

# Melt Blends of SAN with SAN-graft-Polybutadiene (PB)

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## SYNOPSIS

Melt blends of SAN with SAN-graft-polybutadiene (PB) (*g*-ABS) were prepared in a Brabender plasticorder. The effect of *g*-ABS on the morphology and mechanical and viscoelastic properties of the blends was studied up to 60 wt % *g*-ABS. The brittle-tough (BT) transition occurred around 20 wt % *g*-ABS, and the viscosity increased monotonically with *g*-ABS, showing yield behavior at  $\geq 20\%$ . The lower and higher glass transition temperatures ( $T_g$ ) of *g*-ABS, each corresponding to the  $T_g$  of PB and grafted SAN, decreased and increased with the addition of free SAN, and this was interpreted in terms of *graft* SAN-PB phase separation. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

It is of practical importance to improve the toughness of brittle polymers by adding a rubber phase. Typical of such examples include rubber-modified polypropylene,<sup>1-4</sup> nylon,<sup>5-8</sup> styrene-acrylonitrile copolymer (SAN),<sup>9,10</sup> and poly(methyl methacrylate).<sup>9</sup> In these systems, the degree of toughness improvement, or brittle-tough (BT) transition, is governed by a number of factors, such as the type, size, and concentration of the rubber and the level of adhesion between rubber and matrix.<sup>11,12</sup> According to Wu,<sup>5</sup> the BT transition in nylon-rubber is determined solely by interparticle distance, independent of rubber volume fraction and particle size. For toughening, the interparticle distance must be smaller than the critical value, the value determined by the matrix. Wu's model was later verified by Borggreve et al.,<sup>6</sup> and the model seems generally valid for ductile as well as for brittle matrix, as long as the interfacial adhesion is constant.

Rubber-toughened SAN is a most successful thermoplastic. With butadiene rubber, the blend is called ABS (acrylonitrile-butadiene-styrene).

Commercially available ABS resin is manufactured mainly by graft polymerization of acrylonitrile and styrene onto polybutadiene (PB), followed by blending with free SAN.<sup>13</sup> Therefore, ABS may be regarded as a multiphase blend where *g*-ABS forms a dispersed domain in the SAN matrix, and it finds extensive industrial applications where toughness and surface gloss are required properties.<sup>13,14</sup>

When the literature concerning the effect of rubber particles on ABS properties are summed up, little was evolved in the past in spite of their practical significance. Bucknall,<sup>11</sup> Baer,<sup>15</sup> and Parsons and Suck<sup>16</sup> reported that the toughness increased with increasing particle size; however, an optimum particle size of 0.1–1  $\mu\text{m}$  was also reported by other investigators.<sup>11,17,18</sup> The disagreement is probably due to the uncontrolled interfacial adhesion.<sup>5</sup> Recently, Paul et al.<sup>10</sup> reported a synergistic toughening effect by using two types of rubber that differ in size and composition. With regard to the melt properties of rubber-modified SAN, several useful reports are available<sup>19-21</sup>; however, these are confined mainly to capillary measurement.

In this work, we have studied the effect of rubber concentration on ABS properties. Up to 60 wt % of SAN-*g*-PB (*g*-ABS) was added to SAN, and the subsequent effect on morphology and melt, mechanical, and viscoelastic properties as well as the *graft* SAN-PB phase separation in *g*-ABS were examined.

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## EXPERIMENTAL

### Base Resins and Compounding

SAN and *g*-ABS used in the experiments were donated by Hyosung BASF. The degree of grafting, defined as [styrene (St) + acrylonitrile (AN)] grafted onto PB/(St + AN + PB), was 34 wt %, and the overall composition of *g*-ABS was 66(PB):24(St):10(AN) by weight. SAN matrix (MW = 80,000) contained 35% AN.

Base resins were dried in vacuum at 80°C for 24 h. Dried resins were mixed in a Brabender plastimeter with a temperature profile of 212–218°C, followed by quenching in water and pelletizing. Pelletized chips were compression-molded at 230°C, 200 kg/cm<sup>2</sup>, to prepare the specimen for tests.

### Tests

The morphology of the blends was studied using a transmission electron microscope (TEM, Hitachi H300). Samples were stained with OsO<sub>4</sub> for 1 week before viewing.

Viscoelastic properties of the blends were measured using a Rheometrics Dynamic Spectrometer (RDS, Type II) rheometer. For melt property measurement, a cone-and-plate fixture with disk specimens was used. The frequency sweep was done at 220°C with a 10% strain, which is the upper limit where the linear viscoelastic behavior was maintained. Temperature sweep measurements from –150 to 150°C were made using a stick bar sample, at a condition of 2°C/min, 0.2% (strain), and 6.28 rad/s.

Tensile properties were measured using an Instron tensile tester, following the standard procedures described in ASTM(D-638) at a crosshead speed of 5 mm/min. Impact strength was determined using a notched  $\frac{1}{8}$  in. specimen. The above test was made at room temperature. At least five runs were made to report the average.

## RESULTS AND DISCUSSION

### Morphology

TEM micrographs of the microtomed thin section of the compression-molded specimen show the bimodal distribution of the rubber particles, with the larger ones about 2500 Å and the smaller ones about 500 Å in diameter [Fig. 1(a) and (b)]. The spatial distributions are fairly uniform; however, there are particle aggregations, especially with larger ones.

### Mechanical Properties

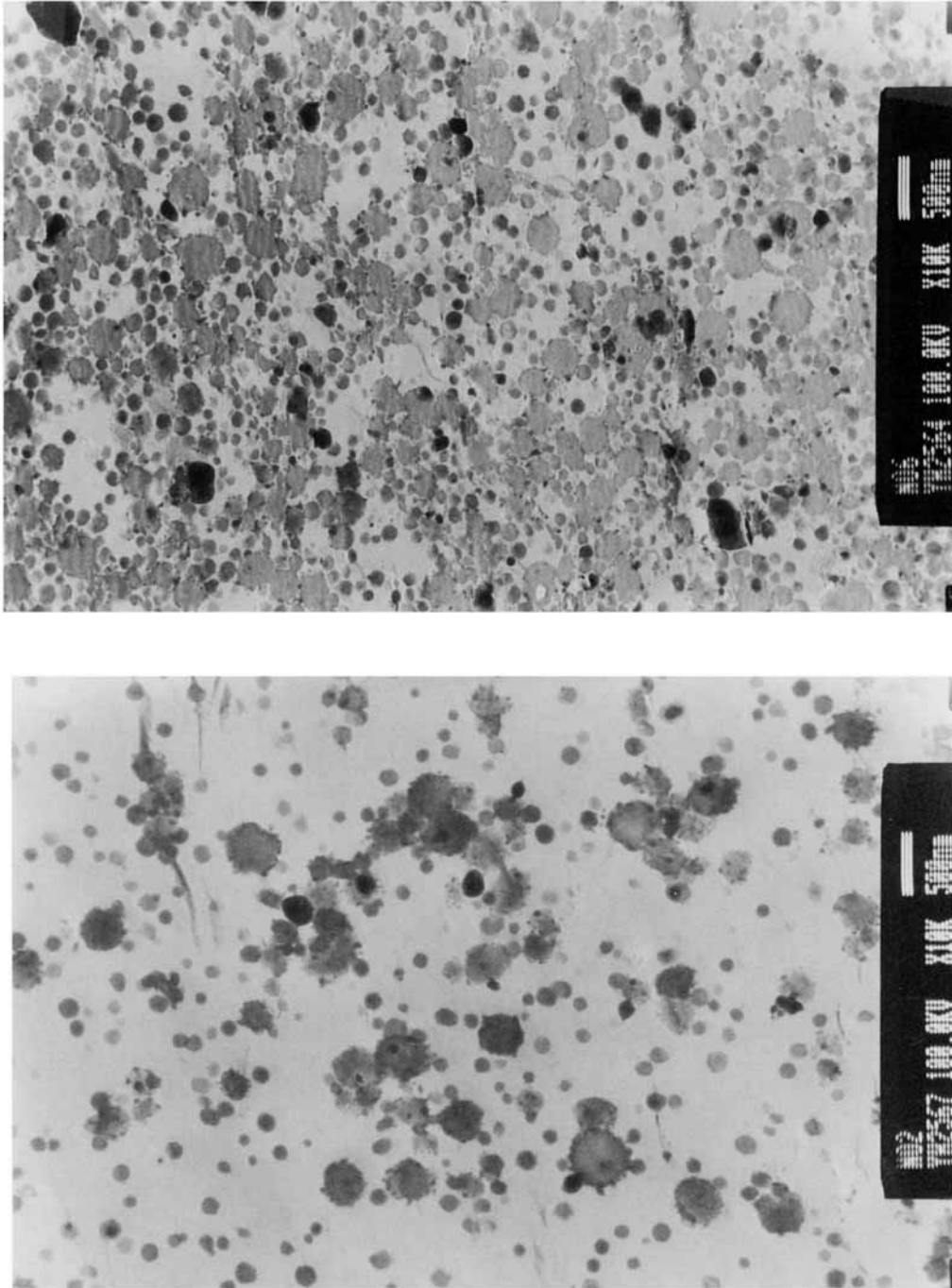
Impact strength of the blends as a function of rubber content is shown in Figure 2, where a BT transition is found at about 20 wt % rubber. The impact strength at 30% rubber (assumed ductile) is 28 kg cm/cm, and it is approximately 15 times greater than that of SAN. The BT transition extends relatively wide compositions, due probably to the bimodal distribution of the rubber particles.<sup>10</sup>

Figure 3 shows the tensile modulus of the blends. The tensile modulus decreases almost linearly with rubber content, indicative of the good dispersion of rubber without the inclusion of SAN in rubber domains.<sup>6</sup> One of the functions of rubber domains is to create stress concentrations, forcing the material to yield at lower applied stress.<sup>6</sup> Figure 4 shows yield and break strength of the blends. The yield strength is kept at about the matrix level up to 20 wt % rubber and decreases beyond the concentration. The break strength of SAN is slightly higher than the yield strength. Upon blending with rubber, break strength significantly decreases below that of the yield.

The elongations at yield and break are shown in Figure 5. The scatter of data at break is probably due to the immiscible nature of the blends. The elongation at yield is slightly increased in blends and that of break up to about four times that of SAN at 60% rubber content. This suggests that the toughening involved in the blends is a purely post-yield behavior, as noted in dual rubber-modified SAN.<sup>10,11</sup>

### Viscoelastic Properties

Figures 6 and 7 show the storage modulus ( $G'$ ) and  $\tan \delta$  of the blends with varying rubber content. It is seen that *g*-ABS shows two loss peaks at –79.4 and 117°C, each representing the glass transition temperature ( $T_g$ ) of PB and grafted SAN segment. It is of interest to note that the lower  $T_g$  moves toward the lower temperature by several degrees as the rubber content decreases, whereas the higher  $T_g$  in blends is higher than that of *g*-ABS alone. This should be an indication of *graft* SAN–PB phase separation<sup>1,22</sup> with the addition of free SAN. Though *graft* polymer/free polymer blends are not always miscible,<sup>23,24</sup> it seems that the *graft* SAN component in *g*-ABS is miscible with free SAN.<sup>10</sup> With the increase of free SAN, the phase separation of *g*-ABS into PB and *graft* SAN becomes clear. It is conceivable that the *graft* SAN forming the outer layer of *g*-ABS improves adhesion with matrix SAN. The sign of *graft* SAN–PB phase separation in blends is



(a)

(b)

**Figure 1** TEM micrographs of the compression-molded specimens: (a) 10 and (b) 50 wt % *g*-ABS.

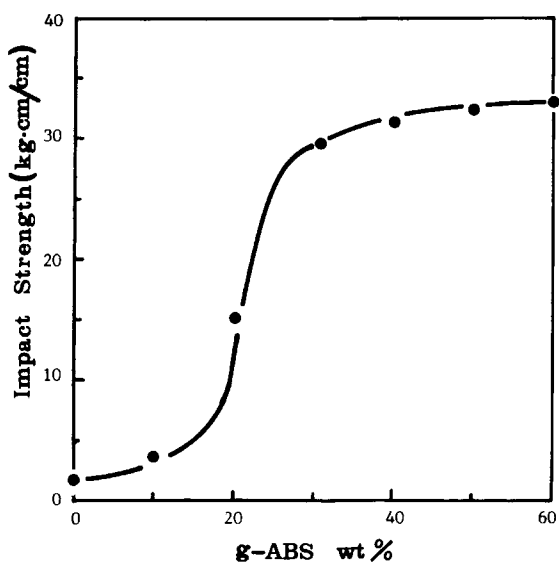


Figure 2 Notched Izod impact strength vs. composition.

also noted from the narrowed temperature range of PB transition. The above finding is in line with the soft-hard phase separation of polyurethane (PU), observed by Rutkowska and Eisenberg.<sup>25</sup> These authors blended PU (not phase separated) with sulfonated PS and found blends of sulfonated PS with the hard segment in one phase with the exclusion of soft segment into a separate phase. The result was to lower the soft-segment  $T_g$  and increase the hard-segment  $T_g$ . In blends or segmented polymers, the  $T_g$ 's of the two components approach each other

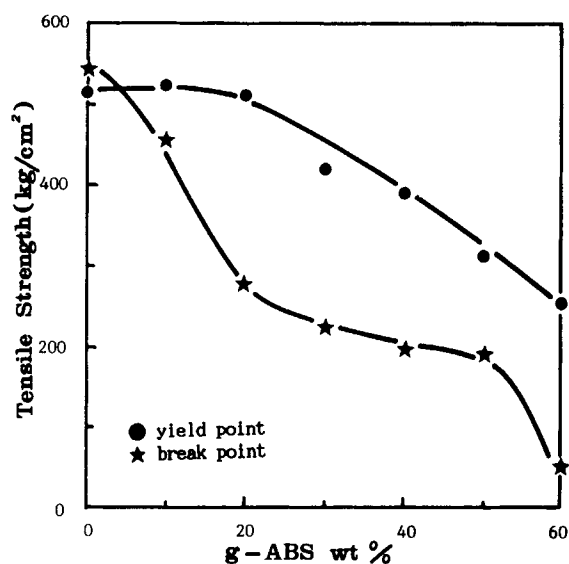


Figure 4 Tensile strength vs. composition.

when there are specific interactions between them.<sup>22</sup> The *graft* SAN and PB in *g*-ABS is believed to interact with van der Waals force. With the addition of free SAN, the  $T_g$  of PB is lowered in proportion to the amount of free SAN added. However, the  $T_g$  of SAN is increased in blends, but not in a regular fashion, due probably to the small concentration of *graft* SAN in *g*-ABS. Similar phenomenon is often observed in segmented PU,<sup>26,27</sup> where PUs containing less than about 40% hard domain do not show hard-domain  $T_g$ .

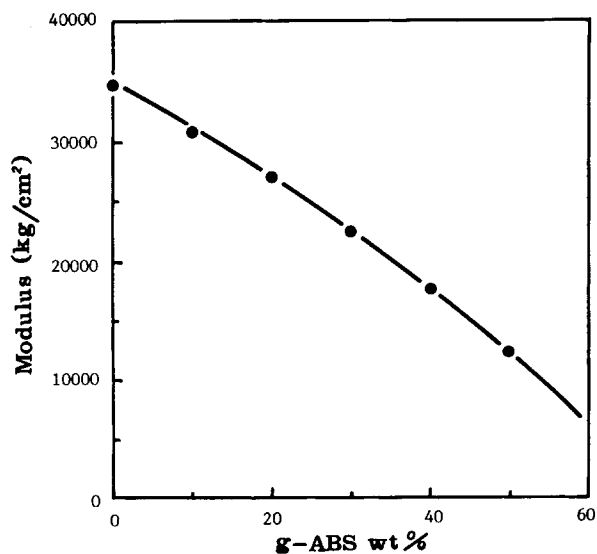


Figure 3 Initial modulus vs. composition.

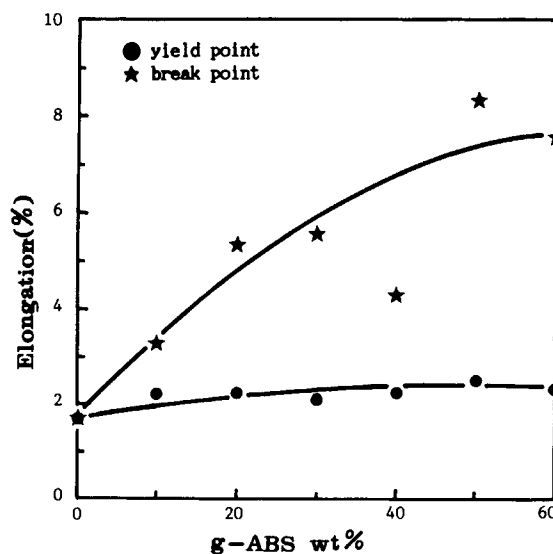


Figure 5 Elongation vs. composition.

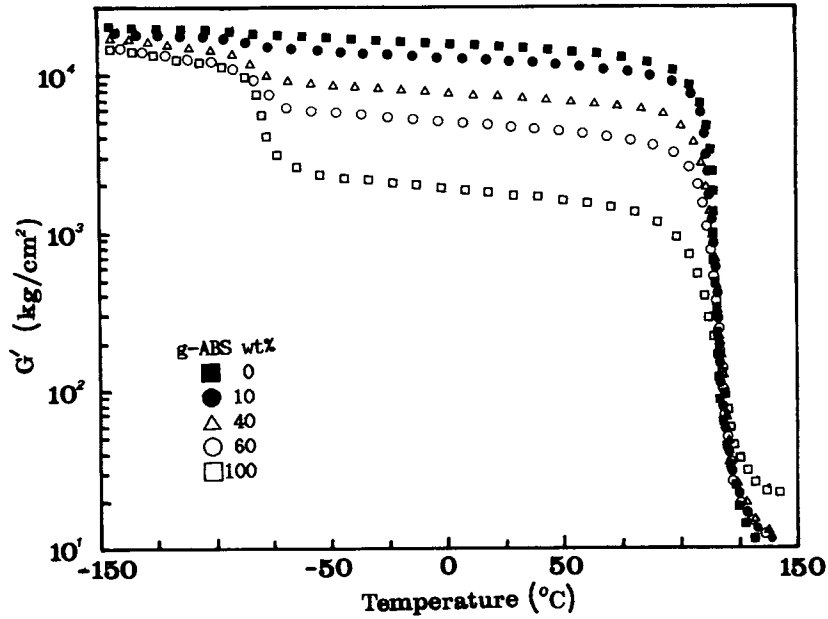


Figure 6 Storage modulus vs. temperature.

It is of interest to see how the tensile fracture occurs with rubber inclusion from the measured values of tensile ( $E$ ) and shear ( $G'$ ) modulus, which are related by

$$G = \frac{E}{2(1 + \nu)} \quad (1)$$

where  $\nu$  is the Poisson's ratio. For infinitesimal volume change, volumetric strain may be defined as<sup>28</sup>

$$\Delta = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \quad (2)$$

where  $\epsilon_{ii}$  is the normal strain.

For simple extension in the X direction,

$$\epsilon_{yy} = \epsilon_{zz} = -\nu\epsilon_{xx} \quad (3)$$

and, hence,

$$\Delta = (1 - 2\nu)\epsilon_{xx} \quad (4)$$

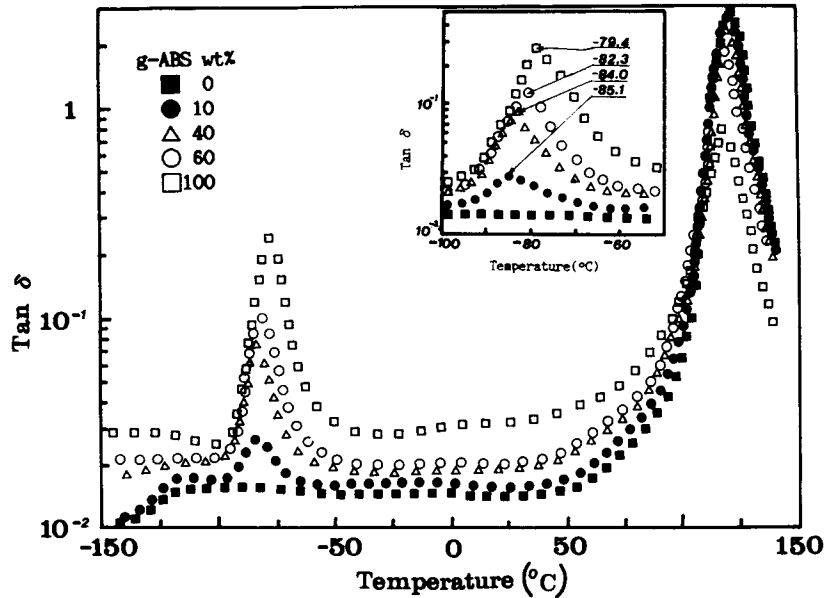


Figure 7 Loss tangent vs. temperature.

**Table I** Modulus and Poisson's Ratio at 20°C

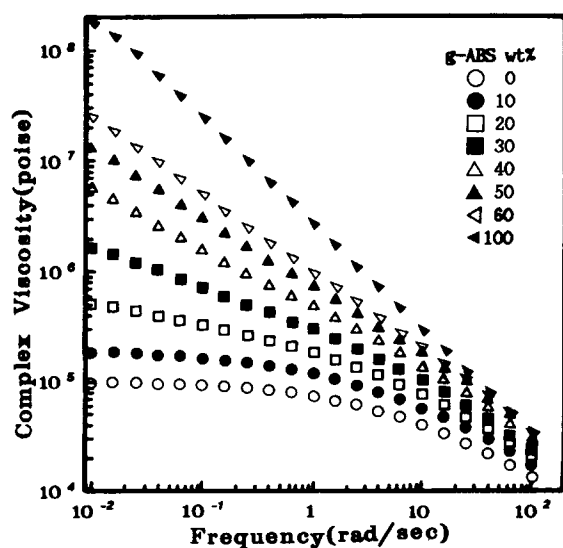
<i>g</i> -ABS (wt %)	Storage Modulus ( <i>G'</i> ) (kg/cm <sup>2</sup> )	Young's Modulus ( <i>E</i> ) (kg/cm <sup>2</sup> )	Poisson's Ratio ( $\nu$ )	(1 - 2 $\nu$ )
0	$1.25 \times 10^4$	$3.5 \times 10^4$	0.400	0.200
10	$1.20 \times 10^4$	$3.2 \times 10^4$	0.333	0.334
40	$7.01 \times 10^3$	$1.7 \times 10^4$	0.212	0.576
60	$4.50 \times 10^3$	$1.0 \times 10^4$	0.111	0.778
100	$1.71 \times 10^3$			

Using the tensile (Fig. 3) and shear modulus (Fig. 6) data, the Poisson's ratio was calculated (Table I). From the table, it is seen that  $\Delta$  should be positive and that it increases with the increase of *g*-ABS in blends. A positive value indicates an increase in volume during tensile straining,<sup>28</sup> which implies that the fracture is due mainly to the craze formation, rather than to the shear yielding. With more rubber inclusion, craze formation, due to the stress concentration around the rubber particle, requires a more significant mechanism of fracture.

### Melt Properties

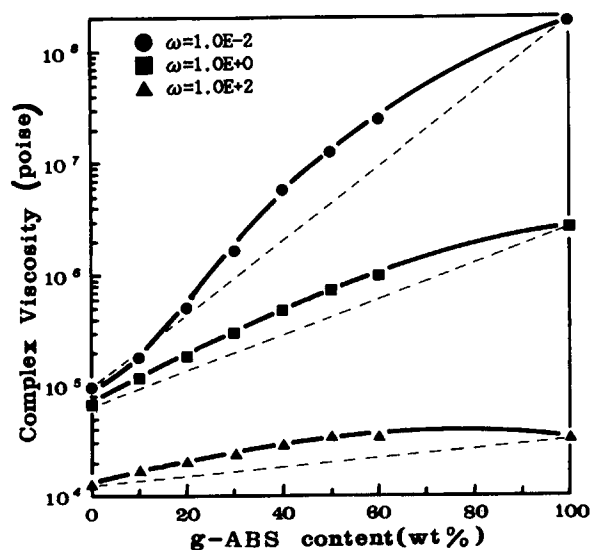
The melt properties of rubber-filled thermoplastics are important since the modified polymers have to be processed similarly to the unfilled polymers. In this regard, it is also of importance to know how the rheological behavior of the modified polymers can be related to that of their base resins.<sup>20</sup>

Figure 8 shows the complex viscosity of the blends as a function of oscillating frequency. The viscosity

**Figure 8** Melt viscosity vs. frequency.

function of SAN is typical of thermoplastic with narrow molecular weight distribution (extended Newtonian plateau) and that of *g*-ABS is of typical elastomer, showing a straight line in a log-log plot. With rubber addition, viscosity increases monotonically: more in low and less in high frequency. Up to 10% rubber, the viscosity function shows a Newtonian plateau; however, yield behavior is seen from 20 wt % loading. The viscosity function at high frequency has a straight-line segment, with a higher slope at higher rubber concentrations; i.e., the pseudoplasticity is increased with rubber content and the flow behavior index (*n*) of the power law becomes smaller from unity. This should lead, e.g., in a tubular flow, to a blunt velocity profile, and, eventually, to a plug flow.<sup>21</sup>

Figure 9 summarizes the viscosity of the blend as a function of rubber content. Deformation at a low rate of shear or frequency corresponds to the viscous one, rather than to the elastic one, and represents the interactions between particles. Positive deviation from additivity is often observed when there

**Figure 9** Viscosity vs. composition.

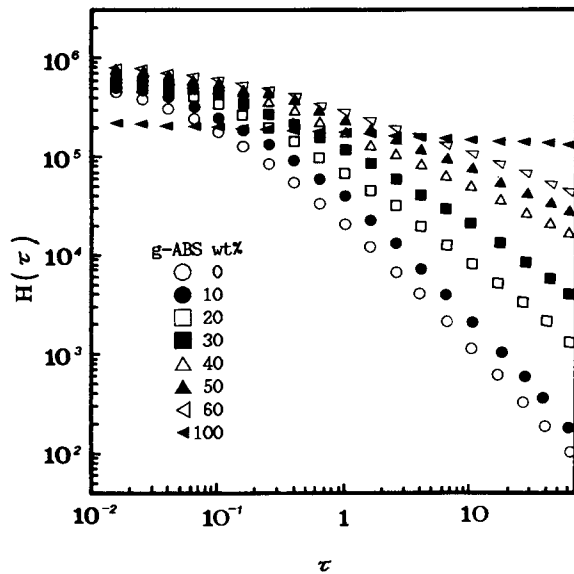


Figure 10 Relaxation spectrum of the blends.

are strong interactions among particles at a low rate of shear or when the blend has an interlocked morphology.<sup>29</sup> The *g*-ABS/SAN blends show positive deviation throughout the frequency range tested, and this should imply that the particle effect is dominant.

Figure 10 shows the relaxation spectrum of the blends. The spectrum was calculated by Niyomiya-Ferry's first-order approximation using loss modulus ( $G''$ ) data from RDS.<sup>30,31</sup> It is seen that *g*-ABS extends its relaxation for a much longer time than does SAN, representing the elastic nature of the material. As the rubber content increases, the relaxation time becomes longer, and, hence, a longer cycle time is required in the injection molding,<sup>32</sup> as expected.

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Received April 24, 1992

Accepted July 15, 1992