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Modeling the Vulcanization of Rubber Blends

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Summary: Kinetics and heat transfer during vulcanization of various blends of polybutadiene (BR) and polyisoprene (NR) were studied simultaneously using mechanistic approach for description of reaction kinetics. Fourier transform infrared spectroscopy (FTIR) was used to study the kinetics of accelerator and retarder chemistry. Differential scanning calorimetry (DSC) and dynamic rheometry were applied in order to retrieve the data for heat transfer modeling during induction period and kinetic modeling throughout the process. Model reaction scheme was based on one of the best possible proposed individual reaction mechanisms. Molecular modeling was applied to differentiate between the reactions of chemically similar species. Physical and chemical model parameters were calculated from the experimental data. A minimum of average rubber heat transfer coefficient was found to be at equal BR and NR weight fractions in the blend while activation energies of crosslinking and reversion reactions increased linearly with increasing BR weight fraction.

Keywords: blends; kinetics; modeling; rubber; vulcanization

Introduction

Rubber applications demand vulcanized products due to improved properties of crosslinked elastomers. Therefore, numerous crosslinking agents such as sulfur, organic peroxides, phenolic resins, alkoxysilanes, etc. may be applied depending on rubber type. Sulfur is the most widely used crosslinking agent and is often accompanied by accelerators (thiazoles, sulphenamides, thiurams, dithiocarbamates), retarders (N-(cyclohexylthio)phtalimide), activators (zinc oxide, stearic acid) and other components.

In order to achieve the desired product properties it is essential to understand the underlying reactions which are generally responsible for the formation of crosslinked network. Kinetics of these reactions have been studied in two manners. Phenomenological models generally tend to fit the vulcanization curve, but seldom try to encompass the chemistry and the reactions during vulcanization. The macrokinetics described by phenomenological models are often represented by power law and other models developed by Piloyan,[1] Kamal et al.,[2] Isayev[3] and others. However, predictability of these models is limited to systems which are similar to ones for which the model parameters had been determined. That is, if the amount of certain component in vulcanization formulation is changed, the fitted parameters no longer apply, since the concentrations of individual components are not directly incorporated into the model. Consequently, Monte-Carlo simulations,[4] reaction schemes[5–13] and mechanistic models were developed in an attempt to treat a variety of species present in vulcanization compound individually. The first and the most widely recognized reaction scheme was proposed by Coran.[6–8] Ding et al.[11] introduced a competitive parallel reaction to crosslink formation. Since the reversion was not considered in this last scheme Ding and

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Leonov[12] proposed yet another reaction scheme, adding a consecutive reaction to crosslinking. Ghosh et al.[13] presented an overview of different reactions and their mechanisms for sulfur vulcanization of natural rubber in bezothiazole accelerated formulations. They developed a model consisting of population balance equations for various species present in the system during vulcanization.

Despite extensive attention which has been paid to kinetics of reactions during vulcanization there are still some shortcomings of the proposed models. The rate of formation or breakage of the bonds in the polysulfidic chains which occur during vulcanization was previously considered independent of the position of the bond.[6–13] The aim was to developed a kinetic model which takes into account the exact location in the molecule where the reaction takes place. Moreover, the model should also be able to allow for crosslinks to be formed even prior to the end of induction period when rubber elasticity starts to increase. The concentration of crosslinks was previously considered zero before the end of induction period i.e. the onset of curing period.[1–3,11–13] Finally, the model was intended to be used for description of the course of vulcanization for various rubber blends of polybutadiene and polyisoprene in order to extract physical and chemical model parameters and thus obtain a deeper insight into the crosslinking process.

Experimental

Materials

A very high cis homopolymer polybutadiene, with density (ρ) of 910 kg/m^3 and weight average molecular weight (M_w) of 6.0 10^5 g/mol and a polyisoprene, with density of 920 kg/m^3 and M_w of 8.2 10^5 g/mol were used. The accelerators used were N-t-butylbenzothiazole-sulfenamide (TBBS) with industrial name Westco TBBS from Western Reserve Chemical and N,N-di-t-butylbenzothiazole-sulfenamide (TBSI) with industrial name Santocure TBSI from Akzo Nobel Chemicals. A mixed N,N′-diaryl-p-phenylenediamine (DTPD) with industrial name Vulkanox 3100 from Bayer and N-(cyclohexylthio)phtalimide (CTP) with industrial name Westco CTP from Western Reserve Chemical were used as antioxidant and retarder, respectively. The formulations of vulcanization compound are laid out in Table 1.

Techniques

Vulcanization experiments were either performed on Mettler Toledo DSC 821^e instrument purged with nitrogen (50 ml/min) or on Alpha Technologies RPA (Rubber Process Analyzer) 2000 instrument. DSC measurements were conducted under isothermal conditions. The samples were put in 40 μl aluminum crucibles with a pin and vulcanized for 30–60 minutes. During RPA measurement conditions were isothermal with the exception of initial thermal equilibration. The samples underwent dynamic oscillation at 7 % strain amplitude and 0,1 Hz frequency. FTIR spectra of various accelerator and retarder compounds were obtained from the 2000 NR FTIR spectrometer (Perkin Elmer) using a high temperature measuring cell. The samples analyzed by means of FTIR spectroscopy were prepared by mixing TBBS, TBSI or TBBS + CTP with the inert KBr. Sample spectra were then collected over a period of time and the spectra evaluated with Spectrum 5.0.1.

Table 1.
Formulations of vulcanization compound.

Ingredient	Weight (g)
BR	100/75/50/25/0
NR	0/25/50/75/100
TBBS (accelerator)	2.05
TBSI (accelerator)	0.82
CTP (retarder)	0.10
Sulfur	0.70
ZnO (with fatty acids)	2.36
ZnO (neat)	1.00
Stearic acid	2.00
DPTD (antioxidant)	1.50

HyperChem 7.5 was used for molecular modeling while Matlab 7.1 was used for numerical computations and modeling.

Results and Discussion

Vulcanization of the compounds was performed in an oscillating bicone cell (RPA 2000 instrument). Storage (G′) and loss (G″) moduli, dynamic (η′) and out-of-phase (η″) viscosities and upper/lower cone temperatures were obtained at various times. These quantities along with sample temperature (T) may be expressed in a following manner for the oscillating bicone cell,[15,16] where the Equation 1 represents the expression obtained from the literature which was modified in order to correspond with the common expression for isothermal vulcanization[11–13] when the set temperature is reached.

$$G'(t) = G'(T_0)\left(\frac{T(t)}{T_0}\right)^{X(t)} \times \exp\left(\frac{\Delta H'}{R}\frac{T_0 - T(t)}{T_0 T(t)}(1 - X(t))\right) + X(t)(G'(t)_{max} - G'(t)_{min}) \quad (1)$$

$$\eta'(t) = \eta'(T_0) \times \exp\left(\frac{\Delta H''}{R}\frac{T_0 - T(t)}{T_0 T(t)}(1 - X(t))\right) \times \exp(C_1 X(t) + C_2 X(t)^2) \quad (2)$$

$$G''(t) = \eta'(t)\omega \quad (3)$$

$$\eta''(t) = \frac{G'(t)}{\omega} \quad (4)$$

$$\rho V C_V \frac{dT(t)}{dt} = h_0(1 + K_1 X(t))A(T_0 - T(t)) + \rho V \Delta H_{tot}\frac{dX(t)}{dt} + \dot{W}, \quad T(t=0) = T_i \quad (5)$$

$$\dot{W} = V'\dot{\gamma}_0^2(\eta'(t)\cos^2(\omega t) + \eta''(t)\sin(\omega t)\cos(\omega t)) \quad (6)$$

In Equations (1–6, X is the degree of vulcanization, R is the gas constant, A is the area between instrument measuring cell and sample (31.05 cm^2),[17,18] V is the volume of sample (3.50 cm^3)[17,18] and V′ is the volume of sample subjected to deformation (2.87 cm^3).[15–18] T_i and T_0 represent the initial and the set (upper/lower cone) temperature of the vulcanization, respectively, ω is the oscillation frequency (0.628 s^{-1}), $\dot{W}$ represents friction energy dissipation, γ_0 is the strain amplitude (0.07), $\dot{\gamma}_0$ is the strain rate amplitude (0.044 s^{-1}), ΔH_{tot} is the heat evolved during vulcanization obtained from DSC experiments, ρ is the rubber density and C_V is the rubber heat capacity (1905 J/(kgK) and 647 J/(kgK) for NR and BR, respectively).[19,20] C_1, C_2, ΔH′ and ΔH″ are the adjustable parameters which encompass the temperature and crosslinking dependency of viscoelastic properties while h_0 and K_1 signify average rubber heat transfer coefficient and the parameter of its variation proportionate to X.

The degree of vulcanization, X, affects all viscoelastic properties as it may be seen in Equations 1–4. It is a relative criterion for concentration of crosslinks with any number of sulfur atoms in polysulfidic chain in comparison to the maximal value of this concentration.

$$X(t) = \sum_{x=1}^{\infty}[Vu_x] \Big/ \left(\sum_{x=1}^{\infty}[Vu_x]\right)_{max} \quad (7)$$

These crosslinks are formed and cloven with certain reaction rates dependent directly or indirectly on all components in vulcanization compound and the products of their reactions. Thus an overall kinetic scheme based on the one of the best proposed individual reaction mechanisms should be written.[13,14] The kinetic scheme for our specific system is presented in Figure 1. The vital aspects of this kinetic scheme include the relevant chemical reaction mechanisms, explicit incorporation of the polysulfidic nature of the various molecular species and additionally, the influence of the exact location in the molecule

accelerator chemistry:

$$\mathrm{TBBS} \xrightarrow{k_{TBBS}} \mathrm{MBT} + \mathrm{amine} \quad \textbf{(R.1)}$$

$$\mathrm{TBSI} \xrightarrow{k_{TBSI}} \mathrm{MBT} + \mathrm{TBBS} \quad \textbf{(R.2)}$$

$$\mathrm{TBBS} + \mathrm{MBT} \xrightarrow{k_{TBBS-MBT}} A_0 + \mathrm{amine} \quad \textbf{(R.3)}$$

$$\mathrm{TBSI} + \mathrm{MBT} \xrightarrow{k_{TBSI-MBT}} A_0 + \mathrm{TBBS} \quad \textbf{(R.4)}$$

$$A_X \xrightarrow{k_B} E^*_Y + E^*_Z \quad 0 \le X \le N-2 \quad X = Y + Z \quad \textbf{(R.5)}$$

$$A_0 + A_X \xleftrightarrow{k_{A-A}} A_Y + A_Z \quad 0 \le X \le N-2 \quad X = Y + Z \quad \textbf{(R.6)}$$

crosslinking chemistry:

$$A_X + \mathrm{rubber} \xrightarrow{k_{A-R}} B_X + \mathrm{MBT} \quad 0 \le X \le N-2 \quad \textbf{(R.7)}$$

$$B_X \xrightarrow{k_{B-R}} B^*_Y + E^*_Z \quad 1 \le X \le N \quad X = Y + Z \quad \textbf{(R.8)}$$

$$B^*_X + \mathrm{rubber} \xrightarrow{k_{VU}} \mathrm{Vu}_X \quad 1 \le X \le N \quad \textbf{(R.9)}$$

post-crosslinking chemistry:

$$\mathrm{Vu}_X \xrightarrow{k_{DEG}} \mathrm{dead\ ends} \quad 2 \le X \le N \quad \textbf{(R.10)}$$

$$\mathrm{Vu}_X + A_0 \xrightarrow{k_{DESULF}} \mathrm{Vu}_{X-1} + A_1 \quad 2 \le X \le N \quad \textbf{(R.11)}$$

retarder chemistry:

$$\mathrm{CTP} + \mathrm{MBT} \xrightarrow{k_{RET}} \mathrm{CDB} + \mathrm{phtalimide} \quad \textbf{(R.12)}$$

$$\mathrm{CDB} + \mathrm{MBT} \xrightarrow{k_{CDB}} A_0 + \mathrm{cyclohexylhydrodisulfide} \quad \textbf{(R.13)}$$

other reactions:

$$E^*_X + S_Y \xrightarrow{k_{E-S}} E^*_{X+1} + S_{Y-1} \quad 0 \le X \le N-1 \quad 1 \le Y \le 8 \quad \textbf{(R.14)}$$

$$E^*_X + \mathrm{rubber} \xrightarrow{k_{E-R}} B_X \quad 0 \le X \le N \quad \textbf{(R.15)}$$

$$B^*_X + S_Y \xrightarrow{k_{BST-S}} B^*_{X+1} + S_{Y-1} \quad 0 \le X \le N-1 \quad 1 \le Y \le 8 \quad \textbf{(R.16)}$$

$$B^*_X \xrightarrow{k_{LOOP}} L_X\ (\mathrm{dead\ end}_X) \quad 1 \le X \le N \quad \textbf{(R.17)}$$

$$B^*_X + A_0 \xrightarrow{k_{A-BST}} B_X + E^*_0 \quad 1 \le X \le N \quad \textbf{(R.18)}$$

$$E^*_Y + E^*_Z \xrightarrow{k_{E-E}} A_X \quad 0 \le X \le N-2 \quad X = Y + Z \quad \textbf{(R.19)}$$

Figure 1.
Reaction scheme for sulfur vulcanization of polybutadiene and polyisoprene with accelerators TBBS and TBSI.

where the reaction takes place on the reaction rates.

According to kinetic scheme TBBS reacts in one step forming MBT (2-mercapto benzothiazole and amine products. TBSI, on the other hand, reacts in two steps. CDB is 2-(cyclohexyldisulfanyl)-1,3-benzothiazole, and amine is actually 2-amino-2-methyl propane. The formation of dead ends can be attributed to a number of reactions such as formation of inactive pendant groups, sulfur loops (L_X, loop with X sulfur atoms), etc. A_X represents accelerator polysulfide or the zinc-accelerator complex, B_X the crosslink precursor, B^*_X the activated form of the crosslink precursor, Vu_X the crosslink, E^*_X the accelerator-terminated polysulfidic radi-

cal and S_Y Y connected sulfur atoms (elemental sulfur in the case when Y is 8). The kinetic constants ascribed to each reaction in Figure 1 apply solely to the reactions where the end-group effect in the molecule or radical species is negligible, that is if the polysulfidic chain is long enough. Taking this into consideration, each reaction, where indexed polysulfidic species are involved should be kinetically treated individually,[14] using molecular modeling, and not in a lumped manner as it was the practice in former works.[6–13]

According to Figure 1 the corresponding rate equations and consequently, the component mass balance equations for various species which are involved in the vulcanization process were written. Kinetic scheme in Figure 1 also introduces N as an arbitrary chosen maximum number of sulfur atoms in polysulfidic chain which has to be selected great enough, so that the calculated model parameters no longer vary with increasing N.

Since a distinction had to be made between reaction rates of chemically similar species, molecular modeling was applied. Stable conformations of numerous species had to be found, meaning that the geometry for a variety of species that are produced during vulcanization or directly added to the rubber compound, had to be optimized. This was achieved by semi-empirical PM3 (Parametrized Model 3) method calculations.[21] Generalized geometries of all species subjected to geometry optimization are presented in Figure 2(a–e). Instead of rubber chains with large number of repeating monomer units, a sequence of five units of isoprene or butadiene was used as a rubber component model. This is sufficiently long chain, since our calculations with longer chains yielded basically no difference in the calculated parameters. The search for the transition state geometry was carried out. The activation energies were not calculated per se and considered as true intrinsic properties of the system but more with regard to reactivity depending on the length of the polysulfidic chain. It was assumed that all kinetic constants follow the temperature dependency according to Arrhenius law

$$k_{i,j} = cf_{i,j} A \exp\left(-\frac{E_A}{RT}\right) = cf_{i,j} k \tag{8}$$

where $k_{i,j}$ is the kinetic constant and $cf_{i,j}$ the correction factor for the reaction where i and j indexed species are consumed or produced. A, E_A and k are the pre-exponential factor, the activation energy and the kinetic constant for the reaction, respectively, where influences of end-groups are minimized. To illustrate this principle, reaction $A_{10} \xrightarrow{k_{B,0,10}} E_0^* + E_{10}^*$ may be taken as an example. Apparently an S-S bond in the A_{10} molecule is broken very close to the benzothiazole end-group, resulting in specific activation energy for the formation of products due to various effects of the end-group. Activation energies from molecular modeling calculations were used to define correction factors, taking into account the Eyring equation.

$$cf_{i,j} \exp\frac{\Delta H^{\#} - \Delta H_{i,j}^{\#}}{RT} \tag{9}$$

$\Delta H^{\#}$ represents the difference between the formation enthalpies of the transition structure and the energy minimum before energy rise towards the transition structure location on the reaction pathway. For the mentioned reaction, $\Delta H_{i,j}^{\#}$ would be $\Delta H_{0,10}^{\#}$ and $\Delta H^{\#}$ the value of formation enthalpy difference towards which all values of $\Delta H_{i,j}^{\#}$ for the specific reaction converge with elongation of the polysulfidic chain. If X in Reaction 5 (Figure 1) is great enough and polysulfidic chain split far enough from end-groups $\Delta H_{i,j}^{\#}$ becomes $\Delta H^{\#}$, the value of $cf_{i,j}$ becomes 1 and $k_{i,j}$ becomes k, k_B for the Reaction 5, specifically.

FTIR measurements were used to measure the change in concentration of both accelerators (TBBS and TBSI) versus time. In view of the fact that all other components needed for the vulcanization of rubber were not added to the sample, only Reactions 1, 3 and 5 (for $x = 0$) or 1–4 and 5 (for $x = 0$) in Figure 1 take place for TBBS and TBSI formulations, respectively. According to IR

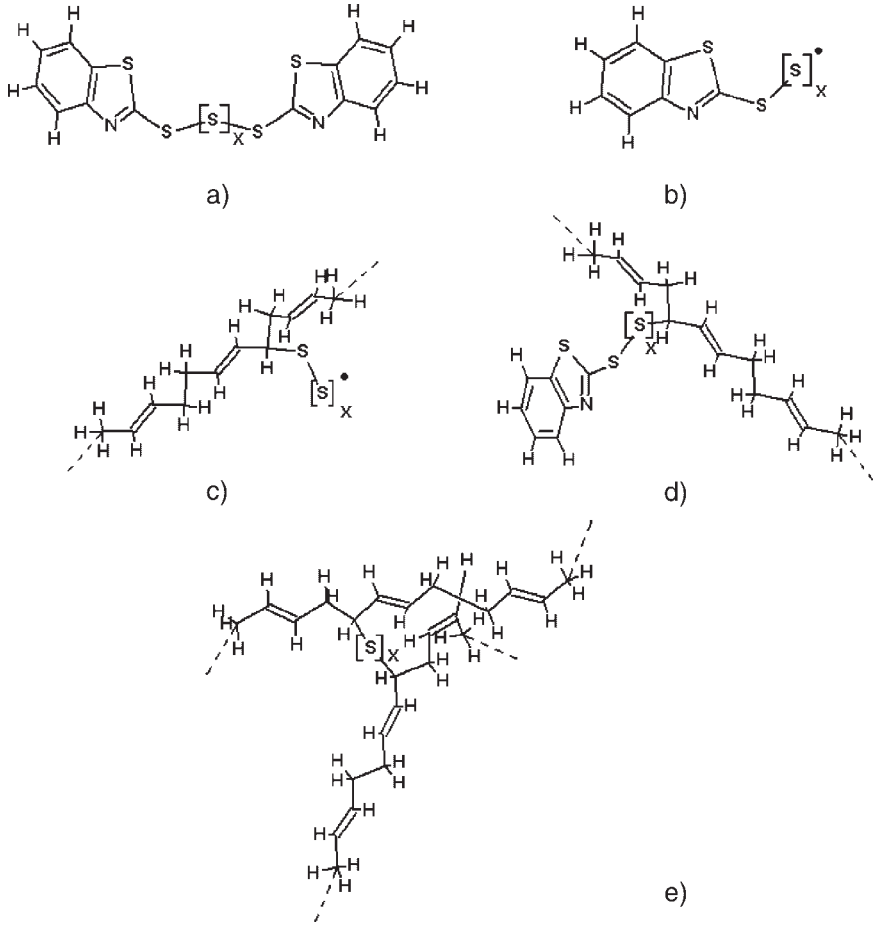

Figure 2.
A_X molecule (a), E^*_X molecule (b), B^*_X molecule (c), B_X molecule (d), Vu_X molecule (e).

spectroscopy literature, signal for t-butyl group in the TBBS is found at wave numbers 1365 and 1389 cm^{-1} while the amine group characteristic signal may be seen at 3248 cm^{-1}. The peak at 3248 cm^{-1}, representing a secondary amine group of TBBS, varied with time, while the t-butyl peaks remained the same throughout our experiment. No peaks can be observed in the vicinity of 3248 cm^{-1} in the TBSI spectrum, since there is no secondary amine group in the accelerator molecule. FTIR spectra were analyzed at different temperatures and reaction times. Conversions were then calculated from spectra using the Beer-Lambert equation and kinetic constants were calculated at different temperatures. Retarder chemistry kinetics were also studied. As the characteristic peaks of phtalimide, formed through Reaction 12, at 3205 cm^{-1} for N-H stretch and 1774 cm^{-1} and 1745 cm^{-1} for C=O stretches, overlap with those of TBBS, the reactions of the retarder could not be dealt with directly. Anyhow, the FTIR data may be fitted indirectly, since application of the retarder causes partial consumption of generated MBT through Reaction 12 and 13, thus reducing the overall TBBS disappearance rate.

DSC experiments were used to study the system by measuring ΔH_{TOT} using isothermal DSC technique at temperatures corresponding to that of RPA experiments.

These results, however, were not used for modeling, except for ΔH_{TOT} calculations, because the heat flow versus time obtained from DSC experiments could not be directly linked to the concentration of crosslinks, though degree of cure may formally be calculated.

The modeling proceeded as follows. In the initial stage of induction period when X is practically zero Equations 1–6 were applied and calculated G', G'', η' and η'' were fitted to experimental data. Adjustable parameters $\Delta H'$, $\Delta H''$ and h_0 were calculated. Then the procedure was repeated for the whole cure curve using Equations 1–7 and 5 $N+17$ differential equations with appropriate boundary conditions which represented mass balances for components involved in kinetic scheme.[14] Correction factors obtained from molecular modeling were introduced into component mass balances to alter the reaction rates which are influenced by the end-group effect. The assumptions were $k_{DESULF} = k_{A\text{-}BST} = = k_{A\text{-}A}$, $k_{E\text{-}R} = k_{VU}$, $k_{BST\text{-}S} = k_{E\text{-}S}$ and $k_{LOOP,i} = cf_{R.17,i}\ k_{VU,i}$. These assumptions are quite justified, since with the introduction of correction factors, these constants are not the same for all lengths of the sulfur backbone in various species, but only for the main chain where the effects of end-groups are not present anymore. Kinetic constants k_B, $k_{A\text{-}A}$, $k_{A\text{-}R}$, $k_{B\text{-}R}$, k_{VU}, k_{DEG}, $k_{E\text{-}S}$ and $k_{E\text{-}E}$ were calculated at various temperatures and compound formulations and consequently activation energies for reactions presented in Figure 1 were calculated at different polybutadiene and polyisoprene weight ratios.[14]

Figure 3 depicts the behavior of BR compound's viscoelastic properties when the rubber compound sample is exposed to increased temperature of the measuring system. Alongside with experimentally determined properties, model predictions may be seen. Analogous diagrams may be constructed for all applied set vulcanization temperatures, which were in the range of 140–190 °C, and all compound formulations. An initial drop of G' may be observed and is mostly ascribed to thermal equilibration of the sample. However, there is some extent of crosslinking present, even as G' decreases. Crosslinking should not be

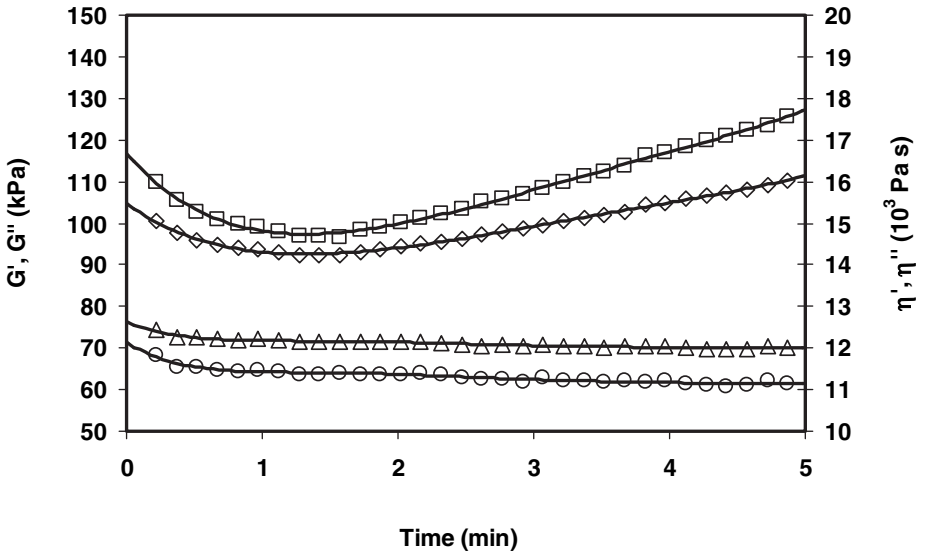

Figure 3.
Experimental data for BR compound viscoelastic properties and the model predictions for vulcanization at set temperature 160 °C (induction and the beginning of cure period): (◇) G'; (△) G''; (○) η'; (□) η''; (–) model prediction.

neglected even during induction period i.e. before G′ reaches minimal value. Model predictions of G′ which would exclude the formation of crosslinks during induction period would be lower, while the combined model which includes crosslinking quite well suits experimental data (Figure 3. In Equation 1 G′ is written as a sum of two contributions. Evidently, during the induction period the first term in Equation 1 plays the decisive role in determining G′, since X is relatively small or practically zero. By using Equation 1, we thus describe the whole vulcanization curve. However, when the sample reaches the set vulcanization temperature, T_0, the whole expression is reduced to frequently used relation between the degree of vulcanization, X, and the storage modulus,[11–13] where $G'(T_0) = G'(t)_{min}$, as the predicted temperature of the compound reaches its set point at the storage modulus minimum.

$\Delta H'$ and $\Delta H''$ represent activation energy equivalents in the exponential term and, presumably, they should not vary greatly with temperature, which was confirmed when these two parameters were calculated. On the other hand, the BR/NR weight ratio influences these two parameters to some extent so that there is a local minimum and maximum at composition 50/50 for $\Delta H'$ and $\Delta H''$, respectively (Figure 4). There is some parallel between this finding and the behavior of h_0 with temperature and composition of the vulcanization compound. The heat transfer coefficient, h_0, rises from its value between 100 and 150 W/(m^2K) depending on set vulcanization temperature, for BR compounds to its value between 250 and 400 W/(m^2K) for NR compounds, the local minimum being at the weight ratio of 50/50, where the h_0 minimum is the more distinctive the lower the set vulcanization temperature. This is probably due to the specific interaction between BR and NR phases in the compound at this composition. The rise of h_0 with fraction of BR in the compound is the greater the higher the applied set temperature of vulcanization.

The developed model describes relatively well the time dependence of the storage modulus during the cure and overcure period. It may be observed in Figure 5 that even for various rubber compound formulations and set vulcanization temperatures the model well describes the course of vulcanization. The storage modulus rises

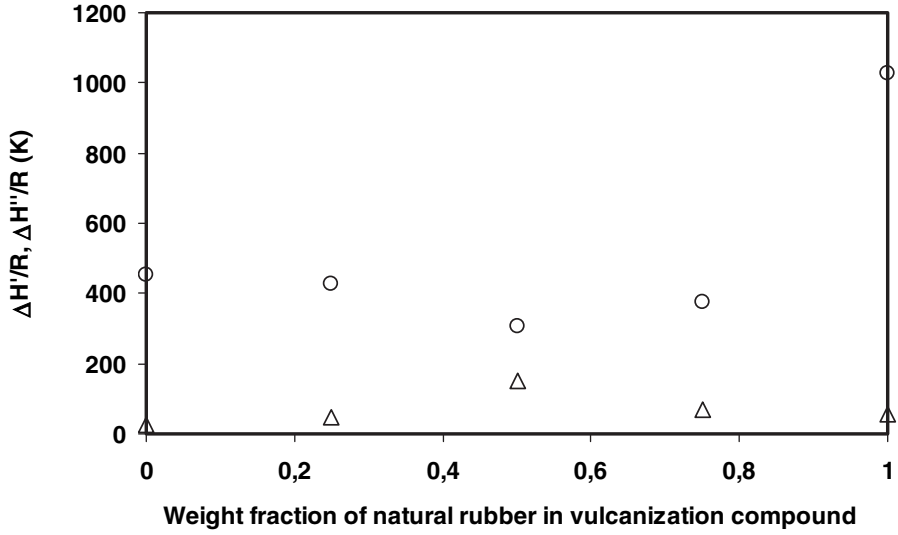

Figure 4.
Influence of weight fraction of natural rubber in the vulcanization compound on parameters $\Delta H'$ and $\Delta H''$: (○) $\Delta H'$; (△) $\Delta H''$.

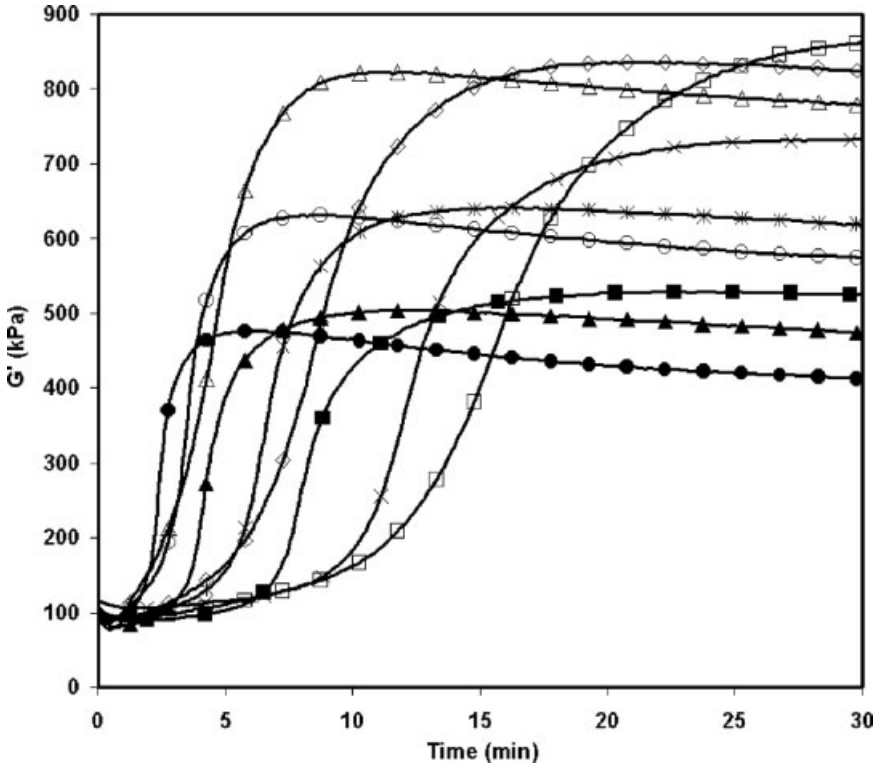

Figure 5.
Influence of the vulcanization compound and temperature on vulcanization curves: (–) vulcanization model; (□) BR, 160 °C; (◇) BR, 160 °C; (△) BR, 180 °C; (×) 50BR/50NR, 160 °C; (∗) 50BR/50NR, 170 °C; (○) 50BR/50NR, 180 °C; (■) NR, 160 °C; (▲) NR, 170 °C; (●) NR, 180 °C.

faster, with increasing set temperature, where at 140 °C there is practically no rise in the modulus within 30 minutes of vulcanization, implying that vulcanization reaction rates are relatively low at this temperature, resulting in long induction times.

It was investigated how the weight ratio of BR and NR in the vulcanization formulation affects the main reactions, responsible for product properties. Reactions 1–4, 12 and 13 (Figure 1) were kinetically treated individually using experimental data from FTIR spectroscopy. TBBS and TBSI react practically with the same reaction rate, TBSI being useful for vulcanization because of its bifunctionality resulting in initial formation of MBT and TBBS. The TBBS formed during this reaction reacts even in later stages of the scorch-delay when the TBBS added to the initial vulcanization mixture is gradually depleted. The reaction between primary or secondary accelerator and MBT is a little faster than reaction of accelerator dissociation, making the latter reaction a rate limiting step of the induction period. BR/NR ratio in vulcanization compound had practically no influence on the activation energies of Reactions 5, 6, 14 and 19 which may be explained by the fact that rubber is not directly involved in these reactions as it may be seen in Figure 1. Activation energies for Reactions 7, 8, 9, 10 and 11 (Figure 1) rise as the percentage of BR increases. This rise of activation energies with increasing BR fraction in vulcanization compound may be interpreted considering vulcanization curves on Figure 5. If BR and NR samples at

identical set vulcanization temperatures are compared it may be observed that although the crosslinking reactions appear to be faster for NR samples (thus the lower activation energies for Reactions 7, 8 and 9 (Figure 1)) the same applies for the reversion reactions embodied in Reactions 10 and 11 (Figure 1).

Conclusions

A model which incorporates heat transfer and complex kinetics of numerous reactions during the process of rubber vulcanization has been developed. Heat transfer parameters and activation energies for a range of reactions have been calculated and compared for various polyisoprene and polybutadiene blends. Reaction kinetics were developed considering location in the polysulfidic chain where the reaction takes place using correction factors obtained from molecular modeling data. The model predicts the formation of crosslinks even before the end of induction period due to combining of temperature and crosslinking dependence of viscoelastic properties. The experimental and predicted values of rubber's viscoelastic properties were in relatively good agreement during induction, cure and over-cure periods. The developed model could be applied for other similar rubber blends and formulations. However, if a different component, for example, is added to vulcanization formulation, the kinetics of its reactions with other species must first be considered, while kinetics of other reactions remain unchanged. In order to prove its predictive abilities, the model should be used for various other fomulations and blends, which was not the scope of this work.

The extracted model parameters may after some further research and model testing be linked to the properties of the vulcanized elastomers and eventually, these parameters may be used to foretell the suitable formulation choice for certain crosslinked rubber application.

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