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Cure Characteristics and Mechanical Properties of Maleic Anhydride Grafted Reclaimed Rubber/ Styrene Butadiene Rubber Blends

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ABSTRACT

Blends of styrene butadiene rubber (SBR) with maleic anhydride grafted whole tire reclaim (MA-g-WTR) have been prepared and the cure and mechanical properties have been studied with respect to the reclaim content. The grafting was carried out in the presence of dicumylperoxide (DCP) in a Brabender Plasticorder at 150°C. The presence of anhydride group on the WTR was confirmed by infrared spectrometry (IR) study. The properties were compared with those of the blends containing unmodified WTR. Though the cure time was

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marginally higher, the mechanical properties of the blends containing grafted WTR were better than that of the unmodified blends.

Key Words: Styrene butadiene rubber; Maleic anhydride grafted reclaimed rubber; Blends and mechanical properties.

INTRODUCTION

Reclaimed rubber, prepared from scrap rubber has been used as a substitute for virgin rubber in many rubber compounds.[1–13] The properties of such blends depend critically on the compatibility of the component matrices. Whole tire reclaim (WTR), a popular form of reclaimed rubber prepared from used and scrap tires, is inherently nonpolar and has been used to prepare blends with nonpolar rubber such as NR, BR and polar rubber NBR.[14–16] Kim and Burford studied the utilization of waste tires in polar and nonpolar rubbers.[17]

Maleic anhydride has been used for functionalization of polymer chains. Grafting is usually accompanied by the formation of cross-links and, hence, improves the mechanical properties of the polyolefins and their blends.[18–21] Farmer and Wheeler patented the method of modifying rubber with maleic anhydride. Maleic anhydride is grafted onto the double bond of the rubber hydrocarbon. Functionalization is usually accelerated in the presence of organic peroxide like dicumylperoxide (DCP). Maleic anhydride readily reacts with polymeric double bonds and free radicals by an ENE reaction.[22–24] In this work we report the results of our study on the grafting of maleic anhydride onto WTR and properties of its blends with styrene butadiene rubber (SBR).

EXPERIMENTAL

Materials Used

Styrene butadiene rubber (Synaprene-1502) with a Mooney viscosity [ML (1+4) at 100°C] of 52 and a styrene content 23.5% by mass was supplied by Synthetics and Chemicals Ltd., Bareily. Reclaimed rubber, WTR, was obtained from Kerala Rubber and Reclaims, Mamala, Kerala, India. The characteristics of WTR used are given in the Table 1. Dicumyl peroxide (DCP), zinc oxide, stearic acid, sulfur, mercaptobenzothiazoledisulfide (MBTS), and tetramethylthiuramdisulfide (TMTD), were obtained from Sameera Enterprises, Kottayam. Antioxidant 4020 i.e., [*N*(1,3-dimethyl-butyl) *N'*-phenyl-*p*-phenylene diamine] was obtained from Bayer India Ltd. Maleic anhydride was supplied by Merck India Ltd.

Table 1. Characteristics of reclaimed rubber.

Property	Value
Acetone extract (%)	15
Carbon black (%)	30
Gel content (%)	68
Mooney viscosity	24
Particle size	30 mesh

Grafting of Maleic Anhydride on Reclaimed Rubber

A Brabender Plasticorder (torque Rheometer) model PS 3S, having a capacity of 40 g, was used for grafting maleic anhydride on reclaimed rubber.

Fourty grams of reclaimed rubber was mixed with 2 grams of maleic anhydride in the presence of 1 g of dicumylperoxide (DCP) at a temperature of 150°C in the Brabender Plasticorder at 30-rpm speed for 3 min. Grafting reaction was completed within 3 min. At the end of 3 min of mixing, the samples were taken out and homogenized on a two-roll mill. Fourier Transform infrared Spectroscopy (FTIR) spectrum of the modified and unmodified samples was taken on a Nicolet AVATAR 360 ESP FTIR Spectra.

Preparation of Blends

Formulations of the mixes are given in Table 2.

The mixes were prepared on a laboratory size two roll (150 × 330 mm) mill as per ASTM D 3182(1989). Cure characteristics were determined by using a Goettfert Elastograph model 67.85 at 150°C. Vulcanization was carried out at 150°C under a pressure of 180 kg/cm^2 in an electrically heated hydraulic press. For thicker samples, sufficient extra cure time was given to get the same extent of cure. The different mechanical properties of the vulcanizate were tested according to ASTM standards. Tensile and

Table 2. Formulation of the mixes.

Ingredient	Mix. no A	B	C	D	E	F	G	H	I	J	K
SBR	100	90	80	70	60	50	90	80	70	60	50
Unmodified WTR	—	20	40	60	80	100					
Maleic anhydride grafted WTR							20	40	60	80	100

Note: SBR = Styrene butadiene rubber. ZnO–5 phr, Stearic acid–2 phr, 4020–1 phr, MBTS–0.8 phr, TMTD–0.4 phr, Sulfur–2 phr are common to all mixes.

tear properties were measured using a tensile tester from Lloyd Instruments, LRX PLUS, according to ASTM D 412. The abrasion resistance of the blend was measured using a DIN abrader as per DIN 53516, and values were expressed as volume loss per hour. Compression set at constant strain was measured according to ASTM D 395-86 method B. Resilience was measured according to ASTM D2832-88 using a vertical rebound Resilience tester from Modex Industries. The heat build-up test was carried out using a Goodrich Flexometer as per ASTM D 623-99 method A. The test samples were preconditioned at oven temperature for 20 min. The heat developed at the base of the sample was measured using a thermocouple. The temperature rise at the end of the specific time interval (20 min) was taken as heat build up. For aging resistance studies, samples were aged in an air oven for 48 h at 70°C (ASTM D 573-88). The tensile and tear properties were measured after aging in an air oven.

RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of modified and unmodified reclaimed rubber. An additional peak appearing at 1783 cm^{-1} corresponding to carbonyl vibration in the case of modified WTR indicates that the anhydride has been grafted.

Cure Characteristics

Figure 2 shows the variation of minimum torque of the blends containing modified and unmodified WTR. The blends containing modified WTR show consistently higher torque values indicating a more viscous matrix. This may result from improved polar interaction of SBR with the grafted WTR. However, with increasing loading of maleic anhydride-grafted WTR (MA-g-WTR), the minimum torque value decreases as in the case of blends with unmodified WTR. The change of minimum torque values in the unmodified and modified reclaim blend was 0.02954 to 0.01514, and 0.02954 to 0.0264 N.m., respectively. The reclaimed rubber contains 15% plasticizer in addition to rubber hydrocarbon and filler (Table 1). Increasing the proportion of WTR also increases plasticizer content of the blends, which results in the reduction of the initial viscosity.

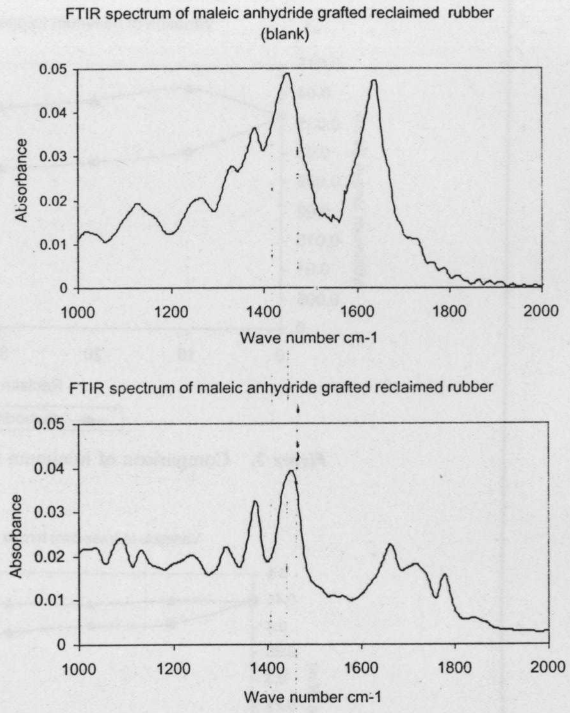

Figure 1. FTIR spectrum of modified and unmodified reclaimed rubber.

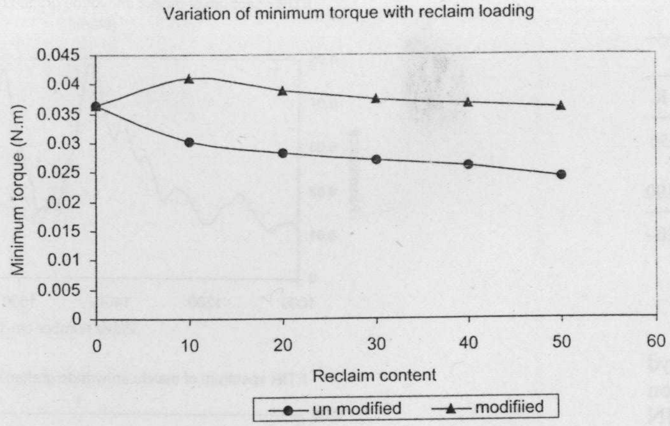

Figure 2. Comparison of minimum torque with reclaim loading.

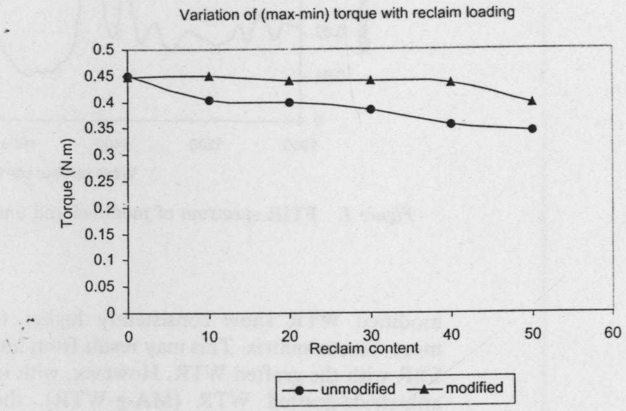

Figure 3. Comparison of maximum–minimum torque with reclaim loading.

The Fig. 3 shows the variation of (maximum–minimum) torque (ΔT). In all the cases the ΔT of the blends containing modified WTR is higher than that of the unmodified blends. In the case of unmodified sample the (maximum–minimum) torque value changes from 0.4783 to 0.2407 and for the modified sample the change is only 0.4783 to 0.3989 at 50 phr reclaim loading, indicating a relatively more restrained matrix in the case of modified blends resulting from the combined effect of higher interaction between blend components and higher levels of cross-links formed. With increasing reclaim content in the blends, the ΔT is found to be gradually decreased, the effect being less significant in the case of MA-g-WTR blends. The lower level of cross-links at higher reclaim loading may be attributed to the fact that the reclaim is already a partially cross-linked matrix and, hence, there are relatively fewer reaction sites available for further cross-linking. However the improved matrix interaction compensates for this and, hence, the observed higher ΔT for the modified blends.

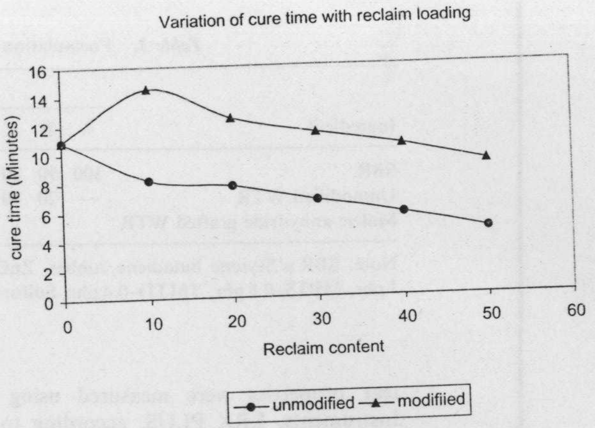

Figure 4. Comparison of cure time with reclaim loading.

Figure 4 gives a plot of cure time vs. reclaim loading. In the case of unmodified blends, the cure time decreases from 10.9 to 4.6 min at 50 phr reclaim loading, while it is reduced to 9.2 min only in the case of blends containing grafted WTR. At all reclaim loading (mixes A-K), the cure time, those blends containing MA-g-WTR is higher than that of the unmodified blends. This may be attributed to the presence of the anhydride group introduced on the WTR backbone by grafting. Anhydrides are known cure retarders. Curative contained in the reclaim reduces the cure time in modified and unmodified blends. The reduced cure time is also supported by change in cure rate in all mix ratios (Fig. 6). In all reclaim loading scorch time is marginally affected by grafting (Fig. 5).

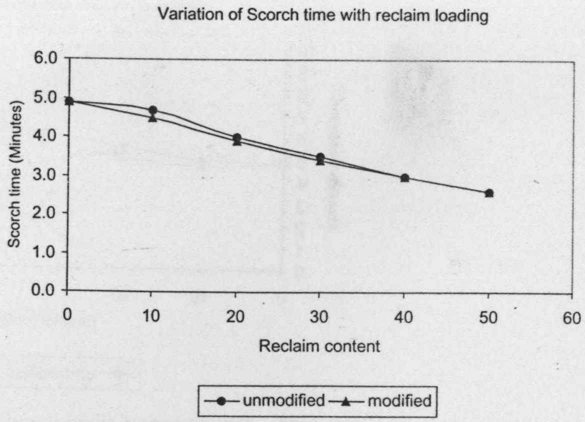

Figure 5. Comparison of Scorch time reclaim loading.

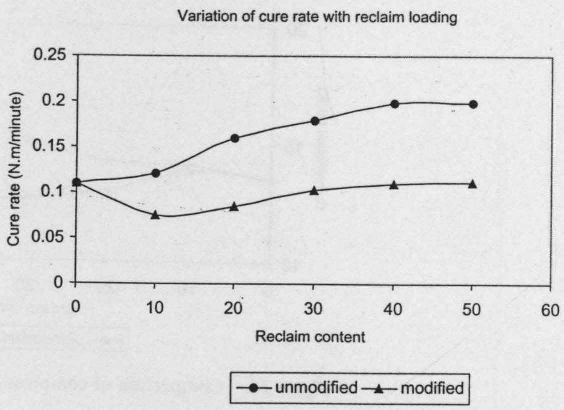

Figure 6. Comparison of cure rate with reclaim loading.

Mechanical Properties

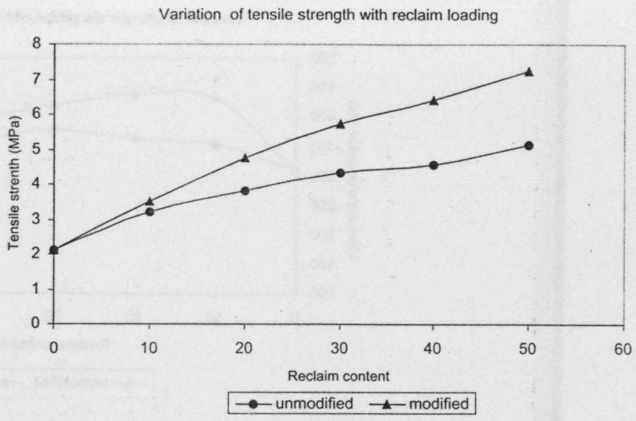

Figure 7. Comparison of tensile strength with reclaim loading.

Figure 7 shows the tensile strength of mixes A–K. In all the cases, the tensile strength increases with reclaim content. This may be attributed to the reinforcing fillers present in the WTR. Similar results in the case of NBR and BR has been reported earlier.[14–16] The tensile strength of the blends containing MA-g-WTR is higher than that of the blends with unmodified WTR at all blend ratios. Tensile strength changes from 2.1 MPa to 5.1 MPa at 50 phr WTR whereas in the MA-g-WTR loading, the tensile strength is 7.2 MPa at 50 phr. This may be attributed to the possibility of the improved polar–polar interaction between the blend components and the filler particles.

Figure 8 gives a plot of ultimate elongation vs. reclaim loading. As expected from tensile strength, ultimate elongation of the blend is also increased with the reclaim loading. Blends with higher reclaim contents show higher elongation at break values. This may be attributed to the presence of plasticizers in the WTR (Table 1). The blends containing grafted WTR shows marginally higher elongation.

Figure 9 shows comparison of tear strength with reclaim loading. The tear strength of the blends with modified and unmodified WTR shows the same pattern with increasing reclaim content. Both the blends show improved tear resistance at higher reclaim loading. The improved resistance to tear can be attributed to the presence of reinforcing filler in the WTR matrix. Tear strength of the modified blends is higher than that of the unmodified at all reclaim loading, again resulting from better interaction between the blend components.

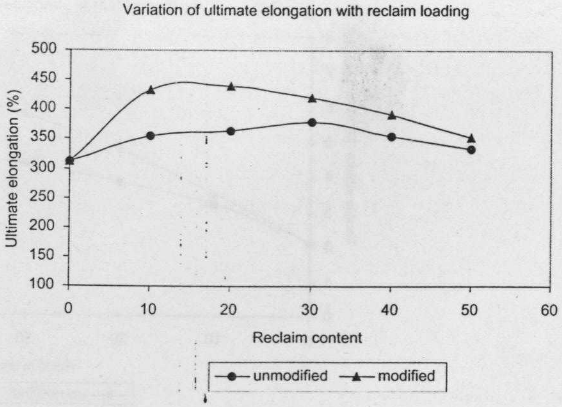

Figure 8. Comparison of ultimate elongation with reclaim loading.

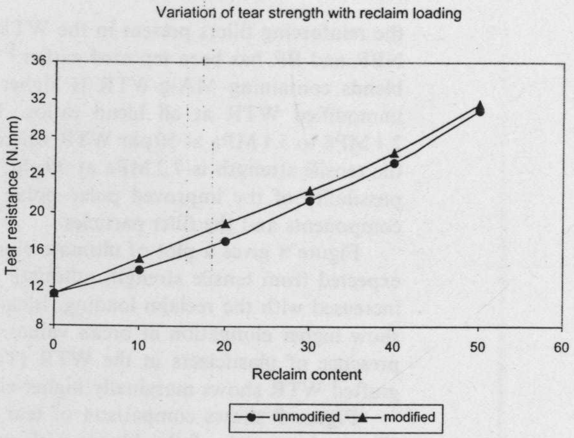

Figure 9. Comparison of tear resistance with reclaim loading.

Figure 10 shows a plot of abrasion loss vs. reclaim loading. Modified reclaim blend shows a low abrasion loss, and hence, better abrasion resistance than the unmodified reclaim blend. The low abrasion loss in the case of the modified blend also indicates improved matrix-filler interaction. A better interface interaction restrains the matrix better, resulting in better abrasion resistance.

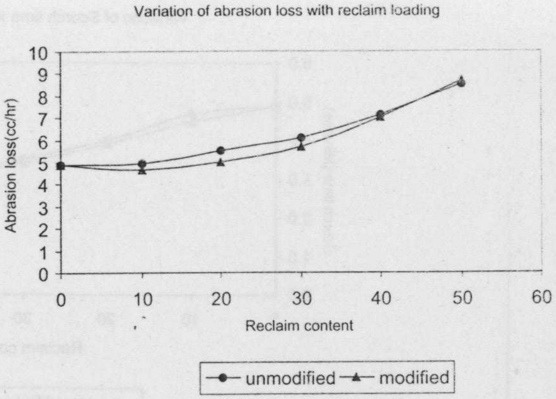

Figure 10. Comparison of abrasion resistance with reclaim loading.

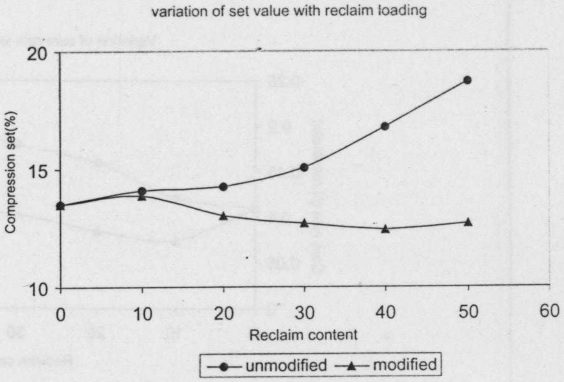

Figure 11. Comparison of compression set with reclaim loading.

Figure 11 shows the comparison of compression set with reclaim loading. Compression set values of the modified reclaim blend are found to be lower than those of the unmodified reclaim blend. The reduced

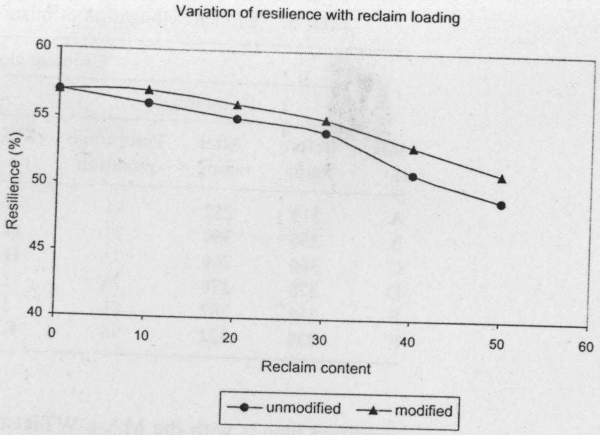

Figure 12. Comparison of resilience with reclaim loading.

compression set values indicates a more restrained matrix. This also supports the view that the grafting improves the interaction between the blend components. The increased set values at higher reclaim loading may result from combined defect of filler, plasticizer, and elevated temperature, all of which reduce the elasticity of the matrix. Low elastic matrices facilitate irreversible flow under stress, resulting in higher set values.

The increased elasticity is also evident from Fig. 12, which is a plot of resilience values of modified and unmodified reclaim blends vs. reclaim loading. The resilience of the modified blend and unmodified blends decreases with reclaim loading. The modified reclaim blends show marginally higher resilience values.

Figure 13 shows comparison of heat build up with the modified and unmodified reclaim loading. The heat generation under dynamic loading is higher at higher reclaim loading in the case of modified and unmodified blends. This is in contrast to the observed resilience values. The difference can mainly be attributed to the difference in the level of strains. In the heat build-up test, the samples are strained to a larger extent than in the case of the resilience test. At higher strains, the chance of the energy loss by interfacial bond breakage is more and, hence, the higher heat generation. The higher hysteresis loss in the case of modified blends indicates that the polar interaction introduced by

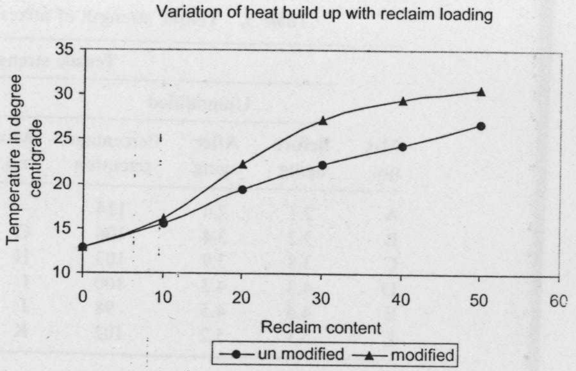

Figure 13. Comparison of heat build-up with reclaim loading.

grafting is not very strong and energy loss occurs at these points under dynamic loading.

Aging Resistance

Table 3 shows the tensile strength of the blends before and after aging. In all the cases the tensile strength value was found to be increased by the grafting of maleic anhydride on the reclaimed rubber. The percentage of retention values, calculated as the ratio of tensile strength after and before aging, now shows a gradual reduction. As a synthetic matrix with better resistance to degradation, the SBR gum compound (mix A) gives a percentage retention of 114. Whereas in the blends, the presence of reclaim, which is relatively more prone to degradation lowers the retention values. Kutty et al. reported similar results in the case of NR, NBR, and BR reclaim blends.[14–16] A similar trend is also observed in the case of tear retention on aging (Table 4).

Table 5 shows the retention values of ultimate elongation of the modified and unmodified sample. Ultimate elongation value of the aged sample is lower than that of the unaged sample. Percentage retention values of the modified reclaim blend are higher than unmodified reclaim blends. The percentage retention values of the modified reclaim blends are almost similar. Percentage retention value reveals that aging resistance of the modified reclaim blend is higher than that of unmodified reclaim blend.

Table 3. Tensile strength of mixes before and after aging.

	Tensile strength (MPa)						
	Unmodified			Modified			
Mix no.	Before aging	After aging	Percentage retention	Mix no.	Before aging	After aging	Percentage retention
A	2.1	2.4	114	—			—
B	3.2	3.4	106	G	3.5	3.8	108
C	3.8	3.9	103	H	4.7	5.0	106
D	4.3	4.3	100	I	5.7	6.5	114
E	4.6	4.5	98	J	6.4	7.4	115
F	5.1	5.2	102	K	7.2	7.8	108

Table 4. Tear resistance of mixes before and after the aging.

	Tear resistance (N/mm)						
	Unmodified			Modified			
Mix no.	Before aging	After aging	Percentage retention	Mix no.	Before aging	After aging	Percentage retention
A	11.4	10.2	89	—			
B	13.9	13.3	96	G	15.2	17.3	114
C	17.0	15.9	94	H	18.9	23.2	123
D	21.3	19.1	90	I	22.4	27.3	122
E	25.4	22.6	89	J	26.4	29.7	113
F	30.9	28.3	92	K	31.6	31.6	100

CONCLUSIONS

Grafting of maleic anhydride to whole tire reclaim affects the cure characteristics and mechanical properties of the styrene butadiene/whole tire reclaim blends. Minimum torque, (Max–Min) torque, and cure time are increased with maleic anhydride grafting. Cure rate and scorch time are decreased with modification of the blends. Tensile strength, ultimate elongation, and tear strength are improved with modification. Abrasion resistance and compression set are improved. Heat build-up and resilience are higher for the modified blend. The aging resistance of modified blends with the MA-g-WTR/styrene butadiene rubber blend is higher compared to that of unmodified blends.

Table 5. Ultimate elongation of mixes before and after the aging.

	Ultimate elongation						
	Unmodified			Modified			
Mix no.	Before aging	After aging	Percentage retention	Mix no.	Before aging	After aging	Percentage retention
A	313	252	81	—	—	—	—
B	355	359	73	G	433	369	85
C	364	266	73	H	440	377	88
D	378	276	73	I	420	403	96
E	355	287	81	J	392	363	93
F	334	322	96	K	353	330	93

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Comparative Studies of Interpenetrating Polymer Networks Derived from Soybean Oil–Based Polyurethane and Cardanol *m*-Aminophenol Dye

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ABSTRACT

Soybean oil and its polymeric products find a wide range of industrial applications due to their higher thermal stability and mechanical strength. Refined Soybean oil, on treatment with glycerol at 210°C in presence of litharge, produces mixed ester polyol (MEP). The probable structure of MEP was established by infrared (IR) spectra. A number of polyurethanes (PU) were synthesized from MEP and di-isocyanates like diphenyl methane di-isocyanate (DPMDI), hexamethylene di-isocyanate (HMDI), and toluene-2,4-di-isocyanate (TDI). Then interpenetrating polymer networks (IPNs)

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