

Maleic Anhydride Grafted Rubbers for Metallic Surfaces Lamination

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ABSTRACT: Modification of two synthetic rubbers, namely polybutadiene (BR) and bromobutyl (BIIR), were carried out to enhance their adhesion performance and their lining to steel to protect it against corrosion. Two different feasible and industrially applicable techniques were used for grafting the two rubbers under investigation individually with maleic anhydride (MAH), namely the reactive extrusion and the mechanochemical techniques. The modified rubbers were characterized by FTIR-spectroscopy, chemical analysis, elemental analysis, and by measuring the surface wetting tension. These applied techniques improved

the adhesion performance of the rubber towards steel surface markedly. Grafting of BR with MAH via mechanochemical technique increased the adhesion strength of BR by four to five times, whereas grafting of BIIR with MAH via reactive extrusion techniques increased the adhesion strength of the parent BIIR up to more than five times. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 850–857, 2008

Key words: rubber grafting; rubber to metal bonding; lining of steel with rubber; bromobutyl modification; polybutadiene rubber modification

INTRODUCTION

The industrial need for metallic equipment such as gas scrubber, valves, and chemical storage tanks is an essential requirement. These metallic substrates suffer from drastic corrosion due to environmental reasons, gas leak, or chemical attack of these surfaces.¹ The protection of these surfaces is an important demand. Among the different methods for protection is the lining of metallic substrates with rubber to withstand corrosion. The factors that may affect the efficiency of the lining are the adhesion performance between the rubber and the metal,² which plays an important role in increasing the life-time of the lined substrate. Also, the nature of the rubber and subsequently, its mechanical and chemical properties of its vulcanizates have a significant effect. The adhesion performance may be increased by modifying the synthetic rubber by incorporation of a functional moiety in the backbone of the rubber chains. Among these is the grafting of the rubber with a monomer bearing carboxylic, anhydride, or epoxy groups.^{3,4} Furthermore, the feasibility and economics of the grafting process is an important task. The reactive extrusion^{5–8} grafting of the polymers with a given monomer is a well-known art, which has the advantages of its industrial feasibility, little or no use of solvent, simple product isolation,

short reaction time, continuous process, and low infrastructure costs. Also, the mechanochemical technique presents an economic solution for polymer grafting in the industrial scale.^{9–11} This work deals with these two techniques individually to graft two synthetic rubbers with maleic anhydride (MAH), namely polybutadiene rubber (BR) which is characterized by its high-abrasion resistance beside its fatigue resistance, and bromobutyl rubber (BIIR) which is characterized by its high gas impermeability.¹²

MATERIALS

Bromobutyl rubber (BIIR 2244) was supplied by EXXON Chemical, with a halogen content of 2–3 wt % and Mooney viscosity $M_L(1 + 8)$ of 46 at 125°C. Polybutadiene rubber (Diene 35AC10), supplied by Firestone Polymers, had a Mooney viscosity $M_L(1 + 4)$ of 37 at 88°C. Maleic anhydride was imported from Aldrich Co. for Chemical Industries with a melting point of 45°C and boiling point of 200°C. 4,4',4''-Triisocyanate triphenyl methane (Desmudor N), imported from Bayer AG Germany, had a isocyanate content of 7.8–8.2%. The other rubber ingredients were of technical grades.

Experimental techniques

Reactive extrusion grafting of the rubber under investigation¹³

The rubbers under investigation were mixed with different ratios of maleic anhydride (1, 2, 3, and 4 phr), in

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presence of 0.05 phr dibenzoyl peroxide as an initiator, by using two-roll mill for 3 min. This mix was then extruded in a brabender premixer with three heating zones at 160°C. The ceiling temperature of maleic anhydride is low enough to assure that this operating temperature is suitable for grafting. The residence time inside the extruder was about 3 min to confirm the complete dissociation of the initiator into free radicals. The extrudate was then extracted with acetone via soxhlet extraction method to remove the excess maleic anhydride. The grafting process was confirmed by means of FTIR and elemental analysis.

The mechanochemical grafting of the rubber under investigation with maleic anhydride¹¹

The rubbers under investigation and 1, 2, 3, and 4 phr of maleic anhydride monomer were milled individually for about 6 min in a two-roll mill, so that the gap between two rolls was 1 mm. The high mechanical shear of the mill induced free radicals across the chain of the rubber due to the cleavage of the Π -bonds. The intimate monomer attacked these active sites to form a grafted rubber. This grafting process was confirmed by spectroscopic (FTIR) and elemental analysis.

Determination of the gel fraction of the modified rubber¹⁴

A predetermined weight sample of the modified rubber (which is previously soxhlet extracted by acetone) was taken and placed in sintered glass (G4) of definite weight. Then the sample was washed with toluene several times to remove the ungelled portion of the rubber. Then the sintered glass with the residual gelified portion was dried and weighed to evaluate the gel fraction.

$$\text{Gel fraction \%} = \frac{\text{The residual gel}}{\text{Sample weight}} \times 100$$

Characterization of the maleated rubber by Chemical analysis¹⁵

Given weights, about 0.5 g of both of the parent rubber (blank sample) and the modified rubber were dissolved in excess of toluene, after soxhlet was extracted from acetone. These rubber solutions were titrated by using a standard potassium hydroxide in methanol (0.1N) and phenolphthalein as indicator. The calculation is based upon estimation of the pendant succinic anhydride moieties as a result of grafting maleic anhydride.

Measuring of the wetting tension¹⁶

In this test method, drops of a series of mixtures of formamide and ethylene glycol monoethylether, of

gradually increasing surface tension, were applied to the surfaces of the rubber films, until a mixture was found that just wets the film surface. The surface tension of the given rubber film will be approximated by the surface tension of this particular mixture.

The adhesion peel strength¹⁷

The rubber under investigation was molded upon a strip of carbon-steel 37. This strip was prepared previously by degreasing with acetone, mechanical cleaning with a grit blasting, and finally rinsing with acetone. Then, the strip was coated with a thin layer of desmudor N. The time of the molding is the optimum cure time (t_{c90}) for each individual sample.

The dimension of the steel strip was 10 cm length \times 1 cm width \times 1 mm thickness. The cavity of the mold had a depth of 1 cm.

The adhered samples were tested by a 90°-peel test procedure using a Tensile Testing machine (ZWICK 1425) with a constant crosshead speed 50 mm/min.

The rubber samples, which were bonded to the steel strips, were subjected to 100% humidity for different time intervals 2, 4, and 6 days in weathering apparatus (QUV—Weathering accelerating tester instrument). Then these samples were tested by 90°-peeling, so that five readings for each individual sample were taken.¹⁸

The mechanical properties

The tensile strength and elongation at break were tested according to ASTM^{19,20} by using tensile testing machine (ZWICK 1425).

The samples were subjected to thermal aging at 90°C, in a good aerated oven for different time intervals. The mechanical properties of the aged samples were determined and compared with those before aging.²¹

RESULTS AND DISCUSSION

The mechanochemical technique was used for grafting the two rubbers under investigation with different ratios of MAH, in order to select the most efficient ratio. Table I shows the tensile strength, elongation at break, and the peel strength of these vulcanizates with different maleic anhydride concentrations. It is obvious that BR-g4 exhibits the highest peel strength and reasonable tensile strength, i.e., the use of 4 phr MAH in grafting of BR gives the most adequate properties. Below this ratio, the peel strength decreases whereas by using 5 phr MAH, a gelified rubber was obtained.

TABLE I
Properties of Vulcanizates Modified with Different Ratios of MAH by Mechanochemical Technique

Samples Properties	BR-g0	BR-g1	BR-g2	BR-g3	BR-g4	BIIR-g0	BIIR-g1	BIIR-g2	BIIR-g3	BIIR-g4
Cure time, t_{c90} , min., at $(152 \pm 1)^\circ\text{C}$	13.5	19	20	26	21.5	21.5	17.5	18.5	17.5	16.5
Mechanical properties										
Tensile strength (MPa)	3.85	4.7	4.9	5.4	5.1	8.18	14..8	16.1	15.3	14.8
Elongation at break (%)	210	356	300	300	265	200	500	510	500	500
Peel strength (N/cm)	20	21	81	86	100	20	23.6	40	48	49.3

The basic recipe is rubber 100, ZnO 5, stearic acid 2, paraffinic oil 3, HAF 40, Sulfur 2.5, CBS, and PBN 1 phr. g0, without MAH; g1, 1 phr MAH; g2, 2 phr MAH; g3, 3 phr MAH; g4, 4 phr MAH.

Also, it is seen that the tensile strengths of the grafted BIIR vulcanizates are nearly in the same order but higher than that of ungrafted one. The highest value is exhibited by BIIR-g2 whereas BIIR-g4 has the highest peel strength.

Thus, the ratio 4-phr of MAH was chosen to carry out the grafting process via the reactive extrusion technique to compare between it and the mechanochemical technique. Both the two rubbers under investigation (BR and BIIR) were reactive extruded in a Brabender premixer, at 160°C , in presence of 4 phr MAH and 0.05-phr dibenzoyl peroxide as an initiator for 3 min.

Characterization of the grafted rubbers with 4 phr MAH

Both the blank rubber and the grafted rubbers (by both mechanochemical and reactive extrusion techniques) were soxhlet extracted individually with acetone for 18 h, to remove the excess unreacted MAH. The grafted rubbers were characterized by the following techniques:

- *FTIR spectroscopy characterization of the maleated rubbers.* The FTIR spectra for BR-R, BR-M, BIIR-R, BIIR-M, and their blanks (where R denotes grafting by reactive extrusion, while M represents the grafting by mechanochemical technique) show that characteristic bands for carbonyl groups have appeared in case of the maleated rubbers at $1700\text{--}1800\text{ cm}^{-1}$. This band is absent in case of the blank samples.
- *Chemical titration of the pendant succinic anhydride moieties.* Table II shows the graft ratios of MAH,

TABLE II
Chemical Analysis of BR Grafted in Presence of 4% MAH, by Both Mechanochemical and Reactive Extrusion Processes

Samples	Grafted MAH (%)	Graft efficiency (%)	Gel fraction (%)
BR-R	0.89	22.25	2.1
BR-M	1.24	31.1	0.08
BIIR-R	1.03	25.75	1.95
BIIR-M	0.71	17.75	0.64

which are 1.24% and 0.89% for BR-M and BR-R, respectively. As indicated in Table II, the mechanochemical grafting of BR with MAH leads to a higher grafting efficiency with lower gel fraction, than in case of the reactive extrusion process. On the other hand, it is seen that the graft ratios of MAH for BIIR-M and BIIR-R are 0.71 and 1.03%, respectively. It is noticed that the grafting efficiency of BIIR with MAH in case of reactive extrusion is higher than in case of mechanochemical technique, whereas the gel fraction in the former technique is higher than that in the latter. That is, grafting of BIIR, in case of a more drastic condition, is more efficient, in contrast to BR which is susceptible for grafting in a mild condition such as the mechanochemical technique.

- *Elemental analysis.* The rubbers BR, BIIR, and their maleated derivatives, either by mechanochemical or reactive extrusion technique, were soxhlet extracted for 18 h by using acetone, and then dried under vacuum. These samples were subjected to elemental analysis of their C, H, Br, and estimation of O (%). The results were listed in Table III. It is obvious from the table that an appreciable increase of the oxygen (%) takes place. These results are in a good agreement with those results for the grafting efficiencies which are previously listed in Table II. This in turn reveals the grafting of the maleic anhydride, which is enriched in oxygen content.
- *Evaluation of the wetting surface tension.* Measuring the wetting surface tensions of both the blank and the modified rubbers gave further

TABLE III
Elemental Analysis of BR, BIIR, and Their Maleated Derivatives

Samples	C (%)	H (%)	Br (%)	O (%)
BR	88.0	10.46	–	1.54
BR-M	75.9	7.68	–	16.42
BR-R	87.3	7.51	–	5.13
BIIR	84.2	12.55	3.1	0.13
BIIR-M	81.2	9.06	2.2	7.54
BIIR-R	74.17	8.28	1.87	15.65

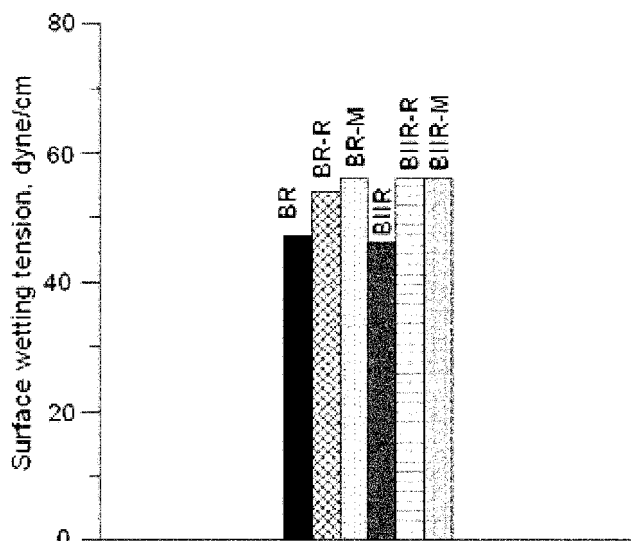


Figure 1 Surface wetting tension, dyne/cm, of the blank rubbers and their maleated forms.

confirmation of the grafting process. Figure 1 illustrates the wetting surface tensions in dyne/cm of BR and BIIR rubbers. It is obvious that the grafting with 4 phr MAH improves the wetting surface tensions of the maleated rubbers rather than the parent rubbers, whatever the used technique. This increase in wetting surface tensions reflects how far will be the extent of the adhesion.

The mechanical properties of the vulcanizates

Both the blank and the maleated rubbers were mixed individually in a two-roll mill with the other ingredients. The mechanical properties were determined and listed in Table IV. It is seen that the cure time t_{c90} for BR-M is less than that for BR-R. It is noticed from the mechanical properties that both the tensile strength and elongation at break of the vulcanizate BR-M are higher than those for BR-R. This may be due to the slight higher extent of degradation of the rubber chains during the reactive extrusion than in the mechanochemical technique.

TABLE IV
Characterization of the Vulcanizates BR, BIIR, and Their Maleated Derivatives

The vulcanizate sample	BR	BR-R	BR-M	BIIR	BIIR-R	BIIR-M
Cure time, t_{c90} , min., at $(152 \pm 1)^\circ\text{C}$	13.5	26	22	21.5	18	16.5
Mechanical properties						
Tensile strength (MPa)	3.85	2.1	5.1	8.18	13.7	14.8
Elongation at break (%)	210	125	265	200	480	500
Peel strength (N/cm)	20	45	100	20	114.7	49.3

The basic recipe is rubber 100, ZnO 5, stearic acid 2, paraffinic oil 3, HAF 40, Sulfur 2.5, CBS 1, and PBN 1phr.

R, maleic anhydride grafted by reactive extrusion technique; M, maleic anhydride grafted by mechanochemical technique.

On the other hand, it is noticed that t_{c90} of BIIR-M is lower than that associates BIIR-R.

Also, from the mechanical properties, it is clear that the grafting of BIIR with 4 phr MAH improves its mechanical characteristics, whatever the technique has been used.

The adhesion peel strength of the bonded vulcanizates to carbon-steel strips shows an enhanced adhesion performance of the maleated forms of BR rubber than in case of the unmodified one. The adhesion peel strength of BR increases from 20 to 100 N/cm in case of mechanochemical technique, and up to 45 N/cm in case of reactive extrusion. It is noticed that the adhesion peel strength of BR-M is twofolds more than that for BR-R. This result may be explained as a consequence of higher graft percentage, in case of BR-M rather than in case of BR-R, as listed in Table II. On the other hand, the grafting of BIIR with 4-phr MAH by using the mechanochemical technique increases its adhesion performance from 20 to 49.3 N/cm, whereas the grafting by using reactive extrusion technique increases BIIR adhesion performance from 20 to 114.7 N/cm. It is seen that BIIR-R exhibits more than twofolds of peel strength than in case of BIIR-M. This is in accordance with the graft MAH, %, listed in Table II. The latter result is unlike the corresponding result as in case of the maleated polybutadiene rubber, which may be attributed to that BIIR rubber, requires more drastic conditions to undergo grafting compared with BR rubber.

The vulcanizates of BR, BIIR, and their maleated derivatives were subjected to thermal aging in good aerated oven at 90°C for different time periods up to 7 days. The mechanical properties were determined after aging and compared with those results obtained before aging.

Figure 2 illustrates the tensile strength, MPa, versus thermal aging time, day, of the vulcanizates BR and its maleated derivatives. It is obvious that the two forms of maleated BR, are thermally stable throughout the entire period of thermal aging, i.e., the maleation of BR acquires it thermal aging stability. Also, it is noticed that the vulcanizates of BR-M

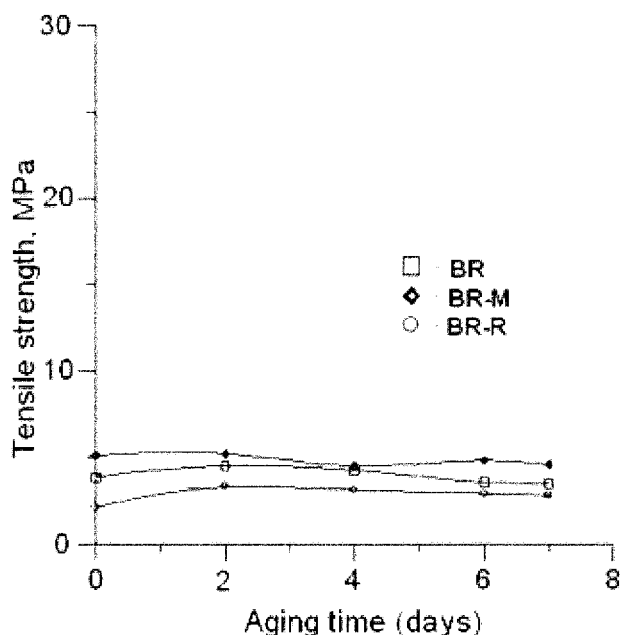


Figure 2 Tensile strength, MPa, versus thermal aging time, days, of the vulcanizate BR and its maleated derivatives, at 90°C.

exhibit higher tensile strength than BR, while the vulcanizates of BR-R exhibit lower values for all the aging periods.

Figure 3 shows the elongation at break, %, of BR vulcanizates versus thermal aging time, day, at 90°C. The highest values of elongation at break are showed by BR-M, the subsequent values associate BR, but the lowest values are for BR-R. These results,

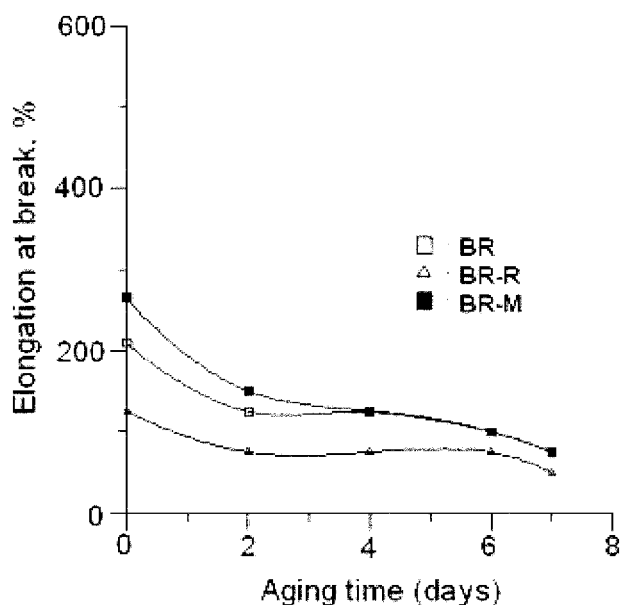


Figure 3 Elongation at break, %, versus thermal aging time, days, of the vulcanizate BR and its maleated derivatives, at 90°C.

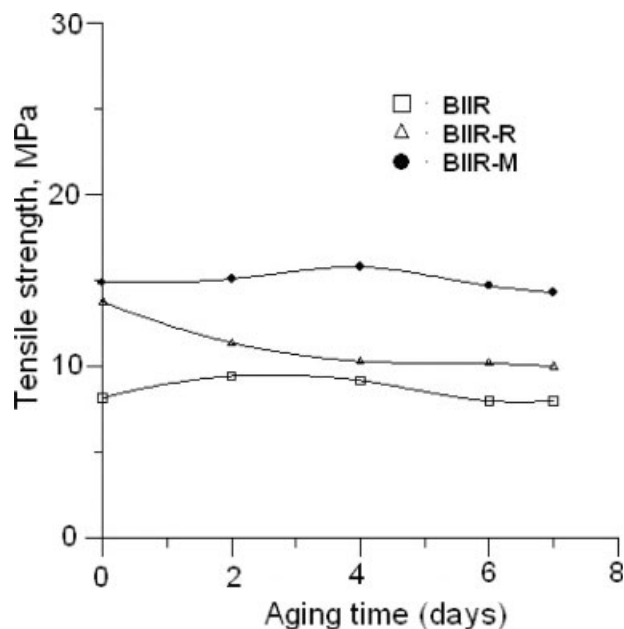


Figure 4 Tensile strength, MPa, versus thermal aging time, days, of the vulcanizates BIIR and its maleated derivatives, at 90°C.

in turn, clarify that grafting of BR under mild conditions with 4 phr MAH improves the mechanical properties, while drastic conditions causes partial chain-scission and decreases the mechanical properties relatively.

Figure 4 illustrates the tensile strength, MPa, versus thermal aging time, day, of the vulcanizates BIIR and its maleated derivatives. The highest and most

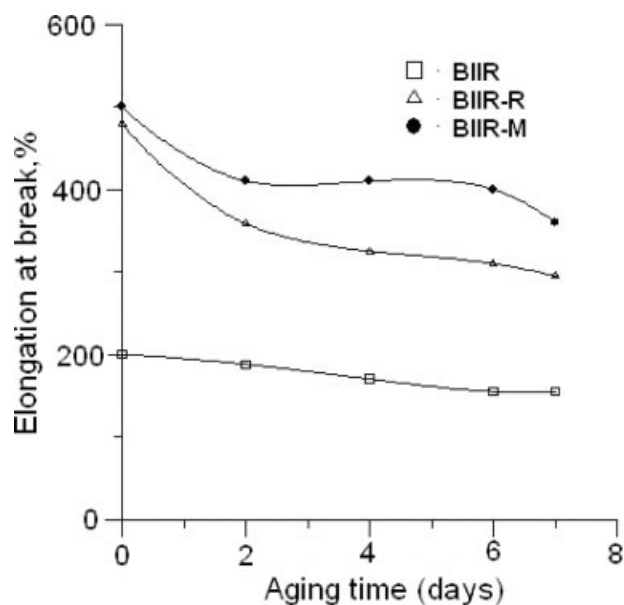


Figure 5 Elongation at break, %, versus thermal aging time, days, of BIIR and its maleated derivatives, at 90°C.

TABLE V
Swelling and Soluble Fractions (%) of Various Rubber Samples in Either 1N H₂SO₄ or 1N KOH after 7 Days Dipping

Properties	BR	BR-M	BR-R	BIIR	BIIR-M	BIIR-R
Swelling in H ₂ SO ₄ (%)	0.64	1.20	1.11	1.01	1.29	1.38
Soluble fraction in H ₂ SO ₄ (%)	0.38	0.53	0.4	0.52	0.60	0.74
Swelling in KOH (%)	0.80	1.44	1.41	1.03	1.19	1.29
Soluble fraction in KOH (%)	0.45	0.33	0.01	0.60	0.83	0.90

thermally stable values throughout the entire period of aging are exhibited by BIIR-M, the moderate values associate BIIR-R, while BIIR has the lowest values.

Figure 5 illustrates the elongation at break, %, versus thermal aging time, day, for BIIR vulcanizates. The obtained results lead to the same conclusion, i.e., grafting of BIIR with 4 phr MAH improves its mechanical properties, whatever the technique of grafting.

From the aforementioned results, it is concluded that grafting of both BR and BIIR with 4 phr MAH by mechanochemical technique improves their mechanical properties, whereas the reactive extrusion technique improves the mechanical properties of BIIR slightly and deteriorates them in case of BR.

Chemical resistance

The vulcanizates were cut into rectangular samples of weights ~ 0.5 g each, these samples were soaked in both 1N H₂SO₄ and 1N KOH for 7 days. After

that the samples were surface dried gently with a filter paper and weighed. These samples were put in an air oven at 70°C for 24 h and weighed again. The swelling, %, and soluble fraction, %, were calculated and listed in Table V.

It is seen that the change in swelling, %, and soluble fraction, %, of these vulcanizates is considered to be in the same order of the chemical resistance. It is concluded that modification of both BR and BIIR by grafting with MAH leads to an improvement of the mechanical characteristics with a very low sacrificing of the chemical resistance.

Evaluation of the adhesion performance

The vulcanizates were molded at $(152 \pm 1)^\circ\text{C}$, according to their t_{c90} , upon cleaned strips of carbon-steel, with surface dimensions 1 cm \times 10 cm, which are previously primed with 4,4',4''-triisocyanate triphenyl methane. These samples were divided into two groups; the first group was subjected to thermal aging at 90°C, for different intervals 2, 4, 6, and 7

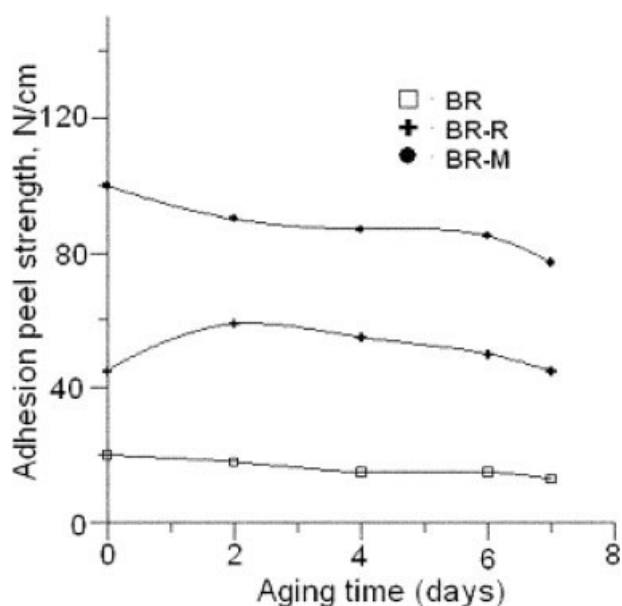


Figure 6 Adhesion peel strength, N/cm, versus thermal aging time, days, of the vulcanizates BR and its maleated derivatives, at 90°C.

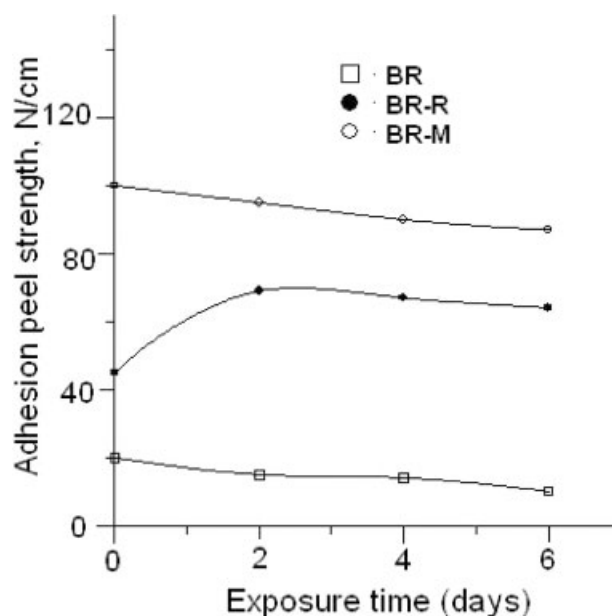


Figure 7 Adhesion peel strength, N/cm, versus 100% humidity exposure time, days, of the vulcanizates BR and its maleated derivatives.

days, the second group was subjected to 100% humidity exposure for time intervals 2, 4, and 6 days, and then tested by peeling with an angle of 90°.

Figure 6 illustrates the adhesion peel strength, N/cm, versus thermal aging time, days, at 90°C for the vulcanizates BR and its maleated derivatives. The vulcanizates BR-M exhibit adhesion peel strength more than four- to five-folds that of the parent BR rubber throughout the entire intervals, while BR-R vulcanizates exhibit adhesion peel strength more than twofolds that of BR.

Figure 7, on the other hand, illustrates the peel strength, N/cm, versus humidity exposure time, days, of the vulcanizates BR and its maleated derivatives. The highest values are exhibited by BR-M. In case of BR-R, the peel strength reaches its maximum after 2 days humidity exposure and then it shows a nearly steady state at 4 and 6 days of humidity exposure, whereas the lowest values associate the unmodified BR.

Figure 8 illustrates the adhesion peel strength, N/cm, versus thermal aging time, days, of the vulcanizates BIIR and its maleated forms. It is obvious that BIIR-R has the highest values, which began high and decreased steeply, but still higher than the other two vulcanizates. The moderate values are exhibited by BIIR-M, this may be explained according to the graft ratio of MAH as listed in Table II. The unmodified rubber BIIR has the lowest values.

Figure 9 illustrates the adhesion peel strength of the aforementioned vulcanizates versus 100% humidity exposure time, days. The vulcanizate BIIR-R

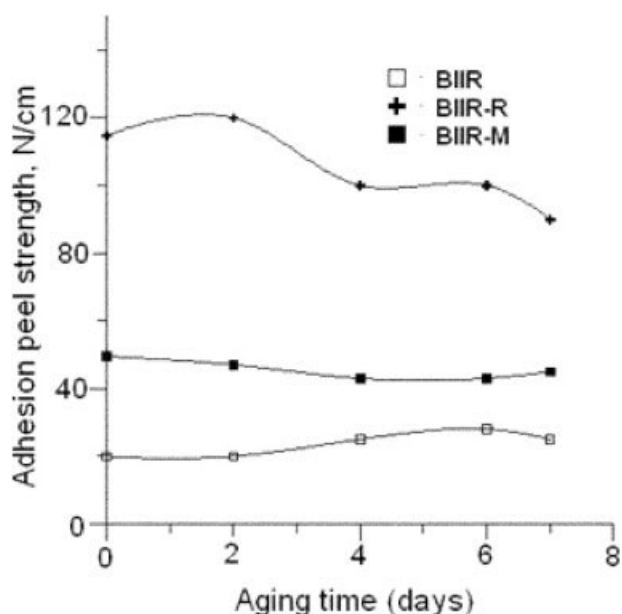


Figure 8 Adhesion peel strength, N/cm, versus thermal aging time, days, of the vulcanizates BIIR and its maleated derivatives, at 90°C.

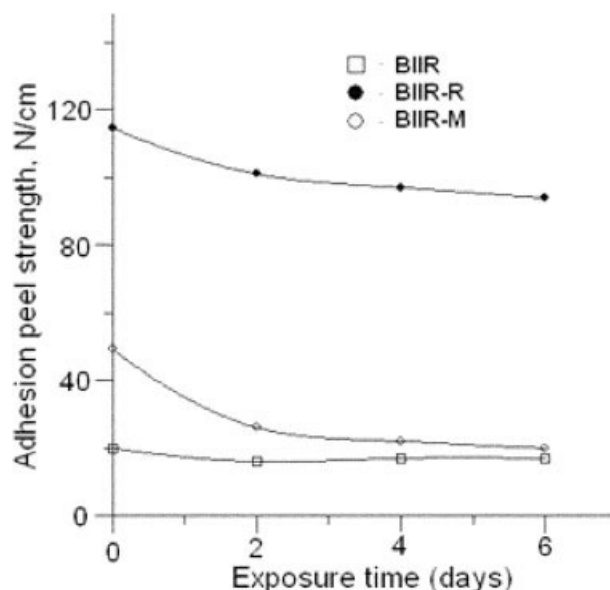


Figure 9 Adhesion peel strength, N/cm, versus 100% humidity exposure time, days, of the vulcanizates BIIR and its maleated derivatives.

shows the highest and the most stable values throughout the entire intervals of humidity exposure. The vulcanizates BIIR-M exhibit less than one third of the values, which are exhibited by BIIR-g-, MAR. Also, it shows inadequate stability towards humidity exposure. The lowest values are displayed by BIIR vulcanizate.

CONCLUSION

It can be concluded that mechanochemical grafting of BR in presence of 4 phr MAH acquires it the highest mechanical and adhesion performance, while the reactive extrusion technique of grafting BIIR in presence of 4 phr MAH acquires it the highest adhesion performance in addition to reasonable mechanical properties.

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