Facilitating high-temperature curing of natural rubber with a conventional accelerated-sulfur system using a synergistic combination of bismaleimides

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Abstract. It is well known that high-temperature curing of natural rubber (NR) with a conventional accelerated-sulfur (CV) system is limited because of reversion. This paper describes the curing behavior and the reversion resistance characteristics of unfilled NR with a CV system in the presence of two different bismaleimides: Perkalink 900 (PL) and Maleide F (MF). Rheometer studies reveal that MF can directly interact with the NR during accelerated-sulfur curing and forms some thermally stable bismaleimide type crosslinks in the beginning via Alder-ene reaction. However, even with the use of 4 phr of MF, a considerable reversion was noticed during the curing of NR with CV at 180 °C for 1 hr. A high dosage (5 phr) of MF was therefore required for a complete reversion free plateau type cure pattern. On the other hand, PL has no direct interaction with the NR at the beginning of the curing reaction. Moreover, even 1 phr PL exhibits a marching modulus curing behavior via Diels-Alder reaction. Therefore, to solve the individual issues of these chemicals, a synergistic combination of MF and PL has been identified and applied to facilitate the high-temperature curing of NR /CV devoid of reversion with a plateau type cure pattern.

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

1. Introduction

As is well known, the accelerated-sulfur curing systems are classified as conventional vulcanization (CV), efficient vulcanization (EV), and semi-efficient vulcanization (SEV) based on the amount of sulfur and the accelerators used in the respective systems. Generally, the CV system is characterized by a high dosage of sulfur (2–3.5 phr) and a low dosage of accelerators (0.4–1.2 phr). A low level of sulfur (0.4–0.8 phr) and a high dosage of accelerator (2–5 phr) are used for the EV system. An intermediate level of sulfur (1.0–1.7 phr) and accelerator (1.2–2.4 phr) is employed for SEV system [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 crosslinks will be poly- and di-sulfidic, and the rest will be mono-sulfidic. However, the amount of mono-sulfidic crosslinks will be around 80% if the rubber is cured with an EV system. Because of the low bond dissociation energy of the polysulfidic crosslinks (252 kJ/mol) compared to the disulfidic (268 kJ/mol) and mono-sulfidic (285 kJ/mol) crosslinks, the curing of highly unsaturated elastomers like natural rubber (NR) with a CV system generally shows reversion at a temperature greater than 140 °C [2]. Many research works have been performed to address the reversion in accelerated-sulfur cured diene elastomers. Based on these research works, it has been identified that the breakage of the polysulfidic crosslinks during curing, particularly at a higher temperature, is one of the primary reasons behind

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the reversion [5–8]. The declination in the rheometric torque after a maximum value with time is the direct evidence for reversion during the curing process. Excessive generation of heat due to severe service conditions on sulfur-cured NR based rubber products like tire may also cause reversion. This will cause NR to lose its physical properties like tensile strength, modulus, tear strength during service and thereby reduce the service life of the tire [9]. Therefore, enhancing the reversion resistance of accelerated-sulfur cured NR based compounds is one of the demanding research topics in the rubber industry.

Many strategies have been adopted to avoid the reversion during the curing of highly unsaturated elastomers with a CV system. One of the common methods is the incorporation of certain chemicals known as anti-reversion agents into the curing recipe. Hexamethylene bithiosulphate disodium salt (Duralink® HTS), bis (triethoxysilylpropyl)-tetrasulphide (TESPT), thiuram accelerators, dithiophosphate accelerators (Vocol ZBPD) are some of the anti-reversion chemicals to enhance the reversion resistance during the curing of truck tire tread compounds based on NR-CV system [9, 10]. It has been realized that these chemicals can heal the reversion tendency through the formation of stable crosslinks with the rubber chains at the point of the reversion without adversely affecting the accelerated-sulfur curing reaction. In addition to this, 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 semi efficient curing (SEV) system in addition to its role as a processing aid [9].

For many years, maleimide-bearing compounds such as bismaleimides or biscitraconimides are widely used as anti-reversion agents for unsaturated elastomers. For instance, Schotman *et al.* [11] investigated the use of bis(citraconimidomethyl)benzene (BCI) as anti-reversion agent in the NR matrix. Datta and coworkers [12, 13] also investigated the anti-reversion activity of BCI in squalene and NR. Based on this study, they have elucidated a mechanism behind the anti-reversion ability of this chemical in diene rubbers. Kumar *et al.* [14] investigated the effect of BCI on the cure characteristics and the physical properties after anaerobic and aerobic aging of an NR based truck tire tread compound. The author has reported the effect of 4,4'-(bismaleimido) diphenyl methane (BMDM) as an anti-reversion agent during

the curing of NR with a CV system. The physicochemical properties and the crosslink densities of the NR/CV vulcanizate were evaluated as a function of BMDM content [15].

This study primarily describes a comparative analysis of Maleide F (a combination of *N,N'*-m-phenylene dimaleimide and a 25% blending agent) and Perkalink 900 (PL) (1,3-bis(citraconimidomethyl)benzene) on the curing behavior and anti-reversion characteristics of NR with a CV system at a higher curing temperature. PL is a commercially available anti-reversion agent for enhancing the reversion resistance during the accelerated-sulfur curing of diene elastomers like natural rubber. One of the disadvantages of PL is its marching modulus curing behavior. To solve this issue, a synergistic combination of PL with Maleide F has been identified and applied to facilitate a high-temperature reversion free plateau type curing of NR with the accelerated sulfur. To the best of our knowledge, no work has been reported in the literature regarding the enhancement of reversion resistance using such a synergistic combination of two different anti-reversion chemicals.

2. Experimental

2.1. Materials

Natural rubber (standard Vietnamese rubber having Mooney viscosity ML(1+4) at 100 °C: 60±5) was kindly supplied by Binh Phuoc, Vietnam, under the trade name SVR CV60. 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)benzene was procured from Lanxess Deutschland GmbH, Leverkusen, Germany. The chemical structures of MF and PL are shown in Figure 1. Other

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

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 cc. A fill-factor of 0.8 was taken for the efficient mixing of the ingredients. The neat NR has masticated at 50 °C under 50 rpm for 1 min. To this, the ZnO, stearic acid, and bis-maleimides 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 sheets having 1 and 2 mm of thickness by applying a constant force of 200 N using a compression molding heat press LaBEcon 300 (Fontijne Presses, The Netherlands) 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 curing

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 (20 °C) 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 crosslink density n of the samples was calculated using the Flory-Rehner equation given in Equation (2) [16–18]:

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

where V_r is the volume fraction of rubber in the equilibrium swollen sample and is calculated using the Equation (3) [19]. V_s is the molar volume of the solvent (106.3 ml/mol for toluene at room temperature) and χ is the Flory-Huggins interaction parameter. For NR-toluene system, the value of χ (0.385) was determined using the Equation (4) [20]:

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

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

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

Sample ID	Ingredients	NR	ZnO	Stearic acid	Sulfur	CBS	MF	PL 900
NR-CV							–	–
NR-CVP1							–	1.0
NR-CVP3							–	3.0
NR-CVP4							–	4.0
NR-CVP5							–	5.0
NR-CVM1		100	4	2	2.5	0.5	1	–
NR-CVM3							3	–
NR-CVM4							4	–
NR-CVM5							5	–
NR-CVM3P0.5							3	0.5

where W_s is the weight of the equilibrium swelled rubber, and W_d is the dried weight of the swelled rubber and ρ is the density. β is the lattice constant (typically 0.34) [20], 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 NR and toluene were taken as 17.18 and 18.20 MPa^{1/2}, respectively [15].

2.3.3. Viscoelastic studies using rubber process analyzer (RPA)

To understand the strength of the network developed at different stages of curing, the viscoelastic properties like shear storage modulus were evaluated via a strain sweep measurement using a Premier RPA, Alfa Technologies, USA. For that, a cure test was first performed at 180 °C for predetermined curing time. The cured sample is then cool down to 40 °C within the RPA die and conducted a strain sweep experiment by varying the strain from 0.5 to 100% at a constant frequency of 1 Hz.

2.3.4. Mechanical (tensile) properties

The stress-strain behavior and the corresponding tensile properties of the vulcanizates were measured using a universal testing machine (Testometric M350, Testometric Company, Ltd. UK). The testing was performed under ambient conditions at a crosshead speed of 500 mm/min as per ISO 37 using S2 type specimen having 2 mm thickness. The results were reported an average of five tested specimens.

3. Results and discussion

3.1. Influence of Maleide F on the curing behavior of NR-CV at 180 °C

Represented in Figure 2 is the curing behavior of NR with a CV system in the presence of different contents of MF at 180 °C for 1 hr. Their cure characteristics are represented in Table 2. The cure curve of NR-CV achieved a maximum torque at 2.25 min and decreased thereafter due to reversion. The percentage reversion that is calculated using Equation (5) at different intervals of time are listed in Table 3.

Table 2. Cure characteristics of the mixes at 180 °C.

Compounds	S'_{min}	S'_{max}	$\Delta S'$	T_{S2} [min]	T_{90} [min]	Cure rate index [min ⁻¹]
NR-CV	0.63	5.62	4.99	0.87	1.42	181.18
NR-CVP1	0.56	5.89	5.33	1.13	1.90	129.87
NR-CVP3	0.52	8.11	7.59	1.12	34.47	2.99
NR-CVP4	0.56	9.08	8.52	1.10	35.76	2.88
NR-CVP5	0.59	9.37	8.78	1.10	37.77	2.72
NR-CVM1	0.73	5.87	5.14	1.17	2.08	109.89
NR-CVM3	0.58	6.76	6.18	1.28	2.75	68.02
NR-CVM4	0.66	6.88	6.22	1.24	2.93	59.17
NR-CVM5	0.64	7.22	6.58	1.05	2.65	62.50
NR-CVM3P0.5	0.63	7.09	6.46	1.28	3.12	54.34

Figure 2. (a) Curing behavior of NR-CV with different contents of MF and (b) an enlarged view from the highlighted region of Figure 2a.

Table 3. Percentage reversion of the compounds at different time intervals from the maximum torque at 180 °C.

Compounds	Reversion [%]		
	$S'_{\max} + 5 \text{ min}$	$S'_{\max} + 10 \text{ min}$	$S'_{\max} + 30 \text{ min}$
NR-CV	15.5	20.1	24.7
NR-CVP1	10.4	10.9	5.1
NR-CVP3	3.3	No reversion (+1.8)	No reversion (+20.3)
NR-CVP4	No reversion	No reversion (+9.4)	No reversion (+36.0)
NR-CVP5	No reversion (+1.0)	No reversion (+9.7)	No reversion (+36.3)
NR-CVM1	9.7	14.2	17.0
NR-CVM3	3.1	5.0	7.5
NR-CVM4	1.6	2.5	7.9
NR-CVM5	No reversion	No reversion	No reversion
NR-CVM3P0.5	1.3	1.0	No reversion (+2.5)

*Values in the parenthesis indicate the additional torque generated in percentage after reversion due to the marching modulus curing.

$$\text{Reversion [\%]} = \frac{S'_{\max} - S'_{\max+t}}{S'_{\max}} \cdot 100 \quad (5)$$

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

It is clear that the percentage reversion increases as the time of curing increases. For instance, a reversion of 15.5% was observed in NR-CV as the cure time extended 5 minutes beyond its maximum torque. The reversion further rose to 24.7% as the cure time extended 30 minutes beyond the maximum torque. The addition of MF gradually improves the curing torque of NR-CV without significantly altering the scorch time and the optimum cure time. For instance, the addition of 1 phr of MF improves the $\Delta S' = (S'_{\max} - S'_{\min})$ of NR-CV by 3%. The $\Delta S'$ was further rose to 31.8% with the addition of 5 phr MF. This improvement in the $\Delta S'$ indicates that the crosslink density of NR-CV increases with the addition of MF. To substantiate this, the crosslink densities of NR-CV with different contents of MF were measured using the Equation (2), and the results are reported in Figure 3. From this figure, it is clear that the chemical

Figure 3. Crosslink densities and $\Delta S' = (S'_{\max} - S'_{\min})$ values of NR-CV with different contents of MF.

crosslink density also increased as the content of MF increased.

One of the probable reasons behind the enhanced crosslinking density might be due to the Alder-ene reaction, as depicted in Figure 4 [21, 22]. This reaction is believed to take place at the beginning of the curing along with the accelerated-sulfur reaction. It is important to note that because of this Alder-ene reaction, some maleimide based crosslinks are getting

Figure 4. Alder-ene reaction between NR and Maleide F.

incorporated into the network of NR-CV/MF systems in addition to the usual sulfur crosslinks at the initial stage of the curing reaction. As a result, the overall thermal stability of the network might be improved. From Table 3, it is clear that the reversion in NR-CV significantly reduced with the addition of MF. For instance, the reversion in NR-CV under $S'_{\max}$ + 5 minutes of curing could be reduced from 15.5 to 3.1% with the addition of 3 phr MF. The reversion in NR-CV could be eliminated throughout the given curing time (1 hr) by raising the content of MF to 5 phr.

3.2. Influence of Perkalin 900 on the curing behavior of NR-CV at 180 °C

Depicted in Figure 5 is the curing behavior of NR-CV with different contents of PL. All the curves followed the same trace irrespective of the PL contents and showed a maximum torque ($S'_{\max}$) value after the completion of the accelerated-sulfur reaction at a point between 5.5 to 6 dNm within 2.5 to 3 minutes of curing as highlighted in the figure. For better understanding, the highlighted portion of the curves of NR-CV/PL in Figure 5 is enlarged and indicates their maximum percentage reversions, as shown in Figure 6. It is clear that, after the initial reaction (accelerated-sulfur reaction), all the NR-CV/PL curves exhibit a sharp declination in the torque (reversion) for a while and then follow a marching modulus curing behavior till the end of the given cure time. Therefore, the percentage changes in the rheometric torque were calculated based on the first peak maxima's, as highlighted in the figure. The calculated percentage changes in the rheometric torque in NR-CV/PL systems at different intervals of time are also reported in

Figure 5. Curing behavior of NR-CV with different contents of PL.

Figure 6. Enlarged view of the highlighted portion of NR-CV/PL curves of Figure 5 with maximum percentage reversions.

Table 3. The addition of 1 phr PL (NR-CVPL1) suppresses the intensity of reversion that was observed after 5 minutes of curing in NR-CV, from 15.5 to 10.4%. Since the cure curve of NR-CVPL1 becomes marching modulus after an initial reversion, the intensity of reversion in NR-CV after 30 minutes of over curing could be reduced from 24.7% to just 5.1%. As the content of PL rose to 3phr, the percentage of reversion after 5 minutes of curing in NR-CV could be reduced from 15.5% to 3.3%. Because of marching modulus curing behavior, NR-CVP3 exhibits no reversion. Instead, it increases the torque by 20.3% when its cure time extended 30 minutes beyond the initial maximum torque. A similar trend was observed as the content of PL increased beyond 3 phr. Based on the above rheometer studies, it can be perceived that PL is inactive at the beginning of the curing reaction. However, it becomes active after a short reversion (after 3–5 minutes of curing) and forms some additional chemical crosslinks in the cured network. To further confirm this, the chemical crosslink densities of NR-CV/PL systems were measured using 5 and 30 minutes cured sheet. Depicted in Figure 7 are the crosslink densities of NR-CV with different contents of PL. The crosslink densities of 5 minutes cured sheet having different contents of PL were almost comparable to the crosslink density of NR-CV. However, the crosslink densities of 30 minutes cured sheet, especially with 3 and 5 phr PL was considerably higher than the crosslink density of NR-CV molded for 30 minutes. Based on this curing behavior and the crosslink density measurements, one of

Figure 7. Crosslink densities of NR-CV with different contents of PL.

the probable chemical reactions behind the enhanced reversion resistance in NR-CV/Perkalink system is considered as the Diels-Alder reaction as depicted in Figure 8 [23–26]. As per this mechanism, the conjugated diene units generated *in-situ* at the point of reversion is acting as the precursor for the Diels-Alder reaction with the maleimide moieties of PL. This means that unlike MF, PL has no direct reaction with the NR chains. To prove this, virgin NR was mixed with 3 phr each of MF and PL, and its cure behavior was measured at 180 °C for 1 hr as depicted in Figure 9. It is evident that the reaction between NR and MF exhibits considerable curing torque confirming the Alder-ene reaction, as mentioned in Figure 4. On the other hand, no considerable curing torque was observed between NR and PL. From this information, it is understandable that for PL to function, the system (NR-CV) should generate conjugated diene units, which is possible only at the point of reversion. Therefore, PL cannot be considered as a good anti-reversion agent because its action begins only after a short reversion. Moreover, once it starts its healing

Figure 9. Curing behavior of pristine NR with MF and PL.

action via Diels-Alder reaction, the curing behavior becomes marching modulus and never attains a plateau region till the end of the given cure time.

3.3. Synergistic effects of MF and PL on the reversion behavior of NR-CV

The curing behavior of NR-CV with different contents of MF reveals that around 5 phr of MF is required for a complete reversion free cure pattern. However, being a crosslinking agent, the use of 5 phr MF in a composition may adversely affect the mechanical properties such as the stiffness and hardness of the resultant rubber products. On the other hand, the use of even 1 phr of PL exhibit a marching modulus curing behavior till the end of the given cure time. It has to be noted that the marching modulus curing behavior is not acceptable as per the industrial requirements, because a marching modulus curing behavior makes difficulty in determining the actual optimum cure time from the rheogram [27, 28]. Therefore, the marching modulus cure behavior should be eliminated or at least minimized.

Figure 8. Diels-Alder-reaction between the *in-situ* formed diene from NR-CV and Perkalin.

From this study, it has been realized that MF can react with NR-CV at the beginning of the reaction, and PL will be active only after reversion. Therefore, if use a mixture of MF and PL in a composition, it can exhibit both the Alder-ene and the Diels-Alder reactions wherever necessary. Represented in Figure 10 is the cure curve of NR-CV with a combination of 3 phr MF and 0.5 phr PL (NR-CVM3P0.5) at 180 °C for 1 hr. For comparative evaluation, the cure curves of NR-CVM3 and NR-CVP3 are also included in the same figure. The percentage changes in the rheometric torque of these compounds at different intervals of time just after the first stage of curing reaction (Alder-ene reaction) are also reported in Table 3. NR-CVM3 exhibited a reversion of 3.1% when it was cured over 5 minutes beyond its maximum torque. The intensity of reversion further rose to 7.5% as the cure time extended to 30 minutes. NR-CVP3 also exhibits a reversion of 3.3% when it was cured over 5 minutes beyond the completion of the first stage reaction. However, as the cure time extends to 10 minutes, no reversion was observed because of the initiation of the second stage reaction (Diels-Alder reaction). Instead, the curing torque becomes 1.8% higher than the maximum torque that was observed after the first stage reaction. As the curing time extended to 30 minutes, the cure curve becomes highly marching resulting in a 20.3% higher curing torque. It is interesting to note that, application of a combination of 3 phr MF and 0.5 phr PL to NR-CV (NR-CVM3P0.5) reduces the reversion that was observed after 5 minutes of curing beyond the maximum torque in NR-CVM3 from 3.1 to 1.3%. As the curing time extended to 30 minutes, the cure curve

of NR-CVM3P0.5 exhibits a slight marching modulus behavior with a 2.5% increment in the rheometric torque. This implies that the addition of 0.5 phr of PL on to NR-CVM3 significantly reduces its reversion throughout the given time (1 hr) of curing. In another way, it can be stated that the marching modulus curing behavior of NR-CVP3 can be significantly minimized by promoting the Alder-ene reaction (suppressing the Diels-Alder reaction) by replacing 2.5 phr of PL with 3 phr of MF.

3.4. RPA studies

To understand how the curing time and the second stage crosslinking reaction affects the shear storage modulus, a combination of a cure-strain sweep experiment was performed using RPA as per the procedure mentioned under the experimental section. Represented in Figure 11 are the RPA cure curves and the corresponding shear storage modulus versus strain sweep curves of NR-CVM3, NR-CVP3, and NR-CVM3P0.5. It is evident from the RPA cure curves that both the NR-CVM3 and the NR-CVM3P0.5 exhibits almost the same maximum torque value (2.3 dNm) after the first stage reaction (*i.e.*, due to accelerated-sulfur + Alder-ene reaction). However, the maximum torque after the first stage reaction in NR-CVP3 was slightly lower, because here the curing torque is mainly from the contribution of accelerated-sulfur reaction. At the end of the curing, NR-CVM3 exhibits the lowest torque due to reversion, and NR-CVP3 exhibits the highest torque due to the initiation of the second stage reaction (Diels-Alder reaction). Because of the possibilities of both the Alder-ene and Diels-Alder reactions in NR-CVM3P0.5, it occupies

Figure 10. (a) Curing behavior of NR-CV with a synergistic combination of MF and PL and (b) an enlarged view from the highlighted portion of Figure 10a.

Figure 11. RPA cure curves (a) and the corresponding shear storage modulus vs. strain sweep behaviors (b) of NR-CVM3, NR-CVP3 and NR-CVM3P0.5.

a position in between NR-CVM3 and NR-CVP3. The strain sweep experiments conducted on these samples after 30 minutes of curing (Figure 11b) indicate that the strength (modulus) of these compounds follows the order NR-CVP3 > NR-CVM3P0.5 > NR-CVM3. Based on the curing mechanisms described in Figures 4 and 8, it is understandable that the higher dynamic shear storage modulus of NR-CVP3 after 30 minutes of curing is because of the formation of more numbers of cyclic adduct type crosslinks in its cured network. On the other hand, the network of NR-CVM3 does not possess a cyclic adduct type crosslink, and therefore it shows the lowest shear storage modulus. However, the network of NR-CVM3P0.5 can have the possibilities of both ‘ σ ’ bond type crosslinks because of the presence of MF via Alder-ene reaction and few numbers of cyclic-adduct type crosslinks because of the presence of PL via Diels-Alder reaction. As a result, the shear storage

modulus of NR-CVM3P0.5 occupies a position in between NR-CVM3 and NR-CVP3.

3.5. Tensile properties

Represented in Figures 12 and Table 4 are the stress-strain behavior and the corresponding tensile properties of NR-CV, NR-CVM3, NR-CVP3, and NR-CVM3P0.5 after 5 and 30 minutes of curing. Because of the presence of poly-, di-, and mono-sulfidic crosslinks in the cured network, the stress-strain curve of a 5 minute cured NR-CV sample exhibits a stiffness (E -modulus, measured under a linear strain less than 20%) of 2.65 MPa and tensile strength of 19.5 MPa with a breaking elongation of 715%. As the cure time extended to 30 minutes, the strength of the initially formed cured network gets deteriorated due to the breakage of the polysulfidic crosslinks (reversion) and the subsequent thermal degradation of the polymeric chains. As a result, the E -modulus of the NR-CV

Figure 12. Stress-strain behaviours of (a) 5 minute cured and (b) 30 minute cured samples of NR-CV, NR-CVM3, NR-CVP3, and NR-CVM3P0.5.

Table 4. Tensile properties of the 5 and 30 minutes cured compounds.

Compounds	Curing time [min]	Young's modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
NR-CV	5	2.66±0.03	19.6±0.3	715±25
	30	1.46±0.03	12.3±0.1	804±17
NR-CVM3	5	2.85±0.02	22.2±0.5	626±41
	30	2.08±0.02	18.6±0.7	768±70
NR-CVP3	5	2.04±0.03	18.4±0.5	752±31
	30	2.51±0.01	19.5±0.2	803±9
NR-CVM3P0.5	5	3.23±0.01	21.6±0.4	661±33
	30	3.01±0.01	20.8±0.4	646±41

sample reduces to 45%, and the tensile strength reduces to 37%. However, the vulcanizate of a 5 minute cured NR-CVM3 exhibits an *E*-modulus of 2.85, which is around 7% higher compared to NR-CV. The presence of some bismaleimide crosslinks from MF generated at the beginning of curing via Alder-ene reaction in addition to poly-, di-, and mono-sulfidic crosslinks and the subsequent increase of crosslinking density in NR-CVM3 can be considered for this enhanced *E*-modulus. Similar to NR-CV, the vulcanizate of a 30 minute cured NR-CVM3 also exhibits a loss in their stiffness and strength. However, because of the thermal stability of the bismaleimide crosslinks, the property loss in NR-CVM3 was not severe, as observed in the 30 minutes cured NR-CV. On the contrary, the *E*-modulus of 30 minutes cured NR-CVP3 was around 23% higher than the same cured for 5 minutes. The additional crosslinks generated from PL after the reversion via Diels-Alder reaction is responsible for the enhanced strength and stiffness in the 30 minutes cured NR-CVP3. Here it is interesting to note that the *E*-modulus of a 5 minute cured NR-CVM3P0.5 is around 13% higher compared to the 5 minutes cured NR-CVM3 and 58% higher compared to NR-CVP3. Similarly, the 30 minute cured NR-CVM3P0.5 is around 45% higher compared to the 30 minutes cured NR-CVM3 and about 20% higher compared to NR-CVP3. Moreover, the 5 and 30 minutes cured NR-CVM3P0.5 exhibit almost comparable mechanical properties indicating that its properties are independent of curing time. This confirms the synergistic action of MF and PL because of the possibilities of Alder-ene reaction for the 5 minutes cured NR-CVM3P0.5 and the possibilities of both Alder-ene and Diels-Alder reaction for the 30 minutes cured sample.

Based on this scientific analysis, the state of the cured network of NR-CVM3, NR-CVP3, and NR-CVM3P0.5 after 5 and 30 minutes of curing can be

pictorially depicted as in Figure 13. From the figure, it can understand that the 5 minutes cured network of NR-CVM3P0.5 comprises a mixture of mono-, di-, and poly-sulfidic crosslinks and some bismaleimide crosslinks from MF via Alder-ene reaction. When the polysulfidic crosslinks break due to extended curing time, the PL in the system will immediately react with the in-situ formed dienes and generate some Diels-Alder adduct type crosslinks. Therefore, the vulcanizate of NR-CVM3P0.5 after 30 minutes of curing comprises a mixture of mono-, di-, and the two types of thermally stable crosslinks from MF and PL. It may be one of the reasons why the mechanical properties of NR-CVM3P0.5 are independent of curing time.

4. Conclusions

The curing behavior of NR-CV was evaluated at a temperature (180 °C) in the presence of two different anti-reversion agents: Perkalin 900 and Maleide F. Here, MF directly interacted with the NR at the beginning of the curing via Alder-ene reaction and produced some thermally stable crosslinks in the cured network. As a result, the curing torque, crosslinking density and reversion resistance were enhanced as the contents of MF increased. On the other hand, the curing curves of NR-CV/PL exhibit a short reversion just after the completion of the initial curing reaction and then proceeds with a marching modulus curing behavior due to the Diels-Alder reaction. Therefore, to make use of the benefits of Alder-ene reaction offered by MF and the Diels-Alder reaction offered by PL, a synergistic combination of both MF and PL has been applied. From the curing studies of NR-CV with a combination of 3 phr MF and 0.5 phr PL, it has been realized that three types of curing reactions are taking place in this composition in two stages. The first stage involves the accelerated-sulfur curing and the Alder-ene reaction. The second stage reaction is

Figure 13. Pictorial representations of the network developed in NR-CVM3, NR-CVP3, and NR-CVM3P0.5 (a) after 5 minutes of curing and (b) after 30 minutes of curing.

the Diels-Alder reaction. The first stage reaction is recommended because it is responsible for enhancing both the crosslinking density and reversion resistance without significantly altering the scorch and the optimum cure time. The second stage reaction is also essential if any immediate reversion is taking place after the first stage reaction. However, it needs to be controlled by adjusting the concentration of PL. Otherwise, it will go for a marching modulus cure behavior, which gives a wrong value of optimum cure time.

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