

# Highly Grafted Polystyrene-Modified Natural Rubber as Toughener for Polystyrene

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Received 29 August 2003; accepted 18 February 2004

DOI 10.1002/app.20576

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A polystyrene-modified natural rubber (SNR) with 80% degree of grafting was evaluated against natural rubber (NR) in their blends with polystyrene (PS). The rubber loading of the PS-SNR and PS-NR blends was varied from 5 to 20% by volume. At 10–15% rubber loading, the PS-SNR blends were found to be approximately 8–10% higher in tensile strength and 7–13% higher in Young's modulus than the PS-NR blends. Over the range of rubber loading investigated, it was also observed that the PS-SNR blends were 5–42 and 14–36% higher in flexural strength and flexural modulus, respectively. The most pronounced difference between the two blend systems is in their impact

strength, where the former is about 55–230% higher than the latter. Relative to the pure PS, the PS-NR and PS-SNR blends are approximately 50–250 and 140–1050% higher, respectively, in impact strength. Morphological observations, which are consistent with the relative tensile, flexural, and impact properties of the two systems, indicate that SNR is more compatible with PS than NR and more homogeneously dispersed in the PS matrix. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1660–1665, 2004

**Key words:** tensile properties; flexural properties; impact strength; PS-NR blends; PS-SNR blends

## INTRODUCTION

For immiscible polymer blends, the addition of compatibilizer is the most efficient method to create a high performance polymeric material.<sup>1–2</sup> The addition of poly(styrene-*g*-ethylene oxide) as compatibilizer in polystyrene (PS)/polyamide-6 blends was observed to give a yield point in the stress-strain behavior, improving the elongation at break and impact strength.<sup>3</sup> Maleated elastomer similar to EPR-*g*-MA and SEBS-*g*-MA may also function as good compatibilizers and coimpact modifiers which improved the dispersing of EPDM-*g*-SAN in the nylon 6 matrix.<sup>4</sup> Some studies on impact modification of PS-EPDM blends by the addition of EPDM-*graft*-styrene, EPDM-*g*-(styrene-*co*-methyl methacrylate), and EPDM-*g*-(styrene-*co*-maleic anhydride) as compatibilizers were reported,<sup>5–7</sup> where improvement in impact strength was achieved because of the better compatibility and interfacial adhesion of the copolymers with the PS matrix. Various styrene-butadiene copolymers were investigated as compatibilizers in polystyrene-butadiene blends.<sup>8</sup> A good compatibilization effect through solubilization of chemically identical segments was achieved when LLDPE-*g*-PS was used as compatibilizer in LLDPE-SBS blends.<sup>9</sup> Rubber toughening of syndiotactic poly-

styrene and poly/(styrene/diphenylethylene) with hydrogenated styrene-butadiene-styrene block copolymer increased the toughness in terms of notched impact strength and energy release rate.<sup>10</sup>

The effect of dynamic vulcanization on the mechanical properties of PS-natural rubber (NR) blends was also studied.<sup>11</sup> PS and NR are not compatible at the molecular level; the addition of NR-*grafted*-PS as compatibilizer in PS/NR blends was observed to improve the tensile properties and impact strength<sup>12</sup> and thermal stability.<sup>13</sup>

The preparation and characterization of polystyrene-modified natural rubber (SNR), at 25 : 75 of PS : NR ratio by weight, was reported.<sup>14</sup> The SNR has approximately 80% degree of grafting (i.e., 20% of 25 wt % of the PS portion is chemically bonded to the rubber). The use of SNR as a high molecular weight compatibilizer in PP-NR blends has shown significant improvement in tensile strength and stiffness.<sup>15</sup>

SNR is expected to be more compatible than NR with PS matrix because it contains a PS portion which is highly grafted. Hence, in this study, PS-SNR blends are reported in comparison with PS-NR, without any compatibilizer, to highlight the effect of SNR, which is chemically modified NR. The blends were incorporated with curatives based on a sulfur curing system to crosslink the rubber phase following the principles of dynamic vulcanization. The focus of the study was on rubber-toughened PS. Rubber-toughened plastics contain usually 5–20% rubber, which is dispersed in

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**TABLE I**  
Recipe for Rubber Compounding

	phr
Natural rubber	100.0
Zinc oxide	5.0
Stearic acid	2.0
IPPD	2.0
MBTS	2.5
TMTD	1.5
Sulfur	0.3

the matrix<sup>16</sup>; thus, in this investigation, the rubber loading was limited to 20% by volume. The tensile, impact, morphological, flexural, and aging properties were investigated.

## EXPERIMENTAL

### Materials

The NR used was SMR L grade. The PS used was a general purpose grade, HH 35, purchased from Petrochemicals (Malaysia), with density and melt flow index of 1.04 g/cm<sup>3</sup> and 6.5 g/10min (measured at 200°C and 5 kg load), respectively. SNR used was synthesized in the laboratory and the degree of grafting was determined according to the methods reported previously.<sup>14</sup>

### Mixing and preparation of samples

NR or SNR was compounded on a two-roll mill according to standard compounding procedures by using efficient sulfur vulcanizing system, the recipe of which is shown in Table I. The resultant rubber compound was then blended with PS by using a Brabender Plasticoder model PLE 331.

Melt mixing for PS-rubber blends was carried out at 190°C. First, the PS was preheated in the Brabender for 2 min before it was rotated in the mixing chamber at 50 rpm for another 4 min. Later, either compounded NR or SNR was charged into the mixing chamber and mixing was continued for another 4 min.

### Measurements

Test samples were prepared by preheating for 4 min followed by compressing for 2 min with 100 kg cm<sup>-2</sup> at 185°C. Molded samples were cut by using a Wallace dumbbell cutter (S/6/1/4). Tensile testing was carried out according to ASTM D638 by using a Testometric tensometer M500 with 1 mm/min crosshead speed at room temperature. Flexural tests were carried out according to ASTM D 790 by using the Testometric tensometer M500 at the rate of 3.0 mm/min. For both tensile and flexural testing, five samples were tested

**TABLE II**  
Tensile Properties of PS-NR Blends at Various Blend Ratios

	Pure PS	Rubber loading (% by volume)			
		5	10	15	20
TS (MPa)	27.5	28.64	27.41	23.03	20.44
EB (%)	1.4	1.5	1.9	2.0	2.5
E (MPa)	2390	2380	2183	1908	1702

and the median was reported. Izod impact tests were carried out according to ASTM D 256 on unnotched samples at room temperature by using a Zwick impact tester. The average of 10 measurements was reported for the impact strength. Scanning electron microscopy (SEM) was carried out by using SEM model Leice Cambridge S-360 on the fractured surface. Selected samples were microtomed and then stained with osmium tetroxide (OsO<sub>4</sub>) for 24 h. The samples were then mounted and viewed under the bright field mode with a light microscope, model Olympus BH2, fitted with a surface imaging analysis system.

## RESULTS AND DISCUSSION

### Tensile and impact properties

Generally, the addition of rubber into a plastic is expected to reduce the Young's modulus (*E*) and tensile strength (TS) but increase the elongation at break (EB). The impact strength is also expected to increase because of the toughening effect of the rubber. These properties are expected to behave accordingly in the manner described as the rubber loading is increased. In this comparative study of PS-NR and PS-SNR blends, the rubber loading is defined in terms of the amount of NR present in the blends. Because SNR contains 25% PS and 75% NR, the ratio of PS to SNR in PS-SNR blends was adjusted in such a way that the NR loading was the same as the respective PS-NR blends. This means that, as the rubber loading increases, the amount of grafted PS in the PS-SNR blends also increases.

Tables II and III show the comparative tensile properties of the PS-NR and PS-SNR blends at four rubber loadings (i.e., 5, 10, 15, and 20% by volume). Rela-

**TABLE III**  
Tensile Properties of PS-SNR Blends at Various Blend Ratios

	Pure PS	Rubber loading (% by volume)			
		5	10	15	20
TS (MPa)	27.5	31.01	30.16	25.07	22.12
EB (%)	1.4	1.7	2.1	2.7	10.2
E (MPa)	2390	2397	2340	2166	1906

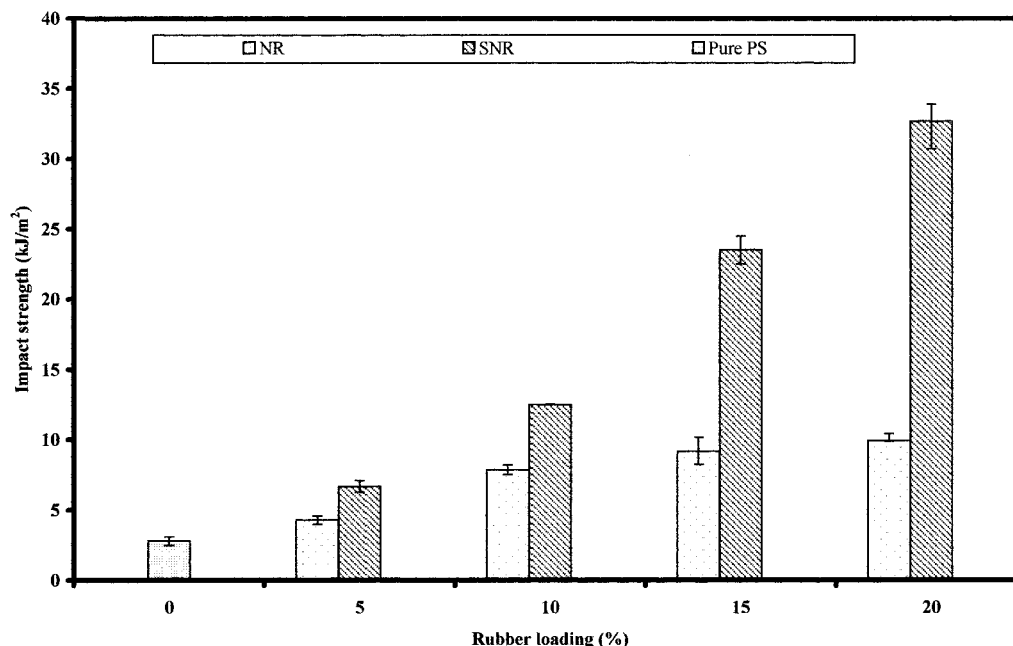


Figure 1 Impact strength of pure PS, PS-NR, and PS-SNR blends.

tively, at 10–20% rubber loading, the PS-SNR blends are approximately 8–10% higher in TS and 7–13% higher in *E*. The increment in EB as a function of rubber loading is more pronounced for the PS-SNR system where at 20% rubber loading, its EB is four times higher than the PS-NR system. Compared with the pure PS, up to 10% rubber loading, the PS-SNR blends are higher in tensile properties and comparable in *E*. For a rubber-toughened system, high tensile properties should give a high toughening effect and high impact strength. Figure 1 shows the impact strength of both blends: the PS-SNR is about 0.5–2.3 times higher in impact strength than the PS-NR. It is observed that the difference in impact strength between the two blend systems becomes more and more pronounced as the rubber loading increases. Using the impact strength of the pure PS as reference, the PS-NR and PS-SNR are approximately 0.5–2.5 times and 2.4–11.7 times higher, respectively.

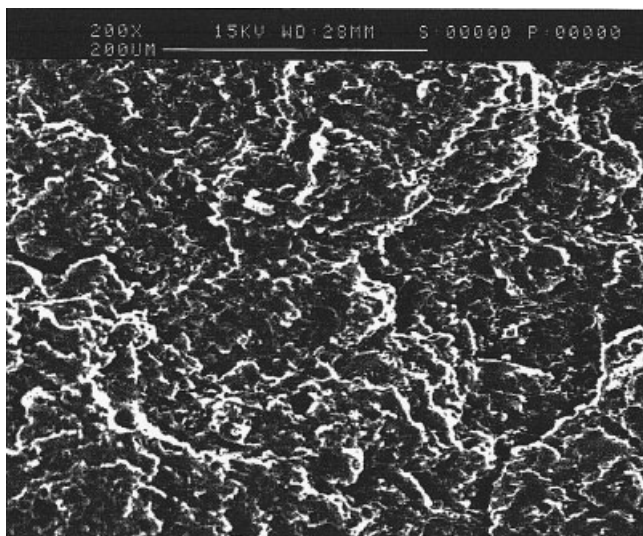
Three main factors are thought to contribute to the better properties of the PS-SNR blends (i.e., the stiffness of SNR, its compatibility with PS, and the homogeneity of the blend). As mentioned earlier, the higher the rubber loading, the higher the amount of the PS-grafted portion in the blends. The PS-grafted portion in SNR contributes to the overall stiffness and strength of the blend, giving relatively high modulus and tensile strength. As a rubber vulcanizate, SNR was found to have higher modulus with TS comparable to NR.<sup>17</sup> Because the PS portion is highly grafted, SNR should be more compatible with PS than NR. Figure 2(a, b) shows SEM photographs of PS-NR 20 and PS-SNR 20 blends, respectively. The fractured surface was ob-

tained from tensile test specimens. The latter has a fractured surface that is smoother and finer compared with the former. Figure 3(a, b) shows the stained photographs of PS-NR 20 and PS-SNR 20 blends. Both blends show a cocontinuous rubber phase but the PS-SNR is much more homogeneous. These observations indicate that SNR is more compatible with PS and more homogeneously dispersed in the PS matrix. The better compatibility and homogeneity of the PS-SNR blends result in higher tensile properties and a more efficient toughening effect given higher impact strength.

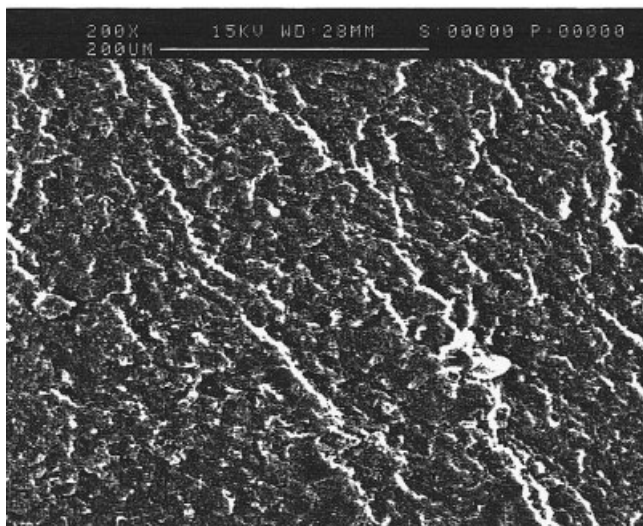
### Flexural properties

Both blend systems were compared in terms of flexural strength and flexural modulus, the results of which are shown in Figures 4 and 5, respectively. As the rubber loading increases, the flexural strength and flexural modulus decrease, a trend that is consistent with and similar to that observed for the TS and *E*. Relatively, over the range of rubber loading investigated, the PS-SNR blends are 5–42 and 14–36% higher in flexural strength and flexural modulus, respectively, compared with PS-NR blends. It is interesting to note that both blends show the highest flexural properties, which are much higher than the pure PS, at 5% loading: a similar observation is noted for the tensile strength. The flexural properties then decrease abruptly at 10% loading, beyond which the decrement is gradual. During the flexural testing, each blend was identified in terms of catastrophic (brittle) or non-catastrophic (ductile) failure. Only the blends at 5%





(a)



(b)

**Figure 2** SEM photographs of (a) PS-NR 20% and (b) PS-SNR 20%.

rubber loading showed brittle failure similar to the pure PS; beyond this loading, ductile behavior was observed. This explains the abrupt drop in flexural properties and the significant increase in EB at 10% loading and beyond as the blends have become ductile.

For an unnotched specimen, the elastic energy at the critical stage ( $U_c$ ) for brittle failure is given by the equation<sup>18</sup>

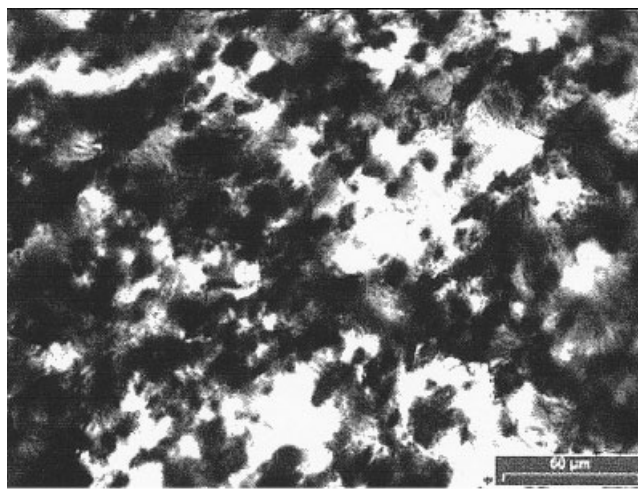
$$U_c = (\sigma_c^2/18E_f)BSW \quad (1)$$

where  $U_c$  is the elastic energy at critical stage (J);  $\sigma_c$  is the critical stress in a centrally loaded and simply supported beam (three point bending) (MPa);  $E_f$  is the

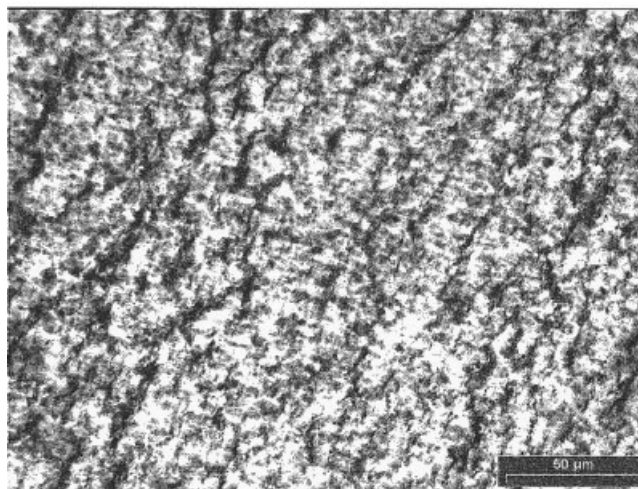
flexural modulus (GPa);  $B$  is the sample depth (mm);  $S$  is the beam span (mm); and  $W$  is the sample width (mm).

The  $U_c$  is an inherent property of a material and should relate well with its mechanical properties such as TS, EB, flexural properties, and impact strength; the higher the  $U_c$ , the higher these properties should be. The  $U_c$  of the pure PS and the PS-NR and PS-SNR blends at 5% loading were calculated to be 0.146, 0.157, and 0.171 J, respectively. These values are consistent with the relative TS, EB, flexural properties, and impact strength observed for the three systems mentioned at 5% loading. The difference in  $U_c$  between the two blend systems is another good indication that SNR is more compatible than NR when blended with PS, and thus, more effective in improving the properties of the blends.

At 10–15% rubber loading, the mechanical properties of the PS-SNR blends, except for the impact



(a)



(b)

**Figure 3** Stained photographs (a) PS-NR 20% and (b) PS-SNR 20%.

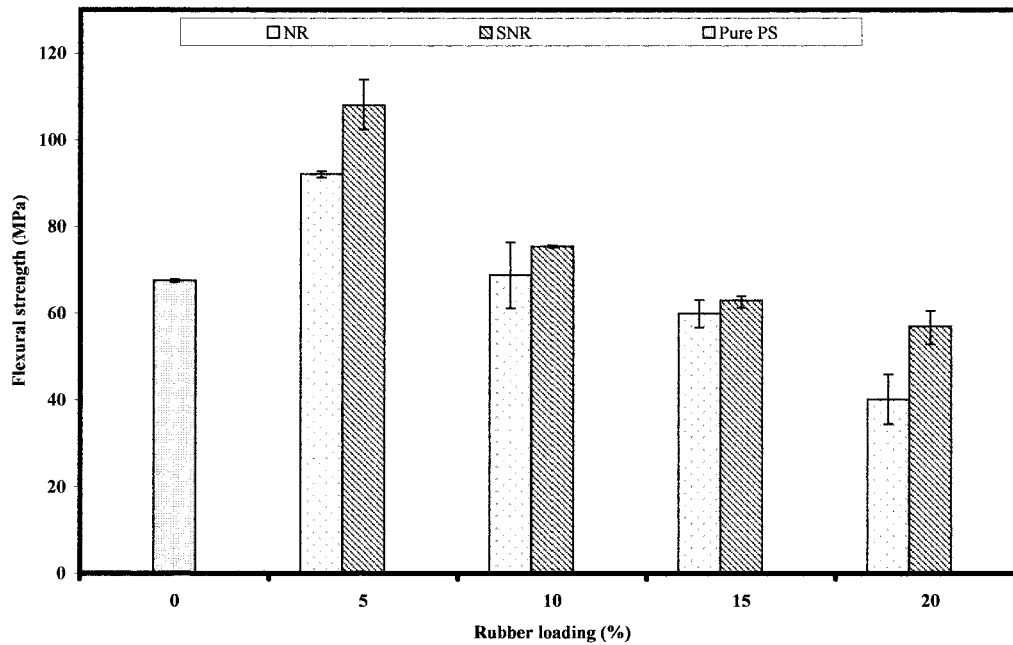


Figure 4 Flexural strength of pure PS, PS-NR and PS-SNR blends.

strength and EB, could be considered quite comparable with those of the pure PS, being slightly higher at 10% loading and slightly lower at 15% loading. At 15% loading, the properties are lower by only about 7% in TS, flexural strength, and flexural modulus, and about 9% in *E*. However, the impact strength and EB are 8.4 times and 1.9 times higher, respectively. This is a good indication, consistent with the SEM observation, that SNR is compatible with PS.

#### Aging retention properties

Table IV shows the aging retention properties of the PS-NR and PS-SNR blends. Except for the EB at 15 and 20% loading, the PS-SNR blends could be considered slightly or considerably better in aging resistance. At 20% loading, the EB aging resistance of the PS-SNR blend is very poor, although at 3.2% after aging, it is still the highest among all the blends. SNR vulcanizate

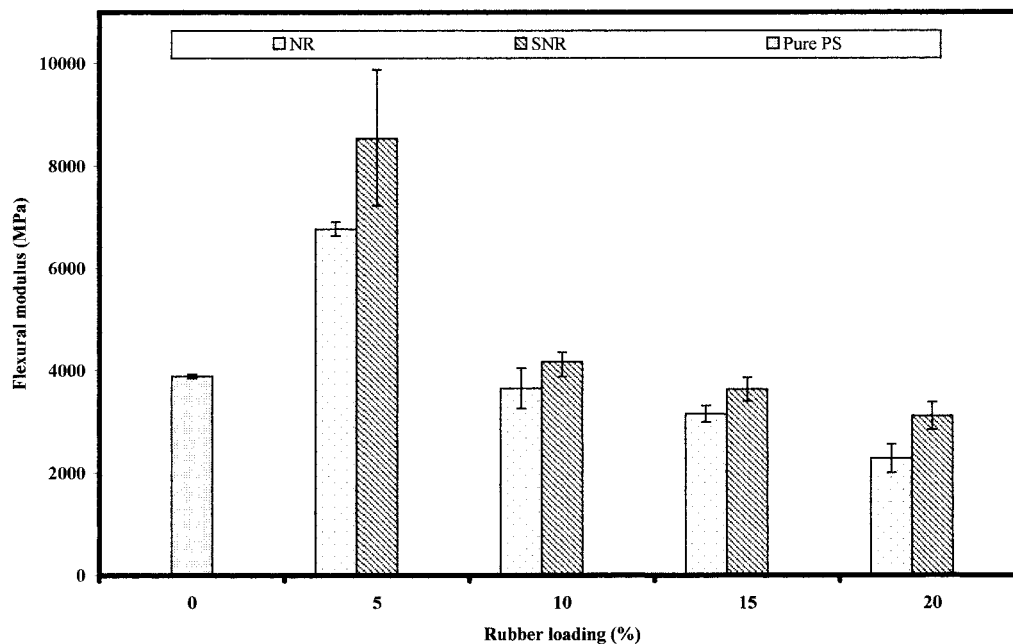


Figure 5 Flexural modulus of pure PS, PS-NR, and PS-SNR blends.

**TABLE IV**  
**Aging Retention Properties of PS-NR Blends and PS-SNR Blends at Various Blend Ratios**

Mechanical properties	Rubber	Rubber loading (%)			
		5	10	15	20
TS (MPa)	NR	-4.1	-10	-8.4	-5.8
	SNR	-0.1	-0.7	-0.9	-5.4
EB (%)	NR	-6.7	-7.0	-5.8	-6.1
	SNR	-0.6	-5.0	-7.4	-68.9
Young's modulus (MPa)	NR	+15.3	+14.1	+10.1	+8.0
	SNR	+14.9	+6.8	+0.5	+1.7
Impact strength (kJ/m <sup>2</sup> )	NR	-8.4	-8.6	-4.7	-4.3
	SNR	-5.0	-5.4	-0.5	-3.3

was observed to be slightly poorer in EB than NR vulcanizate upon aging.<sup>16</sup> A probable explanation is as follows: NR cured with a typical sulfur system usually shows an increase in modulus, as observed in this study, due to further crosslinking reaction upon aging. Also, upon aging, the EB usually drops as a result of main chain scissions that reduce the physical chain entanglements and the average molecular weight (or widen the molecular weight distribution). Because the PS is highly grafted in SNR, it is thought that when the amount is high enough, the chain scissions that occur are sufficient to reduce both the chain entanglement and the average molecular weight significantly. Thus, a significant reduction in EB after aging is observed.

### CONCLUSION

Over the range of rubber loading investigated for PS-NR and PS-SNR blends, the latter displayed better mechanical properties, which are much more pronounced in impact strength. The PS-SNR blends are

0.5–2.3 times higher than the respective PS-NR blends and 2.4–11.7 times higher than the pure PS in impact strength. The results observed could be attributed to the PS-grafted portion of SNR, which resulted in blends that were more compatible and homogeneous. Considering the properties in terms of aging, tensile, flexural, and especially impact, PS-SNR blends at 10–15% rubber loading would give a good balance of overall properties.

### References

1. Rayt, R.; Jerome, R.; Teyssie, Ph. *J Polym Sci, Polym Phys Ed* 1982, 20, 22C9.
2. Heikens, D.; Hoen, N.; Barentsen, W.; Piet, P.; Ladan, H. *J. Polym Sci, Polym Symp* 1978, 62, 309.
3. Jannasch, P.; Wesslen, B. *J Appl Polym Sci* 1998, 70, 1887.
4. Lu, M.; Keskkula, H.; Paul, D. R. *J Appl Polym Sci* 1995, 58, 1175.
5. Shaw, S.; Singh, R. P. *J Appl Polym Sci* 1990, 40, 685.
6. Shaw, S.; Singh, R. P. *J Appl Polym Sci* 1990, 40, 693.
7. Shaw, S.; Singh, R. P. *J Appl Polym Sci* 1990, 40, 701.
8. Cavanaugh, T. J.; Buttle, K.; Turner, J. N.; Nauman, E. B. *Polymer* 1998, 39(18), 4191.
9. Feng, H.; Ye, C.; Tian, J.; Feng, Z.; Huang, B. *Polymer* 1998, 39(10), 1787.
10. Ramsteiner, F.; McKee, G. E.; Heckmann, W.; Oepen, S.; Geprags, M. *Polymer* 2000, 41, 6635.
11. Asaletha, R.; Kumaran, M. G.; Thomas, S. *Eur Polym J* 1999, 35, 253.
12. Asaletha, R.; Kumaran, M. G.; Thomas, S. *Rubber Chem Technol* 1995, 68, 671.
13. Asaletha, R.; Kumaran, M. G.; Thomas, S. *Polym Degrad Stab* 1998, 61, 431.
14. Nguyen, V. Tho; Mohd Omar Abd Kadir; Azanam S. Hashim. *Rubber Chem Technol* 2002, 75, 111.
15. Azanam, S. Hashim; Ong, S. K. *Polym Int* 2002, 51, 611.
16. Bucknall, C. B. In *Toughened Plastic*; Applied Science Publishers: London, 1977; p 2.
17. Hashim, A. S.; Ong, S. K. *Nguyen Van Tho Rubber Stitching: Nat Rubber* 2002, 28, 12.
18. Bucknall, C. B. In *Toughened Plastic*; Applied Science Publishers: London, 1977; p 284.