



Enhancing the efficiency of zinc oxide vulcanization in brominated poly (isobutylene-co-isoprene) rubber using structurally different Bismaleimides

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Abstract

It is a known fact that the bromobutyl rubber can form carbon-carbon crosslinks when it is heating with zinc oxide at a temperature greater than 160 °C. Generally, the rate of ZnO vulcanization is slow at this temperature. If any, attempt to enhance the rate of cure by rising the temperature will lead to an inferior state of cure. It has also been reported that heating of halobutyl rubber with ZnO at higher temperature produces conjugated diene butyl prior to the formation of carbon-carbon crosslinks. In the present work, we tried to exploit the possibility of Diels-Alder reaction between the in-situ formed diene butyl and the maleic moieties of bismaleimide to enhance the rate and extent of curing between BIIR and ZnO. For that, BIIR was heated with ZnO in combination with two types of bismaleimides such as N, N' m-phenylene dimaleimide (HVA-2) and 1,3-Bis(citraconimidomethyl) benzene (Perkalink 900) in different concentrations from 1 to 5phr. The vulcanization studies using oscillating disk rheometer and isothermal scanning calorimetry have proved that the state and rate of curing in BIIR with ZnO have significantly enhanced in the presence of these bismaleimides. However, the efficiency of HVA-2 towards improving the state and rate of curing was considerably higher than that offered by Perkalink 900. The lowest activation energy for HVA-2 from the cure kinetic analysis confirmed the higher activity of HVA-2 over Perkalink 900.

Keywords Rubber · Bismaleimide · Cure characteristics · Crosslink density · Compression set

Introduction

The brominated version of poly (isobutylene-co-isoprene) rubber is commonly known as bromobutyl rubber (BIIR). Based on the detailed microstructure analysis of poly (isobutylene-co-isoprene) rubber (IIR) after brominating, it has been confirmed that the commercial grade of BIIR mainly consists of exo-bromomethyl isomer. It is also reported that the presence of bromine in BIIR can accelerate the rate of conventional sulphur vulcanization. Therefore, the brominated form of IIR shows good cure compatibility with high diene elastomers like styrene-butadiene rubber or natural rubber during accelerated sulphur vulcanization [1–6]. In addition to this, most of

the chemical modifications of IIR were achieved through the chemical modification of BIIR because of the presence of allylic bromide functionality. The functionalization of BIIR via esterification [7], etherification [8], sulphuration [9], N-alkylation [10], nucleophilic substitution reactions with amine [11] and the modification of BIIR into ionomers using tri-aryl phosphine and trialkyl amine nucleophiles [12, 13] are some of the chemical modifications of BIIR reported in the literature.

The possibility of vulcanization with zinc oxide is another notable advantage of BIIR over the parent IIR. It is well known that the vulcanization of BIIR with zinc oxide produces carbon-carbon crosslinks in the vulcanizate. However, the mechanism involved in the ZnO vulcanization is still debatable. Based on the detailed investigation regarding the vulcanization chemistry of BIIR and ZnO, Baldwin et al. [14] and Vukov [15] have reported that BIIR can liberate a conjugated diene butyl via dehydrobromination when it is heating with ZnO. The resulted HBr further reacts with the ZnO to form ZnBr₂, which acts as an initiator for a cationic type of crosslinking with the exomethylene isomer of BIIR and

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subsequently forms a stable carbo-carbon crosslinks. However, Hendrikse et al. [16–18] based on their vulcanization studies of chlorobutyl rubber and ZnO have claimed that a cationic reaction mechanism between the in-situ formed conjugated diene butyl and the isoprenoid carbocation is responsible for the crosslinking reactions.

Even though the vulcanization of BIIR with ZnO produces stable carbon-carbon crosslinks, the speed of vulcanization and the crosslink density of the resultant vulcanizate are rather poor. Therefore, the vulcanization of BIIR with ZnO alone is uneconomical as far as the industrial production standard is concerned. Moreover, the ZnO alone cured BIIR cannot find applications where mechanical performances like compression set resistance are the primary requirements.

In the present investigation, we tried to enhance the rate and state of curing between BIIR and ZnO by using bismaleimides. Bismaleimides are generally the addition products of dianhydride and diamines, which carry maleimide end groups. The electron withdrawing carbonyl groups adjacent to the maleimide terminations makes the double bond in the bismaleimide very active to function as a dienophile for Diels-Alder reaction with conjugated dienes [19, 20]. Two types of structurally different bismaleimides such as N, N'-m-phenylene dimaleimide and 1, 3 bis(citraconimidomethyl) benzene were used in this study. The structural differences of this bismaleimides are represented in Fig. 1. Here, the N, N'-m-phenylene dimaleimide is commercially known as HVA-2 and is widely used as a co-agent for enhancing the peroxide vulcanization in various elastomers [21, 22]. Hassen et al. reported its use as a compatibilizer in a ternary blend of PP/NR/LLDPE [23]. Du et al. studied its compatibilizing effect on a blend of scrap rubber powder (SRP) and NR [24]. Kahar et al. reported the crosslinking effect of HVA-2 in a high-density polyethylene/natural rubber blends [25]. Similarly, 1,3 bis(citraconimidomethyl) benzene is commercially known as Perkalink 900. Several researchers have been successfully tested this material as an anti-reversion agent to enhance the reversion resistance during the accelerated sulphur vulcanization of high diene elastomers [26–28]. Datta et al. studied the performance benefits of employing Perkalink 900 on a model formulation for inner tube based on butyl rubber and a model formulation for inner liners based on chlorobutyl rubber. They have found that in chlorobutyl rubber, Perkalink 900 can be used as a crosslinker [29]. To the best of our knowledge, the vulcanization behavior of these bismaleimides as crosslinking additive in bromobutyl rubber is not being well explored. In this paper, we primarily present a comparative analysis of the effects of these two bismaleimides in the vulcanization chemistry and the vulcanization kinetics of bromobutyl rubber and ZnO. Tensile properties, set properties and the crosslinking densities of the vulcanizates were also evaluated as a function of bismaleimides contents.

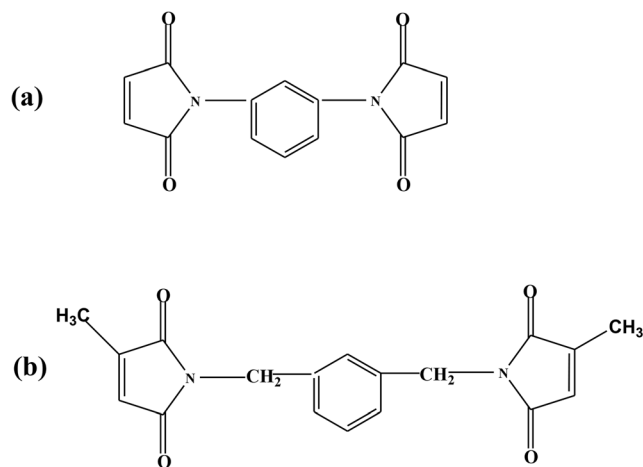


Fig. 1 Chemical structures of (a) N, N'-m-phenylene dimaleimide (HVA-2) and (b) 1, 3 bis(citraconimidomethyl) benzene (Perkalink 900)

Experimental

Materials

Brominated-isobutylene-isoprene rubber (BIIR, Lanxess X_Butyl® BBX2, bromine content: 1.8 ± 0.20 mol%, Mooney viscosity ML₍₁₊₈₎ at 125 °C is 46 ± 4) was used as the base elastomer. The bismaleimides [N, N'-m-phenylene dimaleimide (HVA-2)] with a purity of 97% was obtained from Sigma-Aldrich and 1, 3 bis(citraconimidomethyl) benzene [Perkalink 900, a Rhein Chemie product] with a purity of 85% was procured from Daijin Co., Ltd., South Korea. The zinc oxide (ZnO) was purchased from Sigma-Aldrich.

Preparation of rubber compounds

The formulation of the mixes used in this study is displayed in Table 1. The mix that contains BIIR and 2.5phr ZnO is designated as BIIR-Z. For the mixes that contain a combination of 2.5phr of ZnO and 1 to 5 phr of HVA-2 are designated as BIIR-ZH₁, BIIR-ZH₂, BIIR-ZH₃ and BIIR-ZH₅ respectively. Similarly, for the mixes having a combination of 2.5phr of ZnO and 1 to 5phr of Perkalink 900 are designated as BIIR-ZP₁, BIIR-ZP₂, BIIR-ZP₃ and BIIR-ZP₅ respectively. All the compounds were prepared using an internal mixer (Banbury-type mixer, Nam Yang Corporation, South Korea). The Neat BIIR has masticated at 50 °C under 50 rpm for 2 min. To this, the bismaleimide was added and the mixing was continued under the same rpm for another 5 min to form a better dispersion of the bismaleimide with the rubber matrix. Finally, ZnO was added and the mixing was continued for 3 more minutes. After the mixing, the compound was discharged and then molded into 2 mm sheet at a temperature of 180 °C (except BIIR-Z, which was molded at 160 °C) for the respective cure time obtained from the rheometer cure data at a constant

Table 1 Formulation of the mixes

Compounding ingredients (phr)			
BIIR	^a ZnO	^b HVA-2	^c PERKALINK 900
100	2.5	–	–
100	2.5	1	1
100	2.5	2	2
100	2.5	3	3
100	2.5	5	5

^a zinc oxide, ^b N,N’-m-phenylene dimaleimide, ^c 1,3-bis(citaconimidomethyl)

pressure of 25 ton using a compression molding press (CMV 50H-15-CLPX, CARVER®, USA).

Characterization

Cure characteristics

Maximum torque: M_H , minimum torque: M_L , the difference between maximum and minimum torque: ΔM , 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 generated by an oscillating disk rheometer (ODR, Alpha Technologies, USA) at various vulcanization temperatures. The cure rate index (CRI), a measure of the rate of curing, was calculated using

$$CRI = 100 / (T_{90} - T_{S2}) \tag{1}$$

Crosslink density measurements

The degree of crosslinking was determined by equilibrium swelling method. Round samples with a diameter of 20 mm and a thickness of 2 mm were swelled in a cyclohexane solvent at room temperature until equilibrium was reached. The sample was taken out and removed any adhered solvent from the surface with a filter paper. The weights of the swollen samples were then recorded and the degree of swelling, Q_r was estimated by the equation:

$$Q_r = \frac{W_{sw} - W_i}{W_i} \tag{2}$$

where W_i is the initial dry weight and W_{sw} is the swollen weight of the specimen respectively.

The crosslink density n of the samples was then calculated quantitatively using Flory-Rehner equation [30].

$$n = \frac{-[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2]}{V_s n [\nu_r^{\frac{1}{3}} - 0.5\nu_r]} \tag{3}$$

where ν_r is the polymer volume fraction in the swollen state, ν_s is the molar volume of the solvent (108.1 mL/mol for cyclohexane at room temperature) and χ (0.47) is the coefficient of the interaction between polymer and solvent determined by Bristow-Watson equation [31].

$$\chi = \beta + (\nu_s / RT)(\delta_s - \delta_p)^2 \tag{4}$$

where β is the lattice constant (typically 0.34), ν_s is the volume of solvent per molecule, R is the gas constant, and T is the absolute temperature. The solubility parameters of BIIR (δ_p) and the solvent cyclohexane (δ_s) are 16.5 and 16.8 (MPa)^{1/2} respectively [32].

Mechanical properties

Tensile testing The tensile test was carried out using a LRX plus (Lloyd Instruments, UK) machine in accordance with the ASTM D-412. Dumbbell shaped specimens were prepared from the molded sheets of the samples and tested at a cross-head speed of 500 mm/min at room temperature. Six samples have been taken for each compound and their averages with standard deviations are reported.

Hardness testing Round shaped samples having 6 mm thickness and 10 mm diameter with smooth and uniform surface were used to measure the indentation hardness of the cured samples using a Shore A hardness tester (Asker, Kobunishi Keiki Co. Ltd) as per ASTM D2240 specification. By applying a constant force without any disturbances for a specific time, indentations were made in the various positions. Ten readings were taken from different areas of the testing samples and the average value was estimated.

Compression set The compression set of the vulcanized compounds were determined using cylindrical specimens (12.5 mm height and 29 mm diameter) by applying a 25% compression. The samples were kept in an air oven at the testing temperature (100 °C) for 72 h according to ASTM D 395. At the end of the test, the samples were taken out and allowed to cool at room temperature for 30 min and the final thickness was measured. The compression set (CS) was then calculated using the equation,

$$CS (\%) = \frac{t_o - t_f}{t_o - t_s} \times 100 \tag{5}$$

where t_o and t_f are the original and final thickness of the specimen and t_s is the thickness of the spacer bar used.

Morphological study

The morphological analysis was performed using scanning electron microscopy: SEM (JEOL JSM-6400 model, USA) in conjunction with energy dispersive X-ray spectroscopy (EDX).

Results and discussion

Cure characteristics

Cure behavior of BIIR with ZnO

Represented in Fig. 2 are the cure curves of BIIR with ZnO under different temperatures from 160 to 190 °C and the corresponding cure characteristics are represented in Table 2. The rate of cure at 160 °C was slow and marching modulus, yet it has exhibited the maximum rheometric torque with in the 30 min of curing. As the vulcanization temperature increased, the rate of curing was also increased but the state of curing (ΔM) decreased. For instance, at 160 °C, the onset of curing was started after 14 min and slowly increased to a maximum torque with a ΔM of 4.27 dNm at an optimum cure time (t_{90}) of 27 min. As expected, the onset of curing and the time to optimum cure have been reduced to 2.7 min and 12 min respectively as the vulcanization temperature rose to 190 °C. However, an unexpected decrease in ΔM value was observed in every 10 °C rise in the vulcanization temperature from 160 to 190 °C. The differences in the crosslink densities of the ZnO vulcanized BIIR molded at 160 °C and 190 °C depicted as an inset in Fig. 2. This clearly shows that the crosslink density of the vulcanized sample at 160 °C has reduced to 37% as the vulcanization temperature increased to 190 °C. These results indicated that a simultaneous enhancement of both the rate and state of cure (crosslink density) during the vulcanization of BIIR with ZnO alone might be difficult.

Some previous studies concerning the vulcanization of halobutyl rubber and ZnO reported that heating with ZnO at a temperature greater than 160 °C, the halobutyl rubber undergo dehydrohalogenation and forms zinc dihalide (ZnX_2) and conjugated diene butyl [14, 15]. The in-situ formed ZnX_2 will initiate a carbocation on the polymer chain by abstracting a halogen atom. The carbo-cation thus formed attacks the nearby halogen contain polymer chains and generate carbon-carbon crosslinks. Analysis of the ODR cure behavior in Fig. 2, here it is sensible to make a conjecture that the generation of a carbocation on the polymer chain may be slow at 160 °C. Consequently, the rate of crosslink formation at the initial stages of vulcanization will be slow and therefore exhibited a longer induction period (time to onset of curing). However, as the vulcanization progressing at this temperature, more numbers of crosslinks may gradually get involved in the

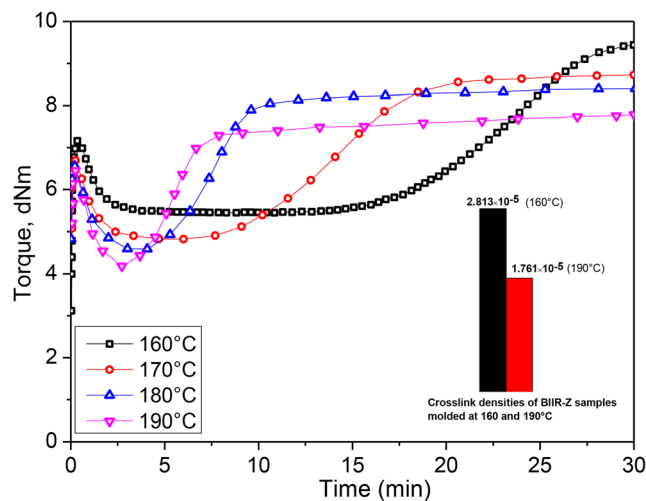


Fig. 2 Cure curves of BIIR with 2.5phr of ZnO under different temperatures

network and therefore showed a marching modulus cure behavior with the highest state of cure (ΔM or crosslink density) at the end of the vulcanization. As the vulcanization temperature increased, the dehydrohalogenation and the subsequent generation of the carbocation will be fast. As a result, the rate of crosslinking to form carbon-carbon crosslinks will be also fast. This high rate of crosslinking may cause a sudden rise in the viscosity (as evident from the relatively higher torque at the early stages curing in the ODR cure curve) of the system. This may cause difficulty for propagating the polymeric chains with a carbocation to find other chains to form crosslinks. As a result, the number of crosslinks gets involved at a temperature above 160 °C may gradually decrease. This might be one of the reasons for the lower crosslink density in the vulcanized sample of BIIR with ZnO held at 190 °C.

Vulcanization behavior of BIIR with a combination of ZnO and Bismaleimides

To enhance the rate and state of curing of BIIR with ZnO, two different types of bismaleimides: HVA-2 and Perkalinck 900 have been introduced in the compounding recipe. Represented in Fig. 3 (a, b) are the cure profiles of BIIR with a combination of ZnO and 1phr of HVA-2 and Perkalinck 900 respectively under different temperatures from 160 to 190 °C. Their respective cure characteristics obtained at each temperature are also listed in Table 2. It can be seen that at a given vulcanization temperature, the state and rate of curing of BIIR and ZnO were dramatically enhanced in the presence of bismaleimides than the vulcanization of BIIR with ZnO alone. For instance, the ΔM (state of cure or crosslink density) produced during the vulcanization of BIIR with ZnO alone at 160 °C has been increased to around 86% with 1phr addition of HVA-2 and 68% with the addition of 1phr perkalinck 900. Here it is worth

Table 2 Cure characteristics of BIIR with ZnO and Bismaleimides

Compounds	Temp (°C)	M _L (dNm)	M _H (dNm)	ΔM (dNm)	T _{S2} (min)	T ₉₀ (min)	CRI (min ⁻¹)
BIIR-Z	160	5.2	9.5	4.3	23.0	27.0	very slow
	170	5.0	9.2	4.2	12.4	24.8	8.1
	180	4.9	8.9	4.0	7.0	18.5	8.7
	190	4.4	8.2	3.8	5.1	15.7	9.4
BIIR-ZH ₁	160	5.7	13.6	7.9	13.8	19.0	19.2
	170	5.3	13.4	8.1	7.6	10.4	35.7
	180	5.1	13.3	8.2	4.7	6.4	58.8
	190	4.6	12.9	8.2	3.3	4.3	102.0
BIIR-ZP ₁	160	5.4	12.6	7.2	15.5	26.7	8.9
	170	4.8	13.3	8.5	9.5	19.9	9.6
	180	4.6	13.4	8.8	5.6	14.2	11.6
	190	4.3	13.2	8.9	3.9	10.5	15.1

noting that unlike in the vulcanization behavior of BIIR and ZnO alone, the ΔM values (state of cure) remains unaffected or marginally increased with an increase in the vulcanization temperature.

Though both the HVA-2 and perkalink 900 increased the state and rate of curing of BIIR with ZnO, the rate of vulcanization offered by HVA-2 was much better than that offered by Perkalink 900. As a result, at a given temperature, the

composition consists of HVA-2 take a lower time (*T*₉₀) to achieve the maximum state of cure than the composition contains Perkalink 900. For instance, at 160 °C, the *T*₉₀ of BIIR-Z has been reduced from 27 min to 19 min with the addition of 1phr HVA-2. Under the same condition, the addition of 1phr Perkalink to BIIR-Z marginally reduced its *T*₉₀ from 27 min to just 26.7 min. As the vulcanization temperature rose to 190 °C, the *T*₉₀ value of BIIR-Z was reduced from 15.7 min to 4.3 min with 1phr addition of HVA-2. However, even at 190 °C, the presence of Perkalink has reduced the *T*₉₀ of BIIR-Z from 15.7 min to just 10.8 min.

The vulcanization behavior of BIIR-Z was also evaluated as a function of bismaleimide content. Depicted in Fig. 4 (a, b) are the cure curves of BIIR-Z with different contents of HVA-2 and Perkalink 900 respectively at a representative temperature, 160 °C. From fig. 4(a), it can be seen that the addition of HVA-2 onto BIIR-Z considerably reduced the time to initiate the vulcanization reaction and dramatically enhanced the maximum rheometric torque. Though BIIR-Z showed marching modulus cure behavior till the end of 30 min of curing, the vulcanization of the same in the presence of HVA-2 exhibits plateau (stable torque) regions irrespective of the bismaleimide contents just after 20 min of curing at 160 °C. The variations in their respective ΔM and the minimum torque (M_L) values are represented in Fig. 5. It is clear that the addition of even 1phr of HVA-2 to BIIR-Z has enhanced its ΔM by about 86%, 170% with 2phr addition and further increased to 202% as the content of HVA-2 rose to 3phr. However, beyond 3phr no further increase in the ΔM was noticed and therefore showed a plateau region in between 3 and 5phr of HVA-2 content. Similarly, the minimum torque (an indirect indication of the viscosity or the flow ability of the compound at a given temperature; here 160 °C) gradually increased as the content of HVA-2 increased. This can be attributed to the fact that HVA-2, being a high melting (melting temperature is around 195 °C) solid, will remain as a solid

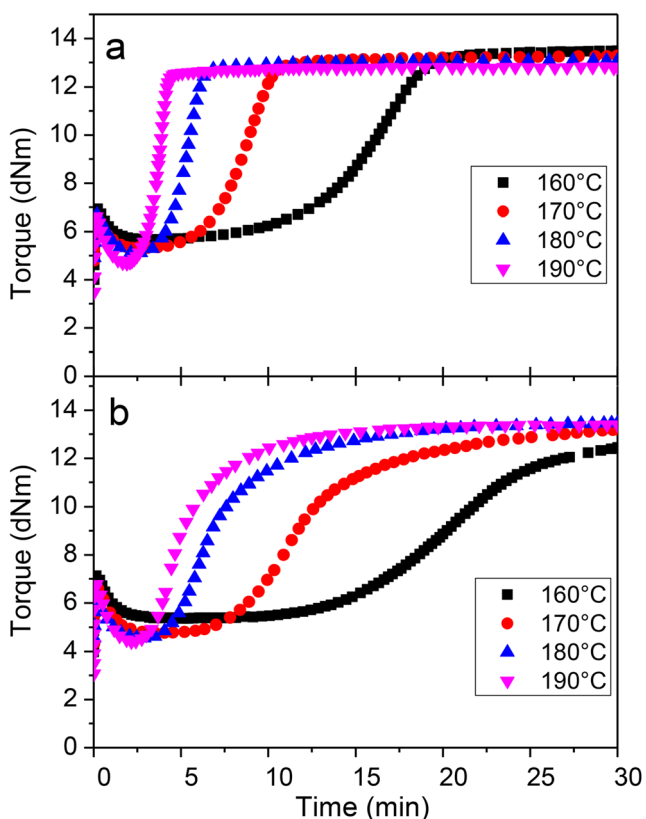


Fig. 3 Cure curves of (a) BIIR-ZH₁ and (b) BIIR-ZP₁ under different temperatures

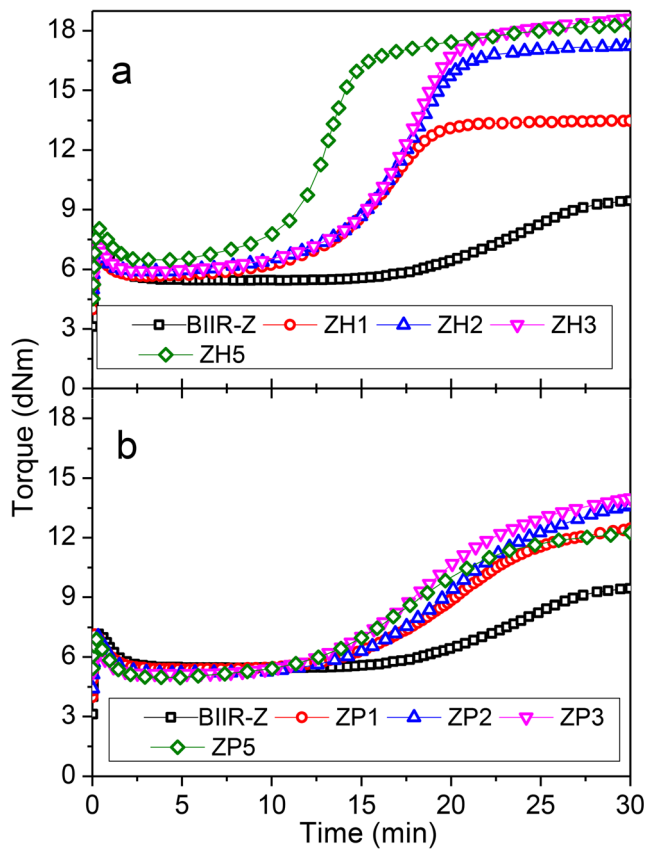


Fig. 4 Cure curves of BIIR with ZnO in combination with different content of (a) HVA-2 and (b) Perkalinck 900 at 160 °C

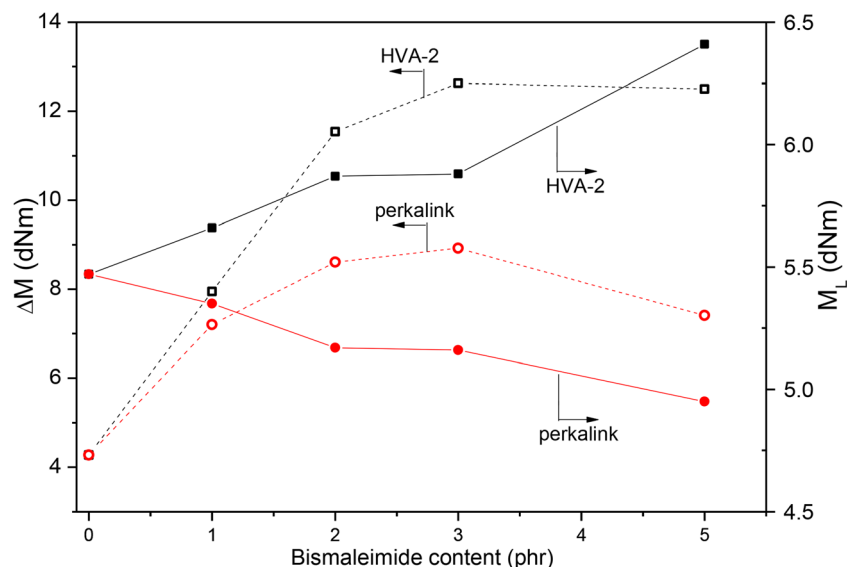
particle at 160 °C. This solid consistency of the HVA-2 might be a reason to enhance the compound viscosity and hence show the M_L values as the content of HVA-2 increased. On the other hand, the vulcanization curves of BIIR-Z with different content of Perkalinck 900 (Fig. 4b) exhibits marching

modulus cure behavior till the end of the 30 min of curing. Also, at a given content, the cure curve of BIIR-Z with Perkalinck 900 was always lower than that produced by HVA-2. As a result, the ΔM values of BIIR-Z vulcanized with Perkalinck 900 shows lower values than those produced by vulcanizing the same with HVA 2 (Fig. 5). This indicated that at a given concentration, the state of cure or the crosslink density offered by Perkalinck 900 will be inferior to that offered by HVA-2. The M_L values of BIIR-Z as a function of perkalinck content was also depicted in Fig. 5. In contrary to the effect produced by HVA-2, the M_L values were gradually decreased as the content of Perkalinck 900 increased. This may be due to the fact that Perkalinck being a low melting (melting temperature is around 80 °C) solid, forms liquid resin well-above its melting point. This liquid resin may act as a softening agent prior to crosslinking and therefore reduces the compound viscosity and hence shows lower values of M_L as the content of perkalinck increased.

Morphological analysis

It was noticed from the Fig. 4b and 5 that the vulcanization curve of a 5phr Perkalinck 900 filled compound (BIIR-ZP₅) showed a reduction in the maximum rheometric torque and therefore exhibited a considerable decrease in the ΔM values. In order to understand this unexpected cure behavior of BIIR-ZP₅, the fracture surface morphology of BIIR-ZP₅ was investigated using SEM. For a comparative purpose, the vulcanizate of BIIR-Z contain 5phr filled HVA-2 (BIIR-ZH₅) was also subjected to the surface morphological evaluation. Depicted in Fig. 6(a, b) are the fracture surfaces of BIIR-ZH₅ and BIIR-ZP₅ under a magnification of X100. As can be seen in Fig. 6a, the surface of the sample was devoid of

Fig. 5 Variations of ΔM and M_L values obtained from the ODR cure curves of BIIR and ZnO in combination with different contents of HVA-2 and Perkalinck at 160 °C



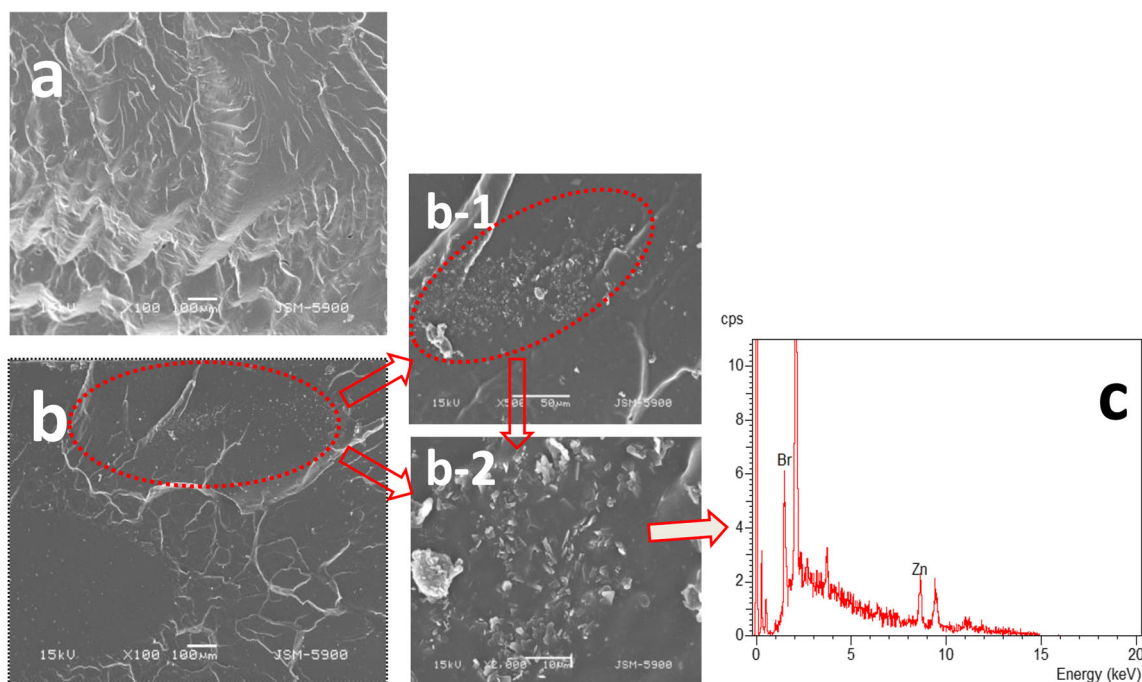


Fig. 6 SEM photomicrographs of the fracture surfaces of (a) BIIR-ZH₅, (b) BIIR-ZP₅ at a magnification of X100, (b-1, b-2) magnified views of BIIR-ZP₁ at X500 and X2000 and (c) EDX analysis of b-2

any aggregated particles. On the other hand, under the same magnification, several scattered aggregated particles were visible on the fracture surface of BIIR-ZP₅ (Fig. 6b). To get more clarifications, the highlighted portion from Fig. 6b was zoomed into X500 and X2000 as shown in Fig. 6b-1 and b-2 respectively. The aggregated particles on the surface of BIIR-ZP₅ by EDX analysis in conjunction with SEM depicted in Fig. 6(c) exhibited signatures of the element Zn, which presumably came from ZnO. From these pieces information, it can be perceived that perkalink, being a low melting solid, will turn into a thick viscous resin like consistency due self-polymerization well above its melting temperature (>160 °C). At a higher concentration of Perkalink (5phr), the self-polymerized viscous resin may reduce the distribution and dispersion of the ZnO particles within the matrix. This may be one of the reasons why the aggregated particles show traces of the element Zn in the EDX analysis. Since, this resinous material inhibiting the full potential of ZnO to take part in the vulcanization process, the efficiency of the reaction to enhance the state and rate of cure will be lower as seen in Fig. 6 b. Moreover, the self-polymerized highly polar Perkalink resin itself may also invite dispersion or incompatibility problems with the relatively less polar BIIR, which can also be a reason for the inferior cure properties observed in BIIR-ZP₅.

Vulcanization kinetics

BIIR-Z, BIIR-ZP₁ and BIIR-ZH₁ were taken as the representative compounds to evaluate how the kinetics of the

vulcanization of BIIR with ZnO affected in the presence of HVA-2 or Perkalink. From the ODR cure profiles of these compounds generated at a given temperature over a period of 30 min, the degree of curing ‘ α ’ was calculated using the equation given below [33–35].

$$a = \frac{M_t - M_L}{M_H - M_L} \quad (6)$$

where M_L is the minimum torque, M_H is the maximum torque and M_t is the torque at time t . Depicted in Fig. 7 (a-c) are the rates of cure conversion (dc/dt) against time for BIIR-Z, BIIR-ZP₁ and BIIR-ZH₁ under various temperatures. It can be seen from the figures that the rate of cure conversions for all the compounds were increased to reach a maximum and then decreased. However, at a given temperature, the rate of conversion for BIIR-ZP₁ and BIIR-ZH₁ was higher than that of BIIR-Z. Nonetheless, among BIIR-ZP₁ and BIIR-ZH₁, the conversion rate for BIIR-ZH₁ was always higher than BIIR-ZP₁. For instance, at 160 °C, BIIR-Z has shown a maximum rate of conversion at 24.4 min whereas BIIR-ZP₁ and BIIR-ZH₁ have achieved the maximum rate of conversion a little over 20.8 min and 16.8 min respectively at the same temperature.

It is evident from the Fig. 7 (a-c) that the maximum reaction rates are attained at a time greater than zero. This indicated that the cure reaction is autocatalytic. Therefore, the autocatalytic model equation as given below was employed to explore the cure kinetics [33].

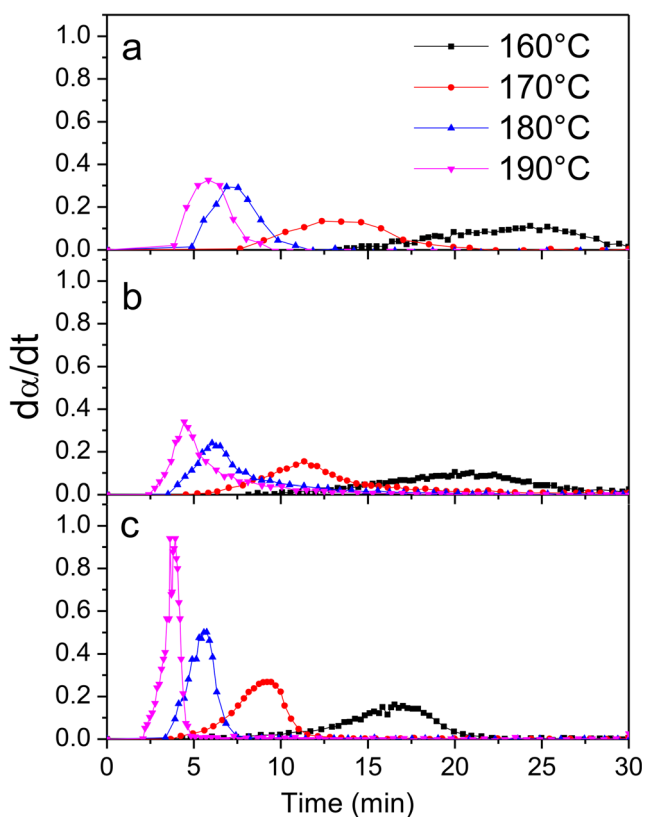


Fig. 7 Rate of conversion ($d\alpha/dt$) vs. time for (a) BIIR-Z, (b) BIIR-ZP₁ and (c) BIIR-ZH₁ under different temperatures

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

where k is the rate constant at temperature, T and m and n are orders of the reaction. The values of k , m and n were determined from the plot of the rate of conversion ($d\alpha/dt$) versus degree of conversion (α) using a non-linear regression fit with the help of computer software OriginPro 8.5. Depicted in Fig. 8 is a nonlinear regression fit curves of BIIR-Z, BIIR-ZP₁ and BIIR-ZH₁ at 160 °C. Similarly, the nonlinear regression curves were also fitted for other temperatures and the fitting parameters (k, m, n) obtained for the respective temperatures are listed in Table 3. It can be seen that the rate constant (k) obtained for all the compounds increased with increasing the vulcanization temperature. However, at a given temperature, the rate constant for BIIR-ZH₁ was always higher than that of BIIR-Z and BIIR-ZP₁. From the values of k obtained for different temperatures, the activation energies were determined using the Arrhenius equation;

$$\ln k(T) = \ln A - \frac{E_a}{RT} \quad (8)$$

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. Fig. 9 represents the Arrhenius plot of $\ln k$ versus

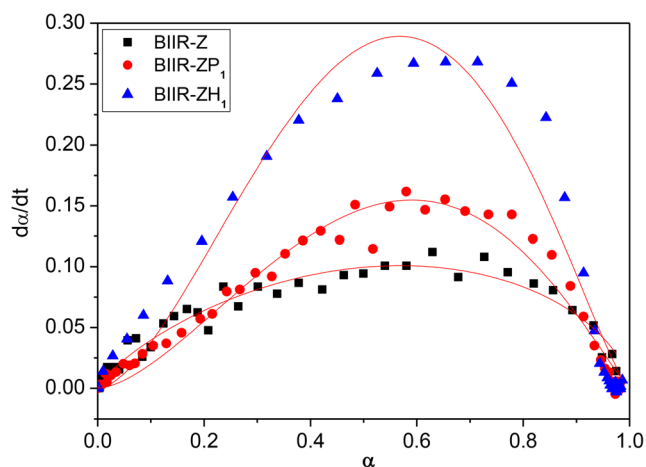


Fig. 8 A representative plot of the rate of conversion ($d\alpha/dt$) vs. degree of conversion (α) for BIIR-Z, BIIR-ZP₁ and BIIR-ZH₁ at 160 °C

$1/T$ for the compounds BIIR-Z and BIIR-ZP₁ and BIIR-ZH₁. The activation energies of these compounds obtained from their respective slope values are also listed in Table 3. It can be seen that the activation energy for the vulcanization of BIIR and ZnO (151.4 kJ/mol) has reduced to 139.4 kJ/mol when vulcanizing the same in the presence of 1phr of perkalink and further reduced to 123 kJ/mol with 1phr of HVA-2. The lower values of activation energy obtained for BIIR-ZP₁ and BIIR-ZH₁ over BIIR-Z confirmed that the efficiency of ZnO vulcanization in bromobutyl rubber can be enhanced in the presence of bismaleimides.

Vulcanization behavior by isothermal DSC analysis

To further endorse the vulcanization behavior described based on the ODR studies, isothermal DSC analysis was performed. It is well known that crosslinking is an exothermic reaction; therefore it will exhibit exothermic peaks in the DSC scan at the vulcanization temperature. From the position and area of

Table 3 Kinetic parameters of the curing reaction obtained from ODR

Compounds	Temp (°C)	k	m	n	E_a (kJ/mol)
BIIR-Z	160 °C	0.17	0.91	0.91	151.4
	170 °C	0.54	1.10	0.83	
	180 °C	1.43	1.31	0.94	
	190 °C	2.62	1.64	1.23	
BIIR-ZP ₁	160 °C	0.33	0.96	0.92	139.3
	170 °C	1.27	1.28	2.03	
	180 °C	2.42	1.24	2.48	
	190 °C	4.36	1.27	3.26	
BIIR-ZH ₁	160 °C	1.04	1.66	1.15	123.0
	170 °C	2.32	1.72	1.31	
	180 °C	5.21	1.83	1.48	
	190 °C	9.44	2.03	1.49	

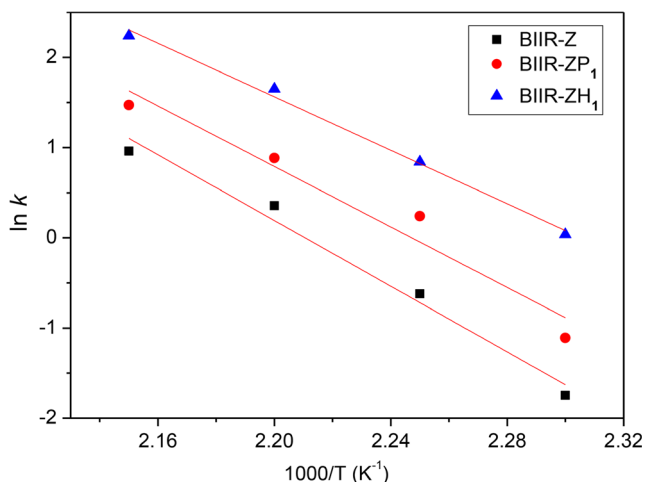


Fig. 9 Arrhenius plot of $\ln k$ versus $1/T$

the curing exotherm, it is possible to understand the nature of crosslinking as well as the extent of crosslinking reactions. Depicted in Fig. 10 (a-c) are the isothermal DSC scans of BIIR-Z, BIIR-ZP₁ and BIIR-ZH₁ under four different temperatures: 160, 170, 180 and 190 °C for a period of 30 min. The heat of reaction (ΔH) liberated at each temperature was calculated from the area under the curing exotherms and are displayed in Table 4. It can be seen from the Fig. 10(a) that the DSC curve of BIIR-Z at a particular temperature exhibited two distinct exothermic peaks. The first peak is considered as the elimination of HBr and the subsequent formation of ZnBr₂ and the second peak is responsible for the crosslinking reaction. The peak positions were shifted to a lower time scale and the ΔH values were gradually decreased as the temperature increased from 160 °C to 190 °C. This behavior was in line with the variation of its ΔM values with the increase in the

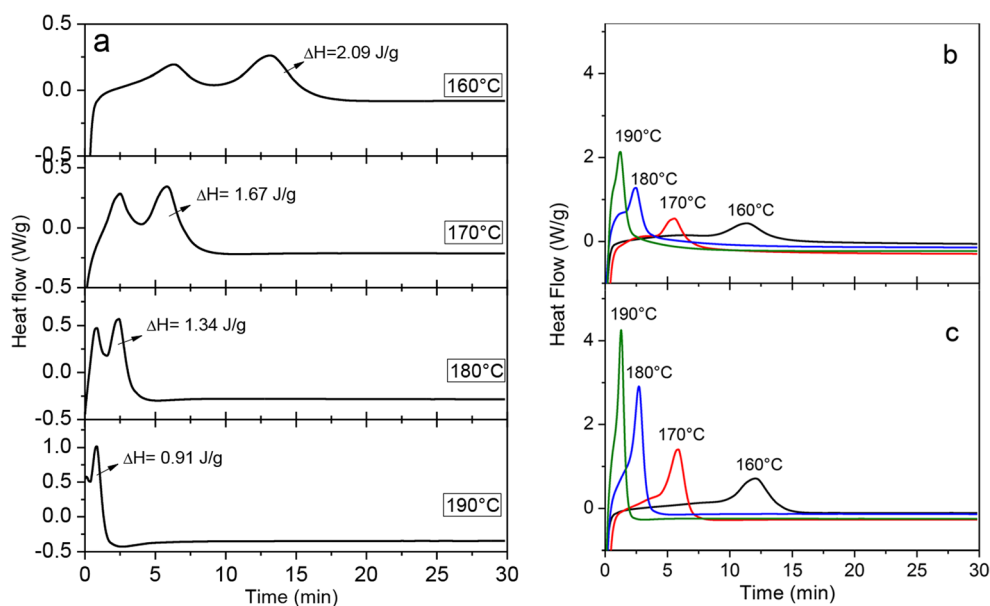
Table 4 Heat of reaction (ΔH) obtained for BIIR-Z, BIIR-ZP₁ and BIIR-ZH₁ from isothermal DSC analysis under various temperatures

Temp (°C)	ΔH (J/g)		
	BIIR-Z	BIIR-ZP ₁	BIIR-ZH ₁
160	2.09	2.16	5.10
170	1.67	2.32	6.13
180	1.34	5.19	11.63
190	0.91	5.83	13.72

vulcanization temperature as observed in the ODR cure studies. On the other hand, the DSC scans of BIIR-ZP₁ and BIIR-ZH₁ exhibited a single cure exotherm with relatively larger values of ΔH indicating that the extent of curing between BIIR and ZnO has dramatically enhanced in the presence of these bismaleimides. Unlike in the case of BIIR-Z, the ΔH values of both BIIR-ZH₁ and BIIR-ZP₁ were increased as the vulcanization temperature increased. However, at a given temperature, the ΔH produced by BIIR-ZH₁ was almost 2 times higher than that produced by BIIR-ZP₁. This trend in the ΔH values with respect to the vulcanization temperature was very well connected to the ΔM values of these compounds from the ODR studies.

To emphasize the effect of bismaleimide content on the vulcanization behavior of BIIR with ZnO as seen in the ODR studies at 160 °C, the isothermal DSC analysis was also performed for BIIR-Z as a function of bismaleimide contents at the same temperature. Depicted in Fig. 11 (a, b) are the DSC scans of BIIR-Z as a function of HVA-2 and perkalink contents respectively. It can be seen from the figure that in both the cases, the ΔH values have been increased as the content

Fig. 10 Isothermal DSC curves of (a) BIIR-Z (b) BIIR-ZP₁ and (c) BIIR-ZH₁ under different temperatures for 30 min



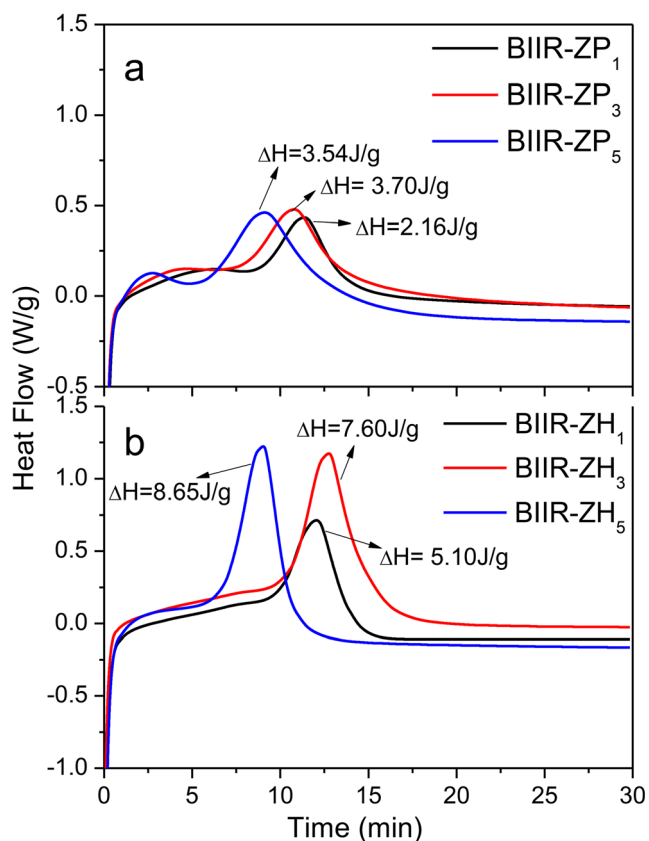
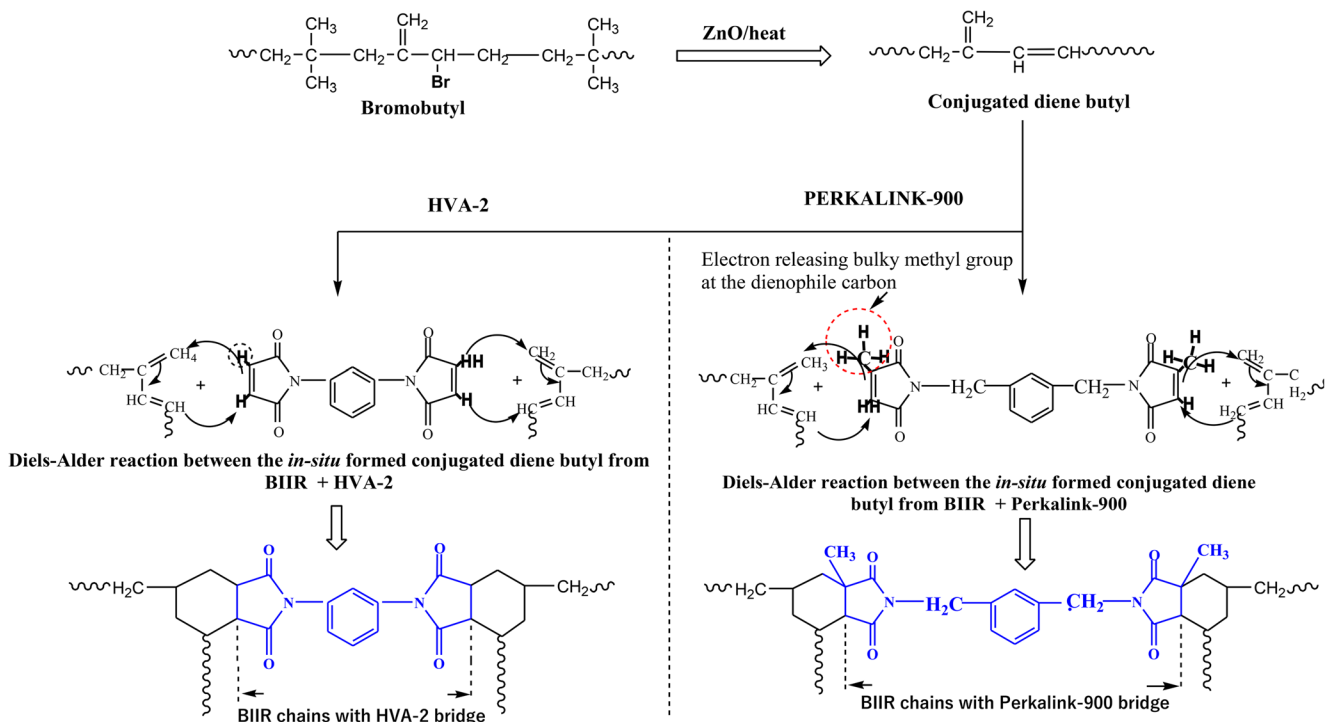


Fig. 11 Isothermal DSC curves of BIIR/ZnO with different contents of (a) Perkalink and (b) HVA-2 at 160 °C

increased from 1 to 3phr and a marginal change has been noticed beyond 3phr. However, at a given concentration, the ΔH produced by HVA-2 was greatly higher than the ΔH produced by perkalink. These DSC results were also well corroborated with the ODR cure behaviors and their respective ΔM values.

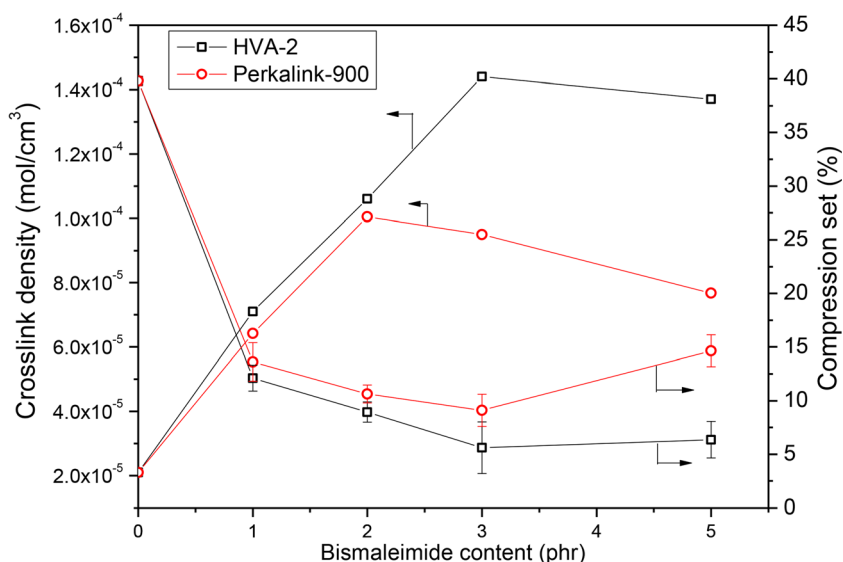
Plausible reaction mechanisms behind the crosslinking reaction

In view of the information gathered based on the vulcanization studies of BIIR with ZnO alone and a combination of ZnO with HVA-2 or Perkalink, an appropriate reaction mechanism was proposed as depicted in scheme 1. It has been reported that heating of BIIR with ZnO at a temperature greater than 160 °C generate ZnBr₂; a precursor responsible for the cationic crosslinking of BIIR with ZnO and conjugated diene butyl. It was also noticed that the in-situ formed conjugated diene butyl will remain unaffected within the system during the vulcanization of BIIR with ZnO alone [14, 15]. Therefore, when BIIR is heating with ZnO in combination with HVA-2 or perkalink at a temperature greater than 160 °C, in addition to the most expected ZnO curing, it is possible to have a parallel reaction between the in-situ formed conjugated diene butyl with the dienophile part of HVA-2 or Perkalink via Diels-Alder reaction as depicted in scheme 1 [36–39]. This is the reason why the vulcanization of BIIR and ZnO in conjunction with either HVA-2 or Perkalink 900 showed higher ΔM values in the



Scheme 1 Plausible reaction mechanism behind the vulcanization of BIIR with ZnO in conjunction with HVA-2 and Perkalink 900

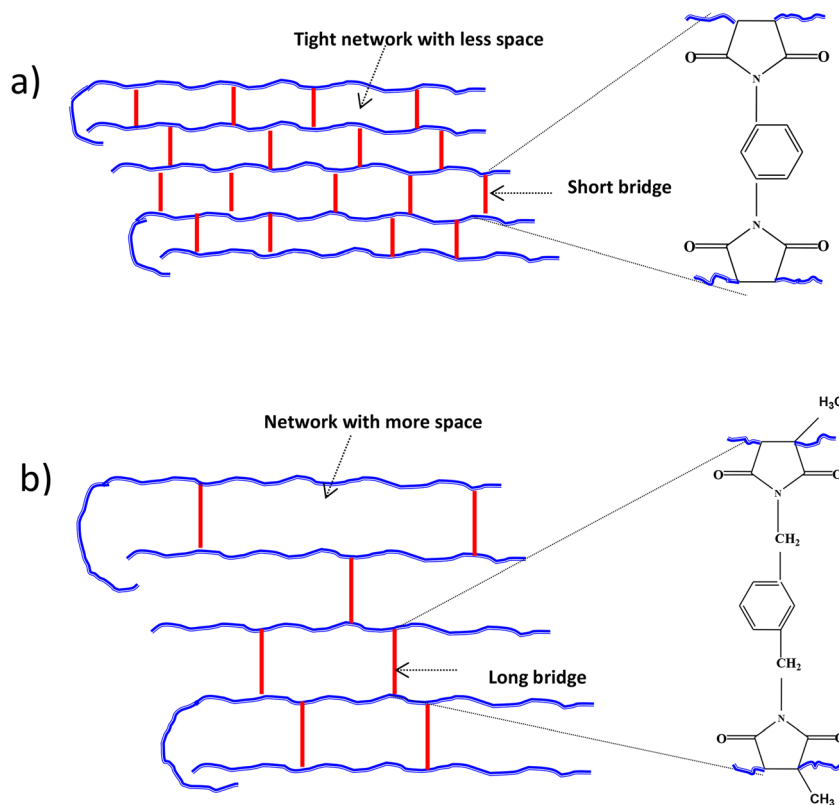
Fig. 12 Crosslink density and compression set values of BIIR/ZnO with different contents of HVA-2 and Perkalinck 900



ODR studies and higher ΔH values in the DSC scans. It has also been reported that the dienophile with an electron donating group will reduce the efficiency of the Diels Alder reaction [40]. Here, in perkalinck, an electron releasing methyl group is being attached to the carbon atom of the dienophile part. This electron releasing methyl group reduces the activity of the dienophile unit in Perkalinck 900 to react with the diene butyl to form crosslinks. Moreover, the bulky nature of the methyl

group may also experience a steric hindrance in the Diels-Alder reaction between the conjugated diene butyl and the dienophile unit of the perkalinck. On the other hand, the dienophile part in HVA-2 is free from any such electron donating bulky groups to reduce its activity towards the Diels Alder reaction. This might be the reason for the higher rate of cure and the lower activation energy for the vulcanization reaction of BIIR with ZnO in the presence of HVA-2.

Fig. 13 Expected network structure in the vulcanizate of BIIR/ZnO (a) with HVA-2 and (b) with Perkalinck-900



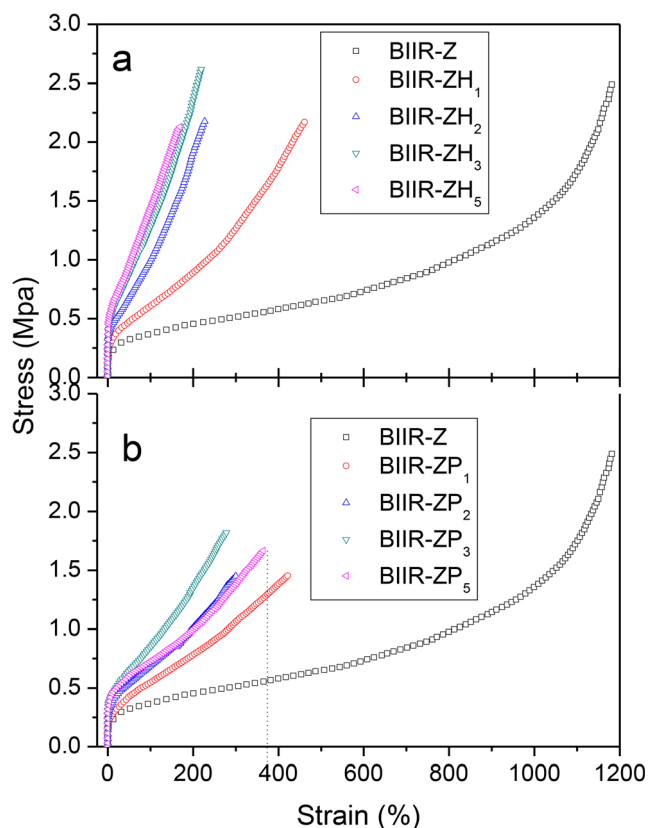


Fig. 14 Stress-strain behaviors of BIIR/ZnO with different contents of (a) HVA-2 and (b) Perkalink 900

Crosslink density and mechanical properties

Crosslink density is generally defined as the moles of crosslinked units per unit weight of the crosslinked polymer. The crosslink density and the type of crosslink can affect various physical and mechanical properties of the vulcanized elastomers. Depicted in Fig. 12 are the chemical crosslink density values of BIIR-Z with different content of HVA-2 and Perkalink 900. It is evident from the figure that the crosslink density of BIIR-Z has considerably enhanced in the presence of HVA-2 up to a concentration of 3phr and then

it shows a plateau region in between 3 and 5phr. Similarly, the crosslink density values of BIIR-Z were also increased as the perkalink content increased up to 3phr and then notably decreased as the content of perkalink increased to 5phr. The variation of this chemical crosslink density values of BIIR-Z as a function of HVA-2 or perkalink 900 were very much similar to the ΔM values (an indirect assessment of the crosslink density) from obtained from the ODR studies and the ΔH values obtained from the isothermal DSC scans. The enhancement in the crosslink densities of BIIR-Z with the presence of these bismaleimides indicating that the network of BIIR-Z becomes tighter due to the formation of bismaleimide bridges in addition to the usual carbon-carbon crosslinks. Here, it is important to note that at a given concentration, the crosslink density offered by HVA-2 was higher than that offered by Perkalink 900. This implies that the number HVA-2 bridges formed in the vulcanized network of BIIR-Z will be higher than that produced by Perkalink presumably due to the higher activity of HVA-2 towards the Diels Alder reaction. Moreover, the structure of Perkalink is relatively large and flexible than HVA-2. As a result, the bridge length of perkalink in the vulcanized network will be higher than that created by HVA-2. This may create more free space in the vulcanized network of BIIR-Z with Perkalink as shown in the Fig. 13. As a result, more solvent can penetrate into their network and therefore shows a higher degree of swelling and lower crosslink density.

In order to understand the influence of these two types of bismaleimide bridges in the vulcanized network of BIIR-Z, its mechanical properties such as tensile strength (TS), elongation at break (EB), modulus at 50% elongation (M50%) and 100% elongation (M100%), hardness and compression set properties were evaluated. Represented in Fig. 14 and Table 5 are the stress-strain behaviors of BIIR-Z and their corresponding tensile properties as a function of HVA-2 or Perkalink content. It is evident from the stress-strain curve that BIIR-Z shows the highest elongation at break with an ultimate tensile strength of 2.4 MPa. Addition of HVA-2 or Perkalink dramatically reduced the EB without altering the TS to a

Table 5 Mechanical properties of the vulcanizates

Compounds	Tensile strength(MPa)	50% Modulus(MPa)	100% Modulus(MPa)	Elongation at break (%)	Hardness (Shore A)
BIIR-Z	2.1 ± 0.3	0.34 ± 0.02	0.39 ± 0.03	1083 ± 54	21 ± 1
BIIR-ZP ₁	1.4 ± 0.02	0.44 ± 0.02	0.56 ± 0.02	424 ± 12	26 ± 1
BIIR-ZP ₂	1.4 ± 0.07	0.51 ± 0.04	0.66 ± 0.03	281 ± 29	30 ± 1
BIIR-ZP ₃	1.7 ± 0.06	0.65 ± 0.03	0.81 ± 0.03	274 ± 10	31 ± 1
BIIR-ZP ₅	2.1 ± 0.38	0.60 ± 0.02	0.72 ± 0.03	435 ± 64	28 ± 1
BIIR-ZH ₁	2.0 ± 0.17	0.47 ± 0.01	0.61 ± 0.02	414 ± 43	27 ± 1
BIIR-ZH ₂	2.4 ± 0.21	0.64 ± 0.03	0.93 ± 0.06	253 ± 22	33 ± 1
BIIR-ZH ₃	2.4 ± 0.39	0.83 ± 0.06	1.23 ± 0.08	209 ± 12	34 ± 1
BIIR-ZH ₅	2.5 ± 0.35	0.92 ± 0.04	1.37 ± 0.04	201 ± 29	35 ± 1

greater extent. Additionally, the stress required to cause a given strain (deformation) was increased as the HVA-2 content increased from 1phr to 5 phr. However, this trend was valid only up to a 3phr addition of Perkalink. It is also worth noting that, at a given concentration, the stress required to cause an initial deformation for the compounds contains HVA-2 were higher than those with Perkalink. This confirms the tighter network structure of the vulcanized network of BIIR with HVA-2 due to the relatively short bridge length. For instance, the stress required to cause a 50% strain for BIIR-Z was increased to 46% with the addition of 1phr HVA-2 and further increased to 187% with the addition of 5phr HVA-2. However, the addition of 1phr of Perkalink to BIIR-Z increased the 50% modulus to around 37% and further increased to 103% with the addition of 3phr. It was interesting to note that as the content of Perkalink in BIIR-Z increased to 5phr, the 50% modulus was slightly decreased. This unusual decrease in the low strain modulus might be due to the low crosslink density of the vulcanized network. Similarly, the shore-A hardness, generally considered as the surface modulus of the vulcanized elastomer showed an almost similar trend as observed in the variation of 50% modulus as a function of HVA-2 or Perkalink content.

The compression set of a vulcanized elastomer is one of the most important property requirements for sealing applications. Vulcanizates having low compression set is considered as better sealing performance. Generally, vulcanizates having higher crosslink density with thermally stable crosslinks exhibited a lower value of compression set. The set values of BIIR-Z as a function of both HVA-2 and Perkalink contents are also displayed in Fig. 12. It can be seen that the set values of BIIR-Z were gradually decreased with the addition of either HVA-2 or Perkalink up to a concentration of 3phr. This reduction in the compression set values can be attributed to the enhanced crosslink densities and the ability of the bismaleimide bridges to withstand and recover from a high-temperature compressive force. However, in the case of BIIR-Z contains HVA-2, almost a stable region was observed between 3 and 5phr. On the other hand, a sharp increase in the set value was noticed in the vulcanizate of BIIR-Z with 5phr of perkalink due to the reduction in the crosslink density.

Conclusions

The detailed vulcanization studies based on ODR and DSC have undoubtedly proved that a simultaneous enhancement in the rate and state of cure could be possible if BIIR is vulcanizing with ZnO in the presence of even 1phr of either HVA-2 or Perkalink. The Diels-Alder reaction between the in-situ formed conjugated diene butyl while heating BIIR with ZnO and the dienophile units in the bismaleimides was proposed as the most appropriate reaction mechanism that is responsible

for the enhanced cure efficiency. A comparative evaluation regarding the activity of these bismaleimides towards the rate and state of cure revealed that HVA-2 is much better than Perkalink 900. The higher activation energy obtained for the vulcanization reaction of BIIR/ZnO in the presence of Perkalink confirmed its lower activity in the curing reaction. The electron releasing bulky methyl group attached on to the dienophile unit in Perkalink 900 was identified for its lower activity towards the Diels-Alder reaction during vulcanization. Owing to the higher state of cure offered by HVA-2, the crosslink density and the mechanical properties of the compounds cured with HVA-2 were better than the compounds vulcanized with Perkalink. Detailed fracture surface morphological studies by SEM in conjunction with EDX have revealed that at a concentration of 5phr, the Perkalink showed severe dispersion problem. This was recognized as the formation of a thick viscous resin due to self-polymerization of Perkalink at the vulcanization temperature. All these experimental results strongly endorse that these bismaleimides with a dosage between 1 to 3 phr can be effectively used as an activator for enhancing the efficiency of ZnO vulcanization in BIIR and also to enhance the crosslink density and mechanical properties of the resultant vulcanizates.

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References

- Hofmann W (1989) Rubber technology handbook. Hanser publisher, Munich
- Chu CY, Watson KN, Vukov R (1987) Rubber. Chem Tech 60:636–646
- Vukov R (1984) Rubber Chem. Tech 57:275–283
- Parent JS, Thom DJ, White G, Whitney RA, Hopkins WJ (2001) *J. Polym. Sci. Part A. Polym Chem* 39:2019–2026
- Malmberg SM, Parent JS, Pratt DA, Whitney RA (2010) Isomerization and Elimination Reactions of Brominated Poly(isobutylene-co-isoprene). *Macromolecules* 43:8456–8461
- Parent JS, White GDF, Thom D, Whitney RA, Hopkins W (2002) Amine Substitution Reactions of Brominated Poly(isobutylene-co-isoprene): New Chemical Modification and Cure Chemistry. *Macromolecules* 35:3374–3379
- Guillen-Castellanos SA, Parent JS, Whitney RA (2006) Synthesis of Ester Derivatives of Brominated Poly(isobutylene-co-isoprene): Solvent-Free Phase Transfer Catalysis. *Macromolecules* 39:2514–2520
- Guillen-Castellanos SA, Parent JS, Whitney RA (2006) *J. Polym. Sci. Part a. Polym Chem* 44:983–992
- Parent JS, White GDF, Thom DJ, Whitney RA, Hopkins W (2003) *J. Polym. Sci. Part A: Polym. Chem* 41:1915–1926
- Whitney RA, Penciu A, Parent JS, Resendes R, Hopkins W (2005) Cross-Linking of Brominated Poly(isobutylene-co-isoprene) by N-Alkylation of the Amidine Bases DBU and DBN. *Macromolecules* 38:4625–4629

11. Parent JS, White GDF, Whitney RA (2002) Amine Substitution Reactions of Brominated Poly(isobutylene-co-isoprene): New Chemical Modification and Cure Chemistry. *Macromolecules* 35: 3374–3379
12. Parent JS, Liskova A, Whitney RA, Resendes RJ (2005) *Polym. Sci. Part A. Polym Chem* 43:5671–5679
13. Parent JS, Penciu A, Guillen-Castellanos SA, Liskova A, Whitney RA (2004) Synthesis and Characterization of Isobutylene-Based Ammonium and Phosphonium Bromide Ionomers. *Macromolecules* 37:7477–7483
14. Baldwin FP (1979) *Rubber Chem. Technol.* 52:77–84
15. Vukov R (1984) *Rubber Chem. Technol* 57:284–290
16. Hendrikse KG, McGill WJ, Reedijk J, Nieuwenhuizen PJ (2000) Vulcanization of chlorobutyl rubber. I. The identification of crosslink precursors in compounds containing ZnO/ZnCl₂. *J Appl Polym Sci* 78:2290–2301
17. Hendrikse KG, McGill WJ (2000) Vulcanization of chlorobutyl rubber. II. A revised cationic mechanism of ZnO/ZnCl₂ initiated crosslinking. *J Appl Polym Sci* 78:2302–2310
18. Hendrikse KG, McGill WJ (2001) Vulcanization of chlorobutyl rubber. III. Reaction mechanisms in compounds containing combinations of zinc dimethyldithiocarbamate, tetramethylthiuram disulfide, sulfur, and ZnO. *J Appl Polym Sci* 79:1309–1316
19. Boris AR, Emma AD, Roger JM, Eugene ES (2002). *Polym Adv Technol* 13:837–844
20. Thomas MD, David R (1992). *Polym Eng Sci* 32:409–414
21. Kovacic P, Hein RW (1959). *J. Amer. Chem. Soc.* 81:187–1190
22. Kovacic P, Hein RW (1959) Cross-linking of Unsaturated Polymers with Dimaleimides I. *J Amer Chem Soc* 81:1190–1194
23. Hassan A, Wahit MU, Chee CY (2003) Mechanical and morphological properties of PP/NR/LLDPE ternary blend—effect of HVA-2. *Polym Test* 22:281–290
24. Du M, Guo B, Jia D (2005) Effects of Thermal and UV-induced Grafting of Bismaleimide on Mechanical Performance of Reclaimed Rubber/Natural Rubber Blends. *J Polym Res* 12:473–482
25. Kahar AWM, Ismail H, Othman N (2013) *J. Appl. Polym. Sci* 128: 2479–2488
26. Datta RN (2003) *Prog. Rubber Plast. Recycl Technol* 19:143–170
27. Kumar NR, Chandra AK, Mukhopadhyay R (1997). *J Mat Sci* 32: 3717–3725
28. Datta RN, Schotman AHM, Weber AJM, van Wijk FGH, van Haeren PJC, Hofstraat JW, Talma AG, Bovenkamp-Bouwman AGVD (1997) *Rubber Chem. Technol.* 70: 129–145
29. Datta RN, Talma AG (2001) *KGK Kautschuk Gummi. Kunststoffe* 54:372–376
30. Flory PJ (1950) Statistical Mechanics of Swelling of Network Structures. *J Chem Phys* 18:108–111
31. Bristow GM, Watson WF (1958). *Trans Faraday Soc* 54:173
32. Brandrup J, Immeraut EH (1974) *Polymer handbook*. Wiley, New York
33. Kader MA, Nah C (2004) Influence of clay on the vulcanization kinetics of fluoroelastomer nanocomposites. *Polymer* 45:2237–2247
34. Choi D, Kader MA, Cho BH, Yang-il H, Nah C (2005) Vulcanization kinetics of nitrile rubber/layered clay nanocomposites. *J Appl Polym Sci* 98:1688–1696
35. Sui G, Zhong WH, Yang XP, Yu YH (2008) *Mater. Sci. Eng. A* 485: 524–531
36. Shibulal GS, Jung JY, Jeong KU, Nah C (2017) *Polym. Adv. Technol.* 28: 742–753
37. Shibulal GS, Jung JY, Jeong KU, Nah C (2016). *J Appl Polym Sci* 133:44082
38. Shibulal GS, Jung JY, Yu HC, Huh YI, Nah C (2016) Cure characteristics and physico-mechanical properties of a conventional sulphur-cured natural rubber with a novel anti-reversion agent. *J Polym Res* 23:237
39. Gopi Sathi S, Park C, Huh YI, Jeon J, Chang HY, Won J, Jeong KU, Nah C (2018) *Rubber Chem. Technol.* doi.org/10.5254/rct-18-82605
40. Kiselev VD, Konovalov AI (2009) Internal and external factors influencing the Diels-Alder reaction. *J Phys Org Chem* 22:466–483