

# Effect of Dynamic Vulcanization on Properties and Morphology of Nylon/SAN/NBR Blends: A New Compatibilization Method of Nylon/ABS Blends

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**ABSTRACT:** Dynamically vulcanized blends of nylon, styrene-acrylonitrile copolymer (SAN), and nitrile-butadiene rubber (NBR) were examined for mechanical properties, Shore D hardness, Vicat softening temperature, impact process, and phase morphology. The effect of a curing system such as phenolic formaldehyde resins (PF), dicumylperoxide (DCP), and a sulfur system on the mechanical properties of the nylon/SAN/NBR blends was studied, and dynamic vulcanization with a PF system was found to lead to outstanding toughness of the blends. The effect of PF content on the mechanical properties, Shore D hardness, and heat resistance of the nylon/SAN/NBR blends was also investigated. With increasing PF content the notched-impact strength and Vicat softening temperature (VST) of the nylon/SAN/NBR (50/25/25) blends evidently improved, but

tensile strength and Shore D hardness of the blends changed slightly. It can be concluded that the nylon/SAN/NBR (50/25/25) blends dynamically vulcanized by high-content PF can attain excellent comprehensive mechanical properties, especially supertoughness, at room temperature. SEM was used to investigate the effect of dynamic vulcanization on disperse-phase particle size, particle size distribution, and phase morphology. It was obvious that disperse-phase particle size decreased with an increasing PF content. Thermal behavior and miscibility of dynamically vulcanized nylon/SAN/NBR with PF were investigated by DMTA. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2057–2062, 2003

**Key words:** nylon; SAN; NBR; dynamic vulcanization; compatibilization

## INTRODUCTION

Nylons, or polyamides, are an attractive class of engineering polymers because of their excellent strength, stiffness, low friction, and chemical and wear resistance.<sup>1</sup> However, they have high moisture sorption, poor dimensional stability, notched-impact sensibility, and bad low-temperature impact properties. Many polymers such as acrylonitrile-butadiene-styrene (ABS) materials have been used to modify nylons so they can attain such characteristics as high notched-impact strength and good dimensional stability. ABS materials consist of a butadiene rubber embedded within a matrix of styrene-acrylonitrile copolymers (SAN), some of which were chemically grafted to the rubber (another type of ABS is a nitrile rubber-modified SAN resin made by simply blending the two copolymers).<sup>2</sup> Blends of nylon and ABS materials are of significant commercial interest because of ABS materials' excellent toughness, dimensional stability, and relatively low cost.

There is extensive technical literature on nylon/ABS blends,<sup>3–10</sup> which mainly focuses on improving the notched-impact properties of nylon by blending nylon and ABS materials. However, simple blends of nylon and ABS have poor mechanical properties. A particularly attractive feature of nylon for reactive coupling to other polymers is its inherent chemical functionality through the amine or carboxyl end groups and through the amide linkage itself. Thus, the preferred compatibilization strategy has been to incorporate a functional polymer capable of reacting with the amine or carboxyl end groups of nylon and also of being miscible with the SAN phase of ABS. Compatibilizers that make nylon/ABS blends have good comprehensive mechanical properties, especially excellent notched-impact properties, such as imided acrylic polymer (IA) and styrene-acrylonitrile-maleic anhydride terpolymer (SANMA), have been reported in a recent series of articles.<sup>11–12</sup>

Dynamic vulcanization is the procedure of using curing agents to crosslink elastomer *in situ* during its melt mixing with molten plastic. At the end of 1980s a series of new commercial blends were prepared using dynamic vulcanization by Coran and Patel.<sup>13–15</sup> It is obvious that in thermoplastic elastomers, dynamic vulcanization of the rubber creates compositions with

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improved mechanical properties (compared with those with uncured or slightly crosslinked compositions). Much of the improvement in the mechanical properties of the dynamic vulcanized blends can be attributed to the stabilization of the rubber particle morphology, which would result from crosslinking. Dynamic vulcanization has been used in polymer blending more and more widely since the introduction of phenolic formaldehyde resins (PF) as a curing system.<sup>16</sup> PF has some active groups such as the hydroxy (OH) group and/or hydrogenous atoms that can react with the active  $\alpha$ -hydrogen atom in rubber molecules, and in dynamic vulcanization the phenolic formaldehyde compound can give rubber and plastic blends a stable morphology and excellent mechanical properties.

There has been little experimental work done using dynamic vulcanization to compatibilize and toughen nylon/ABS blends. In the present study nylon/SAN/NBR blends were prepared as a simulation of nylon/ABS blends. This study investigated the effects of different curing agents such as a phenolic formaldehyde system, a dicumylperoxide (DCP) system, and a sulfur system and of the amount of the PF compound on the properties and morphology of nylon/ABS/NBR blends. The miscibility of the blends was researched using dynamic mechanical thermal analysis (DMTA). This article reports on the beginning of applied research on a series of dynamically vulcanized nylon/ABS blends.

## EXPERIMENTAL

### Materials and specimen preparation

Nylon (PSGN-150), copolymerized by caprolactam (10 wt %), salt of nylon 66 (20 wt %), and salt of nylon (70 wt %) were produced by the Shanghai Cellulose Chemicals Company, Ltd. (People's Republic of China). The melting range of the nylon terpolymer was 140°C–150°C. NBR (JSR N220s, 36%–41% AN) was produced by Japan Synthetic Rubber Company, Ltd. (Japan). SAN (S640, 25%–30% AN) was produced by LG Yongxing chemicals, Company, Ltd. (People's Republic of China). Curing agents such as a kind of alkyl phenolic formaldehyde resin (PF), dicumylperoxide (DCP), and sulfur were industry-grade products. The basic ratio of nylon/SAN/NBR was 50/25/25 unless stated otherwise.

Nylon pellets were dried in a vacuum oven at 80°C for at least 24 h. A mixture of nylon, SAN, NBR, and additives was prepared in a mixing chamber of a HAKKE Rheometer-90 with a rotor speed of 65 rpm at 180°C for 15 min. The prepared blends were compression-molded into sheets 1 and 3 mm thick in an electrically heated press at 180°C under a pressure of 20 MPa for 10 min, followed by cooling to room temper-

ature at 5 MPa. To maintain the overall dimensional stability of the blends, tensile and impact bars were punched from the molded sheet. All specimens were introduced into a desiccator to avoid moisture sorption.

### Mechanical properties testing

Notched Izod impact was performed on a Ray-Ran (UK) pendulum impact tester with an impact rate of 3.5 m/s at ambient temperature according to ASTM D 256-97. The specimen dimension was 63.5 × 12.7 × 3 mm (L × W × H). Notched Charpy impact was performed on an Instron impact tester according to ISO 179. The changes in impact energy of the nylon/SAN/NBR blends were recorded by a Instron Charpy tester. Tensile bars conformed to ASTM D 638-93, Type II. The tensile samples were strained using a crosshead speed of 50 mm/min in an Instron universal testing machine. At least three and typically five replica samples were used for both tensile and impact data.

### Thermal behavior

Vicat softening temperatures were measured according to ISO 306 under a load of 1 kg by a Vicat softening temperature tester of the Ray-Ran Co. (UK) at a heating rate of 500°C/h.

### Hardness

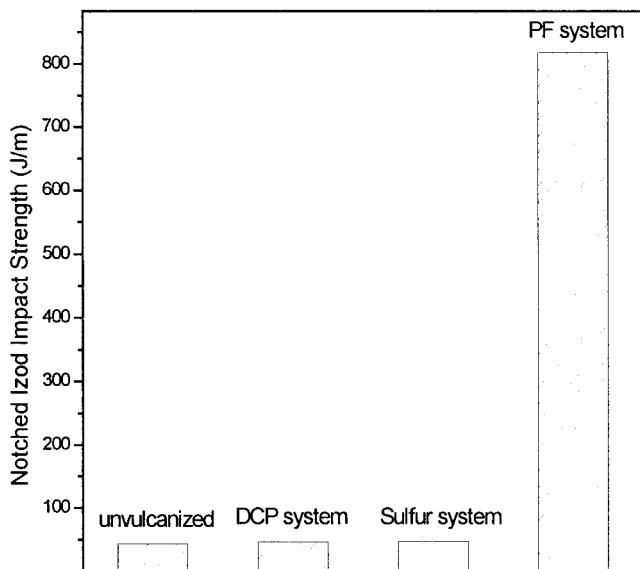
Shore D hardness was measured using a Zwick tester according to ISO 868. The thickness of the specimen was 3 mm.

### Dynamic mechanical properties

Loss tangent ( $\tan \delta$ ), dynamic mechanical thermal analysis (DMTA) data, was obtained under a multiwave dynamic tension mode at 1 Hz by a Rheometric Scientific DMTA IV at a heating rate of 3°C/min. The specimen dimension was 20 × 4 × 1 mm.

### Morphology observation

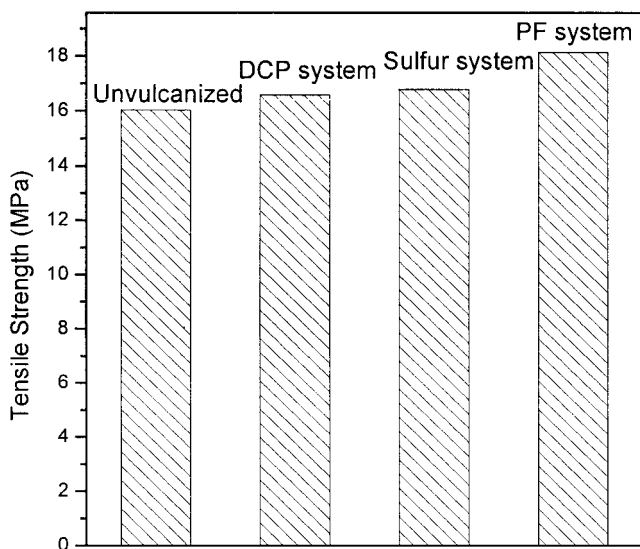
The specimens were fractured under cryogenic condition with liquid nitrogen. Tetrahydrofuran (THF) was used to etch the SAN and NBR phase on the fractured surface for 20 h at ambient temperature. The etched surfaces were coated with thin layers of gold before observation. The morphology of the blends was observed by a Hitachi S-2150 scanning electron microscope.



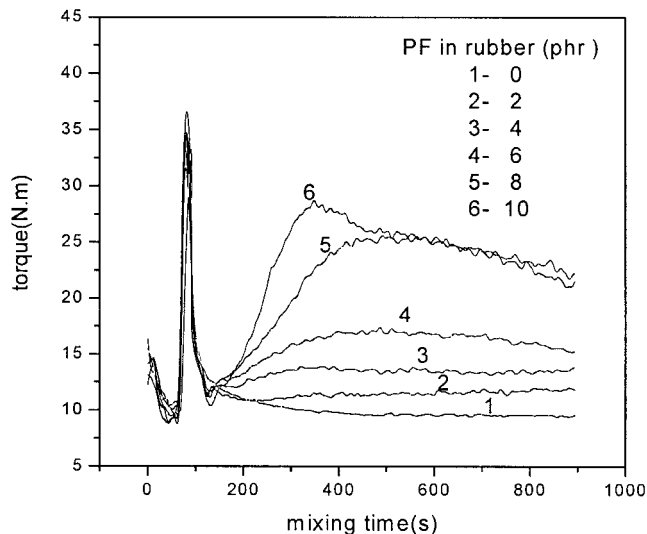
**Figure 1** Effect of uncuring, DCP (2 phr), sulfur (2 phr) and PF (8 phr) system on the notched Izod impact strength of the Nylon/SAN/NBR (50/25/25) blends. The amount of curing agent was based on nitrile rubber content.

**RESULTS AND DISCUSSION**

Figures 1 and 2 show the notched Izod impact strength and tensile strength of a 50/25/25 nylon/SAN/NBR blends vulcanized with different vulcanizing systems. In this study three vulcanizing systems, PF, DCP, and sulfur systems, were used, with the DCP and sulfur curing systems having a slight effect on the notched-impact properties of the nylon/SAN/NBR blends. It should be noted that among these curing systems, the PF system made the nylon/SAN/NBR



**Figure 2** Effect of uncuring, DCP (2 phr), sulfur (2 phr) and PF (8 phr) system on the tensile strength of the Nylon/SAN/NBR (50/25/25) blends. The amount of curing agent was based on nitrile rubber content.

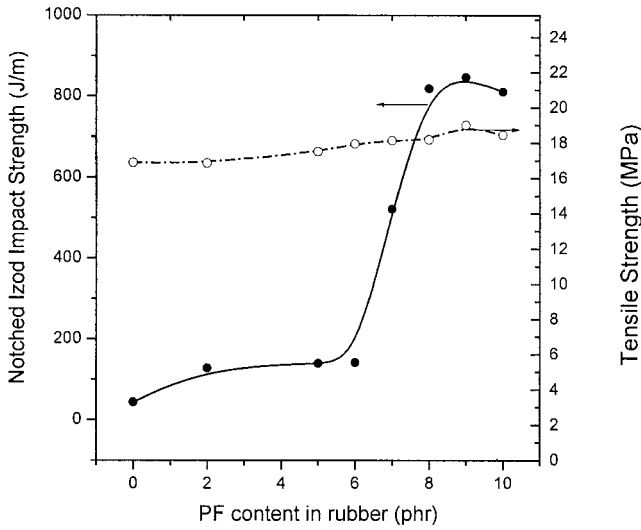


**Figure 3** Comparison plots of torque development during formation of dynamical vulcanized nylon/SAN/NBR (50/25/25) blends with different PF content.

blends attain good notched Izod impact strength at least 10 times greater than the other curing systems. All curing systems used in this study only improved the tensile strength of the blends a bit, so the effect of the PF system is relatively evident. It can be concluded that the PF compound is better at making dynamically vulcanized nylon/SAN/NBR blends attain excellent mechanical properties than the other curing systems. As a result, the blends vulcanized by the PF vulcanizing system and the effect of the PF content on the mechanical properties of the blends were researched in detail as follows. The amount of PF was based on the nitrile rubber content.

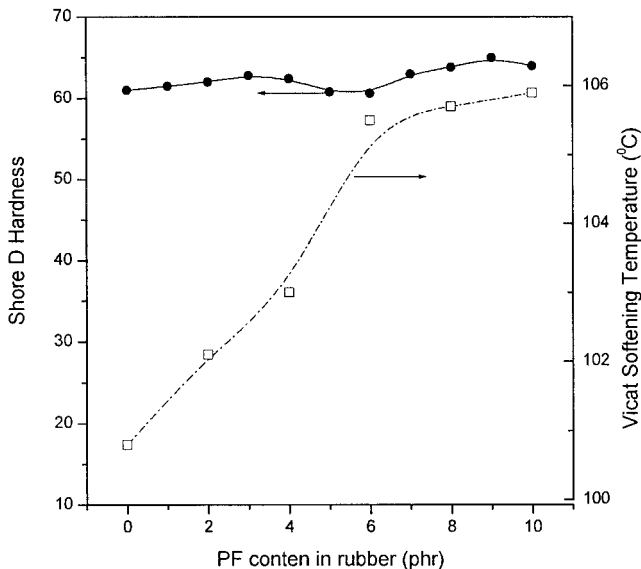
Rheology has an important influence on the morphology structure formed during blend processing and can be used to a certain extent to judge whether a reaction is occurring in functionalized systems. Dynamic vulcanization in rubber is expected to lead to an increase in viscosity relative to the nonreactive system, especially when the vulcanizer content increases. Figure 3 shows the torque versus mixing time for nylon/NBR blends vulcanized with different amounts of PF. It is clear that the balanced torque increased with increasing of the PF compound content. The plot shows that peak values were apparently reached with PF content of more than 4 phr. That should be why the formation of crosslinking and increasing viscosity caused better mixing.<sup>17</sup>

The notched Izod impact strength and tensile strength properties of the blends are shown in Figure 4. It is obvious that the notched Izod impact strength of the blends improved with increasing PF content of the blends. PF content has a bit of an effect on notched Izod impact strength of nylon/SAN/NBR blends when PF content is lower than 6 phr. Although PF

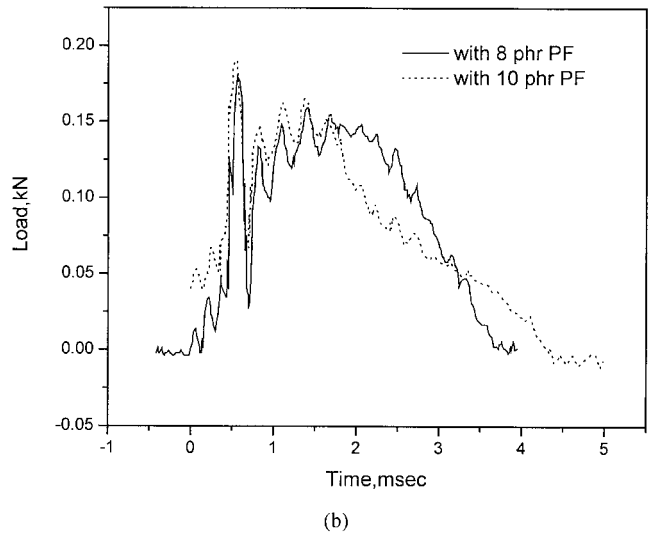
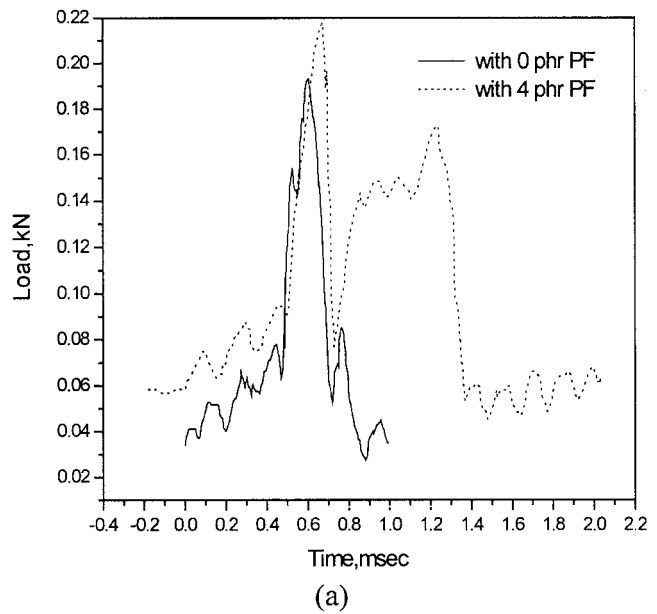


**Figure 4** Effect of the PF content in rubber on the notched Izod impact strength, tensile yield strength of the Nylon/SAN/NBR (50/25/25) blends.

content was greater than 8 phr, the dynamically vulcanized blends become supertough materials with notched Izod impact strength of more than 800 J/m. This may be because some PF compounds can react with nylon and then create interfacial tension between nylon and the lower rubber content.<sup>17</sup> As a result, particle size and particle size distribution decrease, thus improving the toughness of the blends. But the tensile strengths of the dynamically vulcanized blends change slightly when PF content increases. As shown in Figure 5, with increasing PF content, the Shore D hardness increases a little. The VSTs of the nylon/SAN/NBR blends apparently increased when the PF content was less than 6 phr, but the VSTs of the blends



**Figure 5** Effect of PF content in rubber on shore D hardness, VST of the Nylon/SAN/NBR (50/25/25) blends.

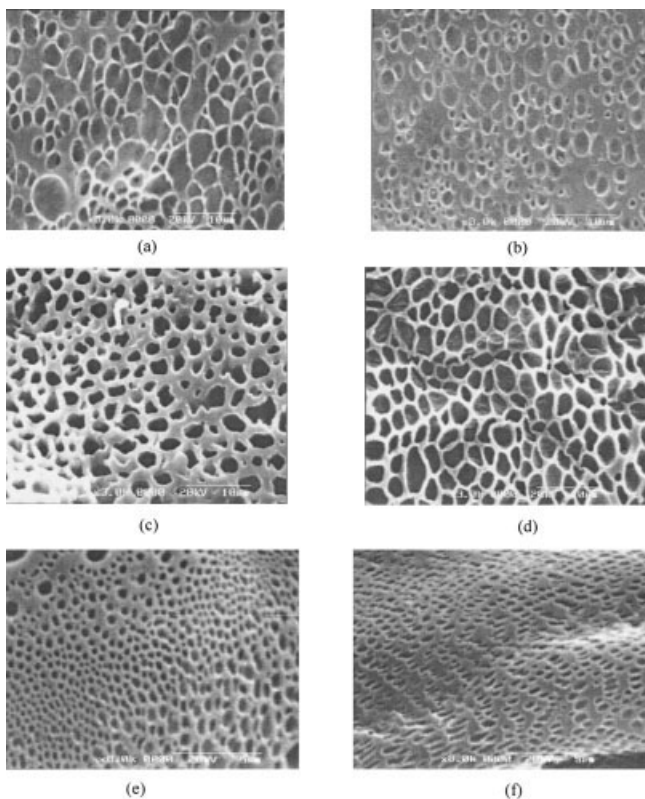


**Figure 6** Charpy force-time traces for the nylon/SAN/NBR (50/25/25) blends

increased slightly when the PF content was more than 6 phr. It can be concluded that the heat resistance of the nylon/SAN/NBR blends can be greatly improved by dynamic vulcanization with the PF compound. In general, nylon/SAN/NBR (50/25/25) blends have excellent comprehensive properties with concentrations greater than 8 phr.

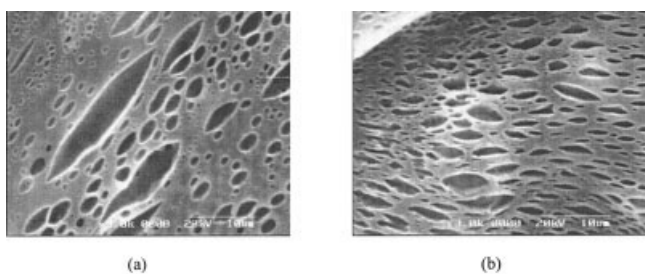
**Impact process**

Figure 6(a) shows the Charpy force-time trace of the unvulcanized nylon/SAN/NBR (50/25/25) blends and the dynamically vulcanized blends with 4 phr PF at a striker impact velocity of 4 m/s. Figure 6(b) shows the Charpy force-time trace of the nylon/SAN/NBR (50/25/25) blends with 8 and 10 phr PF at the same striker impact velocity. From Figure 6(a) it can be seen

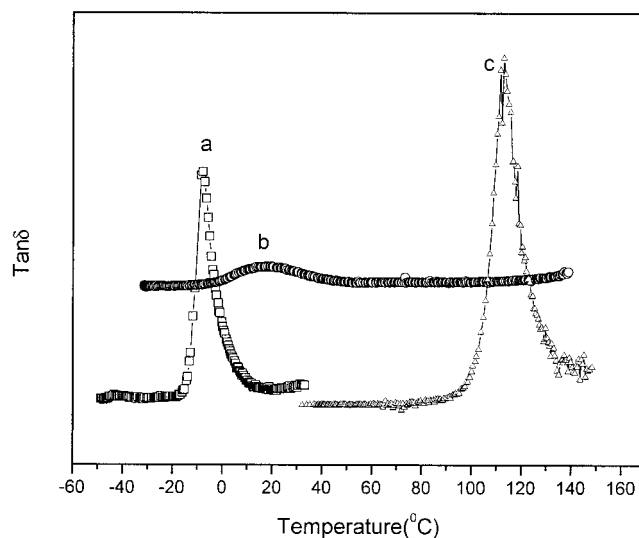


**Figure 7** SEM photomicrographs of the nylon/SAN/NBR (50/25/25) blends vulcanized with different PF content: (a) unvulcanized, (b) 2 phr, (c) 4 phr, (d) 6 phr, (e) 8 phr (f) 10 phr. The blends are all etched by THF (solvent for SAN and NBR) and photographed at  $3000\times$  magnification except for (e) and (f) at  $8000\times$  magnification.

that the uncured nylon/SAN/NBR (50/25/25) blends force-time trace has a simple peak and that the sample of the blends is fractured within 1 ms. It appears to be typically brittle behavior. With increasing PF content, the peak area increased, too. Figure 6(a,b) shows that the dynamically vulcanized nylon/SAN/NBR (50/25/25) blends with 4, 8, and 10 phr PF is fractured within 2, 4, and 5 ms, respectively, and that the dynamic vulcanization with high-content PF increases the toughness of the nylon/SAN/NBR (50/25/25)



**Figure 8** SEM photomicrographs of the nylon/SAN/NBR (50/25/25) blends vulcanized with different curing systems: (a) DCP system; (b) sulfur system. The blends are all etched by THF (solvent for SAN and NBR) and photographed at  $3000\times$  magnification.

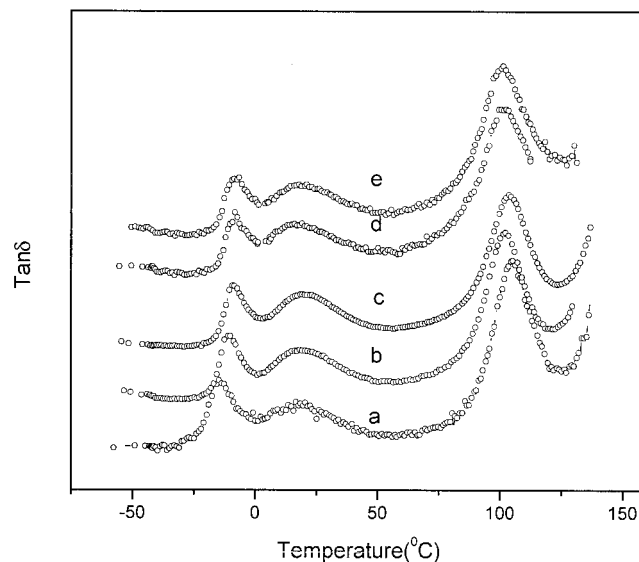


**Figure 9** Temperature dependence of  $\tan \delta$  of (a) NBR, (b) nylon terpolymer and (c) SAN.

blends. As the PF content increases from 0 to 10 phr, the dynamically vulcanized nylon/SAN/NBR (50/25/25) blends appear to go from typical brittle to typical ductile impact-fracture behavior.

### Morphology observation

Mechanical properties of multiphase polymer blends are directly related to their microstructure, especially the size and shape of the disperse phase. Figure 7 shows SEM micrographs of nylon/SAN/NBR (50/25/25) blends vulcanized by different amounts of PF. Figure 7(a) shows the morphology of the uncured



**Figure 10** Temperature dependence of  $\tan \delta$  of the nylon/SAN/NBR (50/25/25) blends dynamically vulcanized with different PF content: (a) unvulcanized, (b) 2 phr, (c) 4 phr, (d) 8 phr, and (e) 10 phr.

blends, used as the blank sample. It can be seen that the nylon has a continuous network structure in the blends and that the disperse phase appears in a relatively large, irregular, and elongated domain. It can be concluded that the sample nylon/SAN/NBR blends are typical immiscible blends with poor mechanical properties, especially bad notched-impact properties, referred to above. With increasing PF content, there was a significant reduction in the SAN and NBR domain sizes and the disperse phase appeared in spherical particles. This tendency was more apparent when the PF content increased. Particle size, shown in Figure 7(d–f), became more uniform and smaller and the particle size distribution became more uniform as the PF content in rubber increased to more than 8 phr, and it can be concluded that the nylon, SAN, and NBR polymers became more miscible because of the dynamic vulcanization with the PF compound. So some tentative conclusions can be drawn: nylon/SAN/NBR blends vulcanized by a PF compound with more than 8 phr have excellent comprehensive properties because of their optimum microstructure morphology.

Figure 8(a,b) shows the size and shape of the disperse phase for the nylon/SAN/NBR (50/25/25) blends vulcanized by the DCP and sulfur curing systems. Compared with what is shown in Figure 7(d–f), it can be seen that the morphology of the blends is more complicated and the disperse-phase particles appear in relatively large and elongated particles with a large particle-size distribution. Poor morphology in the blends shown in Figure 8(a,b) can explain poor mechanical properties of the blends, as the above research indicates. In general, good morphology of the nylon/SAN/NBR blends depends not only on dynamic vulcanization but also on the type of curing system, as does the mechanical properties of the blends.

### Dynamic mechanical properties

The DMTA method can be considered to give the most reliable and reproducible results. These results correlate with the mechanical properties and morphology observation. The DMTA spectra of pure nylon, SAN, and NBR are shown in Figure 9. And the DMTA spectra of the nylon/SAN/NBR (50/25/25) blends with 0, 2, 4, 8, and 10 phr PF are shown in Figure 10. Glass-transition temperatures ( $T_g$ ) is determined as the temperature at the maximum of  $\tan \delta$ . From what is shown in Figures 9 and 10, it can be concluded that the  $T_g$ s of NBR, nylon, and SAN are  $-14.4$ ,  $18.32$ , and  $113^\circ\text{C}$  (the  $T_g$ s of these blends are shown in Table I). Figure 10 shows that the curve of  $\tan \delta$  versus the temperature of the unvulcanized nylon/SAN/NBR (50/25/25) blends exhibits three relaxation peaks. The first relaxation transition temperature, at about  $-14^\circ$ , may be attributed to the glass transition of NBR. The second relaxation peak, at about  $17^\circ$ , and the

**TABLE I**  
The Glass-Transition Temperatures of Dynamically Vulcanized Nylon/SAN/NBR (50/25/25) Blends with PF Compound

PF content (PF)	$T_g$ in rubber phase ( $^\circ\text{C}$ )	$T_g$ in nylon matrix ( $^\circ\text{C}$ )	$T_g$ in SAN phase ( $^\circ\text{C}$ )
0	$-14.33$	16.6	104.82
2	$-10.58$	16.18	102.1
4	$-9.34$	16.05	102.06
8	$-7.95$	15.85	101.92
10	$-7.04$	14.45	101.3

last relaxation peak, at about  $105^\circ\text{C}$ , are related to the glass transition of nylon and SAN copolymer. Compared with curve (a) in Figure 10, the relaxation peaks of the dynamically vulcanized nylon/SAN/NBR (50/25/25) blends appear to go toward one another as PF content increases. In particular, the relaxation peaks related to the glass transition of NBR and SAN are more evidently close to each other. It can be concluded that the changes in  $\tan \delta$  values of the blends are the result of the improved miscibility of the nylon/SAN/NBR blends because of dynamic vulcanization with a PF compound.

### CONCLUSIONS

The dynamically vulcanized nylon/SAN/NBR blends in this study have a multiphase structure and nylon a continuous phase. The dynamically vulcanized nylon/SAN/NBR (50/25/25) blends cured by a more than 8 phr PF compound attained more balanced mechanical properties, especially supertoughness, than those uncured or cured by other curing agents, which could a result of the good compatibility, shown by the SEM and DMTA graphs. It is an effective way to compatibilize and toughen nylon/SAN/NBR blends by using dynamic vulcanization with high PF content compound.

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