

Reversion free high-temperature vulcanization of cis-polybutadiene rubber with the accelerated-sulfur system

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Abstract. The vulcanization of high diene elastomers with conventional or semi-efficient vulcanization systems exhibit reversion at a higher temperature due to the breakage of the polysulfidic crosslinks established in the vulcanized network. As a result, the vulcanizate show inferior mechanical and thermal stability at elevated temperature. In this contest, the anti-reversion ability of Maleide F (75% *N,N'*-meta phenylene dimaleimide and a 25% blending agent: MF) was evaluated on the vulcanization behavior of cis-polybutadiene rubber (BR) with a conventional accelerated sulfur system. The anti-reversion ability of MF was also compared with Perkalink 900 (1,3-bis (citraconimidomethyl) benzene: PL). Based on the vulcanization studies using a moving die rheometer, it has been realized that MF forms carbon-carbon based bismaleimide crosslinks at the beginning of the vulcanization via Alder-Ene reaction. As a result, MF-filled systems exhibit a remarkable reversion resistance and a plateau type cure behavior even at 180 °C for a period of 1hr. On the other hand, PL shows its anti-reversion activity via Diels-Alder reaction after a short reversion. Moreover, the PL filled system exhibits a marching-modulus cure behavior at a higher vulcanization temperature. Therefore, PL cannot be considered as a promising candidate for the high-temperature vulcanization of BR with accelerated sulfur.

Keywords: rubber, vulcanization, bismaleimide, reversion, Diels-Alder reaction

1. Introduction

It has been well-documented in the literature that the accelerated-sulfur systems are classified as conventional vulcanization (CV), efficient vulcanization (EV), and semi-efficient vulcanization (SEV) based on their accelerator to sulfur ratio. Generally, the accelerator/sulfur ratio for a CV system is in the range of 0.1 to 0.6. For SEV, it is about 0.7 to 2.5 and for the EV system, it will be greater than 2.5 [1–4]. It has also been reported that the vulcanizate of a CV cured network comprises 95% poly and disulfidic crosslinks and 5% mono-sulfidic crosslinks. For SEV, 50% of the cross-links will be poly-and di-sulfidic and the rest will be mono-sulfidic. However, the amount of mono-sulfidic cross-links will be around 80% if the rubber is cured with an EV system [1]. Because of the poor thermal stability of the polysulfidic

crosslinks, the high diene rubbers vulcanized with the CV or SEV systems exhibit reversion when exposed to a temperature-time treatment. The breakage of the polysulfidic crosslinks formed during the initial stages of the vulcanization is considered as one of the major reasons behind the reversion process. A gradual reduction in the rheometric torque from its maximum value during vulcanization is one of the direct evidence of reversion. Owing to reversion, the CV/SEV vulcanized diene rubbers show poor physical properties like cross-link density and compression set at elevated temperatures [5–7]. Therefore, the vulcanization of diene elastomers with CV or SEV is limited to a lower curing temperature preferably at 140 to 150 °C. This low-temperature vulcanization for thick rubber products like tire may take a longer time to reach a full state of cure which leads

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to lower production capacity. Therefore, the development of a reversion free accelerated-sulfur vulcanizing system for the diene rubbers is critical.

Various types of chemicals such as hexamethylene bithiosulphate disodium salt (Duralink[®] HTS), bis (triethoxysilylpropyl)-tetrasulphide (TESPT), thiuram accelerators, dithiophosphate accelerators (Vocol ZBPD) have been employed to outwit the reversion during the vulcanization of truck tire tread compounds based on natural rubber (NR) with a CV system [8]. Furthermore, Blok *et al.* [9] explored the use of certain multifunctional acrylates as an anti-reversion agent in NR with a SEV system. Kenneth [10] reported that chemicals such as Struktol[®] ZB47 and Struktol[®] SA1341 (a formulated zinc soap produced by the Struktol Company of America, LLC) can show a considerable anti-reversion property in an NR compound with a SEV system in addition to its role as a processing aid. The bismaleimide based compound like 1,3-bis(citraconimidomethyl)benzene (Perkalink 900) is another important class of chemicals which can show an excellent anti-reversion property in diene rubbers. Many researchers have tested its efficiency as an anti-reversion agent in various NR based rubber compounds [11–14]. Recently, the author has reported the use of a 4,4'-bis(maleimido)diphenylmethane as an anti-reversion agent for the vulcanization of NR with a CV system [15].

In the present work, the anti-reversion efficiency of two different bismaleimide based chemicals such as Perkalink 900 (PL) and Maleide F (MF) was investigated on the vulcanization behavior of an unfilled cis-polybutadiene rubber with an accelerated sulfur system. The influence of these chemicals on the vulcanizate properties like crosslink density, shore hardness and compression set properties was also evaluated. To the best of our knowledge, no reports are available in the literature regarding the anti-reversion ability of MF on polybutadiene rubber.

2. Experimental

2.1. Materials

High cis-polybutadiene rubber, SYNTECA[®]44 (cis-1,4 content: 97%, Mooney viscosity ML(1+4) at 100 °C: 39) was procured from Synthos PBR s.r.o., Czech Republic. Maleide F (MF) is a combination of 75% *N,N'*-meta phenylene dimaleimide and 25% blending agent was procured from Krata Pigment, Tambov, Mentazhnikov, Russia and Perkalink 900 (PL) is chemically 1,3-bis(citraconimidomethyl)

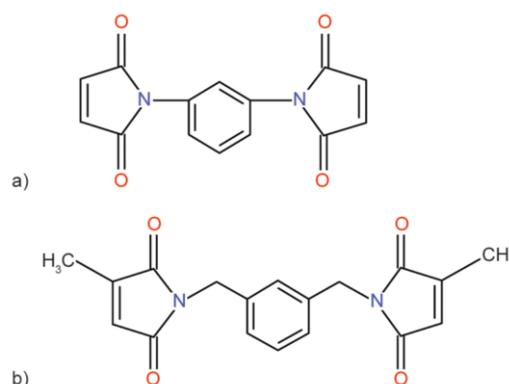


Figure 1. Chemical structures of (a) Maleide F and (b) Perkalink 900.

benzene was procured from Lanxess Deutschland GmbH, Leverkusen, Germany. The chemical structures of MF and PL are shown in Figure 1. Other ingredients such as sulfur, *n*-cyclohexyl-2-benzothiazole sulfenamide (CBS), stearic acid and zinc oxide (ZnO) were purchased from Sigma-Aldrich, Czech Republic.

2.2. Preparation of rubber compounds

The formulations of the compounds with designations are displayed in Table 1. All the compounds were prepared using an internal mixer (Brabender Plastograph, GmbH & Co. KG, Germany) having a chamber volume of 50 cm³. A fill-factor of 0.8 was taken for the efficient mixing of the ingredients. The neat BR has masticated at 60 °C under 50 rpm for 1 min. To this, the ZnO, stearic acid, and bismaleimides were added and continued the mixing under the same rotor speed and temperature for another 2 min. The curatives (sulfur and accelerator) were then added and mixed for 1 more min. After the mixing, the compound was discharged and homogenized using a two-roll mill. It is then molded into a 1 mm sheet by applying a constant force of 200 N using a compression molding heat press LaBEcon

Table 1. Formulation of the mixes (unit: phr).

Ingredients	BR-S ^a	BR-S ^b MF ₁	BR-S ^c PL ₁
BR	100	100	100
ZnO	4	4	4
Stearic acid	2	2	2
Sulfur	2	2	2
CBS	0.6	0.6	0.6
Maleide F	–	1	–
Perkalink 900	–	–	1

^aSulfur,

^bMaleide F,

^cPerkalink 900

300 (Fontijne Presses, The Netherland) for the respective cure time obtained from the rheometer cure data for the selected molding temperature.

2.3. Characterization

2.3.1. Cure characteristics

Maximum torque: S'_{\max} , minimum torque: S'_{\min} , the difference between maximum and minimum torque: $\Delta S'$, scorch time: T_{S2} , optimum cure time: T_{90} (the time required for the torque to reach 90% of the maximum torque) of the rubber compounds were determined from the cure curves from a moving die rheometer (MDR-3000, Mon-Tech, Germany) at various vulcanization temperatures as per ASTM D 5289. The cure rate index (CRI), a measure of the rate of curing, was calculated using the Equation (1):

$$CRI = \frac{100}{T_{90} - T_{S2}} \quad (1)$$

2.3.2. Crosslink density measurements

Samples with a diameter of 20 mm and a thickness of 1 mm were swelled in toluene at room temperature until it reached an equilibrium state of swelling. The swelled samples were then taken out and wiped off the adhered solvent from the surface using a filter paper and immediately recorded the weights (W_s). Afterward, the swollen samples were dried at room temperature for 24 hrs and ensured that the absorbed toluene has completely expelled out. Then, we measured the dried weight of the samples (W_d). From the values of W_s and W_d , the cross-link density n of the samples was calculated using the Flory-Rehner equation given in Equation (2) [16–18]:

$$n = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{V_s [V_r^{1/3} - \frac{V_r}{2}]} \quad (2)$$

where V_r is the volume fraction of rubber in the equilibrium swollen sample, V_s is the molar volume of the solvent (106.3 ml/mol for toluene at room temperature) and χ (0.387) is the coefficient of the interaction between the rubber and the solvent. Here, V_r was calculated using Equation (3) and χ was determined from Equation (4) [19, 20]:

$$V_r = \frac{W_d}{W_d + (W_s - W_d) \frac{\rho_{\text{rubber}}}{\rho_{\text{solvent}}}} \quad (3)$$

$$\chi = \beta + \frac{V_s}{RT} (\delta_s - \delta_r)^2 \quad (4)$$

where W_s is the weight of the equilibrium swelled rubber, and W_d is the dry weight of the swelled rubber. β is the lattice constant (typically 0.34) [21], ρ is the density, R is the molar gas constant, and T is the absolute temperature. The solubility parameters of the rubber (δ_r) and the solvent (δ_s) for BR and toluene were taken as 17.15 and 18.2 MPa^{1/2} respectively [21].

2.3.3. Hardness testing

Cured samples having smooth surfaces with 12.5 mm thickness and 29 mm diameter were used to measure the indentation hardness using a Shore-A hardness tester (Bareiss Durometer, Germany) as per ASTM D 2240. Indentations were made on different areas of the samples by applying constant pressure for 15 seconds. 6 readings were taken from different areas of the sample and reported the average value.

2.3.4. Compression set

The compression set (CS) was measured as per ASTM D 395 using the set produced by Coesfeld GmbH, Germany. Cylindrical samples having 12.5 mm thickness and 29 mm diameter were subjected to a 25% compression. The compressed samples then kept in an air-oven at 100 °C for 22 hrs. After the specified testing time, the samples were taken out and allowed to cool for 30 minutes at room temperature and measured the thickness. The CS was calculated using Equation (5):

$$CS [\%] = \frac{t_0 - t_f}{t_0 - t_s} \cdot 100 \quad (5)$$

where t_0 and t_f are the original and final thickness of the specimen, and t_s is the thickness of the spacer used.

2.3.5. Thermogravimetric analysis

Thermogravimetric analyses (TGA) were conducted to evaluate the thermal stability or the thermal degradation behavior of the vulcanized rubber compounds using a TA instrument (Q500, USA). Cured samples were heated from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

3. Results and discussion

3.1. Vulcanization behavior of BR-S

Represented in Figure 2 is the vulcanization behavior of BR with a conventional accelerated sulfur system (BR-S) at three different vulcanization temperatures

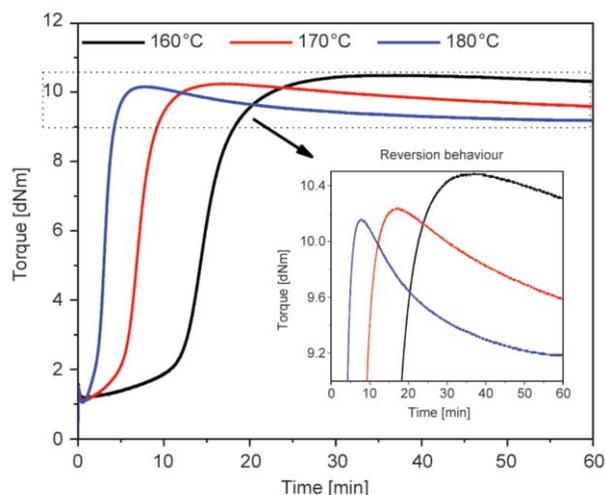


Figure 2. Vulcanization behaviour of BR-S under different temperatures for 60 min.

for 60 min. The detailed cure characteristics are displayed in Table 2. As expected, the speed of vulcanization increased with the increase in temperature, which is evident from the significant increase in the cure rate index. For instance, the T_{S2} value at 160 °C was 12.9 min which has been reduced to 2.5 min by raising the vulcanization temperature to 180 °C. It is important to note that as the vulcanization temperature increased, the torque was found decreased soon after the maximum torque due to reversion. One of the widely accepted reasons for the reversion during the accelerated sulfur vulcanization is the breakage of the polysulfidic linkages which were formed at the initial stages of the vulcanization process. Since the susceptibility of the breakage of a polysulfidic crosslink is more likely at a higher temperature, the severity of reversion was also higher at a higher vulcanization temperature [4, 5]. As a result, the onset of reversion was shifted from 39.3 min at 160 °C to 8.2 min as the vulcanization temperature rose to 180 °C. The intensity of reversion was calculated using the following Equation (6) [11, 14]:

Table 3. Percentage reversion in BR-S at different time intervals from the maximum torque under different temperatures.

Temperature [°C]	Reversion [%]		
	After 15 min ($S'_{\max+15 \text{ min}}$)	After 30 min ($S'_{\max+30 \text{ min}}$)	After 45 min ($S'_{\max+45 \text{ min}}$)
160	0.5	2.1	–
170	2.9	5.9	7.5
180	5.5	8.2	9.0

$$\text{Reversion} [\%] = \frac{S'_{\max} - S'_{\max+t}}{S'_{\max}} \cdot 100 \quad (6)$$

where S'_{\max} is the maximum torque and $S'_{\max+t}$ is the torque at a time t after S'_{\max} .

Represented in Table 3 is the percentage reversion that is observed during the vulcanization of BR-S at different time intervals under different vulcanization temperatures. It is clear that as the time and temperature of vulcanization increases, the percentage of reversion also increases.

3.2. Vulcanization behavior of BR-S in the presence of bismaleimides

To prevent the reversion that is observed during the vulcanization of BR-S, two types of bismaleimides such as PL and MF, were applied as anti-reversion chemicals. Depicted in Figure 3 are the representative cure curves of BR-S in the presence of 1 phr PL (BR-SPL₁) and 1 phr MF (BR-SMF₁) at 160 and 180 °C for 60 min. Their cure characteristics obtained for all the vulcanization temperatures are also displayed in Table 2. The cure patterns of BR-S and BR-SPL₁ were similar during the initial stage of the reaction. As a result, their T_{S2} values were also been similar at all the vulcanization temperatures. From the inset of Figure 3b, it is clear that BR-SPL₁ exhibits a marching modulus cure behavior just after a

Table 2. Cure characteristics of the mixes.

Compounds	Temperature [°C]	S'_{\min}	S'_{\max}	$\Delta S'$	T_{S2} [min]	T_{90} [min]	Cure rate index [min^{-1}]
BR-S	160	1.2	10.5	9.3	13.0	20.0	14.3
	170	1.1	10.2	9.1	6.0	9.7	27.0
	180	1.0	10.2	9.2	2.5	4.4	52.6
BR-SPL ₁	160	1.2	10.5	9.3	13.3	20.8	13.3
	170	1.1	10.7	9.6	6.1	12.0	16.9
	180	1.0	11.3	10.2	2.4	22.7	4.9
BR-SMF ₁	160	1.2	10.9	9.7	14.5	38.2	4.2
	170	1.1	11.2	10.1	6.5	20.2	7.3
	180	1.1	11.5	10.4	2.6	10.3	13.0

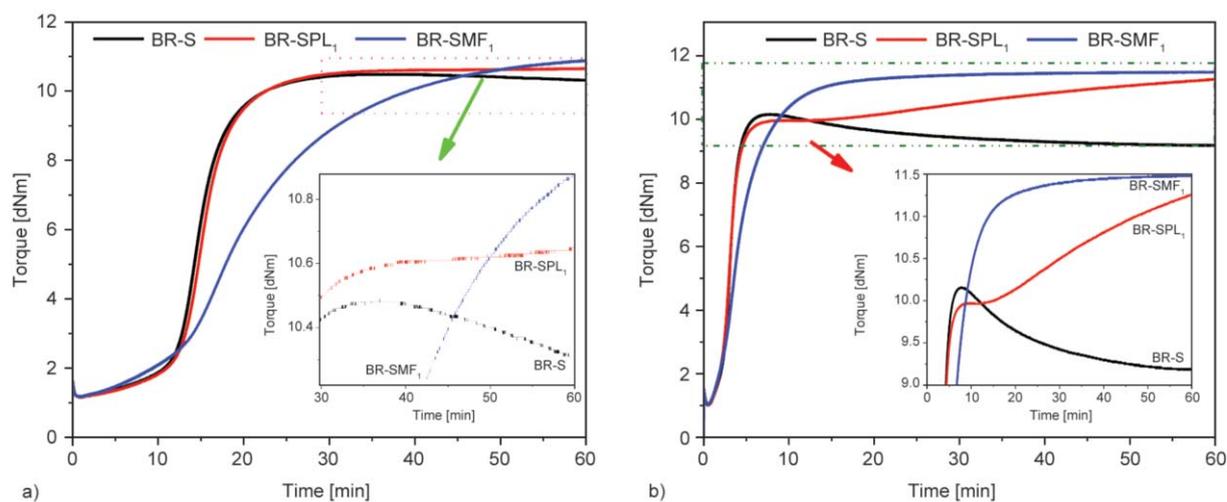


Figure 3. Cure curves of BR-S, BR-SPL₁ and BR-SMF₁ (a) at 160 °C and (b) at 180 °C for 60 min.

short reversion. This means that at a higher vulcanization temperature, the PL can act as an anti-reversion agent only after a small reversion has already happened in the system. Since the curing behavior of BR-SPL₁ exhibits a distinct marching modulus just after the onset of reversion particularly at 180 °C, the time to optimum cure shows a higher value when compared to BR-S. Based on the Fourier transform Raman spectroscopic investigations, it has been reported that the sulfur vulcanized network of diene rubbers comprises isomerized double bonds, conjugated unsaturated bond and cyclic sulfide units in addition to the mono, di and poly sulfidic crosslinks [1, 22–24]. Therefore, it is reasonable to assume that when the polysulfidic crosslink breaks during reversion, the conjugated diene units in the vulcanized network may be exposed to react if any dienophiles are present in the system. Hence, the possibility of Diels-Alder reaction can be considered

high to explain the anti-reversion property of BR-S with PL. As per this reaction mechanism, as soon as the conjugated diene units been exposed at the point of reversion, the maleimide moieties of PL will react with it and produce a cyclic adduct type crosslinks as depicted in Figure 4. From Figure 3a, it is also clear that BR-SPL₁ does not show a significant marching modulus curing behavior at 160 °C even after the onset of reversion till the end of 60 min curing. This may be due to the less breakage of the polysulfidic crosslinks and less availability of the conjugated unsaturation for the Diels-Alder reaction to take place at 160 °C. However, as the vulcanization temperature increased to 180 °C, more polysulfidic cross-links are getting broken and hence the conjugated unsaturation becomes more exposed to react with the maleimide moieties of PL via Diels-Alder reaction. As a result, the vulcanization curve of BR-SPL₁ shows a distinct marching modulus cure behavior

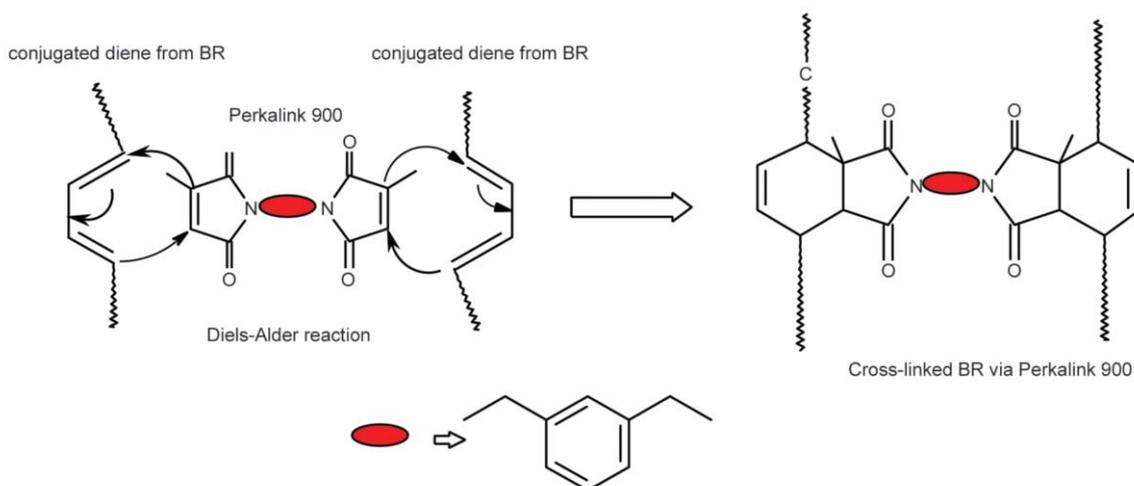


Figure 4. Schematic representation of the cross-linking reaction between the *in-situ* formed conjugated diene from BR-S and Perkalink via Diels-Alder reaction.

just after 10 minutes of curing at 180 °C. Based on these experimental observations, the vulcanized network of BR-S and BRS-PL₁ before and after reversion can be pictorially depicted as shown in Figure 5a and 5b respectively. On the other hand, the speed of the vulcanization of BR-S was considerably reduced particularly at 160 °C with the addition of 1 phr MF. As a result, the cure curve of BR-SMF₁ exhibits a marching modulus behavior right from the beginning of the reaction and therefore never attained a cure plateau till the end of the reaction at 160 °C. However, the cure curve shows a plateau region after 40 minutes of curing at 170 °C and after 25 minutes of curing at 180 °C. Here it is worth noting that the cure curve of BR-SMF₁ does not exhibit any sign of reversion till the end of the vulcanization reaction even at a 180 °C. This indicates that the anti-reversion ability of MF is superior to PL 900 during the vulcanization of polybutadiene rubber with accelerated sulfur.

3.3. Proposed reaction mechanism for the superior anti-reversion property of MF

It has been noticed that the addition of MF significantly affected the speed of the curing reaction in BRS, particularly at 160 °C. This means that MF can interfere with the normal sulfur vulcanization process at the beginning of the reaction. The Alder-ene reaction between the polybutadiene and the maleic moieties of MF can be considered as one of the probable reasons for this [25, 26]. As per this reaction mechanism, the ene group present in MF abstract an allyl hydrogen atom from the polybutadiene and forms bismaleimide crosslinks as represented in Figure 6. The possibility of this Alder-ene reaction between BR and MF may lead to connecting the polybutadiene chains via few numbers of bismaleimide crosslinks before it is getting connected via sulfur crosslinks. If so, the vulcanized network of BR-SMF₁ comprises a mixture of mono, di- and polysulfidic sulfur crosslinks along with the bismaleimide crosslinks as

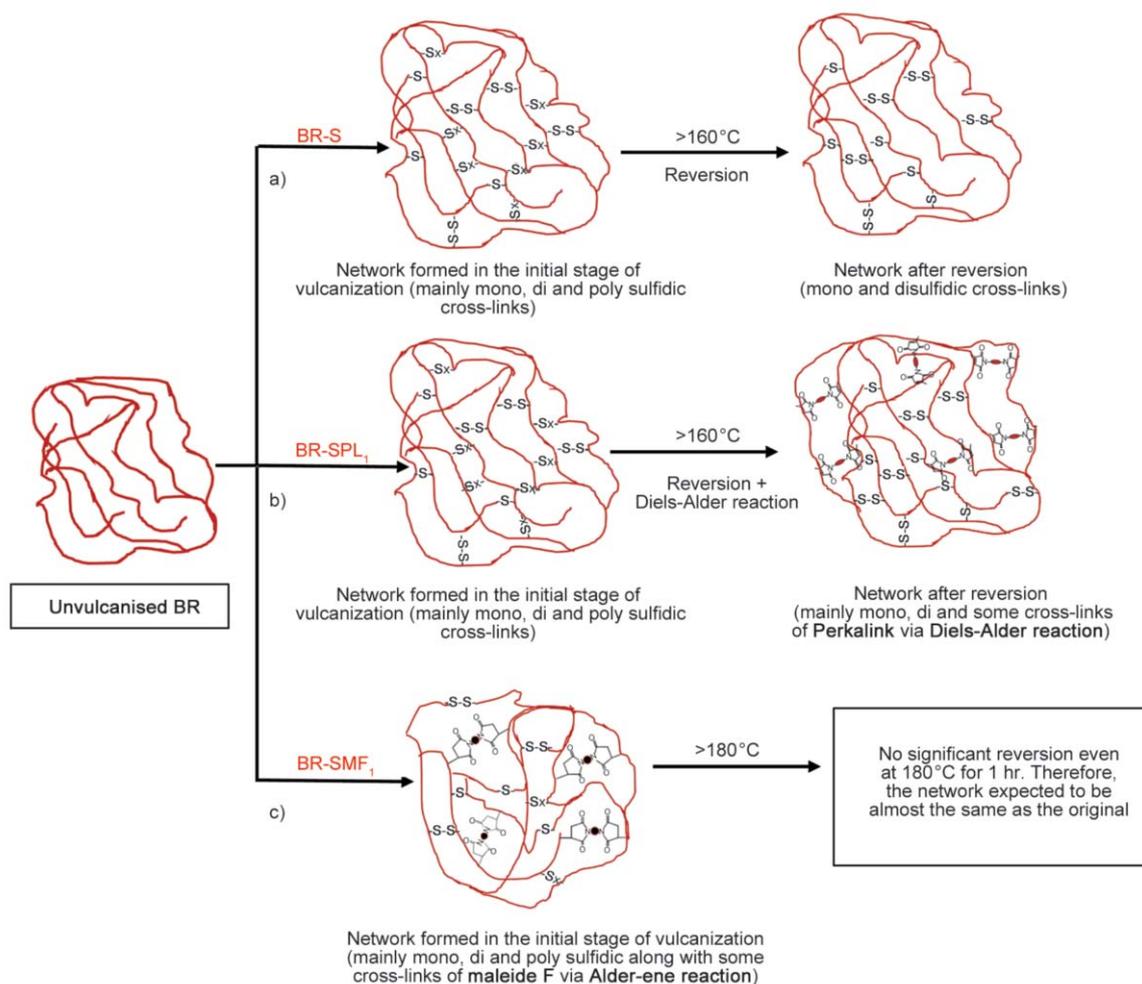


Figure 5. Surmised network structures of (a) BR-S, (b) BR-SPL₁ and (c) BR-SMF₁ before and after the reversion.

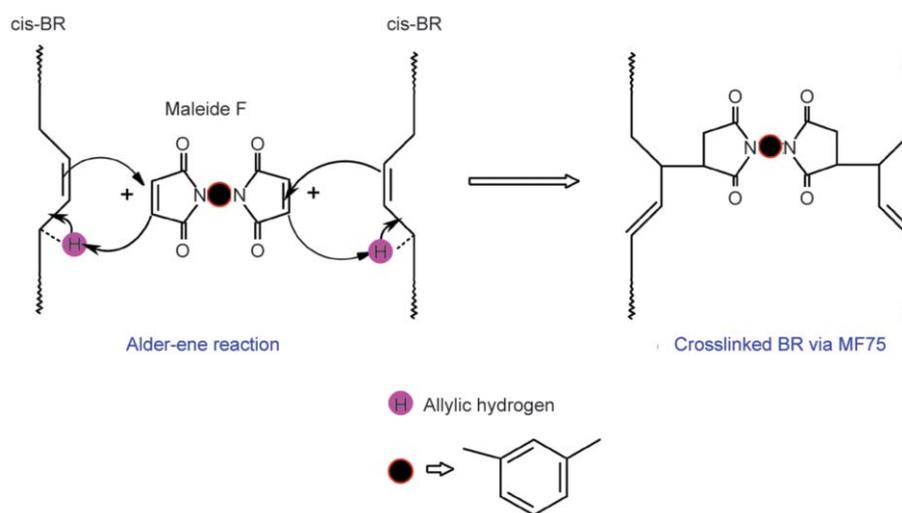


Figure 6. Schematic representation of the cross-linking reaction between polybutadiene and Maleide F via Alder-ene reaction.

depicted in Figure 5c. Because of the aromatic ring structure, the thermal stability of the vulcanizate consist of bismaleimide crosslinks is better than the vulcanizate formed with only a mixture of mono, di and polysulfidic crosslinks as in BR-S. This thermally stable bismaleimide crosslinks which are generated during the initial stages of the crosslinking reaction is responsible for the superior anti-reversion property of MF. However, owing to the bulky nature of the initially formed bismaleimide crosslinks, it may be hindered or delay in the formation of sulfur crosslinks. This may be one of the reasons for the higher T_{S2} and T_{90} values observed in the vulcanization of BR-SMF₁ particularly at 160 °C. On the other hand, because of the electron-donating methyl groups attached to the maleimide moieties, the possibility of Alder-ene reaction between polybutadiene and PL seems somewhat difficult or may take place at a very slow rate [27]. As a result, PL does not interrupt the sulfur vulcanization process at the initial stages of the vulcanization reaction and hence does not alter the speed of the reaction. Since no maleimide crosslinks are being produced in the initial stage of the vulcanization of BR-SPL₁, its vulcanized network after the initial stage of reaction (before the onset of reversion) may consist of only mono, di and polysulfidic crosslinks as shown in Figure 5b. However, after reversion, because of the possibility of Diels-Alder reaction as mentioned earlier, its vulcanized network comprises a mixture of sulfur (mainly mono and di sulfidic) and bismaleimide crosslinks as shown in the figure.

3.4. Evidences supporting the possibilities of Alder-ene reaction between BR and MF

To support the proposed Alder-ene reaction described in Figure 6, we have conducted the curing reactions of polybutadiene with bismaleimides alone. Represented in Figure 7 are the MDR cure curves and the corresponding rate of the curing reactions of polybutadiene with 1 phr MF (BR-MF₁) and 1 phr PL (BR-PL₁) at 160 and 180 °C for a period of 60 min. For a comparative purpose, the cure curve of BR-S was also incorporated in the above figures. The cure curves of BR with MF was relatively fast during the initial stage of the reaction compared to BR-S. For instance, at 160 °C, the vulcanization curve of BR-MF₁ took only 2.3 min to raise 0.5 units of torque from the minimum value. However, BR-S took around 8.7 min to raise the same amount of torque from its minimum torque value. From the inset of Figure 7a, it can be seen that after an initial rapid reaction, the cure curve of BR-MF₁ becomes very slow and exhibits a marching modulus cure behavior. However, the reaction between BR and PL was very feeble at both 160 and 180 °C. Therefore, the cure curve of BR-PL₁ does not show any significant vulcanization torque with time. This experimental evidences strongly confirms that the only possible reaction in BR+MF is the Alder-ene reaction as depicted in Figure 6. Because of the bulky nature of the bismaleimide crosslinks which are initially been generated due to Alder-ene reaction may prohibit or slow down the formation of further bismaleimide crosslinks. This is probably one of the reasons for the low

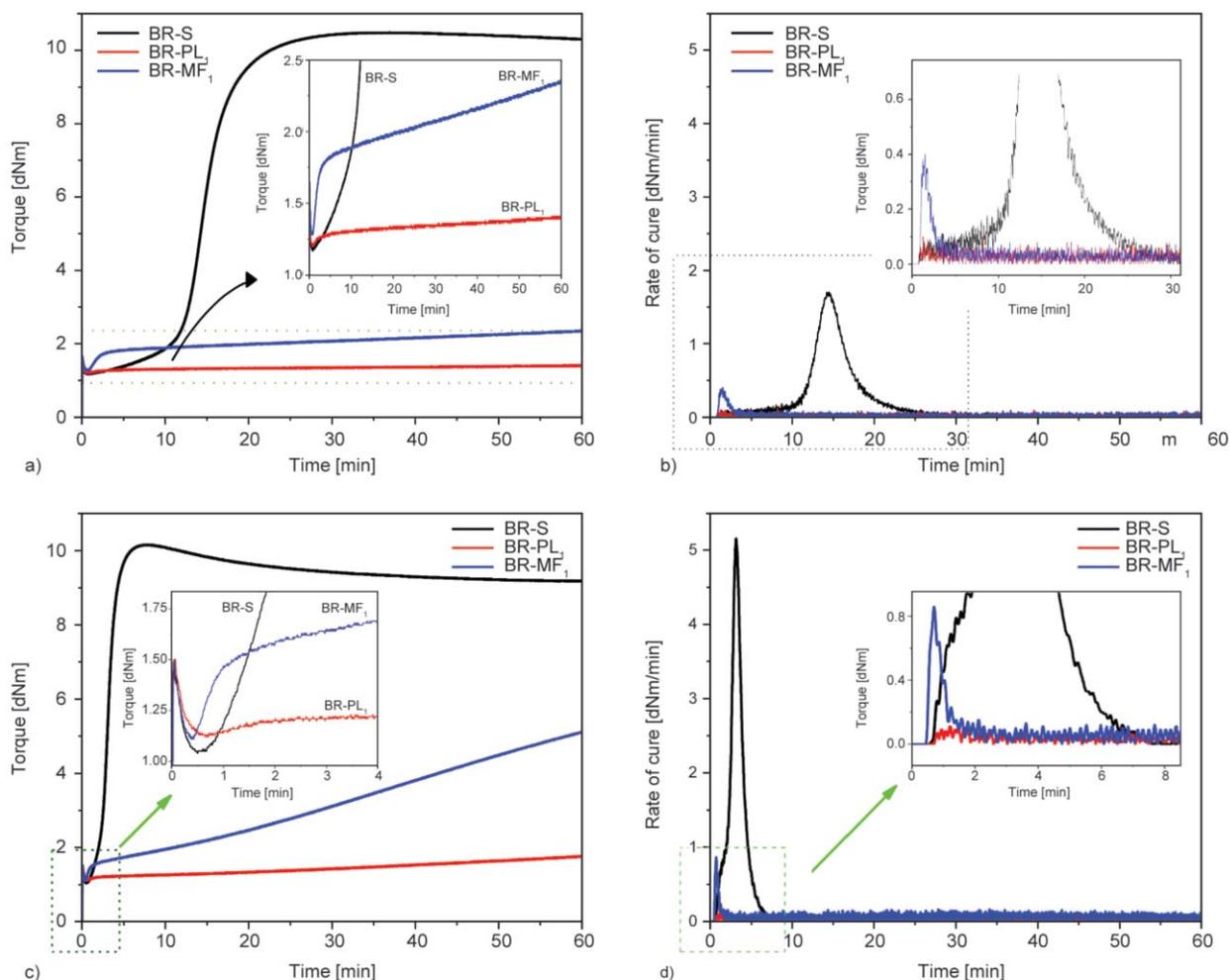


Figure 7. The MDR cure curves and the corresponding rate of the curing reactions of BR-S, BR-MF₁ and BR-PL₁ (a, b) at 160 °C and (c, d) at 180 °C for a period of 60 min.

rate of vulcanization and a marching modulus cure behavior in BR-MF₁ after an initial rapid reaction. On the other hand, because of the electron-donating methyl substituents on the maleimide moieties of PL, the Alder-ene reaction between BR and PL is extremely slow or almost negligible even at 180 °C. Therefore, the vulcanization torque is very poor which can be visualized through the Figures 7.

3.5. Vulcanization kinetics

Represented in Figure 8 are the cure rate curves of BR-S, BR-SPL₁, and BR-SMF₁ at three different vulcanization temperatures (160, 170 and 180 °C) obtained from the MDR analysis. The time required to reach the maximum rate of reaction for BR-S and BR-SPL₁ was almost similar at all the vulcanization temperatures. However, the reaction in BR-SMF₁ proceeds with a lower speed and takes a long time to attain the maximum rate at a given temperature. This can be considered as the interruption of the sulfur

vulcanization in BR-SMF₁ at the initial stage of the reaction due to the formation of some bismaleimide crosslinks via Alder-ene reaction. From the figures, it is clear that the maximum rate of reaction for all the compounds occurs at a temperature greater than zero. This implicates that all the compounds follow an autocatalytic type vulcanization reaction. Therefore, the autocatalytic model equation given in Equation (7) was employed to evaluate the kinetics of the cure reaction [28–30]:

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1 - \alpha)^n \quad (7)$$

where α is the degree of curing, k is the rate constant at temperature, T and m , and n are orders of the reaction. The degree of curing was calculated from the MDR cure curves using the Equation (8):

$$\alpha = \frac{S'_t - S'_{\min}}{S'_{\max} - S'_{\min}} \quad (8)$$

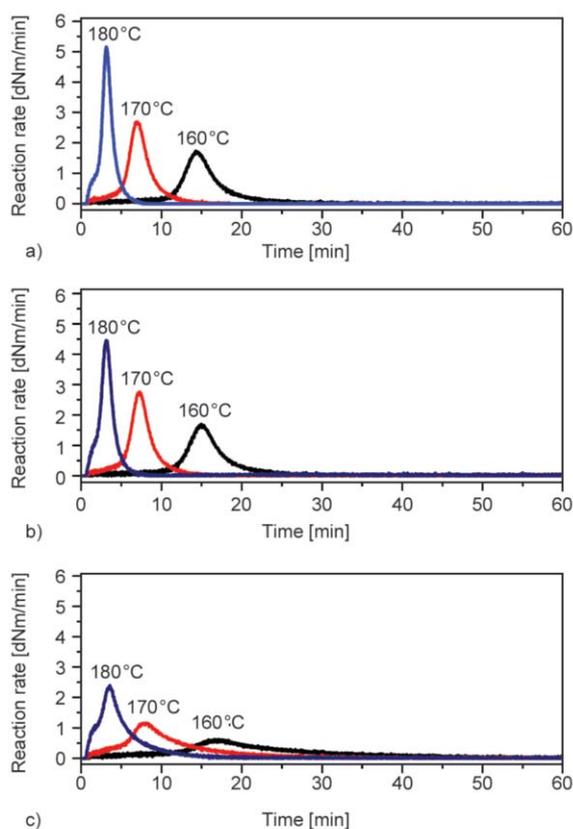


Figure 8. Cure rate curves of (a) BR-S, (b) BR-SPL₁, and (c) BR-SMF₁ obtained from the MDR at different temperatures.

where S'_t is the torque at time t , S'_{\min} is the minimum torque and S'_{\max} is the maximum torque. The values of k , m and n were determined from the plot of the rate of cure conversion (da/dt) versus degree of cure (α) using a non-linear regression fit with the help of a computer software Origin Pro 8.5. A representative curve fitted between da/dt vs. α for all these compounds at 160°C is depicted in Figure 9. The values of the kinetic parameters (k , m , n) obtained from the

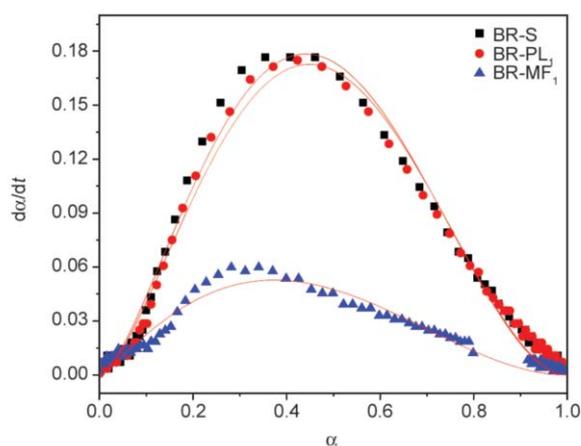


Figure 9. A representative plot between da/dt versus α for BR-S, BR-SPL₁ and BR-SMF₁ at 160°C.

Table 4. Kinetic parameters of the curing reaction obtained from ODR.

Compounds	Temperature [°C]	k	m	n	E_a [kJ/mol]
BR-S	160	2.12	1.59	2.02	44.9
	170	2.51	1.40	1.74	
	180	3.70	1.21	1.62	
BR-SPL ₁	160	2.04	1.61	1.98	42.5
	170	2.66	1.47	1.75	
	180	3.44	1.02	1.50	
BR-SMF ₁	160	0.44	1.19	2.00	53.0
	170	0.59	0.97	1.78	
	180	0.83	0.72	1.66	

respective nonlinear regression fit curves at different vulcanization temperature from 160 to 180°C are represented in Table 4. The rate constant (k) for all the compounds increased with increasing the vulcanization temperature. However, at a given temperature, the rate constants for BR-S and BR-SPL₁ were comparable and that for BR-SMF₁ was always lower than that of BR-S and BR-SPL₁. This confirms that the vulcanization kinetics of polybutadiene rubber with accelerated sulfur will slowdown in the presence of MF. For further clarification, the activation energies of BR-S, BR-SPL₁ and BR-SMF₁ were determined from their respective k values using the Arrhenius Equation (9):

$$\ln k(T) = \ln A - \frac{E_a}{RT} \quad (9)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. Figure 10 represents the Arrhenius plot of $\ln k$ versus $1/T$ for BR-S, BR-SPL₁ and BR-SMF₁. Their activation energies obtained from

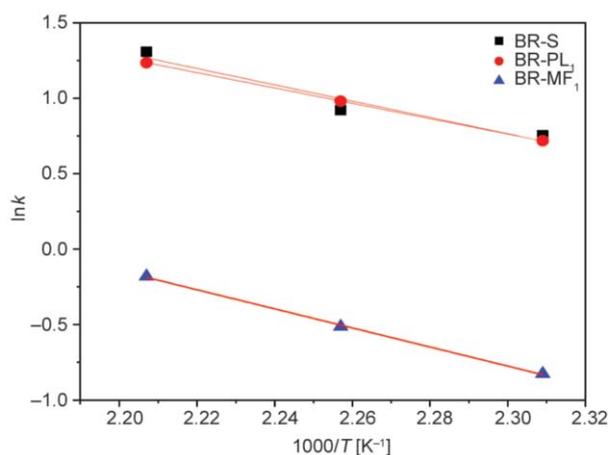


Figure 10. Arrhenius plot of $\ln k$ versus $1/T$ for BR-S, BR-SPL₁ and BR-SMF₁.

the respective slope values are also listed in Table 4. The activation energies of BR-S (44.97 kJ/mol) and BR-SPL₁ (42.4 kJ/mol) were almost comparable. However, BR-SMF₁ showed higher activation energy (52.5 kJ/mol) compared to BR-S and BR-SPL₁. The higher activation energy of BR-SMF₁ further substantiates the fact that the presence of MF will reduce the speed of accelerated sulfur vulcanization in polybutadiene rubber.

3.6. Crosslink density and compression set

3.6.1. Influence of molding temperature on the cross-link density

Depicted in Figure 11 are the chemical cross-link densities of BR-S, BR-SPL₁, and BR-SMF₁ molded at 160 and 180 °C for the respective optimum cure times. Both the molded samples of BR-S and BR-SPL₁ at 160 °C showed almost comparable cross-link densities. This was in good agreement with their respective $\Delta S'$ (an indirect indication of the cross-link densities) values obtained from the rheometer studies. However, the cross-link density of BR-SMF₁ molded at 160 °C was around 37% lower even if its $\Delta S'$ was slightly higher compared to BR-S or BR-SPL₁. This unexpected lowering of the cross-link density in BR-SMF₁ can be explained based on the nature of the vulcanization reaction and the type of cross-links formed in the vulcanized network. From Figures 3a, it can be seen that the vulcanization reaction in both BR-S and BR-SPL₁ proceeds the same pattern with the same speed till 30 minutes of curing. As a result, both these compounds may comprise all the three types of sulfur cross-links (mono-, di- and poly-sulfidic) in their vulcanized network at the same level. This may be the reason

why the samples of BR-S and BR-SPL₁ molded at 160 °C as per their T_{90} (20 minutes) exhibited the same cross-link densities. On the other hand, the speed of the vulcanization reaction in BR-SMF₁ at 160 °C considerably reduced due to a parallel reaction (Alder-ene reaction) between BR and MF as depicted in Figure 6. From Figure 7a, 7b, it has been confirmed that the speed of the reaction between BR and MF is faster than the accelerated-sulfur vulcanization reaction in BR-S in the early stage. Therefore, it is reasonable to believe that the first cross-links formed in the network of BR-SMF₁ might be a carbon-carbon cross-link through the bismaleimide unit. Because of the bulky nature of the initially generated bismaleimide crosslinks, it may be hindered or slow down for the next bismaleimide unit being incorporated into the network as cross-links. Also, the bulky bismaleimide cross-link can slightly slow down the sulfur vulcanization reaction, which ultimately leads to reducing the number of sulfur-based cross-links in the vulcanized network. All these probable factors might be the reasons for the reduction in the overall chemical crosslink density in the samples of BR-SMF₁ molded at 160 °C as per its T_{90} value.

It was noticed that the samples of BR-S and BR-SPL₁ molded at 160 °C as per their respective T_{90} exhibited almost the same values of cross-link densities. However, the cross-link density of BR-SPL₁ molded as per T_{90} at 180 °C was around 30% lower than the same molded as per the T_{90} value at 160 °C. On the contrary, the crosslink density of BR-SMF₁ molded as per T_{90} at 180 °C was around 44% higher than the same molded as per the T_{90} obtained at 160 °C. These discrepancies in the cross-link densities of BR-SPL₁ and BR-SMF₁ can be explained based on the nature of the chemical reactions offered by the PL and MF during the vulcanization process at 180 °C. From the inset of Figure 3b, it is clear that the vulcanization curve of BR-SPL₁ exhibits two distinct stages of cross-linking reaction at 180 °C. The first stage reaction can be considered as accelerated-sulfur vulcanization, which starts at 0.5 minutes and ends at 8 minutes. The second stage reaction seems to be very slow. It starts at around 12.5 minutes and continued till the end of the given 60 minutes curing time. Between 8 and 12.5 minutes, the cure curve exhibits a sign of reversion. Because of the reversion that happened between 8 and 12.5 minutes, BR-SPL₁ loses its initially formed network

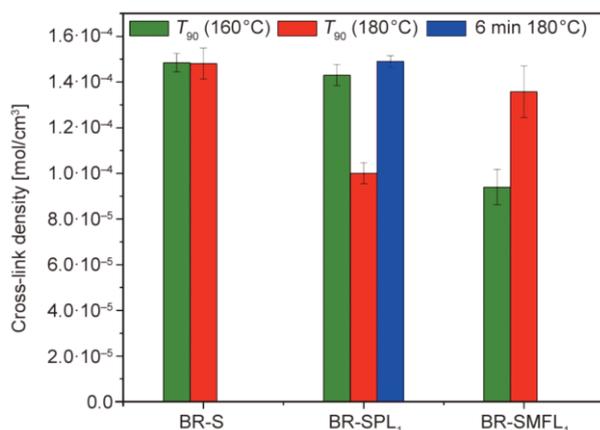


Figure 11. Chemical cross-link densities of BR-S, BR-SPL₁ and BR-SMF₁ molded at 160 and 180 °C for the respective optimum cure times.

integration. This may be the reason why the compound of BR-SPL₁ molded at 180 °C for T_{90} (23 minutes) exhibited a lower cross-link density. However, it is worth noting that the molded samples of BR-SPL₁ at 180 °C for 6 minutes (before reversion) exhibited almost equal cross-link density compared to the same molded at 160 °C as per T_{90} . Unlike BR-SPL₁, the Alder-ene reaction which was responsible for diminishing the speed of the vulcanization reaction in BR-SMF₁ at 160 °C became faster at 180 °C owing to the lower activation energy. Consequently, more numbers of bismaleimide cross-links can get into the vulcanized network along with the sulfur based cross-links. This might be one of the plausible reasons for the enhanced cross-link density for the samples of BR-SMF₁ molded at 180 °C.

3.6.2. Influence of molding time on the cross-link density

To understand the network integrity and stability of the cross-links been formed in BRS, BRS-PL₁, and BRS-MF₁, the cross-link densities of these compounds were determined after molding them at 180 °C under the different extent of time beyond their T_{90} . Represented in Figure 12 are the cross-link densities of BRS, BRS-PL₁, and BRS-MF₁ molded at 180 °C as per T_{90} , $T_{90}+10$ minutes and $T_{90}+30$ minutes respectively. As expected, BR-S molded as per T_{90} exhibited the highest cross-link density owing to its good network integrity. However, when the molding time elapsed 10 minutes beyond its T_{90} , the cross-link density was reduced to around 26%, which further reduced to 46% as the molding time extended to 30 minutes beyond the T_{90} value. Severe breakage of the polysulfidic cross-links and the subsequent

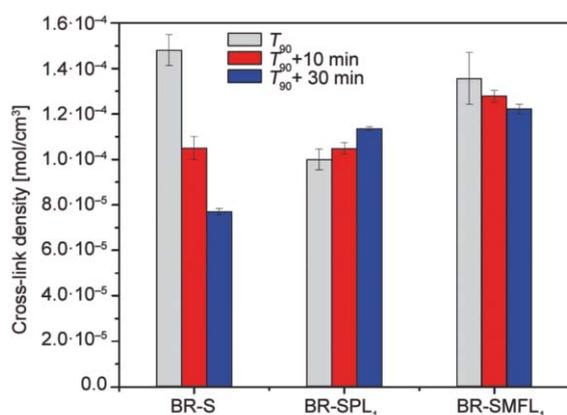


Figure 12. Cross-link densities of BRS, BRS-PL₁, and BRS-MF₁ molded at 180 °C as per T_{90} , $T_{90}+10$ minutes and $T_{90}+30$ minutes.

loss of the network integrity due to over curing was the primary reason for the drastic reduction in the cross-link densities of BR-S. In the case of BR-SPL₁, the one molded as per its T_{90} (23 minutes) showed the lowest cross-link density. However, about 5% improvement in the cross-link density was observed when the molding time extended to 10 more minutes beyond its T_{90} . The improvement in cross-link density was further rose to 36% when it was molded for $T_{90}+30$ minutes. The formation of diene-Perkalink Diels-Alder adducts between the polymer chains beyond its T_{90} is considered as one of the probable reasons for the enhanced crosslink density. Here it is worth noting that, though BR-SMF₁ exhibited a plateau type cure curve with no distinct sign of reversion beyond its T_{90} , the cross-link densities of its samples molded for $T_{90}+10$ minutes and $T_{90}+30$ minutes were also exhibited the same trend as seen in BR-S. However, when compared to BR-S, here, the reduction in the cross-link densities with the extended molding time beyond T_{90} was marginal. For instance, only a 6% decrease in the crosslink density was experienced when the molding time for BR-SMF₁ extended to 10 minutes beyond its T_{90} . The cross-link density was not reduced to more than 10% even if the curing time elapsed 30 minutes beyond its T_{90} . Unlike in the vulcanized network of BR-S or BR-SPL₁, the network formed in BR-SMF₁ within T_{90} comprises some carbon-carbon cross-links via Alder-ene reaction in addition to the sulfur-based cross-links. Since the Alder-ene reaction also consumes certain double bonds from the polymer, the amount of polysulfidic sulfur cross-links in BR-SMF₁ will be lower than those were present in BR-S or BR-SPL₁. Because of the small amounts of the polysulfidic cross-links together with the inherent thermal stability of the carbon-carbon cross-links, the network damage in BR-SMF₁ would not be as severe as observed in either BR-S or BR-SPL₁ in the over-cure region. This may be one of the reasons why we have seen only a marginal reduction in the cross-link densities of the samples of BR-SMF₁ molded for $T_{90}+10$ min and $T_{90}+30$ min at 180 °C.

3.6.3. Influence of molding (curing) time on the compression set properties

The compression set is considered as an important property requirement for the rubber compounds used in the sealing applications. In general, lower the set value higher will be the sealing efficiency. Rubber

compounds having a strong vulcanized network with high cross-link density usually exhibits a low compression set value [31]. Furthermore, the compression set will also depend on the strength of the chemical bonds in the vulcanized network. Generally, the bond energy of a C–C cross-link (354 kJ/mol) is much higher than all the three types of sulfur based cross-links such as C–S_X–C (252 J/mol), C–S₂–C (268 kJ/mol) and C–S–C (285 kJ/mol) [2]. Therefore, it is quite obvious that if any bismaleimide cross-links are generated in the vulcanized network, the overall thermal stability of the network will be higher. Represented in Figure 13 are the set value of BR-S, BR-SPL₁ and BR-SMF₁ molded at 180 °C for different molding times. All these compounds showed a gradually decreasing trend in the set values as the molding time increased. If we evaluate the set properties in terms of cross-link density, this trend was quite unexpected, particularly in BR-S. In terms of cross-link density, the one molded at 180 °C for 30 minutes should have been exhibited the highest set value than the one molded at 10 minutes under the given conditions. But, the reverse was found true here. For instance, BR-S molded at 10 minutes shows a set value of 46.62%, which has been reduced to 29.91% as the molding time was extended for 30 minutes. One of the most probable reasons for the low set value of the 30 minutes molded compounds might be due to the breakage and transformation of the less thermally stable poly-sulfidic crosslinks in its vulcanized network to a more thermally stable mono and di-sulfidic cross-links. Here it is important to note

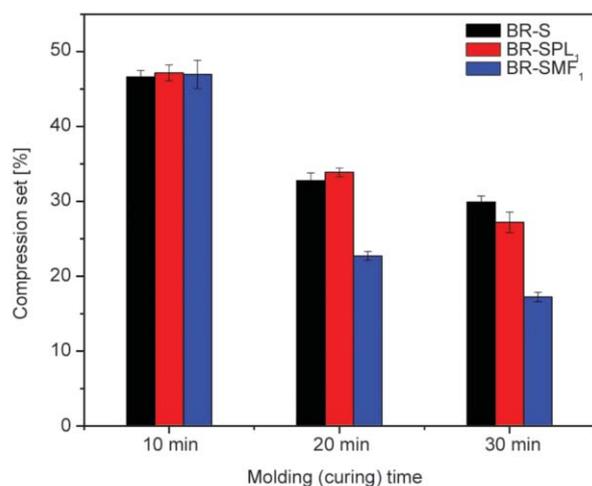


Figure 13. Compression set values of BR-S, BR-SPL₁ and BR-SMF₁ molded at 180 °C for different molding times.

that the set values of all the compounds molded up to 10 minutes and the compounds BR-S and BR-SPL₁ molded up to 20 minutes were almost comparable. This implies that the sulfur-based cross-links generated in the vulcanized network of these compounds within 20 minutes of molding (curing) are largely controlling their set values. On the other hand, BR-SMF₁ molded for 20 minutes exhibits a set value of around 22.7%. At the same time, the set values for the 20 minute molded BR-S and BR-SPL₁ were 32.78 and 33.87% respectively. When the molding time extended up to 30 minutes, the set value of BR-SMF₁ further reduced to 17.24%. This low set value of BR-SMF₁ might be due to the formation of considerable amounts of thermally stable carbon-carbon cross-links in the vulcanized network via Alder-ene reaction between BR and MF.

3.7. Thermogravimetric Analysis

From the compression set studies, it has been observed that when the bismaleimide units through Perkalink or MF get incorporated in the vulcanized network as cross-links, the thermal stability of the resultant vulcanizate become significantly improved. To support this observation, the thermogravimetric analysis of the vulcanized samples of BR-S, BR-SPL₁, and BR-SMF₁ were performed under a nitrogen atmosphere from room temperature to 600 °C. The BR-S taken for this study was molded at 180 °C as per T_{90} . However, the samples of BR-SPL₁ and BR-SMF₁ were used after molding them at 180 °C for $T_{90}+30$ minutes to ensure the presence of the

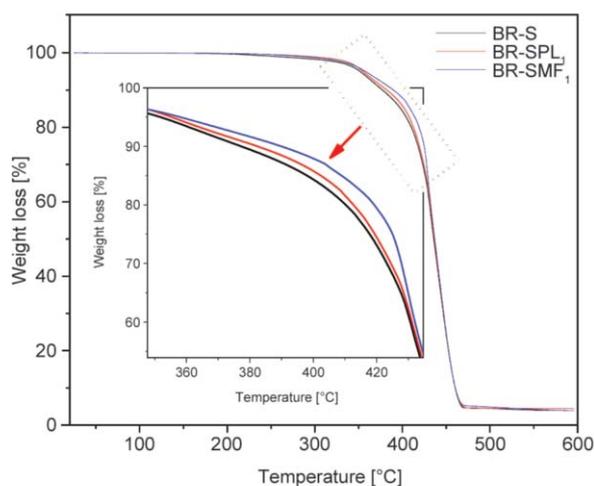


Figure 14. TGA curves of the cured samples BR-S, BR-SPL₁, and BR-SMF₁. (BR-S was cured as per T_{90} and BR-SPL₁ and BR-SMF₁ were cured as per $T_{90}+30$ minutes at 180 °C).

maleimide cross-links in the vulcanized network. Represented in Figure 14 are the weight loss vs. temperature curves of BR-S, BR-SPL₁, and BR-SMF₁. It is clear from the figure that the onset temperature (the temperature at 5% weight loss, $T_{5\%}$) for the thermal degradation of BR-S was slightly improved by 3.5 °C when it was vulcanized in the presence of 1 phr Perkalink 900. The $T_{5\%}$ of BR-S further moved to the higher temperature side by 6.3 °C when it was vulcanized with 1 phr MF. This thermal analysis data substantiate the fact that the bismaleimide cross-links in the vulcanized network improve the overall thermal stability of the system.

3.8. Influence of MF content on the vulcanization behavior and the vulcanizate properties

Based on the above studies, it has been confirmed that MF is a promising chemical to enhance the reversion resistance in an industrially acceptable manner at a higher vulcanization temperature. Moreover, the crosslink density and set properties of the vulcanizate contains MF were better than those with PL900. Therefore, a detailed investigation regarding how the content of MF affects the vulcanization behavior and the vulcanizate properties like cross-linking density, compression set, and shore hardness were also evaluated. Represented in Figure 15 are the MDR cure curves of BR-S with different content of MF at 180 °C for 60 min. Their corresponding cure characteristics are listed in Table 5. The addition of MF does not significantly alter the scorch time (T_{S2}) of BR-S. However, its T_{90} and the S'_{max} were gradually increased as the content of MF increased. The increase of S'_{max} or $\Delta S'_{max}$ with the content of MF is an indication of the enhanced crosslink density. As the content of MF increased, more bismaleimide crosslinks may be produced into the vulcanized network. Because of the bulky nature of the initially formed bismaleimide crosslinks, it may slow down the formation of the most expected sulfur crosslinks and also may slow down the formation of

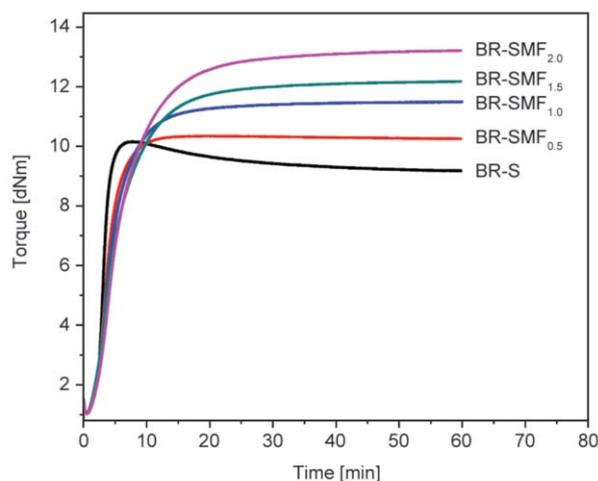


Figure 15. Cure curves of BR-S with different content of MF at 180 °C for 60 min.

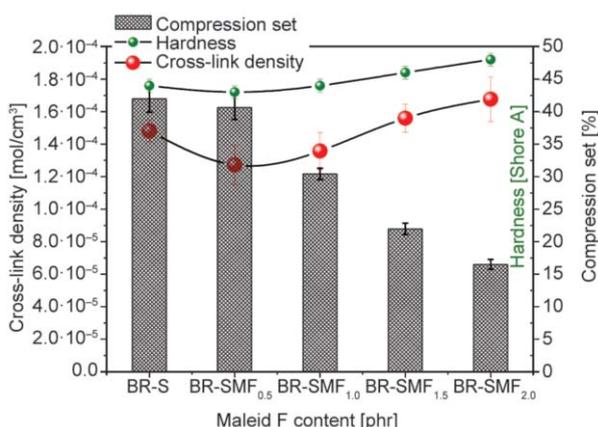


Figure 16. Crosslink density, compression set, and shore-A hardness values of BR-S with different contents of MF. [All the samples were molded as per T_{90} for measuring crosslink density. However, a molding time of $T_{90}+5$ minutes at 180 °C was given for making the samples for measuring both the compression set as well as hardness.]

further bismaleimide cross-links. As a result, BR-S exhibits a slow curing behavior beyond 0.5 phr addition of MF, consequently takes a longer time to reach the optimum cure state. Therefore, the recommended concentration of MF for a balanced T_{S2} and T_{90} with excellent anti-reversion property would be in the range of 0.5 to 1.0 phr. Represented in Figure 16 are the crosslink density, compression set, and

Table 5. Cure characteristics of BR-S with different contents of MF at 180 °C.

MF content	S'_{min}	S'_{max}	$\Delta S'$	T_{S2} [min]	T_{90} [min]	Cure rate index [min ⁻¹]
BR-SMF _{0.5}	1.0	10.5	9.5	2.6	7.0	22.7
BR-SMF _{1.0}	1.1	11.5	10.4	2.6	10.3	13.0
BR-SMF _{1.5}	1.0	12.2	11.2	2.5	13.4	9.2
BR-SMF _{2.0}	1.0	13.1	12.1	2.3	14.2	8.4

shore-A hardness values of BR-S with different contents of MF. Here, the samples used for measuring the cross-link densities were molded as per the respective T_{90} values at 180 °C. However, a molding time of $T_{90}+5$ minutes was given for making the samples for measuring both the compression set as well as hardness. The changes in the cross-link densities of BR-S with the addition of MF was not linear. It is clear from the figure that the cross-link density of BR-S decreased by 14.1% with the addition of 0.5 phr MF. The intensity of reducing the cross-link density was quenched to 8.3% with the addition of 1 phr MF. Later, the cross-link density was slightly improved to 5.3% with 1.5 phr addition of MF and further improved to 13.2% as the MF content rose to 2 phr. However, both the hardness and the compression set values of BR-S have exhibited a linear change as the MF content increased. Here, the hardness gradually increased from 44 to 48 Shore A with the content of MF increased from 0 to 2 phr MF and the compression set values were gradually decreased from 42 to 16.3% as the MF content rose from 0 to 2 phr.

4. Conclusions

From this study, it has been identified that both the PL 900 and MF can show anti-reversion activity during the accelerated sulfur vulcanization of polybutadiene rubber. However, the performance of Perkalink in terms of both its curing and anti-reversion ability was at its best only at 160 °C. As the vulcanization temperature raised to well above 160 °C, the PL exhibits its anti-reversion ability only after considerable damage has happened in the vulcanized network. Therefore, PL cannot be recommended as a promising anti-reversion agent for the high-temperature vulcanization of diene-rubbers with accelerated sulfur. On the other hand, MF can directly react with the polybutadiene chains during the initial stage of the vulcanization reaction and produces bismaleimide crosslinks via Alder-ene reaction along with the sulfur crosslinks. Owing to the high thermal stability of the bismaleimide crosslinks, the compounds contain MF do not exhibit any sign of reversion even at elevated temperatures. Moreover, the crosslink density of the compound with 1 phr MF vulcanized for $T_{90}+30$ min at 180 °C was 58.5% higher than those without any MF and about 7.5% higher than those with 1 phr PL. Similarly, the compound with 1 phr MF vulcanized for 30 minutes at 180 °C exhibits the lowest compression set of 17.24% at 100 °C for 22 hrs.

At the same time, it was around 27.24% for the compound with 1 phr PL and around 29.9% without any bismaleimides. Therefore, MF can be recommended as a trustworthy chemical to enhance the reversion resistance for the high-temperature vulcanization of diene-rubbers with accelerated sulfur and also to improve the vulcanizate properties such as cross-linking density and compression set.

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