# Physical properties of ABS/SMA/nylon-6 ternary blends: effect of blending sequence

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The effect of a blending sequence in acrylonitrile-butadiene-styrene terpolymer(ABS)/nylon-6 blend modified by poly(styrene-*co*-maleic anhydride) (SMA) on the dynamic mechanical and rheological properties, and morphology was studied. When nylon-6 was blended with the preblended ABS/SMA(90/10) blend, the SMA-*g*-nylon-6 formed during the blending process seemed to lie at the interfacial region and act as an effective compatibilizer. However, when ABS was blended with the preblended SMA/nylon-6(10/90) blend, the SMA-*g*-nylon-6 formed during the preblending process seemed to lie preferentially at the nylon-6 domain and improve the thermal resistance and modulus of the nylon-6 rich domain.

**(Keywords: physical properties; ternary blends; blending sequence)**

## INTRODUCTION

The need to broaden the performance spectrum of plastics has stimulated much interest in blending different types of polymers to obtain materials having a balanced combination of specific properties[1-3]. Most polymer pairs are thermodynamically immiscible, and, depending on composition, the viscosity and elasticity ratio of the components, the interfacial tension, and compounding conditions, completely different types of morphology, mechanical and rheological properties were observed[4-6].

The compatibilizers, which act as interfacial agents to reduce the interfacial tension and promote the adhesion at the interface, are commonly used to improve some properties of polymer blends[7-9]. Block or graft copolymers, generally known to be effective compatibilizers, can be preformed and added separately or be formed *in situ* by a reaction between co-reactive functional groups in the polymer or additive during the melt blending process[10-12].

Maleic anhydride (MAH) can react with the terminal amide group of nylons, so the polymers containing the MAH group can effectively be used in the reactive compatibilization process of nylons[13-15]. Poly(styrene-*co*-maleic anhydride) (SMA) can be used as a compatibilizer in the blends of acrylonitrile-butadiene-styrene terpolymer (ABS), because SMA can be mixed in the molecular level with the poly(styrene-*co*-acrylonitrile) (SAN) matrix of ABS when the maleic anhydride (MA) and acrylonitrile (AN) contents do not greatly differ, and there exist some favourable intermolecular interactions even at the outsides of the miscibility window[16-18].

Nylon-6 is a crystalline polymer with high melting temperature ($T_m = 220°C$)[19] and good solvent resistance, but it has defects of dimensional growth due to moisture absorption and a gradual decrease of modulus above the glass transition temperature ($T_g = 45°C$)[20]. ABS has a SAN matrix of relatively high $T_g (= 110 \sim 120°C)$[21] but has poor solvent resistance and shows drastic deterioration of physical properties above $T_g$ because SAN is an amorphous polymer. Ideally, the ABS/nylon-6 blend should combine the merits of component polymers, i.e. a good solvent resistance, retain of modulus at the temperature range between the $T_g$ of SAN and that of nylon-6, have low moisture absorption, etc. In ABS/SMA/nylon-6 ternary blends, the blending sequence should take an important role in determining the blend properties, as in other reactive compatibilization processes[22].

In this study, we examined and discussed the dynamic mechanical, rheological, and morphological properties of the ternary blend of ABS/SMA/nylon-6 with an emphasis on the sequence of blending. One type of ternary blend was prepared by first blending SMA and nylon-6 (10/90 by weight), followed by adding ABS (hereafter called ABS/(SMA/nylon-6) blends). The other type was prepared by adding nylon-6 to the ABS/SMA (90/10 by weight) preblends ((ABS/SMA)/nylon-6). In addition, ABS/nylon-6 blends were also prepared.

## EXPERIMENTAL

ABS resins were kindly donated by Hyosung BASF: rubber content 10 wt% with a bimodal size distribution of rubber particles, and the matrix SAN contained 35 wt% AN. Nylon-6 was the product of Tongyang

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Nylon, with a number average molecular weight of 17 500. The SMA used was Arco Dylark (232) with MA content 8 wt%. Resins were dried under vacuum in appropriate conditions. Blends were prepared using a Brabender Plasticorder, with $L/D=30$, at 220~240°C.

Dynamic mechanical properties of the blends were measured using a Rheovibron (Toyo Baldwin DD V-II). Films were compression moulded at 230°C, with a thickness around 0.3 mm. Measurements were carried out from 10°C to 170°C at 110 Hz, and at 5°C min$^{-1}$.

The morphology of the blends was observed by SEM (Jeol, JSM-35CF) from a fractured (in liquid nitrogen) surface of the extrudate, perpendicular to the extrusion direction.

The melt rheologies of the blends were measured using a RDS (Rheometrics Dynamic Spectrometer, 7700) at 230°C with 10% strain.

## RESULTS AND DISCUSSION

### *Dynamic mechanical properties*

ABS and nylon-6 have damping peaks at 113°C and 25°C, respectively (*Figure 1a*). In ABS/nylon-6 blends, the damping peak of ABS moves towards that of nylon-6 as the content of nylon-6 in the blend increases. This shows the partial dissolution of nylon-6 molecules into the ABS domain.

The nylon-6/SMA blend obtained by reactive pre-blending process[23] shows two damping peaks at 55°C and 127°C (*Figure 1b*), probably corresponding to nylon-6 rich and SMA-rich domains, respectively. The damping peak of a nylon-6 rich domain appeared at a higher temperature than that of pure nylon-6, which indicates that some SMA segments are dissolved in the nylon-6 rich domain, whereas an unmoved damping peak of SMA suggests that the SMA-rich domain is almost pure.

In ABS/(SMA/nylon-6) blends, the damping peak of the nylon-6 rich domain moves toward that of ABS as the content of ABS in the blend increases. But, the downward migration of the ABS damping peak with the increasing content of nylon-6 is not noticeable. This suggests that the dissolution of ABS molecules into the nylon-6 domain is preferred over the reverse direction in the ABS/(SMA/nylon-6) blend. In (ABS/SMA)/nylon-6 blends (*Figure 1c*), the damping peaks of the ABS/SMA blend and nylon-6 come closer, probably due to the mutual dissolution. In these experiments, SMA is not miscible with ABS in a molecular level because the MA content in SMA and the AN content in the SAN matrix differ greatly[17]. So, during the melt blending process, SMA molecules may react with nylon-6 and move toward the interface or nylon-6 rich domain[22]. SMA-*g*-nylon-6 interposed at the interface will act as an effective compatibilizer, and this may be the cause of the inward migration of damping peaks. The damping peaks are broadened in the blend, and this can be ascribed to the increased interfacial region, probably due to the presence of a SMA-*g*-nylon-6 molecular layer at the interface[24,25].

The tensile storage moduli ($E'$) of ABS/nylon-6 blends at 30°C and 50°C show little scatter from simple additive lines (*Figure 2a*), with a certain level of mechanical compatibility shown between the two polymers[19,26,27]. But at 100°C, namely above the $T_g$ of nylon-6, data show a negative deviation at nylon-6 rich compositions. This seems to be due to the decreased modulus of the nylon-6

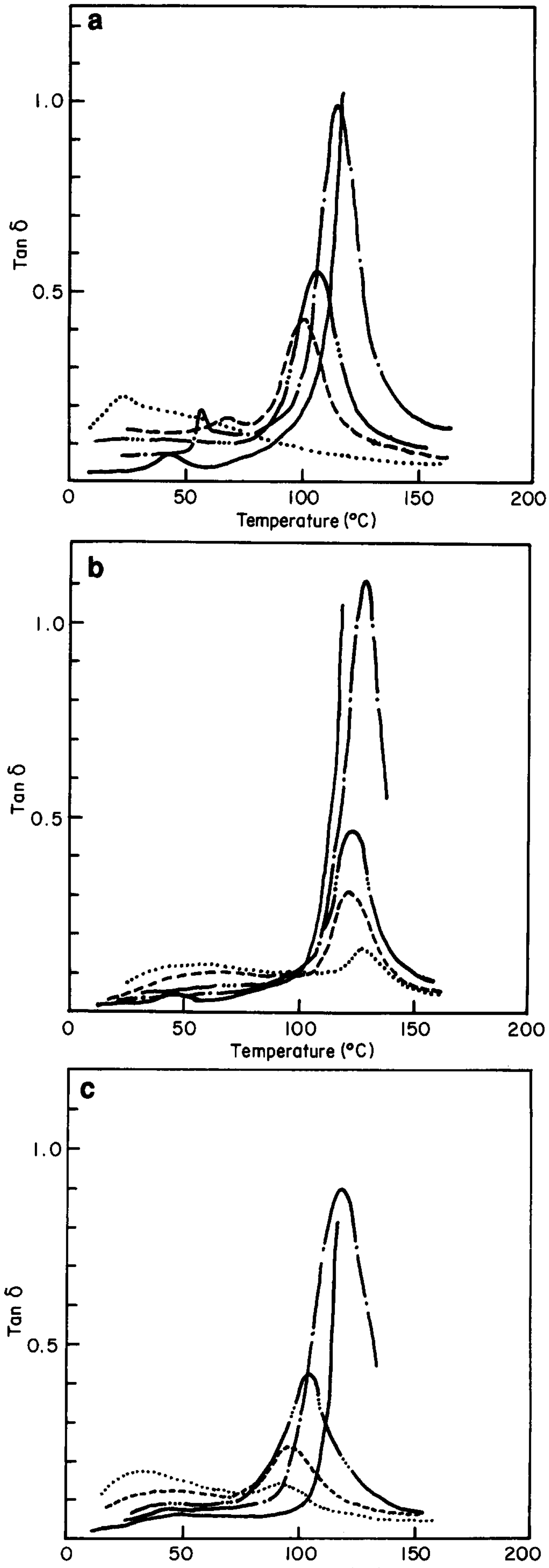

**Figure 1** Tan δ of (a) ABS/Nylon-6; (b) ABS/(SMA/Nylon-6); and (c) (ABS/SMA)/Nylon-6 blends: 100/0 (——), 70/30 (–·–), 50/50 (–···–), 30/70 (– – –), and 0/100 (······) by weight

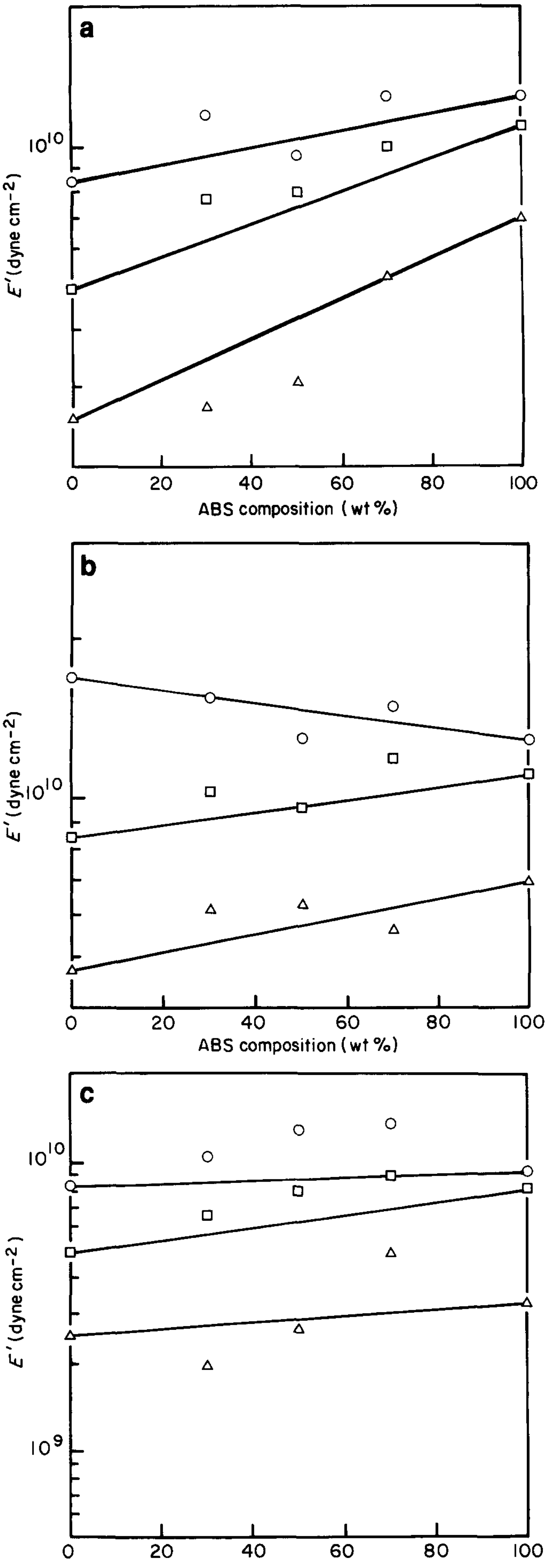

**Figure 2** $E'$ of (a) ABA/Nylon-6; (b) ABS/(SMA/Nylon-6); and (c) (ABS/SMA)/Nylon-6 blends at 30°C (○), 50°C (□), and 100°C (△)

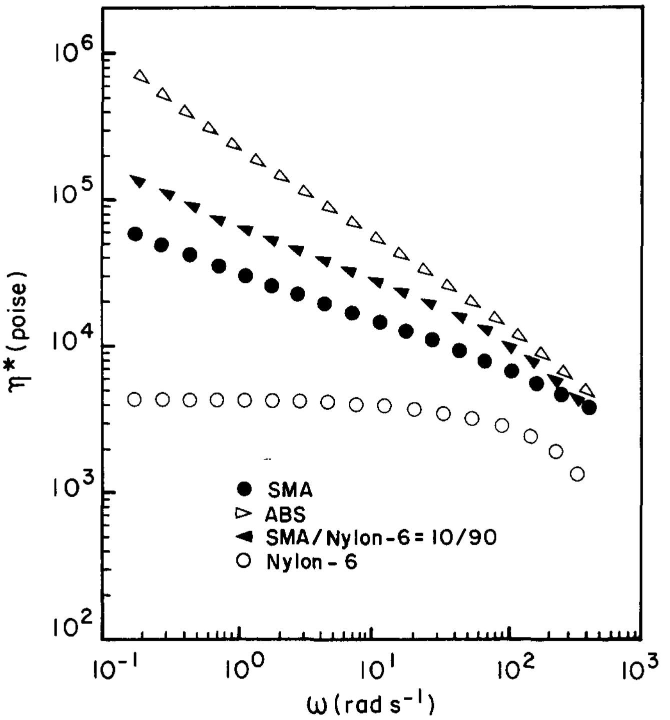

**Figure 3** Complex viscosity *versus* frequency at 230°C

matrix at temperatures above its $T_g$. The $E'$ at 100°C approaches the simple additive value at compositions over 50 wt% ABS, probably indicating a phase inversion at a ABS-rich composition because nylon-6 has a much lower melt viscosity (*Figure 3*)[5,6].

In ABS/(SMA/nylon-6) blends (*Figure 2b*), $E'$s lie near simple additive lines at all temperatures. This shows that the thermal resistance of the nylon-6 rich phase is improved due to the dissolution of SMA segments and ABS molecules as seen in *Figure 1b*[23].

In (ABS/SMA)/nylon-6 blends, the $E'$s at 30°C and 50°C show evident positive deviations from simple additive lines. This shows that the compatibility between the ABS/SAN blend and nylon-6 is better than the one between ABS and nylon-6, or between the SMA/nylon-6 blend and ABS, probably due to the interposal of the SMA-*g*-nylon-6 layer at the interface.

The $E'$s of ABS/(SMA/nylon-6) blends are greater than other blends, and more evidently at nylon-6 rich compositions. This seems to be due to the extension reaction of SMA and nylon-6 at a preblending process, and the consequent dissolution of SMA segments in the nylon-6 rich phase which might act as a crosslinker or filler[23].

### *Morphology*

The morphology of ABS/nylon-6 blends (*Figure 4*) does not significantly vary with composition, and the dominant morphology is apparently a particle-in-matrix structure. However, a sign of domain stratification is also seen in the 50/50 blend. The dispersed domain is smaller in size when nylon-6 forms a dispersed phase than when ABS does. This, among many factors, is due to the large difference in viscosity between the two components. With a higher viscosity of the dispersed phase (ABS), fine break-up would be more difficult[28].

*Figure 5* shows SEM micrographs of ABS/(SMA/nylon-6) blends, and generally better dispersion over the

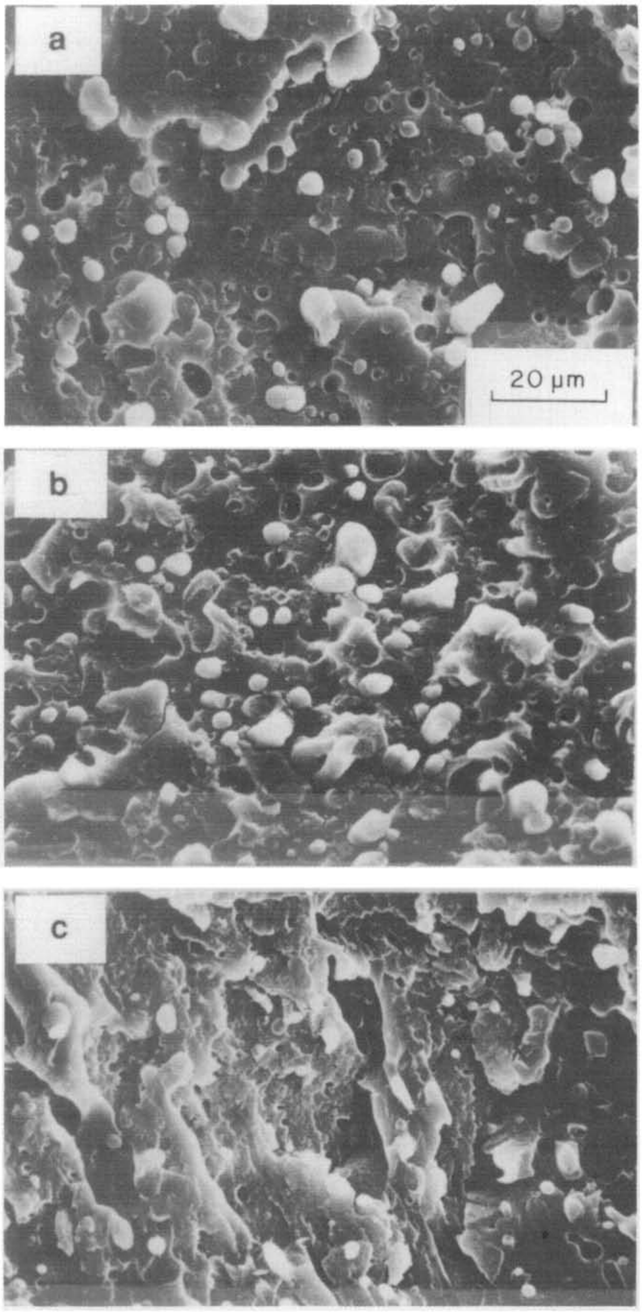

**Figure 4** SEM micrographs of fractured surface of ABS/Nylon-6 blend: (a) 30/70); (b) 50/50; and (c) 70/30 by weight

ABS/nylon-6 blend is observed, especially in the 30/(63/7) blend with high SMA content. This probably comes from the combined effect of the viscosity approach and the compatibilizing effect of SMA-*g*-nylon-6. As mentioned earlier[23], blends of nylon-6 with SMA are subject to a chemical reaction during the melt mixing, which brings the viscosity of the SMA/nylon-6 blend close to ABS (*Figure 3*). With the viscosity ratio of the components close to unity, a fine break-up of the dispersed phase is generally expected[5,28].

The morphology of (ABS/SMA)/nylon-6 blends (*Figure 6*) generally shows better dispersions over the above two blends, with a sign of brittle fracture in (63/7)/30 and (45/5)/50 blends. This seems to be due to the more efficient compatibilizing effect of SMA-*g*-nylon-6 laid at the interface, as previously described.

### *Rheological properties*

In a variety of polymer blends, the use of logarithmic plots of shear storage modulus ($G'$) *versus* loss modulus ($G''$) gives rise to correlations independent of temperature[29,30] and such plots are sometimes useful for distinguishing the rheologically compatible blends from incompatible ones.

*Figure 7a* shows that ABS is more elastic than nylon-6, because $G'$ is the elastic energy stored and $G''$ the energy dissipated in a cyclic deformation.

The elasticity of nylon-6 rises greatly in the SMA/nylon-6(10/90) blend (*Figure 7b*), presumably due to the reaction yielding SMA-*g*-nylon-6 during blending. In both ABS/nylon-6 and ABS/(SMA/nylon-6) blends, the melt elasticities of the blends vary regularly with blend composition, suggesting the rheological compatibility

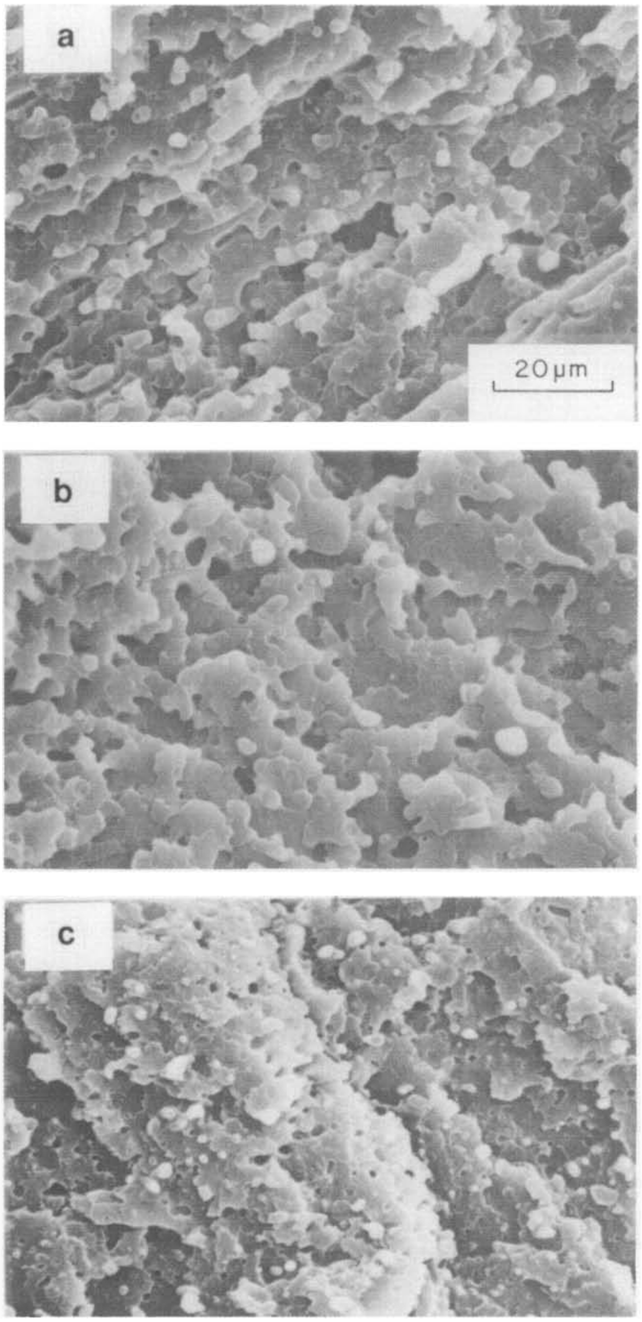

**Figure 5** SEM micrographs of fractured surface of ABS/(SMA/Nylon-6) blend: (a) 30/70; (b) 50/50; and (c) 70/30 by weight

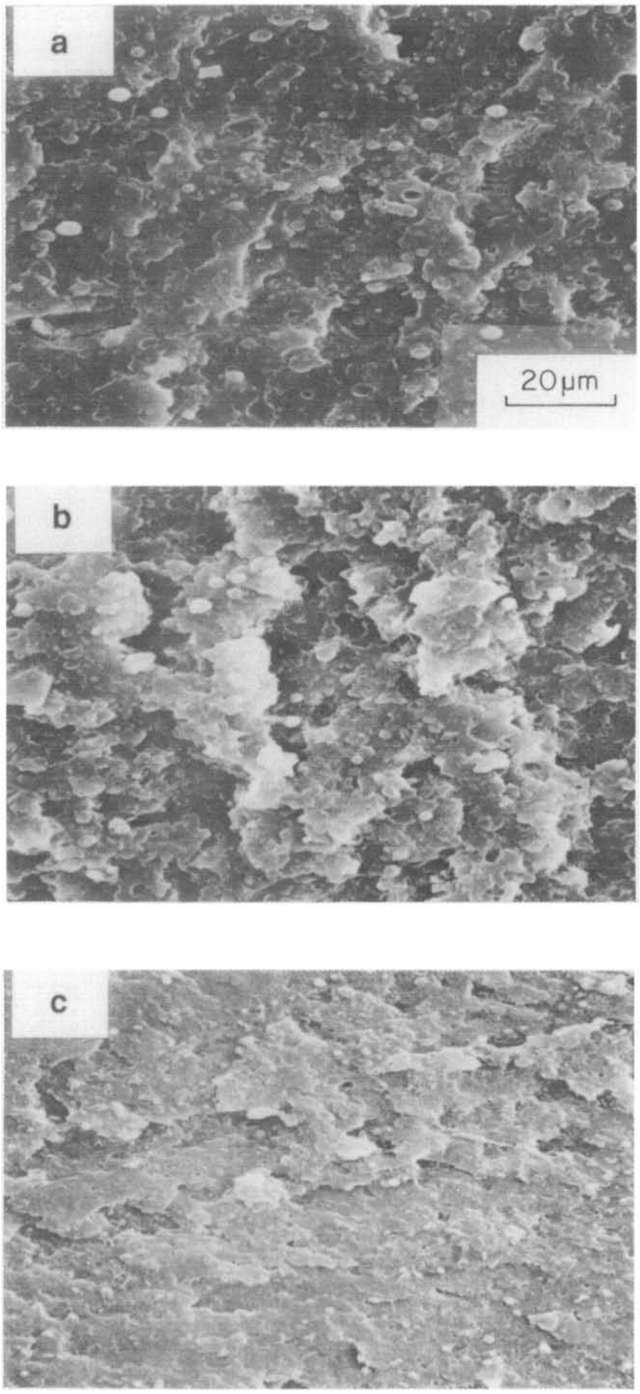

**Figure 6** SEM micrographs of fractured surface of (ABS/SMA)/Nylon-6 blend: (a) 30/70; (b) 50/50; and (c) 70/30 by weight

between ABS and nylon-6, or the SMA/nylon-6 blend and ABS.

However, in (ABS/SMA)/nylon-6 blends (*Figure 7c*), the increase of elasticity by the added ABS/SMA blend over that of nylon-6 is more evident at nylon-6 rich compositions. This also demonstrates the reaction between SMA and nylon-6 during the process of blending.

In phase-separated polymer blends, a negative deviation of the viscosity from the log additive rule is observed when there exists interlayer slip due to poor interfacial adhesion. But positive deviation in viscosity generally occurs when the surface tension between the dispersed particle and matrix is small to give a long relaxation time of associated structure created by the interacting droplets of the dispersed phase[31,32]. Therefore, the positive deviation of viscosity (*Figure 8*) would suggest good adhesion at the interfaces between ABS and nylon-6, or the SMA/nylon-6 blend and ABS. The (ABS/SMA)/nylon-6 blend shows the most evident positive deviation. This should mainly be due to the chemical structure change occurring during blending, but the effective compatibilizing effect of SMA-*g*-nylon-6 laid at the interface should also be accounted for.

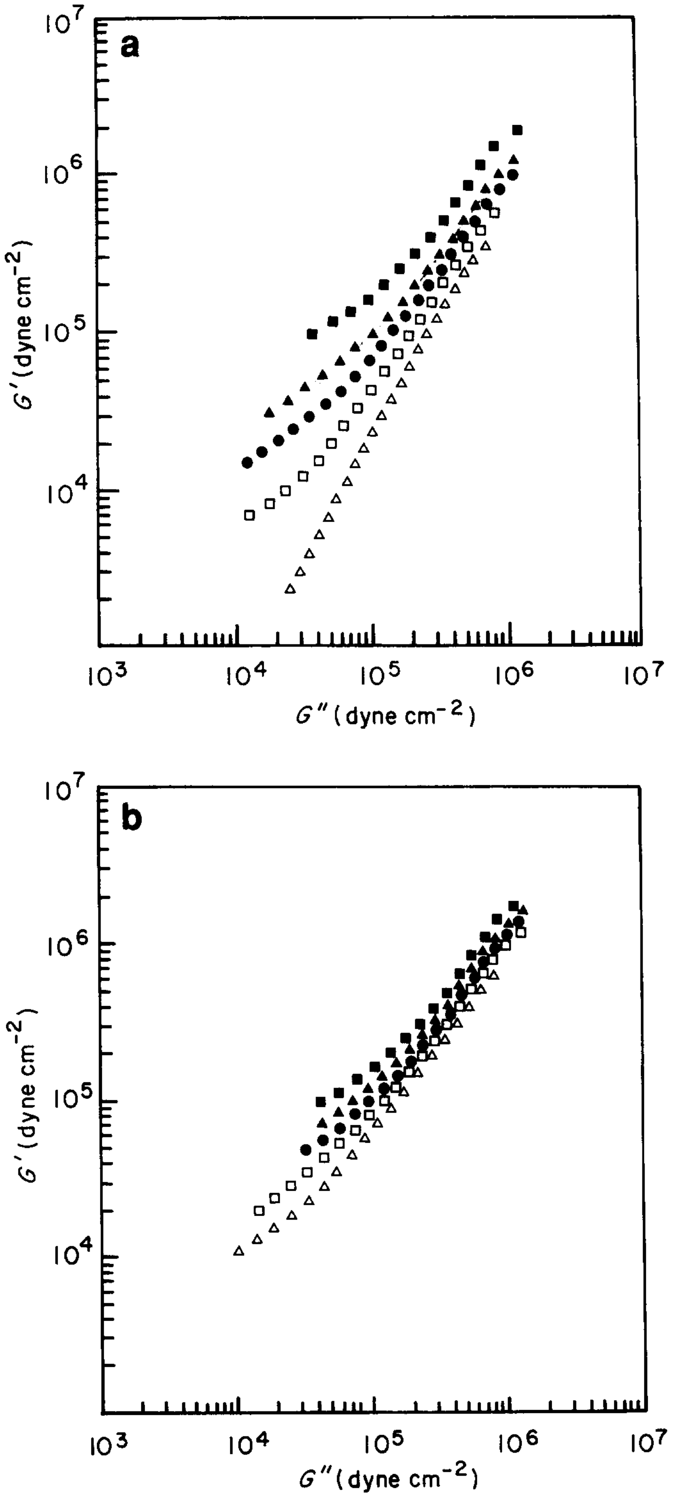

**Figure 7** $G'$ *versus* $G''$ for (a) ABS/Nylon-6; (b) ABS/(SMA/Nylon-6), and (c) (ABS/SMA)/Nylon-6 blends: 100/0 (■), 70/30 (▲), 50/50 (●), 30/70 (□), and 0/100 (△) by weight

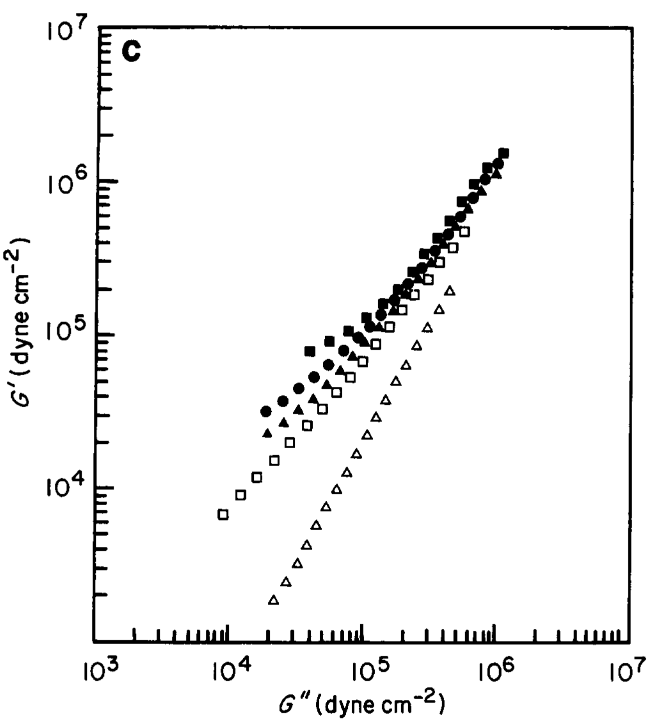

**Figure 7** *continued*

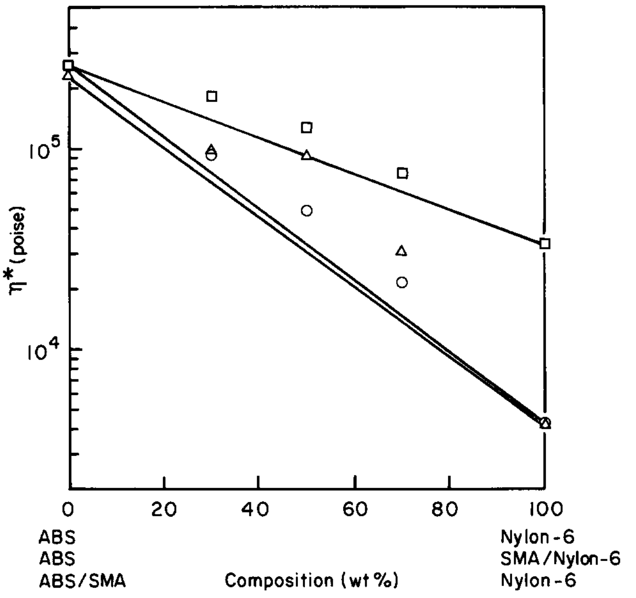

**Figure 8** Complex viscosity *versus* composition for ABS/Nylon-6 (○), ABS/(SMA/Nylon-6) (□), and (ABS/SMA)/Nylon-6 (△) blends at $\omega = 7.493 \times 10^{-1}$ rad s$^{-1}$

## CONCLUSIONS

The ABS/nylon-6 blends modified by SMA showed quite different dynamic mechanical and rheological properties, and morphology depending on the blending sequence. In (ABS/SMA)/nylon-6 blends, SMA-*g*-nylon-6 formed during the reactive blending of the ABS/SMA blend with nylon-6 seems to lie at the interface and works as an effective compatibilizer. However, in ABS/(SMA/nylon-6) blends, the SMA-*g*-nylon-6 formed during the preblending of SMA and nylon-6 seems to lie preferentially in the nylon-6 domain, and improve the thermal resistance and modulus of the nylon-6 rich domain.

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