt flow (E_a) according to the slope of the straight line. The result is shown in Table V. The E_a reflects the sensitivity of the melt viscosity to the temperature change. From Table V we can understand that the E_a of the composites is increased with increasing tremolite content. The E_a of the silane-treated system is small and close to that of the nylon resin, while the E_a of the UP resin-coated system is larger even than the 50% tremolite–nylon composite. This also reflects that the improvement of the silane coupling agent and the UP resin on the interface interaction of the composites is different, resulting in the difference of the sensitivity of the melt viscosity on the temperature.

CONCLUSIONS

The reinforcement effect of tremolite on the nylon 66 resin is marked because of its acicular particle

Table V Activation Energy for Melt Flow of Nylon 66/Tremolite Composites

Composites' Composition Nylon 66/Tremolite (wt %)	Activation Energy (kJ/mol)
100/0	142.18
90/10	223.33
70/30	299.41
60/40	349.81
50/50	346.57
60/40 (silane-treated)	263.09
60/40 (UP resin-coated)	481.64

structure and better interfacial adhesion with the nylon 66 matrix. The mechanical properties of the composites are clearly improved, especially the flexural strength and tensile strength. The smaller filler particle size (10 microns) is more favorable to improve the mechanical properties of the composites and to reach a higher filler content. The silane coupling agent is useful to improve the interfacial adhesion of tremolite–nylon 66 composites and to further improve the reinforced effect of tremolite on the nylon 66 resin.

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