

Reactive Melt Blends of Nylon with Poly(styrene-co-maleic anhydride)

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SYNOPSIS

Melt blends of nylon with poly(styrene-co-maleic anhydride) (SMA) were prepared in a twin-screw extruder. Viscoelastic properties of the melt and morphological, thermal, and mechanical properties of the blends were determined. Fourier-transform infrared (FTIR) spectroscopy measurement indicated reactions between nylon and SMA. Melting peak temperature (T_m) of nylon was not changed in blends. This, together with the FTIR results, assured that the reactions occur mainly with the free amide end groups of nylon. Melt viscosity, elasticity, and the heat-distortion temperature (HDT) of nylon was significantly increased with the addition of SMA. Tensile strength and impact strength of nylon were, respectively, in general, increased and decreased with SMA.

INTRODUCTION

Poly(styrene-co-maleic anhydride) (SMA), a polar polymer, has good compatibility with a number of other materials and has become the basis of several commercial blends. These include blends of SMA with polycarbonate (PC) and SMA terpolymers with acrylonitrile-butadiene-styrene terpolymers (ABS).¹ Blends with SMA generally take the advantage of enhancement of glass transition temperature (T_g) with an increase of maleic anhydride (MA) content in SMA. T_g of SMA increases approximately by 2°C with 1 wt % increase of MA content in SMA.¹

Blends of SMA with poly(styrene-co-acrylonitrile) (SAN) have also been studied by a number of investigators.²⁻⁴ Depending upon the compositions of both copolymers, a miscibility window, leading to a lower critical solution temperature-type phase diagram, exists. Partial miscibility was also reported from melt blends of SMA with ABS.⁵ Recently, SMA was successfully used as a compatibilizer in nylon/SAN blends,⁶ where SMA reduced the size of the dispersed phase significantly.

In this paper, we consider the melt blends of nylon with SMA with regard to viscoelasticity of the melt, thermal properties, and mechanical properties as well. The results were interpreted in terms of chemical reaction between nylon and SMA.

EXPERIMENTAL

Materials and Blending

Injection grade of nylon-6 (Tongyang Nylon, Toplamid 1011) after drying at 80°C under vacuum overnight and SMA (Arco Chemical, Dylark 232, maleic anhydride content, 8 wt %, heat-distortion temperature, 104°C) as received, were used for blending. Blends were prepared using a corotating twin-screw extruder with L/D = 33 and angles of three leading blocks, 30, 60, and 90°. The extruder was operated at 100 rpm and a temperature profile of 230, 225, and 240°C (die). Seven compositions containing 0, 2.5, 5, 7.5, 10, 15, and 100 wt % SMA in nylon were prepared. In the following text, these samples will be identified by the following symbols: nylon, 2.5SMA, 7.5SMA, 10SMA, 15SMA, and SMA. The extrudates were quenched in cold water and pelletized. Prior to testing, the materials were dried under vacuum overnight at 85°C to avoid the plasticizing and hydrolyzing effects of humidity.

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Rheology

Melt rheology of the blends was determined using an RDS (Rheometrics Dynamic Spectrometer, 7700) rheometer. A cone-and-plate fixture, with cone angle of 0.1 rad and radius of 1.27 cm, was employed. The rheometer was operated isothermally at 240°C.

Morphology

Morphologies were determined from the cryogenically fractured surfaces of the extrudates, sputtered with gold before viewing using scanning electron microscopy (SEM).

Thermal Properties

Crystallization temperature (T_c), heat of crystallization (ΔH_c), melting peak temperature (T_m), and heat of fusion (ΔH_f) were determined from a differential scanning calorimetry (DSC DuPont 910). Samples were first heated to 240°C and stayed at that temperature for 5 min. T_c and ΔH_c were recorded during the cooling cycle, at 10°C/min, and the melting thermograms were recorded during the second heating cycle, 10°C/min. Heat-distortion temperature (HDT) was measured following ASTM D648 with 1/4 in. specimen at 2°C/min.

Mechanical Properties

Tensile strength and elongation at break were determined following the standard procedure described in ASTM D638 with type I specimens. An Instron tensile tester was operated at 50 cm/min. The Izod impact test was done on 1/8 in. notched specimens following ASTM D256. The above tests were made at room temperature, and at least five runs were made to report the average.

RESULTS AND DISCUSSION

FTIR Spectrum

The FTIR spectra of the nylon, SMA, and nylon/SMA blend samples are shown in Figure 1. The spectra of nylon [Fig. 1(a)] used in our experiment is essentially identical with those reported by others.^{6,7} The spectrum of SMA [Fig. 1(c)] shows that of a saturated five-membered ring.⁷ The coupling of C=O groups in the anhydride gives rise to two bands for symmetric (1858 cm⁻¹) and the antisymmetric (1780 cm⁻¹) stretching modes.⁴ In the nylon/SMA

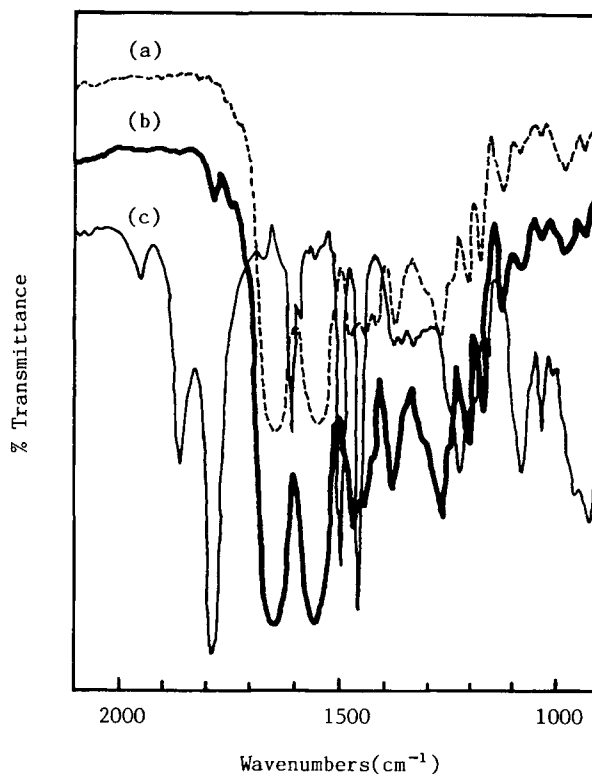


Figure 1 FTIR spectra of (a) nylon, (b) 5SMA, and (c) SMA.

blend [Fig. 1(b)], these peaks disappeared, and this suggests that the anhydride groups of SMA are bonded to nylons to form an SMA-*g*-nylon copolymer.⁶

Morphology

SEM micrographs of the fractured surfaces are shown in Figure 2. No evidence of clean-phase separation is observed from the figure. Apparently, no significant difference is found among the micrographs of various compositions. However, a careful examination reveals that a number of small cracks are seen in 2.5SMA, providing clues to the highest impact strength measured at this composition, to be discussed later.

Thermal Properties

Heat-distortion temperatures of the blends are shown in Figure 3. HDT of the blends increases with SMA content, and the effect is most pronounced in 2.5SMA, where HDT of nylon is increased by approximately 4°C/wt % SMA. The increased HDT in blends is due mainly to MA in SMA.⁸

T_m of nylon essentially was not influenced by

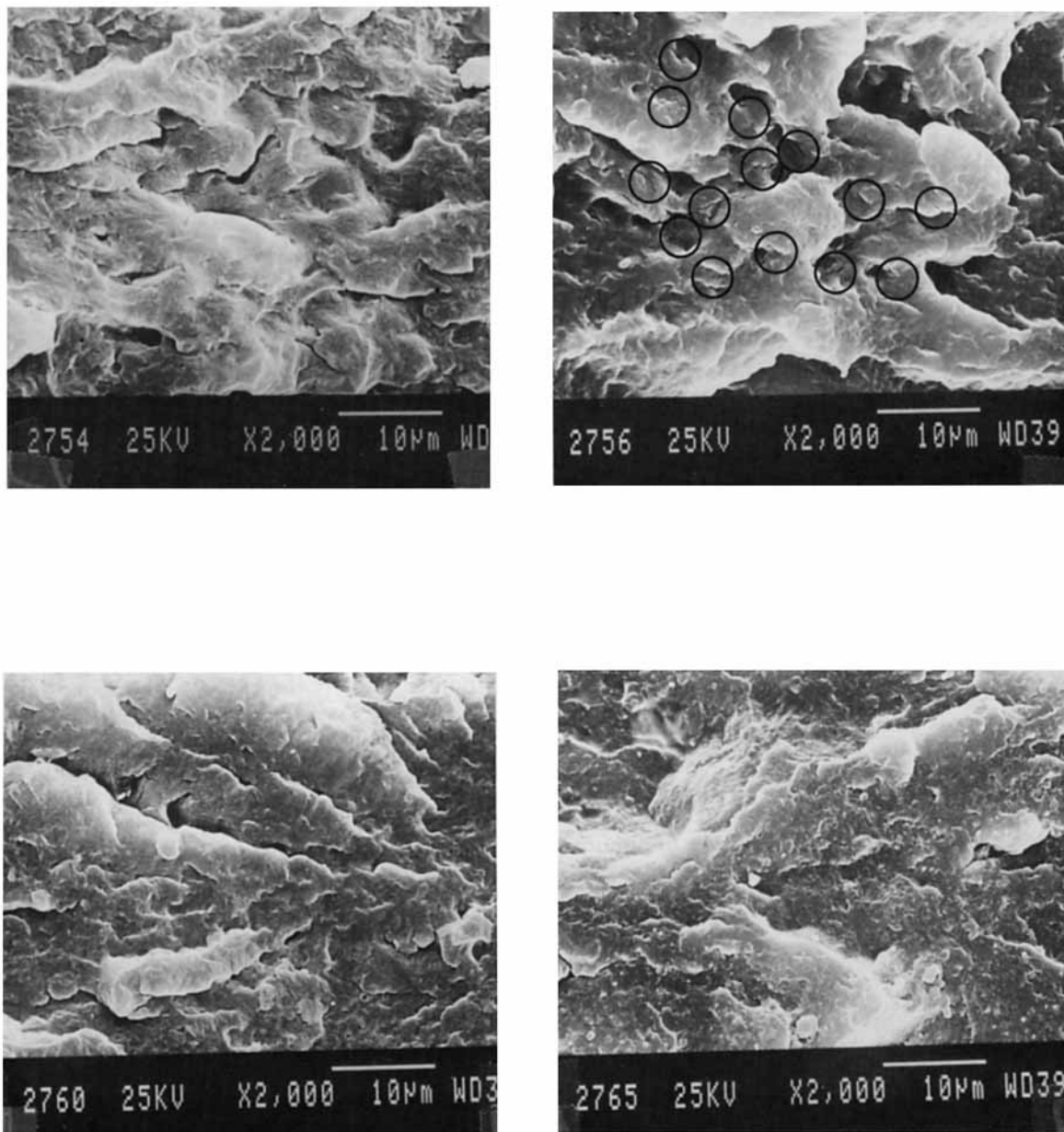


Figure 2 SEM micrographs of fractured surface: (a) nylon, (b) 2.5SMA, (c) 7.5SMA, and (d) 15SMA.

SMA, but T_c was slightly increased in 2.5 and 5SMA (not shown). When the T_c and T_m data are put together, one may conclude that the rigid SMA provides nylon with nucleating sites at low concentrations and gives a dilution effect at relatively high concentrations. The presumed effect is rather clearly verified from the measured ΔH_c , and ΔH_f (Fig. 4). In Figure 4, the straight lines were drawn from $\Delta H = \chi \Delta H_{\text{nylon}}$, where χ denotes the weight fraction of nylon in blends. The blends of SMA with nylon should be subject to chemical reactions between nylon and SMA during the melt mixing process. This

was evidenced from our FTIR measurements and by others.⁶ Further, our T_m data imply that the reactions occur mainly between the free amide end groups of nylon and MAH.⁹⁻¹¹ If reactions occur with amide linkage in nylon backbone, the lamella thickness of nylon will be reduced,¹² leading to lower T_m of nylon in blends than in the homopolymer.

Mechanical Properties

Mechanical properties of the blends are shown in Figures 5-7. Generally, tensile strength increases

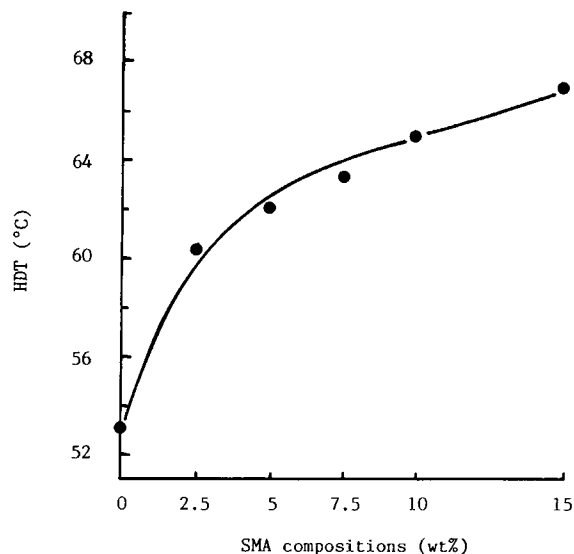


Figure 3 Heat-distortion temperatures of the blends.

and impact strength and elongation at break decrease with SMA addition, as expected. However, the behavior of 2.5SMA seems unusual. In 2.5SMA, tensile strength is smaller and impact strength is larger than those of nylon. The improvement of impact strength in 2.5SMA is probably due to the multiple crazing, observed from fractured surfaces. With impact toughening, tensile strength is at a minimum in 2.5SMA and the value of nylon is recovered in

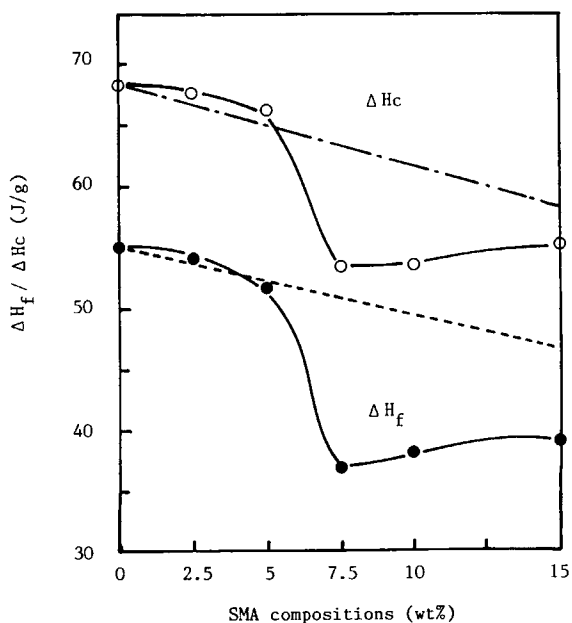


Figure 4 Heat of crystallization (ΔH_c) and heat of fusion (ΔH_f) of the blends.

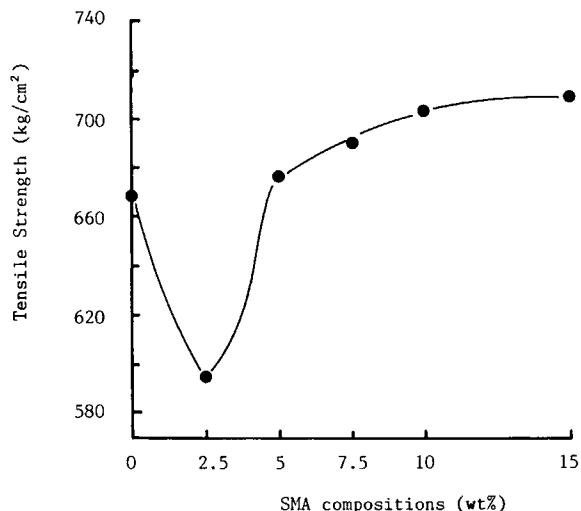


Figure 5 Tensile strengths of the blends.

5SMA, followed by a monotonical increase with SMA content. Though not directly related, such behavior is typical of hybrid composites¹³ and fiber-reinforced rubbers,¹⁴ where the lowered strength of a composite below that of the matrix is known as the dilution effect. It seems likely that essentially identical phenomena happen with nylon/SMA blends. In fiber-reinforced composites, at fiber loading below the critical value, typically around 15 vol %, fiber would be subjected to high strain with only small loads and would break. This results in lowered composite strength below that of matrix. A number of small crazes observed in 2.5SMA may be due to

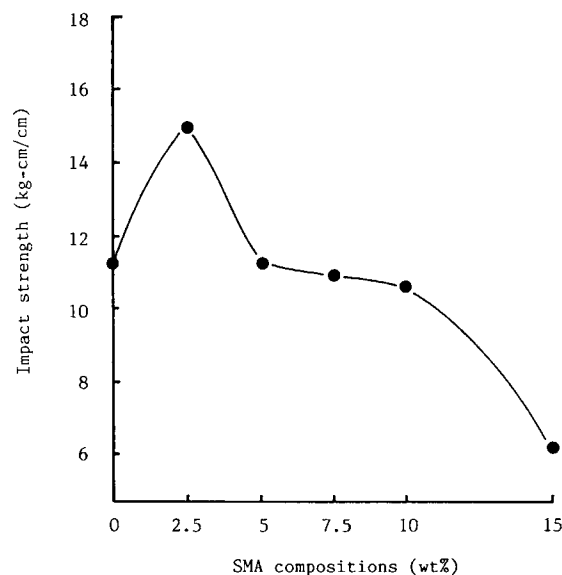


Figure 6 Notched Izod impact strengths of the blends.

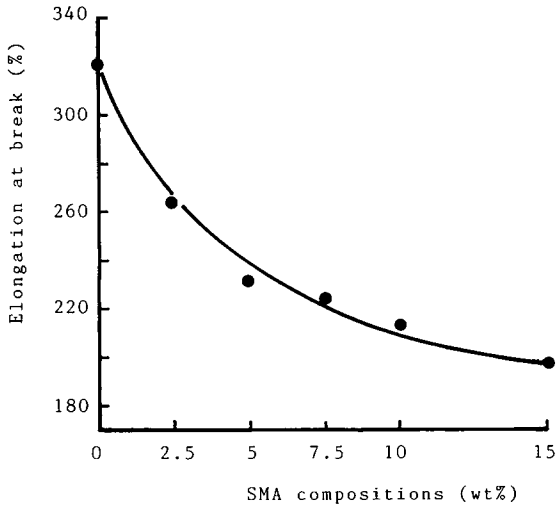


Figure 7 Elongations at break of the blends.

large strain around the SMA. At such small concentrations of SMA, together with strong interfacial adhesion with nylon, SMA would be subjected to high strain, leading to crazes.

Rheology

Complex viscosities at 240°C and viscosity-composition curves of the blends are shown in Figures 8 and 9. With the addition of small amounts of SMA to nylon, viscosities at low frequencies increase approximately seven times in 2.5SMA and over one order of magnitude in 5SMA compared with that of nylon. Two of the above blends show a Newtonian

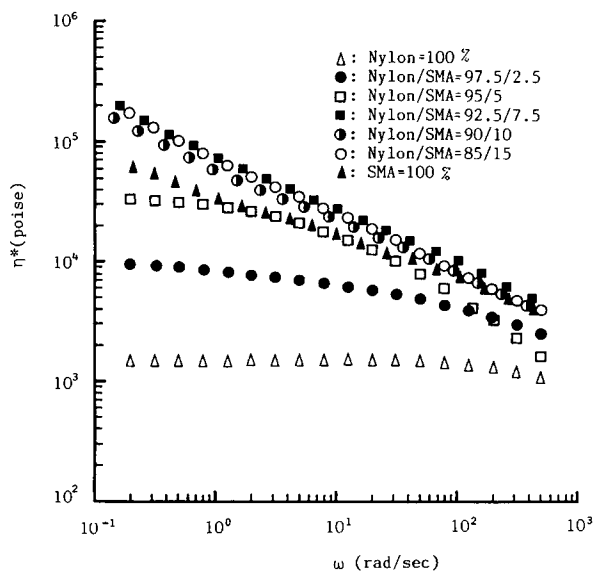


Figure 8 Complex viscosities of the blends at 240°C.

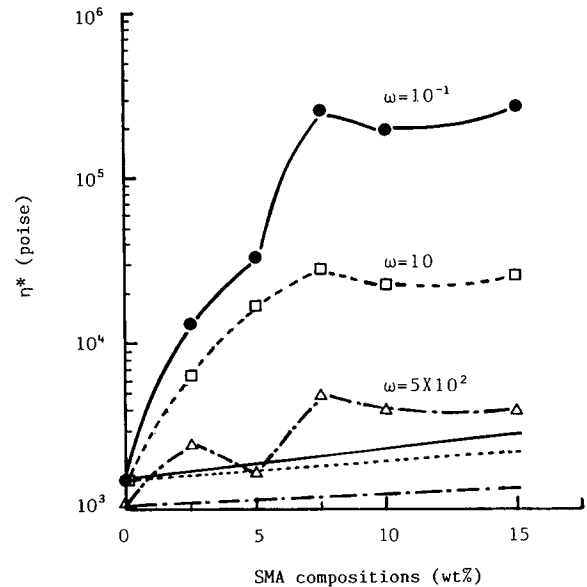


Figure 9 Viscosity vs. composition of the blends.

plateau. Onset frequency of shear thinning viscosity moves toward the lower frequency with SMA addition. Further addition of SMA to nylon eventually induces viscosity yield in 10SMA and 15SMA. The viscosity-composition curves of the blends show positive deviation from the simple additive rule (dotted line in Fig. 9). Positive deviation of viscosity is often observed when there are strong interactions between droplets or when the two component polymers are intimately mixed, leading to interlocked morphology.¹⁵⁻¹⁷ In incompatible blends, viscosity yield is observed when the associated structure has long relaxation times.¹⁷⁻²⁰ In fact, the larger the

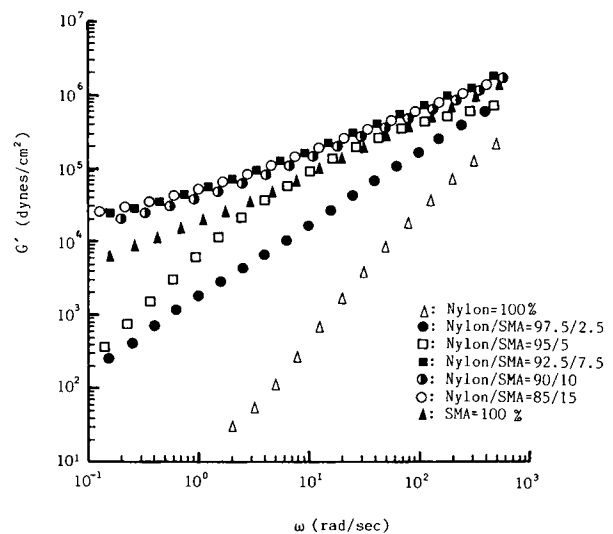


Figure 10 Storage modulus of the blends at 240°C.

droplets and the greater their concentration, the larger the apparent yield stress. However, as our SEM micrographs indicate, the blends do not show clean-phase separation or particle-in-matrix structure. Therefore, positive deviation in viscosity with yield behavior should come from the chemical reactions between the components.¹⁵ With interfacial chemical reactions, blend viscosity should increase over the additive line, and as a matter of fact, this has been verified in a number of systems. In line with this, chemical reaction between the maleic anhydride group attached to the polyolefin backbone with the amide group has been reported.⁹⁻¹¹ The reaction is likely to occur with amide linkages in the nylon backbone, but more likely, however, with free amide end groups, as suggested by others, and by our T_m measurement, described earlier.

Storage modulus (G'), loss modulus (G''), and $\tan \delta$ as a function of ω are given in Figures 10–12, respectively. G' is the elastic energy stored in a cyclic deformation and often interpreted as the melt elasticity.²¹ As expected, the melt elasticity of the blends are significantly higher than that of nylon, and G' for 7.5SMA, 10SMA, and 15SMA is even higher than that of SMA. The enhancement of elasticity of nylon upon blending with SMA should come mainly from the chemical reactions and make the melt processings, like blowing, more feasible.

CONCLUSIONS

Melt blends of nylon with SMA have been studied from morphological, thermal, mechanical, and

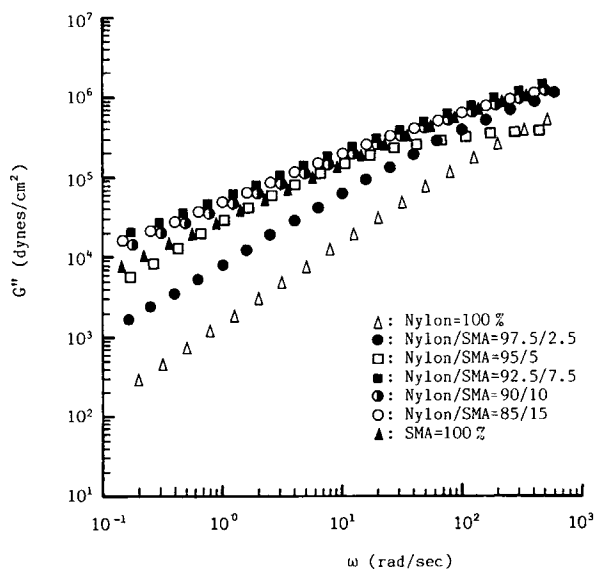


Figure 11 Loss modulus of the blends at 240°C.

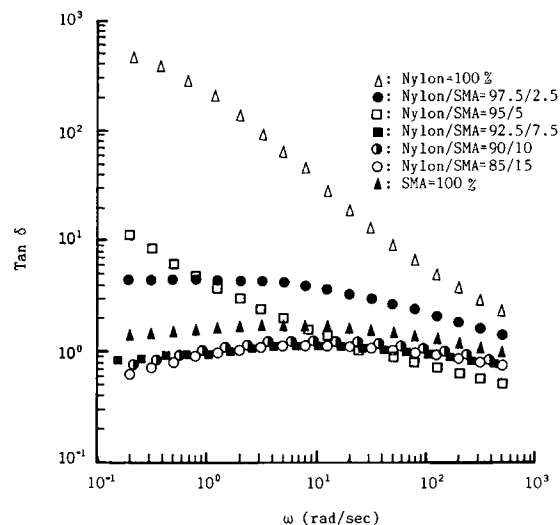


Figure 12 $\tan \delta$ of the blends at 240°C.

rheological points of view. SEM micrographs of the cryogenically fractured surfaces of the blends showed no clean-phase separation. The heat-distortion temperature of nylon was significantly increased with SMA addition. Heat of crystallization and heat of fusion measurements indicated that the rigid SMA provides nylon with nucleating sites at low concentrations and gives a dilution effect at high concentrations. Tensile strength of the blends showed a sharp minimum in 2.5SMA, where a sharp maximum of impact strength was observed. This phenomenon is in close analogy with hybrid composites and fiber-reinforced composites. Melt viscosities of the blends showed a drastic increase over the simple additive rule with viscosity yield at high SMA contents. This is an indication of chemical reactions between nylon and SMA, attested by our FTIR measurement.

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