

# Effects of Coupling Agents on the Rheological Behavior and Physical/Mechanical Properties of Filled Nylon 6

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## Synopsis

An investigation was made on the rheological behavior and physical/mechanical properties of highly filled nylon 6 composites with and without a coupling agent. As fillers, calcium carbonate and calcium silicate were used, and, as coupling agent, two silanes (Union Carbide, A1100 and Y9187) and two titanates (Kenrich Petrochemicals, KR-44 and KR-138) were used. It was found that all the coupling agents used increased the viscosities of the nylon/CaCO<sub>3</sub> system. However, the effect of the coupling agents on the viscosity of the nylon/CaSiO<sub>3</sub> system seems quite complex; namely, the titanate KR-44 decreased the melt viscosity of the nylon/CaSiO<sub>3</sub> composite, whereas the titanate KR-138S and the silane Y9187 increased it. In general, the effectiveness of the coupling agents in improving the physical/mechanical properties of the nylon/CaCO<sub>3</sub> and nylon/CaSiO<sub>3</sub> composites was marginal. A considerable decrease in glass transition was observed upon exposure of all samples to water, regardless of the type of filler and coupling agent.

## INTRODUCTION

In recent years, the use of engineering thermoplastic resins [e.g., nylon 6, poly(ethylene terephthalate)], together with particulate fillers and/or reinforcements, has received an increasing attention of the plastics industry. This is due in part to the continuously increasing cost of the resins. In the use of fillers and reinforcements, two important technical factors must be considered. They are: (1) the rheological behavior of the filled (or reinforced) polymer, which governs its processability, and (2) the adhesion characteristics (or interactions) between the particulates and the resin matrix, which dictate the ultimate mechanical properties and the long-term durability of the composite materials.

When incorporating particulates into a resin, one often encounters processing difficulties and deterioration of the ultimate mechanical properties. In order to overcome this, attempts have been made to add a third ingredient, often referred to as "coupling agent," to a mixture of particulates and a resin. Some success<sup>1,2</sup> has been reported in improving the mechanical properties of CaCO<sub>3</sub>-filled polypropylene, using silane and titanate coupling agents.

As part of our continuing effort toward enhancing the understanding of the role that "coupling agents" play in improving either the processability or the physical/mechanical properties of particulate-filled thermoplastic composites, we recently carried out an experimental study, using highly filled nylon 6. The highlights of our findings are reported in this paper.

TABLE I  
 Test Materials Specifications

Sample code	Resin	Filler <sup>a</sup>	Coupling agent <sup>b</sup>
1	Nylon 6	None	None
2	Nylon 6	Calcium carbonate	None
3	Nylon 6	Calcium carbonate	Silane A1100
4	Nylon 6	Calcium carbonate	Silane Y9187
5	Nylon 6	Calcium carbonate	Titanate KR-44
6	Nylon 6	Calcium carbonate	Titanate KR-138S
7	Nylon 6	Calcium silicate	None
8	Nylon 6	Calcium silicate	Silane A1100
9	Nylon 6	Calcium silicate	Silane Y9187
10	Nylon 6	Calcium silicate	Titanate KR-44
11	Nylon 6	Calcium silicate	Titanate KR-138S

<sup>a</sup> In all cases, the amount of filler used is 50 wt % in a given composite.

<sup>b</sup> In all cases, the amount of coupling agent used is 1.0 wt % of the filler.

## EXPERIMENTAL

Two inorganic fillers, calcium carbonate (Thompson and Weinman Co., Atomite) and calcium silicate, commonly referred to as wollastonite (Nyc Co., Nyad-G), were treated with coupling agents. The coupling agents used were: two silanes, *N*-octyltriethoxy silane (Union Carbide, Y9187) and  $\gamma$ -aminopropyl triethoxy silane (Union Carbide, A1100), and two titanates, isopropyltriethyl-diaminoethyl titanate (Kenrich Petrochemical, KR-44) and oxoethylene, di-(dioctyl)pyrophosphato titanate (Kenrich Petrochemical, KR-138S).

After treatment with the coupling agents, the fillers (calcium carbonate and calcium silicate) were compounded with a commercially available nylon 6 (Allied Fibers and Plastics Co., Capron 8207F), using a twin-screw compounding machine (Werner and Pfleiderer). Table I gives specifications of the test materials prepared.

A cone-and-plate rheometer (Weissenberg rheogoniometer, Model R16) was used to determine the rheological properties of the composites at 230°C.

The compounds were injection-molded to prepare specimens for testing the impact strength and tensile properties, according to the ASTM procedures. Both the notched Izod impact test and the falling dart test were performed at room temperature after the specimens were annealed at 75°C for 1 h. An Instron machine was used to determine the tensile properties at room temperature after the specimens were annealed at 60°C for 2 h. The specimens were annealed to ensure complete crystallization and uniformity of thermal history, because the temperature of the mold, when injection-molded, was kept at room temperature (ca. 20°C), which is below the glass transition temperature of nylon 6.

Dynamic mechanical measurements were conducted using a DuPont 981 Dynamic Mechanical Analyzer (DMA) connected to a 1090 Thermal Analyzer. Specimen dimensions were 30 × 12.5 × 1.25 mm. Tests were run at an oscillation amplitude of 0.2 mm, peak-to-peak, and a heating rate of 5°C/min. Measurements were conducted with the specimens conditioned as follows: (1) injection-molded and exposed to room temperature for an extended period of time; (2) immersed in a deionized water bath at 75°C for 8 h and for 23 h. (The specimens were tested after removal of the free water from their surfaces.)

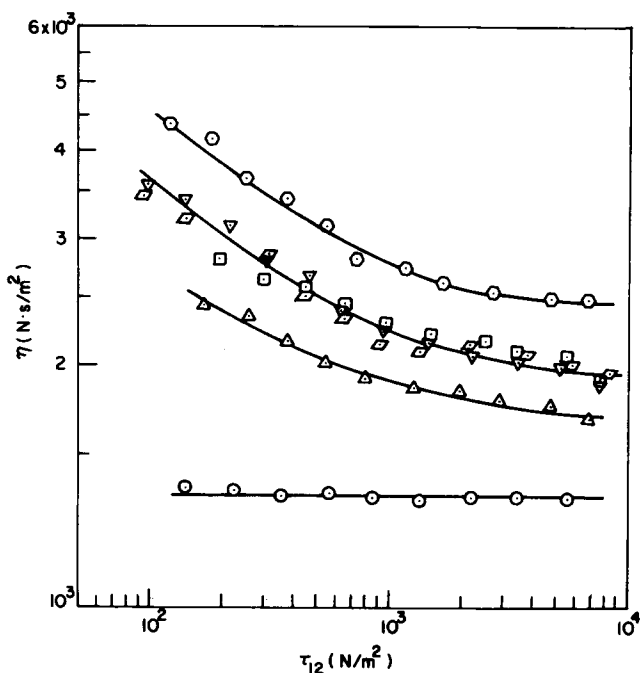


Fig. 1. Viscosity vs. shear stress for nylon 6/CaCO<sub>3</sub> system at 230°C: (○) pure nylon 6; (Δ) nylon 6/CaCO<sub>3</sub>; (◻) nylon 6/CaCO<sub>3</sub>/A1100; (▽) nylon 6/CaCO<sub>3</sub>/Y9187; (⊙) nylon 6/CaCO<sub>3</sub>/KR-44; (◐) nylon 6/CaCO<sub>3</sub>/KR-138S.

## RESULTS AND DISCUSSION

In all composite systems containing fillers treated with a coupling agent, it is of primary importance to determine the effect of the coupling agent on: (1) their rheological properties, (2) their physical/mechanical properties "as processed" and as annealed, and (3) their physical/mechanical properties after exposure to an aggressive environment which simulates the actual service conditions. All of these three aspects of the role of coupling agents in filled nylon 6 were investigated in this study.

The rheological properties of the composites were studied first. Plots of melt viscosity vs. shear stress for the nylon 6/CaCO<sub>3</sub> composites and the nylon 6/CaSiO<sub>3</sub> composites are given in Figures 1 and 2, respectively. It is seen in Figure 1 that the coupling agents used, without exception, increased the melt viscosity of the nylon 6/CaCO<sub>3</sub> system and that the filled systems, both untreated and treated with a coupling agent, tended to exhibit yield values at low shear stresses. More specifically, the titanate KR-44 increased the viscosity of the nylon 6/CaCO<sub>3</sub> composite by the greatest amount, whereas the increase in viscosity caused by the other coupling agents (silane A1100, silane Y9187, and titanate KR-138S) was about equal. In general, if coupling agent/filler and coupling agent/resin interactions occur during flow (i.e., during fabrication of the composite), one would expect to observe an increase in the melt viscosity and also an improvement in the mechanical properties of the final (fabricated) product.

However, when used in the nylon 6/CaSiO<sub>3</sub> composite, some coupling agents

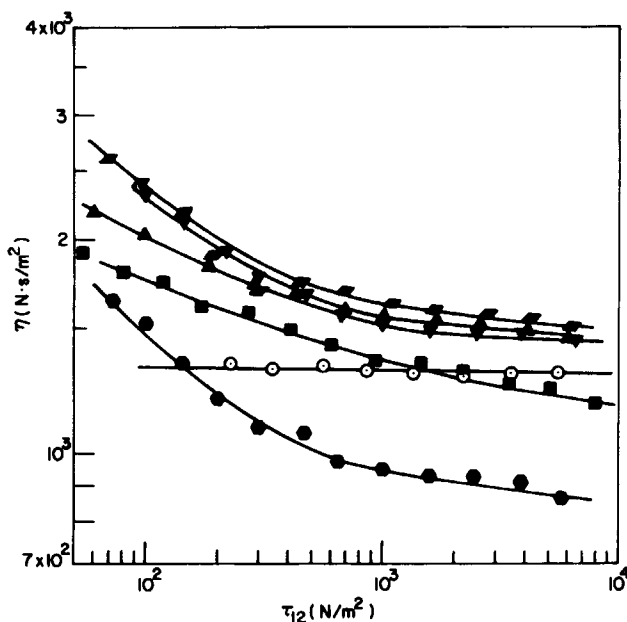


Fig. 2. Viscosity vs. shear stress for nylon 6/CaSiO<sub>3</sub> system at 230°C: (○) pure nylon 6; (▲) nylon 6/CaSiO<sub>3</sub>; (■) nylon 6/CaSiO<sub>3</sub>/A1100; (▼) nylon 6/CaSiO<sub>3</sub>/Y9187; (●) nylon 6/CaSiO<sub>3</sub>/KR-44; (◆) nylon 6/CaSiO<sub>3</sub>/KR-138S.

decreased its melt viscosity significantly. It is seen in Figure 2 that, at shear stresses above 200 N/m<sup>2</sup>, the titanate KR-44 brings the melt viscosity of the nylon 6/CaSiO<sub>3</sub> composite below the viscosity of pure nylon 6. Also, the silane A1100 has a similar but lesser effect. The addition of the other two coupling agents (silane Y9187 and titanate KR-138S), however, has hardly any effect on the melt viscosity, as clearly seen from a comparison with the data on the untreated nylon 6/CaSiO<sub>3</sub> composite.

It can then be concluded that the role of a coupling agent in decreasing (or increasing) the melt viscosities of filled nylon 6 composites is quite complex and that it depends on the chemical structure of the coupling agent, the type of filler, the interaction between the coupling agent and the filler, and the interaction between the coupling agent and the matrix resin.

In the second set of experiments, the effect of various coupling agents on the physical/mechanical properties of "as processed" and then annealed composites was investigated. The results of the falling dart impact strength and Izod impact strength tests are shown in Figures 3 and 4, respectively. It is seen that, in general, the impact strengths are decreased considerably when fillers are added to nylon 6. In nylon 6/CaCO<sub>3</sub> composites, the addition of silane coupling agents (A1100 and Y9187) increases the falling dart impact strength by approximately 50%, whereas the addition of titanates has little effect, as shown in Figure 3. In nylon 6/CaSiO<sub>3</sub> composites a noticeable increase in the falling dart impact strength was observed in the silane-A1100-treated system. That system is also the only one to show some improvement in impact strength as measured by the Izod test, as may be seen in Figure 4.

The ultimate tensile strength and the elongation at break of the composites

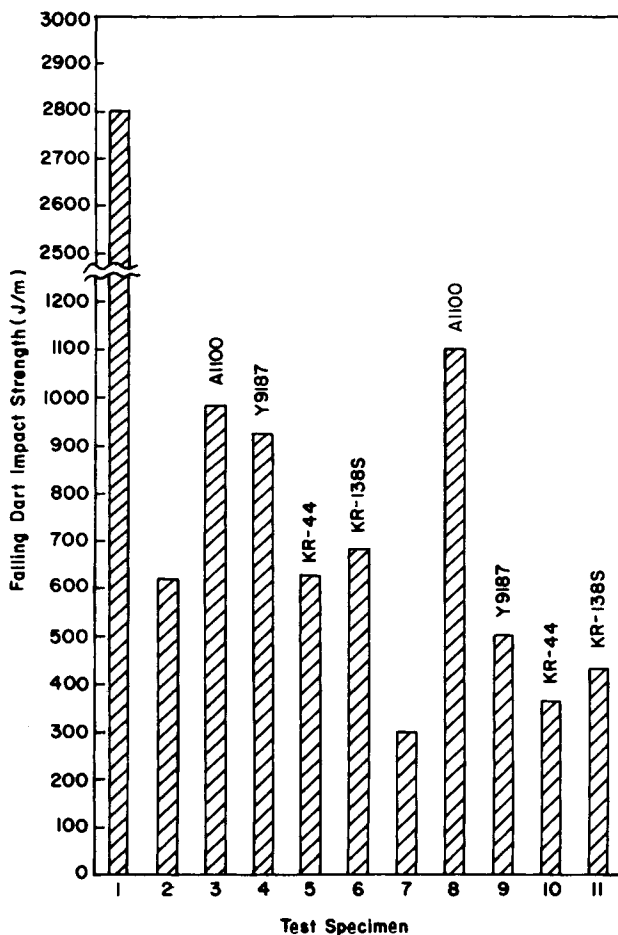


Fig. 3. Falling dart impact strength for nylon 6 composites. Sample codes are the same as in Table I.

were investigated next, and the results are shown in Figures 5 and 6. Interestingly enough, filled nylon 6 composites had tensile strength values almost identical to that of the pure nylon 6, regardless of whether the fillers were treated or not, as clearly seen in Figure 5. As expected, the elongation at break was found to decrease significantly upon the addition of fillers. The only noticeable increase in the elongation at break among the filled systems was observed in the nylon 6/CaSiO<sub>3</sub> composites which contain the silane coupling agents A1100 and Y9187, as seen in Figure 6. The fact that a consistent improvement was not observed in the mechanical properties of either nylon 6/CaCO<sub>3</sub> or nylon 6/CaSiO<sub>3</sub> system in the presence of coupling agents leads us to believe that the observed increase in melt viscosity of the composites may be attributable to poor dispersion of filler particles in the resin matrix. It is possible that the filler particles may have formed lumps (aggregates) in the presence of the coupling agent. In this context, the titanate coupling agent KR-44 would appear to be an effective dispersing agent for the nylon 6/CaSiO<sub>3</sub> system, as seen in Figure 2. On the other hand, however, KR-44 does not appear to play a role in increasing the adhesion

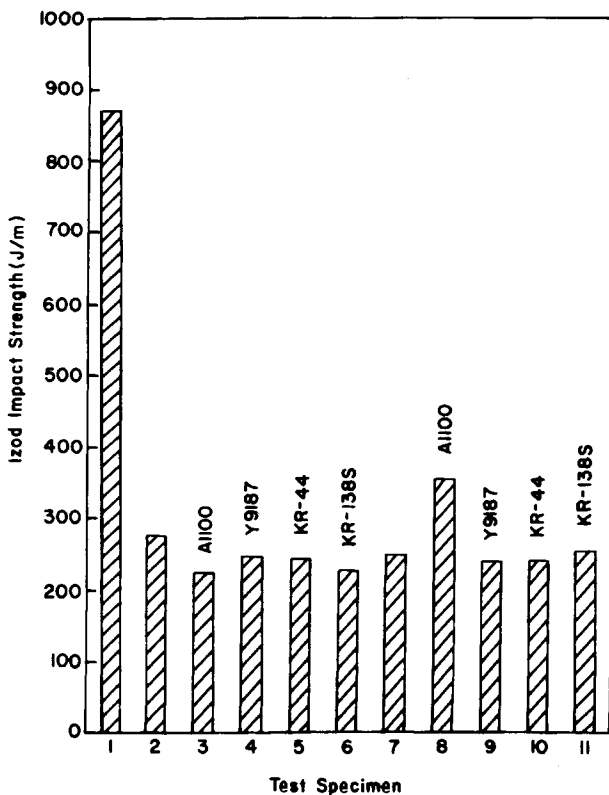


Fig. 4. Izod impact strength for nylon 6 composites. Sample codes are the same as in Table I.

between the filler and the matrix, as judged by the little improvement in the impact and tensile strengths (see Figs. 3 and 5).

In order to understand fully the effect of coupling agents on the properties of composites, one must consider the presence of an interphase. Although the thickness of an interphase is approximately on the order of several thousand angstroms, its importance is paramount. The interactions within the interphase and its morphology are unique and complex. The characteristics of the interphase depend primarily on the type of coupling agent and the coupling agent-filler and coupling agent-resin interactions as well as the morphological gradient in the matrix in the vicinity of the filler. The latter implies that the morphologies of nylon 6 in the bulk and near the filler are not the same. The presence of filler, in that sense, is analogous to the effect of the proximity of the mold surface on the morphology of injection-molded nylons.<sup>3</sup> The variation of morphology means that the physical/mechanical properties vary within the polymer matrix as a function of distance from the filler surface. However, no further direct efforts were made in this study to elucidate the character of the interphase. An excellent review of the state-of-the-art of this subject has been written by Ishida and Koenig,<sup>4</sup> and another one is forthcoming.<sup>5</sup>

In the third stage of our work, the mechanical properties of composites were evaluated prior to and after the exposure of specimens to an aggressive environment. In general, the molecular motions in the solid state and their effect

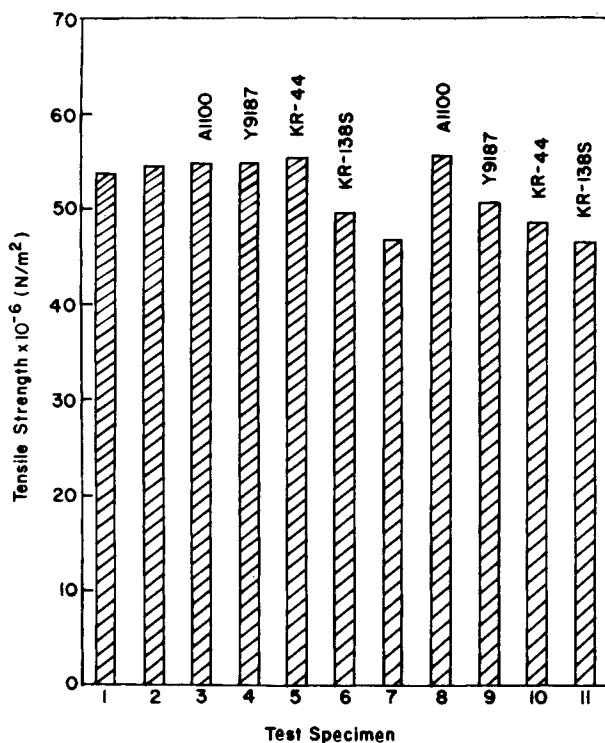


Fig. 5. Tensile strength for nylon 6 composites. Sample codes are the same as in Table I.

on the thermomechanical properties of polymers when exposed to an aggressive environment are best described by dynamic mechanical analysis. This technique is known to be particularly sensitive to various physical and chemical transitions and relaxations, structural heterogeneities, morphological gradients, and interphases. Hence, in the next set of experiments, dynamic mechanical measurements were made on the annealed specimens and on the samples exposed to an aggressive environment. The latter was represented by immersion in water at various temperatures.

A typical dynamic mechanical spectrum is shown in Figure 7, in which the elastic modulus  $E'$ , and the mechanical loss factor  $\tan \delta$  are plotted as functions of temperature for the untreated nylon 6/ $\text{CaSiO}_3$  composite. The first sign of an abrupt drop in  $E'$ , at approximately  $30^\circ\text{C}$ , corresponds to the onset of molecular motions in the polymer, which eventually lead to transformation from glassy to rubbery state. The glass transition ( $T_g$ ) of this sample (and of all samples hereafter) is defined by the location of the  $\tan \delta$  peak in the dynamic mechanical spectrum. Besides the  $T_g$ , recorded at  $60^\circ\text{C}$  for this sample, two additional peaks were observed at approximately  $-50^\circ\text{C}$  and  $-120^\circ\text{C}$ . These peaks, often referred to as  $\beta$  and  $\gamma$  transitions, have been reported in the literature.<sup>6-10</sup> The origin of the  $\beta$  transition is believed to lie in the segmental motions involving methylene groups and adjacent amide groups.<sup>7</sup> The  $\beta$  transition peak temperature was reported to decrease with increasing amount of absorbed moisture as a result of interactions between the water molecules and amide and

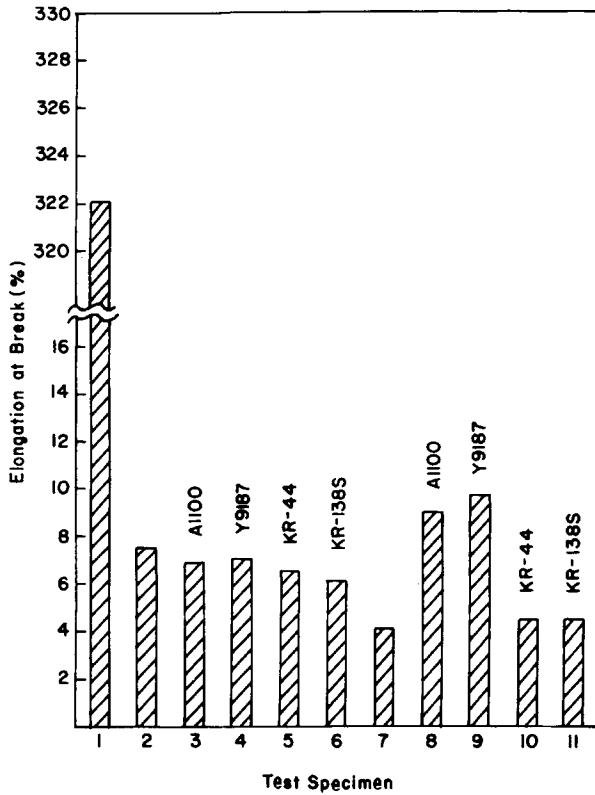


Fig. 6. Elongation at break for nylon 6 composites. Sample codes are the same as in Table I.

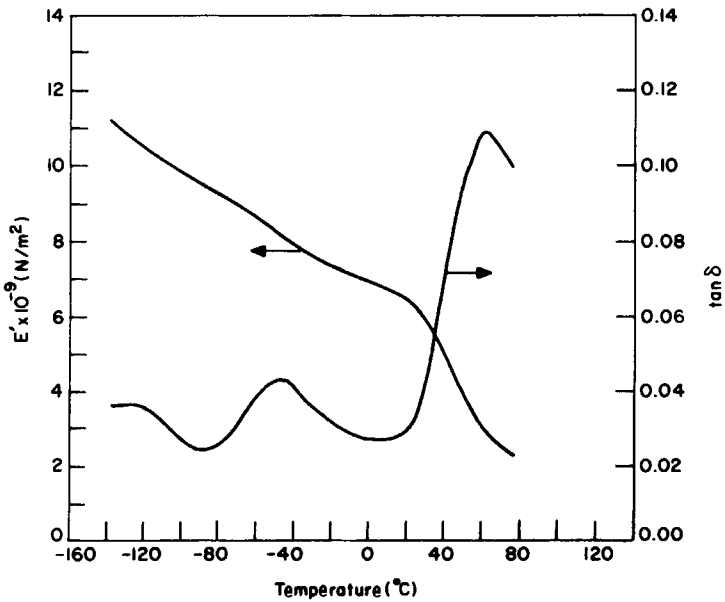


Fig. 7. Dynamic mechanical spectra of nylon 6/CaSiO<sub>3</sub> system showing changes in  $E'$  and  $\tan \delta$  as a function of temperature.



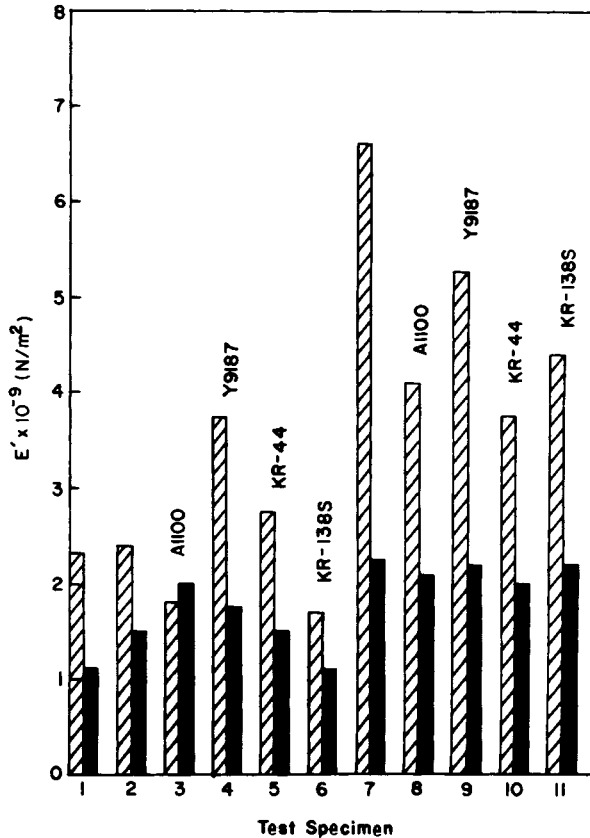


Fig. 8. Dynamic storage (elastic) modulus for nylon 6 composites, measured at 20°C: (▨) as injection-molded; (■) after immersion in water at 75°C for 8 h. Sample codes are the same as in Table I.

methylene groups. The  $\gamma$  transition, on the other hand, is related to the crankshaft motion of methylene groups in the backbone chains.<sup>8</sup>

Two additional general observations are worth noting in the dynamic mechanical spectra of the as-injection-molded samples. First, the  $\text{CaSiO}_3$ -filled samples have higher elastic moduli than their  $\text{CaCO}_3$ -filled counterparts. Second, in the nylon 6/ $\text{CaSiO}_3$  composites, the untreated sample has a higher  $E'$  than any of the treated ones, while in the nylon 6/ $\text{CaCO}_3$  composites no such trend was observed.

The effect of immersion in water at various temperatures (static hydrothermal fatigue) on the physical/mechanical properties of composites was studied next. Figure 8 compares the elastic modulus ( $E'$ ), measured at 20°C, for the specimens as injection-molded and after immersion in water at 75°C for 8 h. It is also seen in Figure 8 that, with the exception of silane A1100 in the nylon 6/ $\text{CaCO}_3$  composite, the use of a coupling agent does not prevent the observed decrease in the elastic modulus of filled composite materials, when they are immersed in water at 75°C. At this point, it is worth noting that, even in the dry samples, the onset of molecular motions, which eventually lead to the glass-to-rubber transition, was recorded in the vicinity of room temperature. Hence, the effect of absorbed

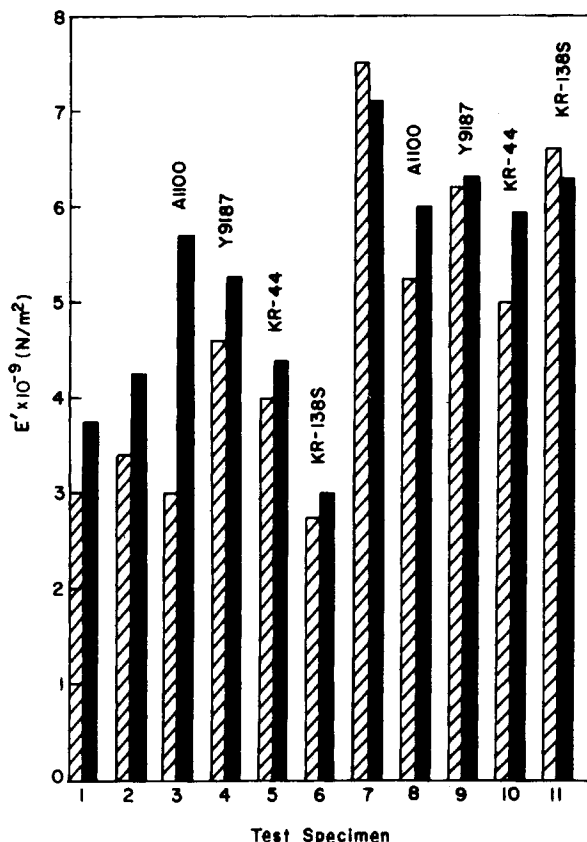


Fig. 9. Dynamic storage modulus for nylon 6 composites, measured at  $-20^{\circ}\text{C}$ : (▨) as injection-molded; (■) after immersion in water at  $75^{\circ}\text{C}$  for 8 h. Sample codes are the same as in Table I.

moisture on the elastic modulus may be diminished by the increased overall molecular mobility of polymeric chains at room temperature. In order to focus more closely on the effect of moisture on the elastic modulus of various composites, we have recorded and investigated the values of  $E'$  at  $-20^{\circ}\text{C}$ , at which temperature the dry samples are well below their  $T_g$ 's. The elastic moduli measured at  $-20^{\circ}\text{C}$  for the specimens, as injection-molded and after immersion in water at  $75^{\circ}\text{C}$  for 8 h, are shown in Figure 9. Interestingly enough, it is generally observed that the elastic modulus of filled composite materials is increased by the presence of moisture. This phenomenon might have been caused by the antiplasticization effect that the absorbed moisture has on the elastic modulus at  $-20^{\circ}\text{C}$ . Simultaneously, the intensity of the  $\beta$  peak was found to decrease, upon immersion of samples in water. Apparently, the absorbed moisture restricts the ease of molecular motions within the polymer and thus causes an increase in stiffness (elastic modulus). Similar results were previously reported for nylon 6,<sup>12,10</sup> namely, an increase in the amount of absorbed moisture decreased the  $T_g$  of nylon and increased the low temperature values of shear modulus.

Figure 10 describes the changes in the glass transition temperature measured first on the specimens as injection-molded and then on the specimens immersed

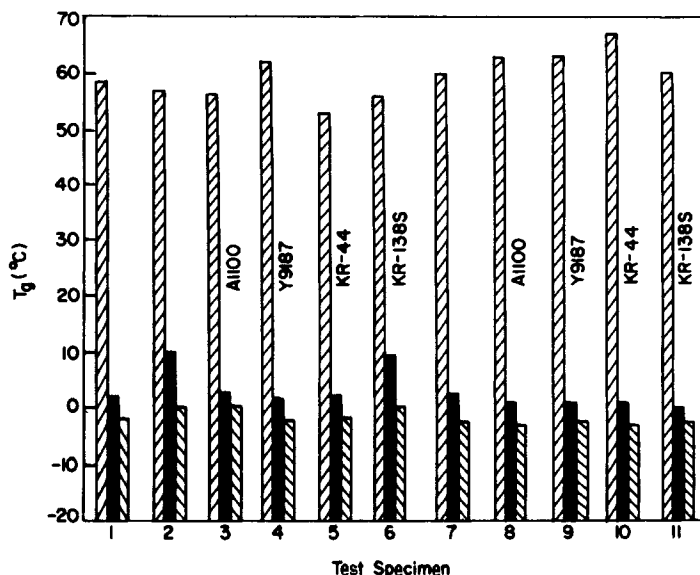


Fig. 10. Glass transition temperature ( $T_g$ ) for nylon 6 composites: (▨) as injection-molded; (■) after immersion in water at 75°C for 8 h; (▩) after immersion in water at 75°C for 23 h. Sample codes are the same as in Table I.

in water at 75°C for 8 h and 23 h, respectively. An abrupt drop in  $T_g$  during the first 8 h is followed by a gradual decrease as the duration of water immersion was increased to 23 h. Since the water bath temperature (75°C) is above the  $T_g$  of nylon 6, the moisture can penetrate into the free volume between the polymeric chains, whereby it acts as an intramolecular plasticizer. It appears that, particularly after the 23-h exposure to water, the coupling agents play no role in influencing the  $T_g$  of composite materials.

We recognize the fact that the presence of moisture has been shown to greatly affect the physical/mechanical properties of nylons and their composites.<sup>3</sup> However, in our investigation, no special effort was made to control the kinetics of moisture penetration, because we were interested in simulating practical situations, where containers made of nylon composites are used under the conditions of static hygrothermal fatigue. A general description of the molecular mechanism of moisture penetration in polymer composites, on the morphological level, has been given elsewhere.<sup>11</sup>

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