

Improvement of the Homogeneity of SBR/NBR Blends Using Polyglycidylmethacrylate-g-Butadiene Rubber

S. H. Botros, A. F. Moustafa, S. A. Ibrahim

National Research Center, Polymers Department, Dokki-12622, Cairo, Egypt

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ABSTRACT: Polyglycidylmethacrylate grafted butadiene rubber (PGMA-g-BR) was synthesized by a graft solution copolymerization technique. The PGMA content was determined through titration against HBr. The PGMA-g-BR was blended with styrene butadiene rubber/butadiene acrylonitrile rubber (SBR/NBR) blends with different blend ratios. The SBR/NBR (50/50) blend was selected to examine the compatibility of such blends. Compatibility was examined using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and viscosity measurements. The scanning electron micrographs illustrate the change of morphology of the SBR/NBR rubber blend as a result of the incorporation of PGMA-g-BR onto that blend. The T_g s of SBR and NBR in the blend get closer upon incorporation of PGMA-g-BR 10 phr, which indicates improvement in blend homogeneity. The intrinsic viscosity (η) versus blend ratio graph shows a straight-line relationship, indicating some

degree of compatibility. Thermal stability of the compatibilized and uncompatibilized rubber blend vulcanizates was investigated by determination of the physicomechanical properties before and after accelerated thermal aging. Of all the vulcanizates with different blend ratios under investigation, the SBR/NBR (25/75) compatibilized blend possessed the best thermal stability. However, the SBR/NBR (75/25) compatibilized blend possessed the best swelling performance in brake fluid. The effect of various combinations of inorganic fillers on the physicomechanical properties of that blend, before and after accelerated thermal aging, was studied in the presence and absence of PGMA-g-BR. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1559–1567, 2006

Key words: brake fluid; compatibility; graft solution copolymerization; inorganic fillers; nitrile rubber; polyglycidylmethacrylate; rubber blend; styrene butadiene rubber

INTRODUCTION

The search for new and interesting polymeric materials with complementary properties has recently intensified. An easy and cost-effective way to produce a new combination of properties is blending. Most blends are immiscible and thus exhibit poor physicomechanical properties. Therefore, compatibilization is needed to obtain blends with the desired properties. The mechanical properties of incompatible polymers can be significantly improved by the addition of a compatibilizer during the processing stage.¹ A common way to improve the compatibility between two immiscible polymers is to add block or graft copolymers.² The segments of block, graft, or random copolymers can be identical with those in the respective phases. These compounds reduce the macroscopic inhomogeneities and improve the morphological stability, by decreasing the interfacial tension and subsequently reducing the dispersed phase size.³ Incorporating either a block copolymer or grafted reactive polymer carrying functional groups into the mul-

tiphase system enhances the physical bonding of dissimilar polymers. PGMA-g-BR has been added to polymers as a reactive compatibilizer, which reacts in the melt and forms chemical bonds between constituents. An example of this process is represented by the peroxide-initiated functionalization leading to grafting or crosslinking reactions.^{4,5} Compatibility studies, on different polymer blends, have been reported where the extent of blend homogeneity depends on the mixing method, solubility parameters, and the nature of blend constituent rubbers.⁶

It has been expected that the styrene in SBR, and nitrile groups in NBR, could act as a donor-acceptor system and therefore allow compatibility of nonpolar SBR and polar NBR. The experimental results obtained showed that SBR is incompatible with NBR.⁷ The effect of unsaturated polyester (UPE) on the compatibility of SBR/NBR in their physical blends was studied with ultrasonic velocity and attenuation measurements.⁸ The effect of some compatibilizers on the compatibility of SBR/NBR rubber blends has been studied. The investigated compatibilizers were a) a polymeric compatibilizer, namely, acrylonitrile-butadiene-styrene (ABS); b) low molecular weight compounds, such as divinylbenzene (DVB) and triethylene glycol dimethylacrylate (TEGDMA); and c) graft copolymers, such as SBR-g-AN, NBR-g-St, BR-g-AN,

Correspondence to: S. H. Botros (sh50_botros@hotmail.com).

and BR-g-St. The compatibility of SBR/NBR blends was evaluated by viscosity, DSC, and DMTA.⁹ Many investigators have worked on comparison of the thermal stability of NBR and SBR vulcanizates cured by different curing systems. That has been performed by thermogravimetric analysis.¹⁰ The present article is concerned with synthesis and application of PGMA-g-BR as a compatibilizer for SBR/NBR blends. Rheological and physicochemical properties of the SBR/NBR vulcanizates over a range of blend ratios were determined. The thermal stability of the blend vulcanizates was evaluated after accelerated thermal aging. The effect of the SBR/NBR blend ratio, with and without PGMA-g-BR, on the swelling performance in toluene and brake fluid is also discussed. The physicochemical properties of an SBR/NBR (25/75) blend with and without different inorganic filler combinations were evaluated.

EXPERIMENTAL

Materials

Glycidylmethacrylate monomer (Merck, Darmstadt, Germany) was vacuum distilled twice before use. Dibenzoyl peroxide (BPO) (Acros, New Jersey, USA) was recrystallized from chloroform/methanol (50/50) v/v twice. Toluene, chloroform, and methanol products of El Nasr Chemical Company, Cairo, Egypt, were used as received. Methyl ethyl ketone, acetone, benzene, crystal violet (indicator), hydrogen bromide 43%, and anhydrous sodium sulfate products of Riedel de Haën, Seelze, Germany, were of analytical grade and used as received. Butadiene rubber (BR) of 35 Mooney viscosity and NBR (Krynac 3450) of 34% acrylonitrile content and 50 Mooney viscosity are products of Bayer Company, Leverkusen, Germany. SBR (1502) of 52 Mooney viscosity is a product of Exxon, Machelen, Belgium.

Synthesis of PGMA-g-BR

Solution copolymerization grafting of PGMA onto BR was carried out in a 2L, nitrogen flushed, three-neck round bottom flask, using a mechanical stirrer. BR toluene solution (15g/L) was introduced into the reaction vessel and heated up to 80°C. BPO (2.7 mmol) and GMA (2110 mmol) were added to the reaction medium drop-wise over 60 min. The solution copolymerization reaction mixture was stirred for 5h at a speed of 600 rpm. The copolymerization reaction product was precipitated in methanol overnight, decanted, washed several times with water and methanol, and finally dried in a vacuum oven at 40°C for a week. The grafted material (BR-g-PGMA) was purified from the homopolymer by Soxhlet extraction for 24 h using methyl ethyl ketone. PGMA-g-BR was then

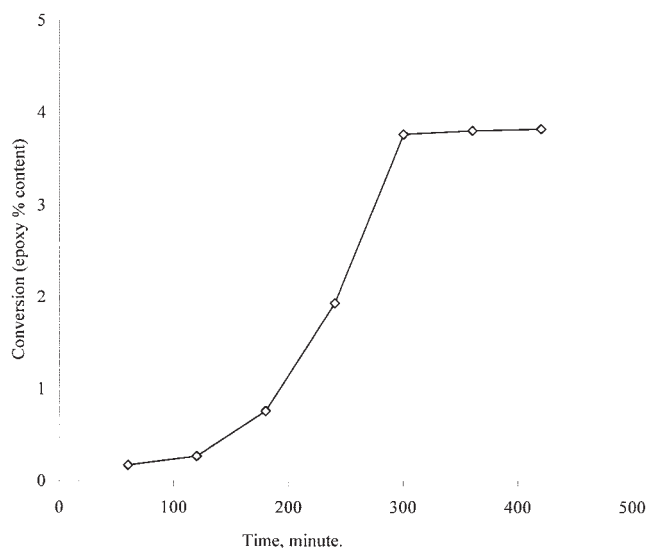


Figure 1 Conversion-time curve of graft copolymerization of glycidylmethacrylate onto butadiene rubber.

dried in a vacuum oven at 40°C for 1 week. The molar % of epoxy groups in the grafted rubber was found to be 8.86×10^4 .

Characterization techniques

PGMA-g-BR was characterized by means of: 1) Direct titration of the grafted epoxy groups against HBr,¹¹ and 2) Agilent GPC-SEC, using an Instrument from Agilent Technologies Deutschland GmbH. A Hewlett-Packard-Strasse8, Waldbronn, Germany, instrument was used to determine number average molecular weights (M_n) and polydispersity (M_w/M_n) with THF (HPLC grade) as eluent at room temperature. The GPC instrument was equipped with a series of PL gel columns (100, 10^3 , and 10^4 Å). Those columns were calibrated with narrow molecular weight distribution polystyrene linear standards. The GPC instrument was connected to an Agilent model G1362A differential refractometer (DRI) detector.

Compatibility investigation

Morphology of compatibilized and uncompatibilized SBR/NBR blends was studied using a scanning electron microscope, Model JXA-840A (JEOL Technics Co. Ltd., Tokyo, Japan) at magnification $M = 500\times$. The surface of the polymer was mounted on a standard specimen stub. A thin coating 10 Å of gold was deposited onto the polymer surface and attached to the stub prior to examination in the microscope to enhance conductivity. T_g s of rubber blends were determined utilizing a DSC calorimeter, Shimadzu, DSC-50 (Foster City, CA, USA). The DSC was operated at a heating rate of $10^\circ\text{C min}^{-1}$ within a -100 to 100°C

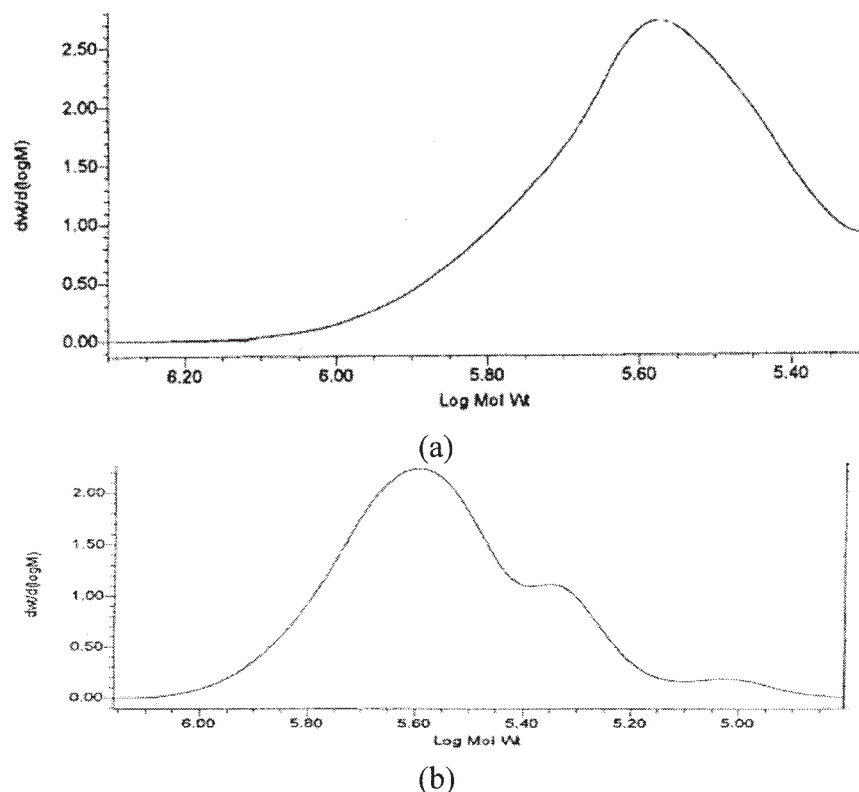


Figure 2 GPC traces of (a) butadiene rubber and (b) glycidylmethacrylate grafted butadiene rubber.

temperature range. Rubber blend specimens were heated up to 100°C , then cooled to -100°C twice to remove their thermal history. η of the blend solutions was determined with a modified Ostwald viscometer at $25 \pm 1^{\circ}\text{C}$. Various blend ratios of uncured SBR/NBR blends, with and without PGMA-g-BR compatibilizer, were dissolved in toluene to obtain 0.8, 0.6, 0.4, 0.2, and 0.1 g/100 mL solutions required for η measurements.

Mixing, vulcanization and testing of rubber

The rubber blends were mixed with curatives and other compounding ingredients, on an open two roll-mill of 170 mm diameter and 300 mm working distance at a 24 rpm speed of the slow roll and 1 : 1.25 of gear ratio at 90°C . PGMA-g-BR was first mixed with SBR, then NBR was added onto the mill followed by the other compounding ingredients. The rheometric characteristics¹² were assessed with a Monsanto (USA) Oscillating Disc Rheometer R-100 at $152 \pm 1^{\circ}\text{C}$. The blends were then cured for their respective optimum cure time, in a hydraulic press at the same temperature and pressure of 4 MPa on the mold. The physicomechanical properties were determined with a Zwick-1425 tensile tester¹³ at $25 \pm 1^{\circ}\text{C}$ and cross-head speed of 500 mm min^{-1} . Accelerated thermal aging of rubber vulcanizates was carried out in an air-circu-

lated oven at 90°C for 7 days. Swelling tests of rubber blend vulcanizates in toluene were carried out at $25 \pm 1^{\circ}\text{C}$ for 48 h¹⁴; however, swelling tests in motor oil were conducted at $100 \pm 1^{\circ}\text{C}$ for 8 days, in a thermo-

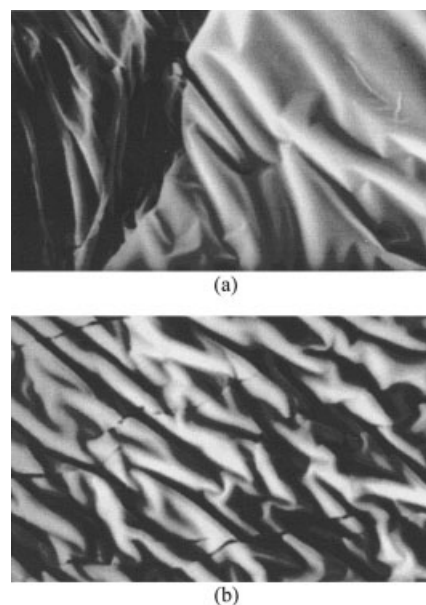
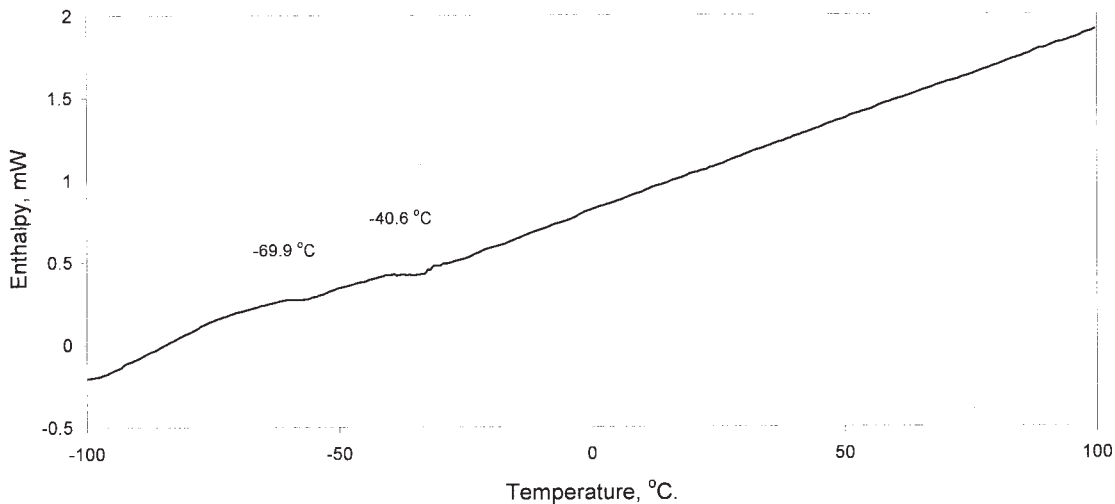
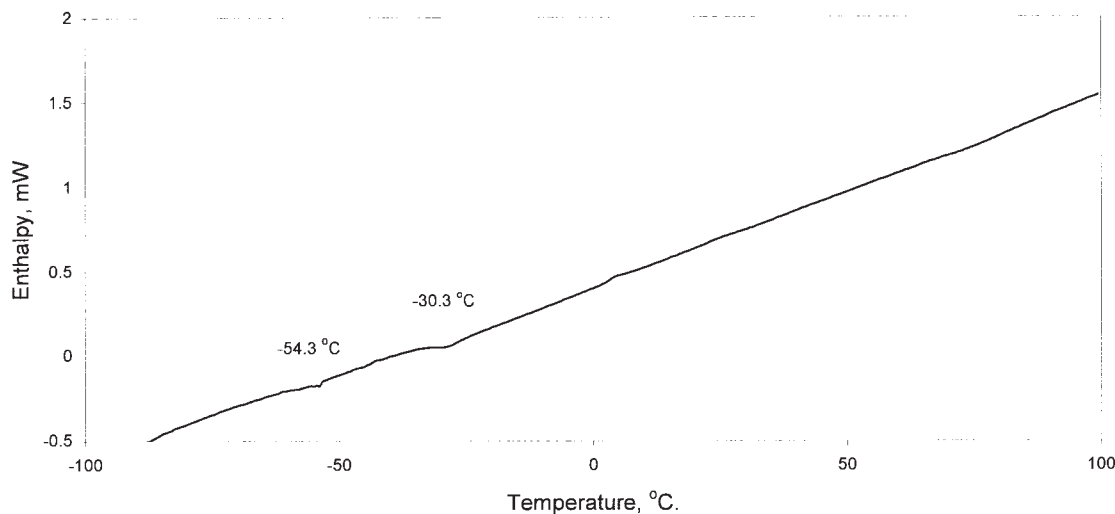


Figure 3 SEM micrographs of SBR/NBR (50/50) blends: (a) uncompatibilized and (b) compatibilized with GMA-g-BR. $M = 500\times$.



(a)



(b)

Figure 4 DSC traces of SBR/NBR (50/50) blends: (a) uncompatibilized and (b) compatibilized with GMA-g-BR.

stated electric oven. The physicomechanical and swelling data were measured in five replicates.

Degree of crosslinking density

The swelling data were utilized to determine the molecular weight between two crosslinks (M_c) by applying the Flory–Rehner equation.¹⁵

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2}$$

$$V_r = 1/(1 + Q_m)$$

where ρ is the density of the rubbers, V_s is the molar volume of the solvent (toluene), V_r is the volume fraction of the swollen rubber, χ is the interaction parameter of the rubber, and Q_m is the weight swell of the SBR/NBR blends in toluene.

The degree of crosslinking density (ν) is given by

$$\nu = 1/(2M_c)$$

The following constant values were used to determine the degree of crosslinking density of SBR/NBR in the presence and absence of AN-g-BR and/or GMA-g-BR.

$$\rho \text{ (SBR) } 0.933 \text{ g/cm}^3 \quad \rho \text{ (NBR) } 1.17 \text{ g/cm}^3$$

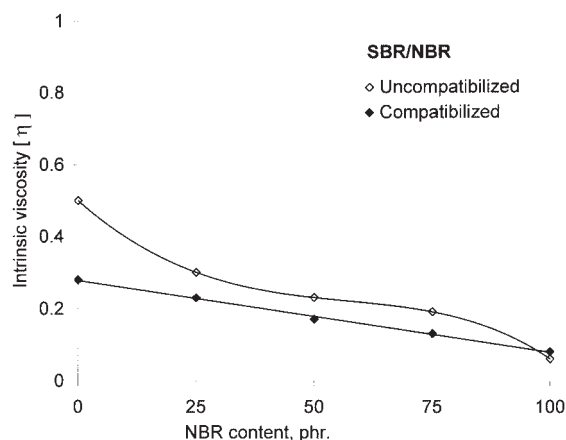


Figure 5 Intrinsic viscosity versus NBR content in SBR/NBR blend, in presence and absence of PGMA-g-BR compatibilizer.

$$\chi(\text{SBR}) 0.446 \quad \chi(\text{NBR}) 0.390$$

$$V_s(\text{toluene}) 106.35 \text{ cm}^3/\text{mol}.$$

RESULTS AND DISCUSSION

Solution copolymerization grafting of PGMA-g-BR

The graft solution copolymerization of PGMA was carried out onto BR. The conversion-time curve, as a function of % epoxy content, is shown in Figure 1. The induction period of the graft copolymerization is quite low, ~ 30 min. The conversion to PGMA-g-BR increases with time up to 5 h, and then levels off at 3.8%.

Gel permeation chromatography

The GPC traces of PGMA-g-BR and BR (Fig. 2) show lower M_n (3.12×10^5) and higher polydispersity index

($M_w/M_n = 1.24$) for PGMA-g-BR when compared with the mother BR, which shows $M_n = 3.66 \times 10^5$ and $M_w/M_n = 1.13$. These results indicate that there is a considerable amount of PGMA-g-BR, which appears as a larger species in the trace with higher molecular weight than the mother BR. The GPC trace of PGMA-g-BR shows a shoulder to the right of the main peak that contributes to the mother BR. The drop in M_n and the elevation of the polydispersity index are attributed to the difference in molecular weights and shapes of the mother linear BR and the branched PGMA-g-BR.

Compatibility of SBR/NBR blends

SBR/NBR (50/50) blends with and without PGMA-g-BR (10 phr) were prepared for microscopy examination. The micrograph (Fig. 3a) of the blend without compatibilizer illustrates two different phases for the individual rubbers, indicating phase separation and incompatibility of the SBR/NBR blend. However, the micrograph (Fig. 3b) of the blend containing PGMA-g-BR shows one phase and no phase separation takes place, indicating a change of morphology and enhancement of the homogeneity of the SBR/NBR blend. Figures 4a and b illustrate DSC traces of SBR/NBR (50/50) blends with and without PGMA-g-BR. T_g s of SBR and NBR in the blend without compatibilizer appear at -69.9°C and -40.6°C , respectively, with a T_g difference of 29.3°C . However T_g s of SBR and NBR in the blend with PGMA-g-BR appear at -54.3°C and -30.3°C , respectively, with a T_g difference of 24°C . These data illustrate that T_g s of SBR and NBR became closer to each other upon incorporation of PGMA-g-BR. This can be attributed to the reduction of interfacial energy and to the increase of adhesion between phases.¹⁶ The intrinsic viscosities of the un-

TABLE I
Formulations, Rheological and Physicomechanical Properties of SBR/NBR Rubber Blends with Different Blend Ratios in Presence and Absence of PGMA-g-BR

Ingredients, phr.	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
SBR	100	75	50	25	0	100	75	50	25	0
NBR	0	25	50	25	100	0	25	50	75	100
PGMA-g-BR	0	0	0	0	0	10	10	10	10	10
<i>Rheological properties</i>										
Minimum torque, Nm	8	9	8.5	8	7	7	8.5	7.5	8	9
Maximum torque, Nm	68	60	64	67	70	71	63	65	68	74
Cure time (t_{C90}), min	25	18.5	17.5	20	23	35	17	18	19	25
Scorch time (ts2), min	4.5	5	5	4.25	3.8	4	3.25	4.25	3.75	3
Cure rate index (CRI), min^{-1}	4.8	7.4	8	6.3	5.3	3.2	7.3	7.3	6.5	4.5
<i>Physicomechanical properties</i>										
Tensile strength, MPa	15.8	14.4	16.8	14.1	12.9	11.7	12.9	18.5	15.4	15
100% modulus, MPa	1.4	2	2.2	2.3	1.9	1.5	1.5	1.6	1.5	1.7
Elongation at break, %	775	665	740	685	675	700	850	1000	935	965

The base recipe contains, in parts by weight, zinc oxide 5, stearic acid 2, high abrasion furnace black (HAF) 40, processing oil 5, N-cyclo hexyl-2-benzothiazole sulfenamide (CBS) 1, sulfur 2.

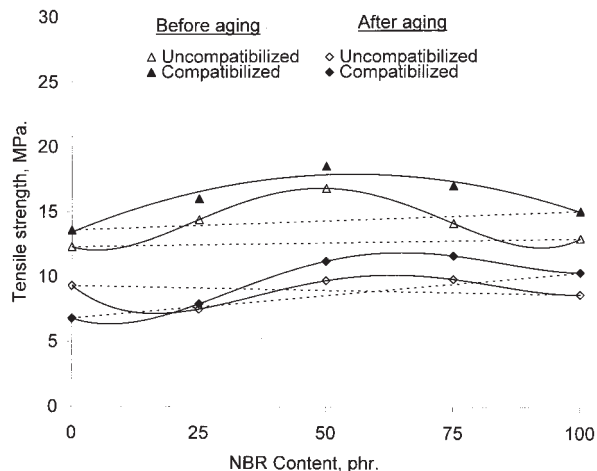


Figure 6 Tensile strength of SBR/NBR blend vulcanizate before and after thermal aging for 7 days in presence and absence of PGMA-g-BR versus NBR content in the blend.

cured blends were determined and plotted versus the SBR/NBR blend ratios (Fig. 5). The blends without PGMA-g-BR (S1–S5) show an S-shape relation whereas the blends with PGMA-g-BR (S6–S10) show a straight line, which indicates homogeneity^{17,18} of the PGMA-g-BR containing SBR/NBR blends.

Effect of PGMA-g-BR on the physicochemical properties of SBR/NBR blends

SBR/NBR rubber blends with different blend ratios were prepared in the presence and absence of PGMA-g-BR. The formulations and the rheological properties of SBR, NBR, and their blends are listed in Table I. Cure times (t_{c90}) of the SBR/NBR blends were shorter and cure rate indices were greater than those of the individual rubbers. The rubber mixes were then vulcanized at their cure times. Physicochemical properties of SBR, NBR, and their blends with different blend ratios, in the presence and absence of a compatibilizer, were measured before and after thermal aging and plotted versus NBR content in the blend. Tensile strength (Fig. 6) of the uncompatibilized SBR/NBR showed an irregular relationship with NBR content in the blend before aging. That points to the incompatibility of that blend.¹⁶ However, the tensile strength of SBR/NBR vulcanizates compatibilized with PGMA-g-BR showed a positive deviation from the additive rule (a desirable phenomenon). The improvement in the mechanical properties can be attributed to the improved interfacial adhesion of SBR/NBR blends by reducing the interfacial energy between phases as a result of incorporation of PGMA-g-BR. Also, the tensile strength of SBR/NBR compatibilized blends after 7 days of thermal aging showed better performance than that of the uncompatibilized blend, which showed a negative deviation from the additive rule.

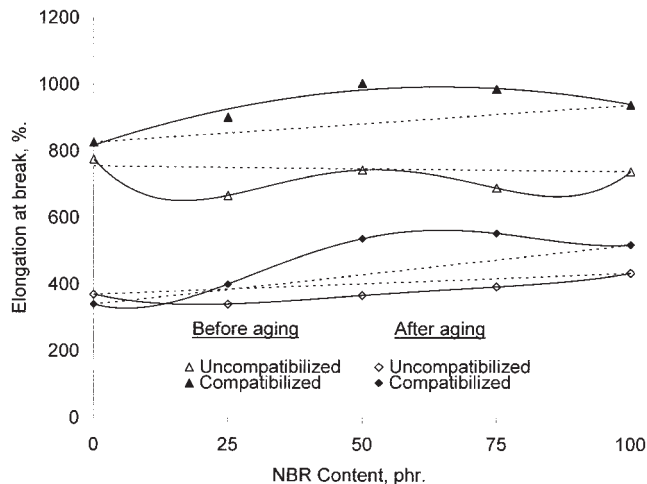


Figure 7 Elongation at break, %, of SBR/NBR blend vulcanizate before and after thermal aging for 7 days in presence and absence of PGMA-g-BR versus NBR content in the blend.

The SBR/NBR (50/50) blend, as well as the 25/75 blend, showed a more pronounced effect of PGMA-g-BR. On the other hand, elongation at break (Fig. 7) before thermal aging of the uncompatibilized blend showed an irregular pattern. However, elongation at break of the compatibilized blend showed a positive deviation from the additive rule. Thus, the compatibilized blend showed a much better elongation at break than the uncompatibilized blend after thermal aging for 7 days. The effect of the compatibilizer is much more pronounced in the 50/50 and 25/75 SBR/NBR blends. The elongation at break and tensile strength data confirm one another. Therefore, 50/50 and 25/75 SBR/NBR blends possess good mechanical properties

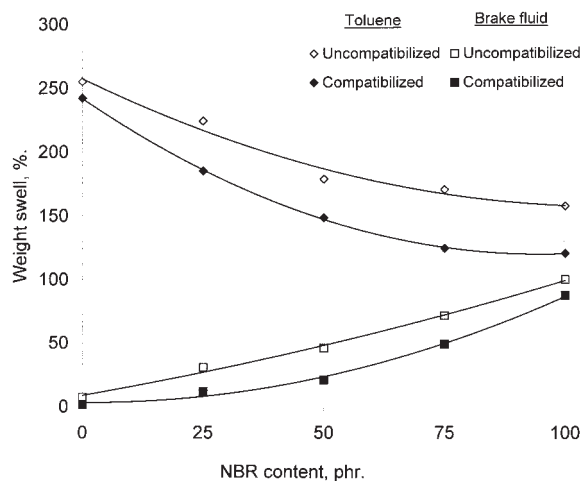


Figure 8 Weight swell after immersion in toluene for 2 days at 25°C and in brake fluid for 8 days at 100°C versus NBR content in SBR/NBR blend with and without GMA-g-BR as compatibilizer.

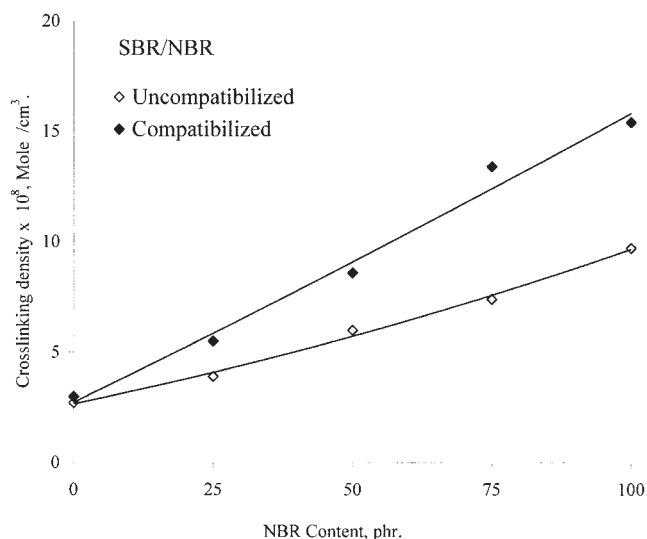


Figure 9 Crosslinking density of SBR/NBR blends in presence and absence of GMA-g-BR versus NBR content in the blend.

together with the best thermal stability. Generally, NBR and the NBR rich blends (Figs. 6 and 7) showed thermally stable mechanical properties. This can be attributed to the increase of the more thermally stable acrylonitrile content.

Figure 8 illustrates that weight swell of the SBR/NBR rubber blend vulcanizates decreased in toluene and increased in brake fluid with increasing NBR content in the blend. That can be attributed to the polar nitrile group of NBR. Thus, SBR/NBR (25/75) exhibited the best swelling behavior in toluene while SBR/NBR (75/25) possessed the best swelling behav-

ior in brake fluid. Therefore, the SBR/NBR blend (75/25) can be recommended to be used in industry for oil seals and hoses subjected to brake fluid.

Weight swell values of the compatibilized SBR/NBR blends are less than those of the uncompatibilized blends. This could be attributed to the increase in crosslink density of SBR/NBR vulcanizates as a result of incorporation of PGMA-g-BR, which contains oxirane groups. Swelling data were used to calculate the crosslinking density^{15,19} of SBR/NBR blends with and without PGMA-g-BR according to the Flory equation. The crosslink density was plotted versus NBR content in the blends, as shown in Figure 9. It is obvious that the crosslink density of the blends increased with increasing NBR content in the blend. The increase in crosslink density is much more pronounced in PGMA-g-BR compatibilized blends. This can be attributed to the epoxy group present in the compatibilizer.

SBR/NBR (25/75) blends were prepared with various combinations of inorganic fillers, namely, silica/talc, talc/kaolin, and silica/kaolin, in the presence and absence of PGMA-g-BR, as shown in Table II. Physico-mechanical properties of the blend vulcanizates were measured before and after accelerated thermal aging. Figure 10 illustrates that the talc/kaolin combined filler possessed the least tensile strength throughout the aging periods. This can be attributed to the fact that talc and kaolin are nonreinforcing fillers. However, the combination of silica with either kaolin or talc resulted in vulcanizates with the highest tensile strength during thermal aging due to the presence of the reinforcing silica filler. The silica/kaolin combination resulted in vulcanizates that possessed the best thermal stability together with high tensile

TABLE II
Formulations, Rheological and Physico-mechanical Properties of SBR/NBR Rubber Blend (75/25) Filled with Various Combinations of Inorganic Fillers in Presence and Absence of PGMA-g-BR

Ingredients, phr.	S11	S12	S13	S14	S15	S16
SBR	25	25	25	25	25	25
NBR	75	75	75	75	75	75
PGMA-g-BR	0	0	0	10	10	10
Silica	20	0	20	20	0	20
Talc	20	20	0	20	20	0
Kaolin	0	20	20	0	20	20
<i>Rheological properties</i>						
Minimum torque, Nm	7	4	8	7	4	7
Maximum torque, Nm	43	25	45	49	31	52
Cure time (t_{c90}), min	30	22.5	26.5	35	30	29.5
Scorch time (t_{s2}), min	6	8.5	6.5	4.5	4.5	4.25
Cure rate index (CRI), min ⁻¹	4.2	7.1	5	3.3	3.9	3.9
<i>Physico-mechanical properties</i>						
Tensile strength, MPa	3.8	1.8	3.9	5	2.5	4.6
100% modulus, MPa	1.9	1.75	1.95	1.7	1.64	1.8
Elongation at break, %	1050	1010	950	1300	1350	1250

The base recipe contains, in parts by weight, zinc oxide 5, stearic acid 2, processing oil 5, N-cyclohexyl-2-benzothiazole sulfenamide (CBS) 1, sulfur 2.

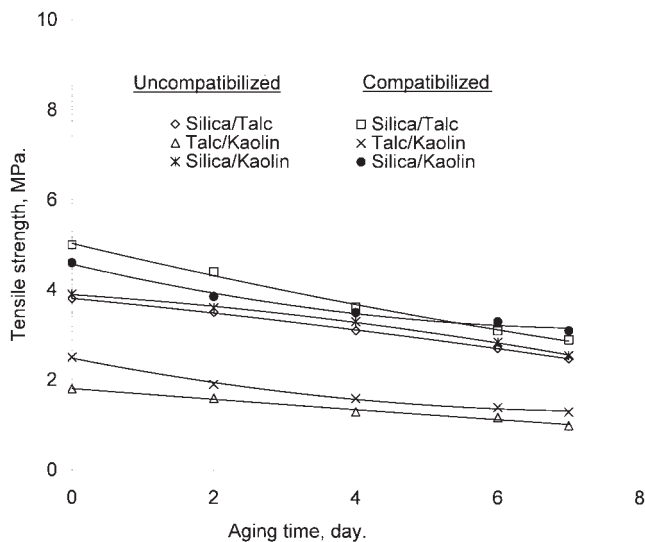


Figure 10 Tensile strength of SBR/NBR (25/75) blend with various combinations of inorganic fillers in presence and absence of PGMA-g-BR compatibilizer versus aging time at 90°C.

strength. This can be attributed to the thermal stability of the oxides of silicon and aluminum present in the silica and kaolin fillers, respectively.

Figure 11 illustrates the variation of elongation at break versus the thermal aging period. It is clear that the vulcanizate filled with the silica/kaolin combined filler and compatibilized with PGMA-g-BR possessed the highest elongation at break as well as the best thermal stability, which is in agreement with the results of tensile strength obtained. Figure 12 reveals that 100% modulus of all vulcanizates under investi-

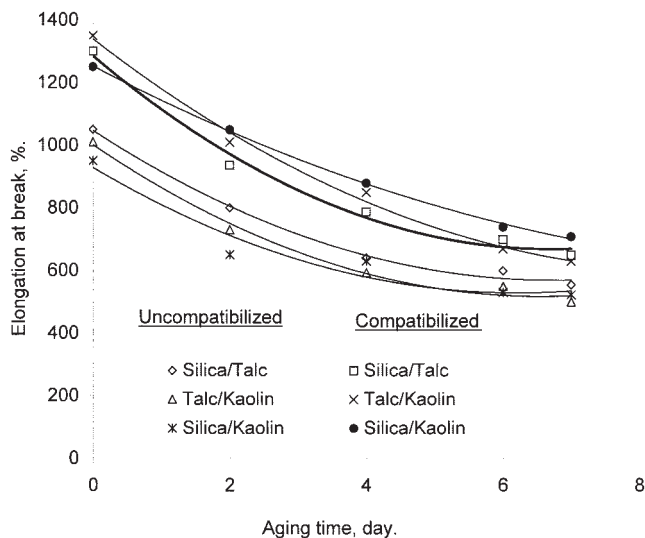


Figure 11 Elongation at break of SBR/NBR (25/75) blend with various combinations of inorganic fillers in presence and absence of PGMA-g-BR compatibilizer versus aging time at 90°C.

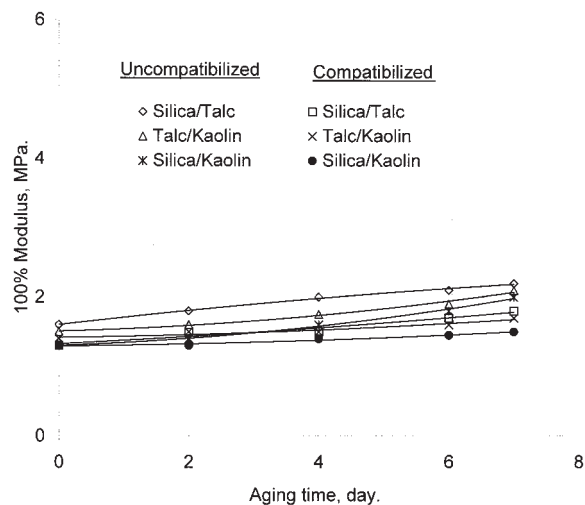


Figure 12 100% modulus of SBR/NBR (25/75) blend with various combinations of inorganic fillers in presence and absence of PGMA-g-BR compatibilizer versus aging time at 90°C.

gation increase upon thermal aging. However, the silica/kaolin filled SBR/NBR compatibilized with PGMA-g-BR vulcanizate exhibits the least change in 100% modulus, confirming its highest thermal stability shown with the tensile strength and elongation at break results obtained. In summation, it can be concluded from Figures 10 through 12 that the compatibilized blends possessed higher mechanical properties than the uncompatibilized blends throughout the aging periods. This can be attributed to the dipole-dipole interaction of the epoxy groups present in PGMA-g-BR and the nitrile groups of NBR, which improved the interfacial adhesion between gross-phase-separated polymer pairs.

CONCLUSIONS

1. Incorporation of PGMA-g-BR into SBR/NBR blends improves the blend morphology and homogeneity, as shown by SEM micrographs and T_g shifts of SBR and NBR in their blend and viscosity measurements.
2. The SBR/NBR (25/75) rubber blend compatibilized with PGMA-g-BR possessed the best thermal stability, together with good physicomechanical properties.
3. The weight swell of SBR/NBR vulcanizates decreased in toluene and increased in brake fluid with increasing NBR content in the blend.
4. The SBR/NBR (75/25) blend vulcanizate possessed the best swelling performance in brake fluid. However, the (25/75) blend vulcanizate possessed the best swelling performance in toluene.

5. Physicomechanical properties of SBR/NBR compatibilized blends filled with silica/kaolin combined fillers possessed the best thermal stability.
6. The conversion % to PGMA-g-BR increases with time up to 5 h, then levels off at 3.8%.

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