

Chemical Sensing Materials II: Electrically Conductive Peroxide Crosslinked SEBS Copolymers Systems

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ABSTRACT: Chemical sensing materials based on electrically conductive styrene-ethylene butylene-styrene (SEBS) triblock-copolymers systems were investigated. Systems based on crosslinked rather than thermoplastic SEBS systems can be exposed to a wide range of chemical environments. Composites of SEBS containing various amounts of CB and Varox DBPH (peroxide crosslinking agent) were prepared by blending at relative low temperatures, limiting the peroxide activation, and then compression molding at elevated temperatures. Samples containing CB at a level near the corresponding percolation threshold were used for the sensing experiments. Structure characterization included crosslink level and density, dynamic mechanical

analysis (DMA), and calorimetry (DSC). The crosslinked SEBS composites exhibit large reversible changes in conductivity on exposure to various solvents and air drying cycles. The observed electrical conductivity changes on solvent sorption/desorption is based on the polymer reversible swelling, resulting in breakdown and reconstruction of conductive CB networks, respectively. Sensing performance depends mainly on the solvents solubility parameter and volatility. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1390–1396, 2009

Key words: block copolymers; crosslinking; elastomers; sensors

INTRODUCTION

Electrically conductive polymers and composites have recently been widely studied for chemical sensors applications.^{1–5} Conductive polymer composites are commonly prepared by mixing insulating polymers and conducting fillers, e.g., carbon black (CB), metal particles.^{6,7} When this type of composites is exposed to organic chemicals compatible with the polymer matrix, their resistance increase drastically.⁸ It is generally believed that the matrix swelling, which enlarges the interfiller particle distance, accounts for the sensing ability.³

Styrene-ethylene/butylene-styrene (SEBS) triblock copolymers, part of a quite large family of styrenic block copolymers, are thermoplastic, elastomeric materials. Because the S and the EB blocks are not compatible, they phase separate, forming polystyrene nanodomains locking both ends of the EB block into a physically crosslinked network structure. Because these crosslinks are physical rather than chemical, SEBS cannot be used at high temperatures (above the glass transition temperature [T_g] of the polystyrene blocks) and in applications where resistance to solvents is required. To overcome these limitations chemical crosslinks are necessary.⁹ SEBS

polymers are difficult to crosslink due to the hydrogenated form of the polymer chain.⁹ Modified SEBS polymers having a small amount of grafted maleic anhydride (MA) are commercially available. They can be used for the crosslink reactions since the (MA) modification of the polymer chain increases the reactivity of the polymer main chain.^{10,11}

The main objectives of the present research were to peroxide crosslink the carbon black (CB) filled SEBS blends and investigate their chemical sensing behavior, in comparison with the behavior of the corresponding thermoplastic systems.¹

EXPERIMENTAL

The studied systems were based on thermoplastic SEBS tri-block-copolymers, Kraton G polymers, (Kraton Polymers, UK). Three types of Kraton polymers were used, G1652, G1657, and FG1901X, differing in styrene/EB ratio (30/70, 13/87, and 30/70, respectively), solution viscosity (1.8, 4.2, and 5 Pa s, respectively, of 25 wt % toluene solutions at 25°C), and group functionality. A highly structured electrically conductive CB, Ketjenblack EC-600 (Akzo-Nobel, Netherlands), was used as the conductive filler. CB content within the polymer is referred to in the text in phr units (part per hundred, by weight). Peroxide crosslinking agent Varox DBPH (R.T. Vanderbilt Company) was used for chemical crosslinking of the SEBS copolymers.

SEBS/CB/Varox blends were prepared in two steps: first, melt blending of polymer/CB mixtures

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in a Brabender Plastograph at 260°C, for 15 min. Afterward the temperature of the mixing cell was air cooled to 145°C (below the initiation temperature of the peroxide) and the crosslinking agent, Varox DBPH, was added and blending continued for an additional minute. The resulting blends were then cut to small pieces and compression molded at 170–180°C. Following molding, the samples were post cured in an air oven at 100°C for 2 h. Crosslink level (% gel) and density (average molecular weight between crosslinks) of compression-molded samples were determined by chloroform Soxhlet extraction and polymer swelling in chloroform for 24 h.

Surface electrical resistivity was measured using the two-point method. The resistance between two silver marks painted on the surface of compression-molded samples ($\sim 3 \times 3 \times 23 \text{ mm}^3$ in sizes) was measured (DIN-53596) using a Fluke 8840A multimeter. Silver paint was applied to minimize contact resistance between the sample and the electrodes.¹

For sensor analysis, $\sim 3 \times 3 \times 23 \text{ mm}^3$ compression-molded samples were used. Two silver paint marks were applied on the surface of the samples, 10 mm apart. Copper electric wires were connected to the sample at the marked areas. Liquid sensing experiments were performed by immersion/drying cycles at $\sim 25^\circ\text{C}$ along with continuous monitoring of the changing resistance. All data are presented as relative resistance, i.e., R_t/R_0 , where R_0 is the initial resistance of the sensor and R_t is the measured resistance at time t . The solvents used in this study included acetone, *n*-heptane, chloroform, cyclohexane, and 1,2-dichloroethane.

Differential scanning calorimetry (DCSQ10) was carried out at heating and cooling rates of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. Samples, $\sim 5 \text{ mg}$ in weight, were heated to a temperature above their T_g , cooled at the same rate, and subsequently reheated. Dynamic mechanical analysis (DMAQ800) was performed using the tension mode with rectangular samples, $\sim 2 \times 3 \times 6 \text{ mm}^3$ in size, at 1 Hz. Heating was carried out in a nitrogen atmosphere, at a rate of $5^\circ\text{C}/\text{min}$.

Sorption of solvents was studied using an immersion/weight gain method at room temperature. Compression-molded samples, $\sim 3 \times 3 \times 23 \text{ mm}^3$ in sizes, were immersed in plastic bottles containing the respective solvents. At various time intervals, the specimens were removed from the solvent, wiped off by a filter paper, and weighed. Solvent content in the samples at time t was calculated as:

$$\% \text{Sorption} = (\text{Weight at time } t - \text{Initial weight}) \times 100 / \text{Initial weight}$$

The crosslink level (% gel) of the samples was determined after Soxhlet extraction in chloroform for 24 h by using the following equation:

$$\text{Crosslinklevel} = 100 \times W_f/W_i [\%] \quad (1)$$

Where W_i —weight before the extraction, W_w —weight after removing from the solvent, and W_f —weight after drying in a vacuum oven at 40°C , for 24 h. The crosslink density (average molecular weight between crosslinks) was determined using the following equation¹²:

$$M_x = \frac{\rho \times V_1}{\left(\frac{\phi_2}{2} - \phi_2^{1/3}\right)^{-1} \times (\ln \phi_1 + \phi_2 + \chi \times \phi_2^2)} \quad (2)$$

where ρ is the density of the polymer, V_1 is the molar volume of the solvent (chloroform), ϕ_2 is the volume fraction of the polymer, ϕ_1 is the volume fraction of the solvent, and χ is the polymer–solvent interaction parameter, modeled as the sum of entropic and enthalpic components¹³:

$$\chi = \chi_H + \chi_S \quad (3)$$

where χ_S is the entropy component, usually 0.3–0.4 for nonpolar systems; 0.34 was used. The enthalpy component, χ_H , can be related to the Hildebrand parameters, δ ¹³:

$$\chi_H = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (4)$$

Therefore,

$$\chi = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 + 0.34 \quad (5)$$

where δ_1 and δ_2 are the solubility parameter of the solvent and the polymer, respectively. The δ_2 value was calculated as follows¹³:

$$\delta_2 = \frac{\rho_2 \sum_i G_i}{M_2} \quad (6)$$

where ρ_2 is the polymer density, M_2 is the polymer molecular weight of a repeating unit, G_i is the Gibbs free energy of component i in the repeating unit determined by small or group contribution method.¹³

RESULTS AND DISCUSSION

Resistivity–Crosslink Relationships

To extend the use of SEBS in the environment of various solvents, selected SEBS blends were chemically crosslinked, preventing dissolution. Three types of SEBS (G1652, G1657, and FG1901) were selected to be crosslinked. These polymers have relatively high melt index (5, 22, and 22 g/10 min, respectively), allowing blending at a temperature below 150°C , the initiation temperature of the peroxide.

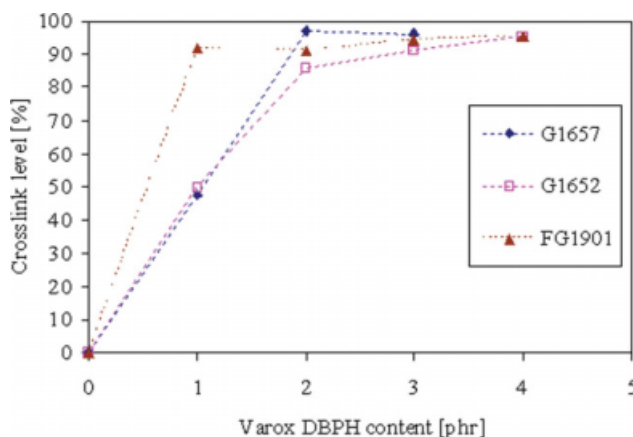


Figure 1 Crosslink level (% gel) of various SEBS vs. peroxide content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 1 depicts the crosslink level of the three SEBS copolymers as a function of Varox DBPH content. It seems that 2-phr peroxide is practically sufficient to fully crosslink (100% gel) the copolymers. The behavior of the G1652 and G1657 polymers, having S/EB ratios of 30/70 and 13/87, respectively, is practically the same. SEBS FG1901 (S/EB ratio of 30/70) is almost fully crosslinked even with just 1phr of Varox DBPH, as seen in Figure 1. The grafted anhydride functionality (1.7% grafted maleic anhydride) increases the reactivity of the polymer main chain.^{10,11} The crosslink reaction takes place in the EB phase of the SEBS copolymer since it is more difficult to extract hydrogen atoms to form a radical from the PS than from the EB phase.

Figure 2 depicts the average molecular weight (M_w) between crosslinks, estimated using eq. (2), as a function of the Varox DBPH content. As expected, the average M_w between crosslinks decreases with an increase of the peroxide content. The crosslink density of FG1901 increases already at Varox content of 1 phr, whereas the crosslink density obtained for the three samples at Varox content ≥ 2 phr is practically the same, though some copolymer molecular effect is clearly seen.

Interestingly, there is no significant difference between the surface resistivity of the three studied copolymers with and without crosslinking (data not shown). Thus, crosslinking has no effect on the surface resistivity.

Thermal behavior

The two phase system in SEBS polymers results in two distinct glass transition temperatures corresponding to poly(ethylene/butylene) at $T_{g1} \sim (-50^\circ\text{C})$ and polystyrene at $T_{g2} \sim 100^\circ\text{C}$. Table I summarizes the glass transition temperature values of the “soft”

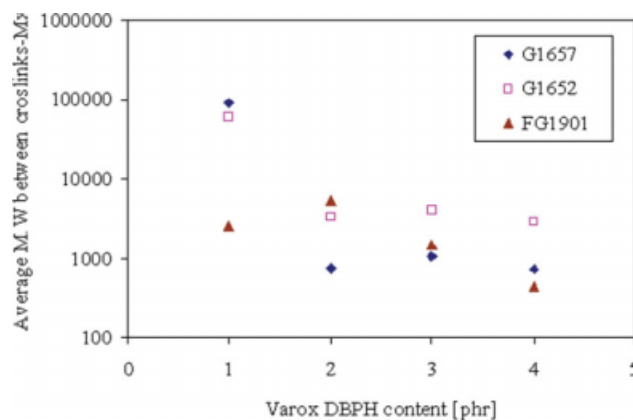


Figure 2 Average molecular weight between crosslinks in various SEBS vs. peroxide content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and “hard” phases of the neat, crosslinked and CB containing SEBS G1652 as measured by DSC. It should be mentioned that it was quite difficult to determine the T_g values due to the shape and width of the transition region in the thermograms.

The data in Table I show that the addition of peroxide to the blend, i.e., crosslinking, increases the T_{g1} value from -57°C to -46°C for the neat G1652, and from -67°C to -51.4°C for the CB-containing blend. Similar tendency was obtained for all three copolymers studied. Hence, it can be concluded and verified that the crosslinking reaction takes place in the rubbery ethylene/butylene phase of the SEBS copolymers. For the same systems, there is no clear tendency of the effect of peroxide on the glass transition temperature of the hard phase (T_{g2}). It was quite difficult to determine accurately the T_{g2} value, probably due to the low content of the hard PS phase.

Figure 3 depicts the loss modulus, the storage modulus, and the $\tan\delta$ curves for neat G1652 (a) and G1652 with 4-phr Varox (b). Two main peaks of both loss modulus and $\tan\delta$ are seen in the DMA

TABLE I
Glass Transition Temperature of THE Neat, Peroxide Crosslinked and CB-Containing SEBS as Determined by DSC

SEBS type	Styrene part in SEBS	Rubber part in SEBS	CB content [phr]	Varox content [phr]	T_{g1} [$^\circ\text{C}$]	T_{g2} [$^\circ\text{C}$]
G1652	30	70	–	–	–57	101
G1652	30	70	–	4	–46	117
G1652	30	70	20	–	–67	87
G1652	30	70	20	4	–51	93
G1657	13	87	–	–	–59	106
G1657	13	87	–	3	–45	109
FG 1901	30	70	–	–	–53	85
FG 1901	30	70	–	3	–45	84

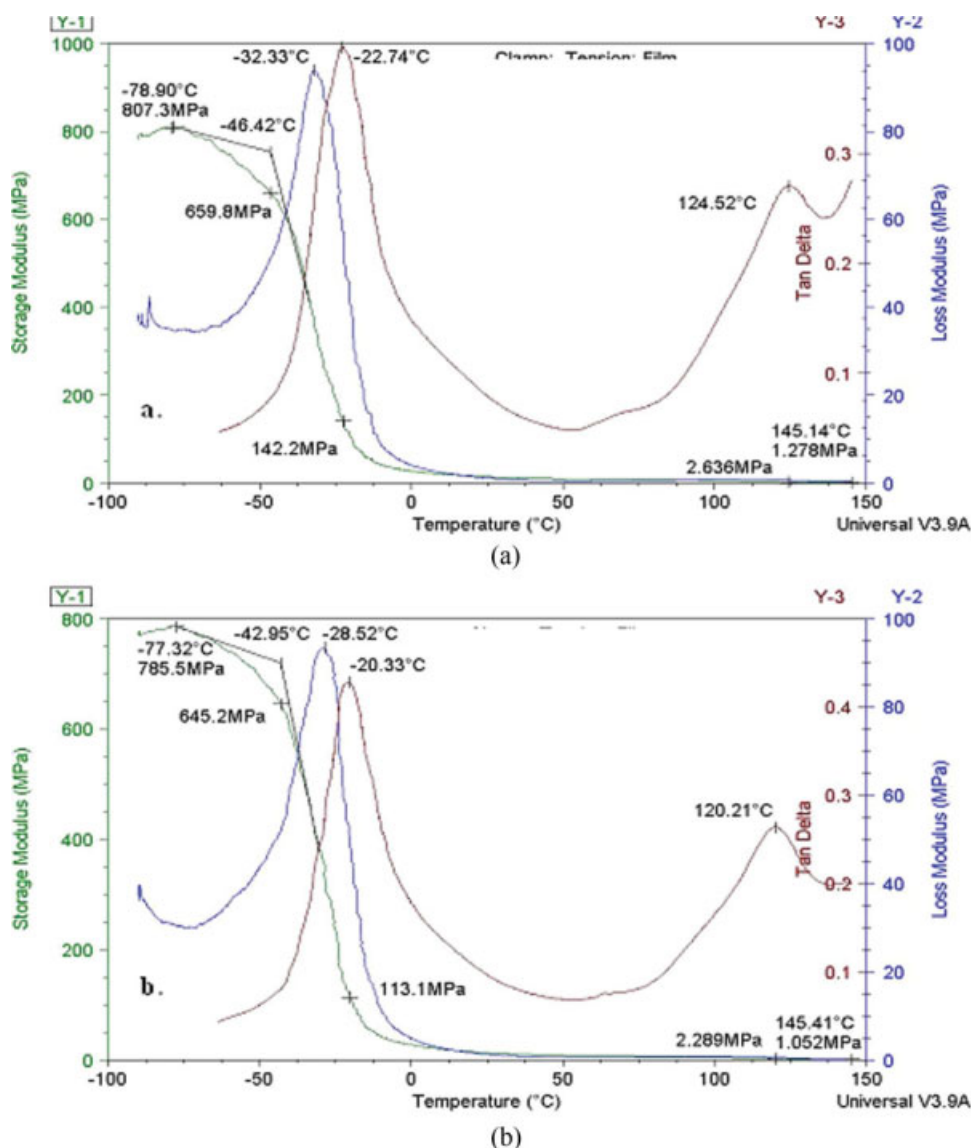


Figure 3 DMA curves of (a) neat G1652 and (b) G1652 with 2 phr Varox. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thermograms, corresponding to the glass transition of the poly(ethylene/butylene) and the polystyrene phases. DMA results are summarized in Table II for the three copolymers studied. For G1652 and FG1901 there is a few degrees increase in T_{g1} on crosslinking, whereas DSC results show an increase of about 10–12°C. There is no change in the T_{g1} of G1657 on crosslinking. FG1901 exhibited the highest T_{g1} value relative to the other copolymers, probably due to main chain modification by the grafted maleic anhydride. T_{g2} was not detected for the G1657 samples; probably due to low PS content in the copolymer, 13%, different from the 30% in the others copolymers. As expected, the T_{g2} value was not affected by the CB presence and the crosslinking as well. Although the DMA T_g values are different from those measured by DSC, they exhibit similar

TABLE II
Glass Transition Temperature of the Neat G1652 and CB-containing G1652 as Determined by DMA

SEBS type	Styrene part in SEBS	Rubber part in SEBS	CB content [phr]	Varox content [phr]	T_{g1} [°C]	T_{g2} [°C]
G1652	30	70	–	–	–32	124
G1652	30	70	15	–	–34	125
G1652	30	70	–	4	–29	120
G1652	30	70	15	4	–34	120
G1657	13	87	–	–	–34	Not detected
G1657 ^a	13	87	–	3	–33	Not detected
FG 1901	30	70	–	–	–30	124
FG 1901 ^a	30	70	–	1	–25	123
FG 1901	30	70	–	2	–27	123
FG 1901	30	70	–	3	–26	122
FG 1901 ^a	30	70	–	4	–25	117

^a Two samples were measured.

TABLE III
Solubility Values and Boiling Point of the Various Solvents Used in this Study

	T_b ($^{\circ}\text{C}$)	δ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$
Acetone	~ 56	9.9
Chloroform	~ 62	9.3
Cyclohexane	81–85	8.2
1,2-Dichloroethane (EDC)	~ 81	9.8
<i>n</i> -Heptane	~ 98	7.45

trends, allowing concluding that the crosslinking of the polymer chain takes place in the rubbery phase.

Table II also shows that CB presence in the blend (G1652) decrease the T_{g1} value by few degrees from -32.3 to -34°C and from -29 to -34°C for neat and crosslinked G1652 SEBS, respectively. Interestingly, it seems that the CB presence affects the crosslinking process, as expressed by the T_{g1} values, determined by both DSC and DMA. For G1652 SEBS, crosslinking resulted in an increase of T_{g1} from -57 to -46°C and from -32 to -28°C , as measured by DSC and DMA, respectively. However, in the presence of CB the changes are from -66 to -51°C by DSC and no change by DMA. Hence, CB interferes with the peroxide activity, probably by interacting with the peroxide radicals.

Sensing properties

Selected SEBS/CB/Varox compression-molded samples were studied as sensing materials for several different liquids. Table III presents the solubility parameter values (δ) and the boiling points (T_b) of the solvents used in this study. These parameters are crucial to understand the different behavior of SEBS in these solvents. *n*-Heptane [$\delta = 7.45$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$], and cyclohexane [$\delta = 8.2$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$] are good solvents for the ethylene/butylene mid-block, whereas 1,2-dichloroethane [$\delta = 9.8$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$] and chloroform [$\delta = 9.3$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$] $^{14-16}$ are good solvents for the polystyrene block. The lower the boiling point of the solvent (high vapor pressure), the faster it can desorb out from the sample during the drying cycle.

Figure 4 depicts the relative resistance, R_r , of crosslinked G1657/15phr CB/2phr Varox and uncrosslinked (dash lines) samples as a function of exposure time to various solvents for three sequential immersion/air cycles of 6 min. These samples displayed an increasing resistance on exposure to the various solvents. In acetone, the crosslinked samples exhibited reversible behavior similar to the uncrosslinked sample but with higher sensitivity; maximal R_r of 14 compare to 10, respectively. In *n*-heptane, the crosslinked samples exhibited accumu-

lative increase in resistance even after 3 min air drying, similar to the G1651/15phr CB/2phr Varox samples, 1 in contrary to the G1657/15phr CB uncrosslinked sample that exhibited reversible behavior due to dissolution of the copolymer in the *n*-heptane.

The chemical crosslinking of the SEBS copolymer allowed the use of SEBS blends for sensing additional solvents, including 1,2-dichloroethane (EDC), cyclohexane, and chloroform. The uncrosslinked SEBS blends dissolved completely in these solvents. The electrical resistance of G1657/15phr CB/2phr Varox samples exposed to these solvent, did not return to its initial values and showed accumulative increase in resistance even after air drying for 3 min. The electrical behavior in cyclohexane [$\delta = 8.2$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$] is similar to that in *n*-heptane [$\delta = 7.45$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$]; both are good solvents for the mid-block EB. 15 During the exposure cycle, the solvent molecules diffuse into the bulk, and cannot diffuse quickly out during the air drying, since cyclohexane and heptane have relative high boiling points of $81-85^{\circ}\text{C}$ and $\sim 98^{\circ}\text{C}$, respectively. Thus, permanent low increase in resistance is observed during several consecutive cycles. The sensitivity of G1657/15phr CB/2phr Varox samples in cyclohexane and heptane are similar and relatively low; maximal R_r of 4.3 and 7.4, respectively. In EDC [$\delta = 9.8$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$], a good solvent for the outer PS block, the sensitivity is higher than in acetone [$\delta = 9.9$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$]; maximal R_r of 60 compare to 14, respectively. G1657/15phr CB/2phr Varox samples exposed to chloroform [$\delta = 9.3$ ($\text{cal}\cdot\text{cm}^{-3}$) $^{1/2}$], a good solvent for the outer PS block, exhibited the highest resistance increase, maximal R_r of 130 (above the resistivity measurement limits, >20 M Ω /sq, of

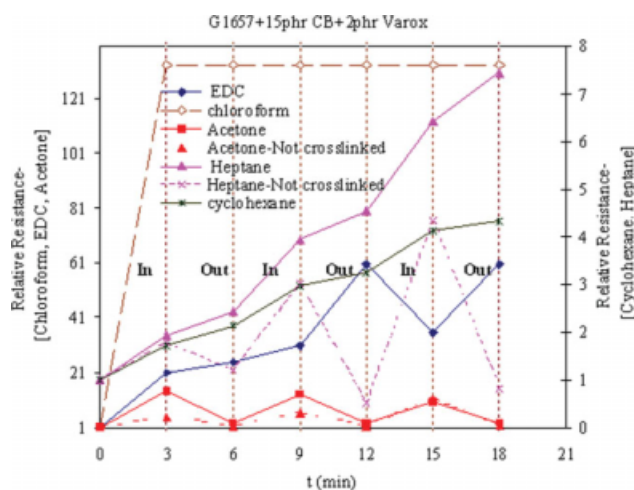


Figure 4 Relative resistance vs. exposure time to different solvents for G1657/15phr CB/2phr Varox. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

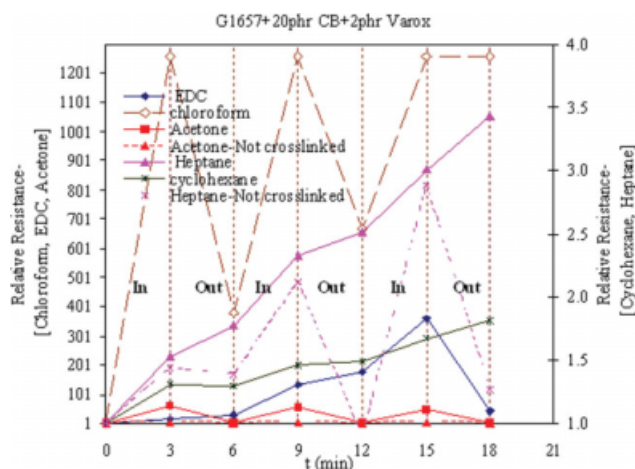


Figure 5 Relative resistance vs. exposure time to different solvents for G1657/20phr CB/2phr Varox. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the instrument). The boiling point of chloroform at 62°C is relatively low compared to that of EDC and cyclohexane at 81–85°C, and 81°C, respectively. Nevertheless, all these solvent have high molecular volume, resulting in slow desorption rates. Thus, owing to their relatively slow rate of desorption their resistance does not return to its initial value during the prescribed relatively short 3 min drying cycle.

Increasing the CB content from 15 to 20 phr, further above the percolation threshold than the 15 phr CB-containing samples, increases the sensitivity to most studied solvents. Figure 5 depicts the relative resistance, R_r , of G1657/20phr CB/2phr Varox (chemically crosslinked) and the uncrosslinked samples (dash lines), as a function of exposure time to various solvents for three sequential cycles of 6 min. For both G1657 crosslinked samples (15phr CB and 20phr CB), the samples with the higher CB content (20 phr) were more sensitivity to acetone, EDC, and chloroform, whereas the 15 phr CB crosslinked samples were more sensitive to cyclohexane and heptane.

In acetone G1657/20phr CB/2phr Varox samples exhibited reversible behavior, similar to the uncrosslinked sample but with much higher sensitivity; maximal R_r of 60 compare to 6, respectively. In *n*-heptane, crosslinked samples exhibited permanent increase in resistance even after air drying for 3 min, similar to the G1657/15phr CB/2phr Varox samples (Fig. 4), in contrary to the G1657/20phr CB uncrosslinked sample that exhibited reversible behavior due to dissolution of the copolymer in the *n*-heptane. The electrical resistance of G1657/20 phr CB/2 phr Varox samples exposed to 1,2-dichloroethane (EDC), cyclohexane, and chloroform, did not return

to their initial values and showed accumulative increase in resistance in cyclohexane, even after air drying for 3 min. The electrical behavior in cyclohexane is similar to *n*-heptane; the sensitivity is similar and relatively low; maximal R_r of 1.8 and 3.5, respectively. In the other studied solvents, the behavior is similar to the system containing 15phr CB; however, the sensitivity is significantly higher, up to an order of magnitude.

The effect of drying time was studied for the crosslinked sample in chloroform. Figure 6 depicts the relative resistance, R_r , of G1657/15phr CB/2phr Varox for three cycles in chloroform. In a single cycle, sample was immersed for 3 min and then allowed to dry in air for 9 min. Reversible behavior was observed, in contrast to the behavior of the same sample exposed to chloroform but allowed to dry in air for only 3 min. This observation indicates that reversible behavior can be achieved when enough time is available for the solvent to diffuse out of the sample. Significant resistance changes are observed in the subsequent immersion/drying cycles. The sensitivity of the SEBS/CB samples significantly increased in the second and third cycle in chloroform, maximal R_r of 2350 (above the resistivity measurement limits, >20 M Ω /sq, of the instrument) compare to 140 in the first cycle. These changes in resistance may be accounted for by the occurrence of structural changes in the sample (occurring mainly in the outer skin regions) due to solvent sorption/desorption during the immersion/drying cycles, respectively. These structural changes may also activate mechanism of solvent penetration into the compound through capillarity and transport through microcracks.

Figure 7 depicts the sorption of various solvents by G1657/15phr CB/2phr Varox as a function of

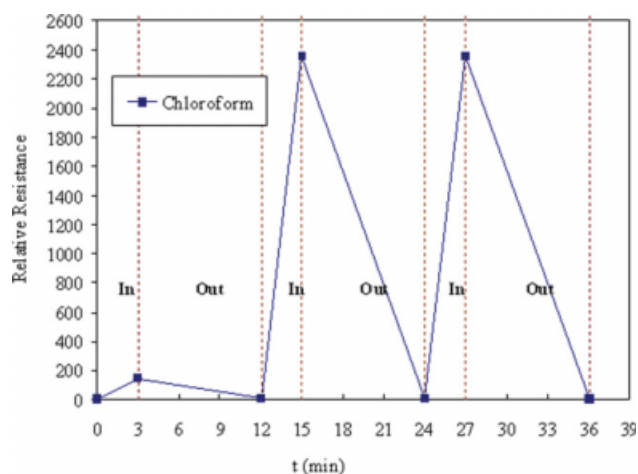


Figure 6 Relative resistance vs. exposure time to chloroform for G1657/20phr CB/2phr Varox with 3 min "in" cycle and 9 min "out" cycle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

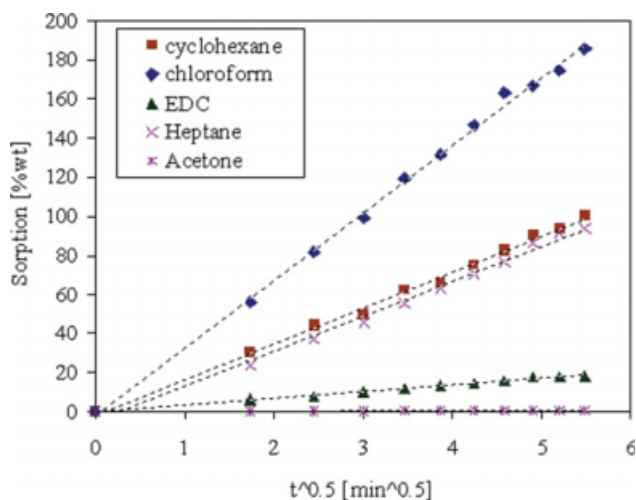


Figure 7 Sorption mass change vs. square (root of time) for (a) G1657/15phr CB/2phr Varox. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

square root of exposure time. The linear relation between the fraction of solvent absorbed and $t^{1/2}$ indicates that Fick's law for diffusion is applicable for all studied solvents. The sorption of acetone [$\delta = 9.9(\text{cal}\cdot\text{cm}^{-3})^{1/2}$] is very low; thus, when a SEBS sample is exposed to acetone, the acetone molecules locate only on the surface of the sample. When the sample is allowed to dry in air, the acetone desorb, resulting in the observed reversible behavior. The highest sorption is observed in chloroform [$\delta = 9.3(\text{cal}\cdot\text{cm}^{-3})^{1/2}$], causing the SEBS sample to swell, causing large resistance increase in proximity to the percolation threshold (Figs. 4 and 5). In chloroform, a reversible behavior is observed when the sample is allowed to dry for long period of time. Similar sorption values achieved in heptane [$\delta = 7.45(\text{cal}\cdot\text{cm}^{-3})^{1/2}$] and cyclohexane [$\delta = 8.2(\text{cal}\cdot\text{cm}^{-3})^{1/2}$] which are good solvents for the EB mid-block, and similar relatively low increase in resistance values are observed in these solvents (Figs. 4 and 5). In EDC, the sorption values are between those for acetone and heptane. Also, a reversible behavior can be achieved when the sample is allowed to dry in air for long enough time (Fig. 6).

CONCLUSIONS

Crosslinking of the SEBS system by adding peroxide to the blend is possible. It expands the use of SEBS/CB systems to solvents including 1,2-dichloroethane, cyclohexane, and chloroform, by preventing the dissolution of the SEBS copolymer in the solvent.

Based on DSC and DMA studies, it is suggested that the crosslinking reaction takes place mainly in the soft ethylene/butylene phase of the SEBS, affecting its glass transition temperature.

Crosslinked samples exposed to chloroform exhibited the highest resistance increase, i.e., highest sensitivity. This behavior was related to the sorption kinetics, affected by the different characteristics of the solvents (solubility parameter, polarity, and molecular volume). The samples' resistance tended to return to its initial value upon short drying in acetone, and longer drying in other studied solvents. Similar low sensitivities were found for *n*-heptane and cyclohexane, both "good" solvents for the mid-block EB. The relative rapid recovery of SEBS/CB samples' initial values for acetone, suggests that morphological changes, owing to solvent sorption, mainly occur in the outer skin regions of the samples, whereas the core region remains essentially intact.

The sensor SEBS/CB sensitivity increases with the amount of solvent absorption during exposure; however, the time required for the drying stage (reversibility) increases.

The sensor sensitivity depends on the CB content proximity to the percolation content.

The different selectivities and sensitivities exhibited by the SEBS/CB system in the studied solvents can be explained by the difference between the solubility parameters of the solvent and the matrix, the sorption kinetics and the volatility of the studied solvents.

The main sensing phase is the rubbery EB whereas the rigid Styrene domains contribute to the materials mechanical stability.

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