Polym. Bull. (2011) 67:1621–1631
DOI 10.1007/s00289-011-0521-0

ORIGINAL PAPER

Crosslinking kinetics of SBR composites containing vulcanized ground scraps as filler

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Received: 1 February 2011 / Revised: 6 May 2011 / Accepted: 24 May 2011 /

Abstract The aim of this study was to characterize the cure reaction of styrene–butadiene rubber (SBR) composites containing industrial rubber scraps. Different proportions of SBR ground scraps (SBR-r), varying from 10 to 80 parts per hundred of rubber, were incorporated into a base formulation of identical composition. Crosslink formation and the kinetics of the cure reaction were evaluated through oscillatory disk rheometry, differential scanning calorimetry, and crosslink density. Cure characteristics, such as scorch time and cure time, decreased with increasing SBR-r content. Minimum torque indicated only a small variation in the viscosity with the incorporation of SBR-r. The maximum torque decreased with the addition of scrap rubber, as a consequence of the reduction in virgin rubber content where crosslinks had been formed. Crosslink density values corroborated these findings, presenting a slight decrease with the increase in the SBR-r content. The kinetic study indicated lower enthalpy values for SBR-r composites compared to those of the control sample. The kinetic parameters, such as activation energy and reaction order, indicated a change in the mechanism of reaction, related to the increased complexity of the systems.

Keywords SBR · Rubber scraps · Recycling · Cure kinetics · Crosslink density

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Introduction

The curing process of rubber materials is one of the key factors that determines their final properties. Sulfur curing systems have been widely studied. Both the chemistry during accelerated vulcanization and the reaction kinetics during curing have been topics of great interest [1–4]. However, if vulcanized rubber scraps are introduced onto a virgin matrix, the curing characteristics of the rubber composites would differ from those of the neat rubber materials [5]. Therefore, understanding of the curing process of rubber composites can help predict and control the curing behavior of materials during the process of revulcanization and achieve good overall performance of the final product [6].

Many authors have studied the cure characteristics of rubber compounds filled with vulcanized rubber scraps through oscillatory disk rheometry [7–13]. However, little information is available on quantitative evaluation of the kinetics of its revulcanization. Isayev and Sujan [2] were the first to study the kinetic approach of devulcanized ground rubber tire (GRT) using nonisothermal vulcanization in an advanced polymer analyzer. Bianchi et al. [14] investigated the crosslinking kinetics of blends of ethylene vinyl acetate and GRT through oscillatory disk rheometry (ODR) and differential scanning calorimetry (DSC). The cure modeling and mechanical properties of devulcanized GRT blended with natural rubber was also evaluated by Balasubramanian [5] using the cure parameters obtained by ODR.

The method proposed in this study involves grinding of the rubber wastes and utilization of the resulting powder as a filler in elastomeric matrices. In this process, the rubber powder is incorporated into a virgin rubber matrix in the presence of curatives and various additives, and then the compound is subsequently revulcanized. This kind of rubber reutilization appears to be a viable economic alternative that is also environmentally friendly [15].

This article is a continuation of previous work in which the mechanical properties of SBR composites filled with vulcanized ground scraps of the same composition of the matrix were evaluated before and after thermal aging [16, 17]. The results obtained showed that up to 50 parts per hundred (phr) of ground rubber scraps (SBR-r) can be added to the virgin matrix without an adverse effect. Presently, the aim is to characterize the crosslink formation and kinetics of the cure reaction of these composites through oscillatory disk rheometer and DSC. Crosslink density of the cured compounds was also determined using the Flory–Rehner equation. The cure characteristics of the developed compositions with SBR ground scraps (SBR-r composites) were analyzed and compared with the control sample (base formulation with 0 phr of SBR-r).

Experimental

Materials

SBR (SBR 1502) was purchased from Petroflex Indústria e Comércio S.A. The SBR extruded profile scraps were supplied by Ciaflex Indústria de Borrachas Ltda.

(Caxias do Sul, RS, Brazil). Approximately 24 kg of scraps were collected from July 2nd to August 11th, 2007, according to ASTM E 300-03, and were ground under ambient conditions. The obtained SBR powder (SBR-r) was physically and thermally characterized in our previous study based on currently used techniques [18–20]. It presented a particle size distribution in the range of 28–35 mesh. The partial composition of the scraps, obtained by thermogravimetric analysis, was as follows: 27.6% SBR, 34.1% $CaCO_3$, 24.1% oil, 12.1% carbon black, and 2.1% other additives [16].

The base formulation was formulated following this partial composition of the scraps. The $CaCO_3$ was supplied by Indústria de Calcários Caçapava Ltda, aromatic oil from Ipiranga Química and carbon black from Evonik Industries. The compositions were prepared with conventional sulfur vulcanization system, using zinc oxide (Votorantin/Metais), stearic acid (SIM Estearina Indústria e Comércio), sulfur (RCN & Phelps Distribuidora Química Ltda), and CBS (*N*-cyclohexyl-2-benzothiazole sulfonamide) from Bann Química Ltda.

Preparation of SBR-r composites

Prior to each crosslinking analysis, the base formulation and eight formulations with different amounts of SBR-r (varying from 10 to 80 phr) were prepared in a laboratory-size, open, two-roll mill (MH, model MH-600C). The two-roll mill temperature was maintained at 50 ± 5 °C, and the mill mixing cycle followed ASTM D 3185-06 and ASTM D 3182-06. The SBR-r was incorporated to the base formulation and then the curing system was added. The compounding ingredients, such as sulfur and accelerators, as well as the time of mixing, were the same and proportional to the neat SBR in all formulations. A control sample (base formulation with 0 phr SBR-r) was also prepared and analyzed in all situations.

Cure characterization

Cure characteristics were determined through ODR and DSC.

The ODR tests were performed using a disk cure meter (Tech Pro-Rheotech OD+), at the vulcanization temperature (160 °C), according to ASTM D 2084-06. The cure rate index (CRI), which is a measure of the rate of vulcanization and related to the scorch time (t_{s1}) and optimum vulcanization time (t_{90}), was determined by:

$$\mathrm{CRI} = \frac{100}{t_{90} - t_{s1}} \tag{1}$$

The DSC analyses were carried out in order to analyze the cure kinetics of SBR-r composites. The measurements were performed in a TA Instruments DSC 2010. The samples were heated from 20 to 250 °C at 20 °C min^{-1} under a nitrogen atmosphere (70 mL min^{-1}).

The reaction conversion data ($\alpha(T)$) were obtained using the following relationship [6, 14, 21]:

$$\alpha(T) = \frac{\int_{T_o}^{T} (\mathrm{d}H/\mathrm{d}T)\mathrm{d}T}{\int_{T_o}^{T_\infty} (\mathrm{d}H/\mathrm{d}T)\mathrm{d}T} \tag{2}$$

In Eq. 2, d*H*/d*T* is the reaction enthalpy at an infinitesimal temperature (d*T*); T_o is the onset reaction temperature; T_∞ is the reaction temperature on finishing the crosslinking process; and *T* is temperature at an arbitrary time (*t*).

For the kinetics data, the empirical assumption represented by Eq. 3 was used:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{3}$$

The conversion rate ($\mathrm{d}\alpha/\mathrm{d}t$) is a linear function of a temperature-dependent rate constant (*k*) and a temperature-independent function of crosslinking conversion (α). The rate constant *k*(*T*) is generally assumed to follow the Arrhenius equation. The function $f(\alpha)$ may be expressed as a solid-state reaction, $f(\alpha) = (1 - \alpha)^n$, where *n* is the reaction order [14]. If the temperature of the sample is changed using a controlled and constant heating rate, $\phi = \mathrm{d}T/\mathrm{d}t$, the variation in the degree of conversion can be analyzed as a function of temperature, with this temperature being dependent on the heating time [6]. Therefore,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\phi}\mathrm{e}^{-E_a/RT}(1 - \alpha)^n \tag{4}$$

The *A* parameter is the pre-exponential factor and E_a is the activation energy. Considering that the parameter *n* is not constant during the reaction, a nonlinear regression is needed for the solution of Eq. 4. Here, a nonlinear regression based on the Levenberg–Marquardt method was used to solve for *A*, E_a, and *n* [22, 23].

Crosslink density

Chemical characterization of the samples involved the determination of crosslink density [*X*]. The crosslink density was obtained by a swelling experiment, using the Flory–Rehner equation [24] with the Kraus correction [25], based on the fact that vulcanized rubbers swell to equilibrium degrees when immersed in liquids [18]. This correction was distinct for each formulation, considering the variation in the elastomeric proportion and the filler content (carbon black and $CaCO_3$).

The Flory–Rehner equation relates the volume fraction of the rubber network in the swollen gel, defined by υ_r, to the crosslink concentration.

$$[X] = \frac{-[\ln(1 - \upsilon_r) + \upsilon_r + \chi\upsilon_r^2]}{V_o(\upsilon_{ro}^{1/3} - \upsilon_r/2)} \tag{5}$$

In Eq. 5, χ and V_o are the rubber–solvent interaction parameter and the molar volume of the solvent, respectively. Data from Eq. 5 were obtained from an adaptation of the swelling experiment previously described by Bilgili et al. [18]. The vulcanized samples with approximate dimensions of 20 × 20 × 2 mm^3 were immersed in *n*-heptane in the dark at 23 ± 2 °C for 7 days, and then immediately weighed to measure their swollen weights. Subsequently, the samples were dried at 60 °C under vacuum for 12 h, cooled at room temperature in a desiccator, and weighed again to find the dry weights after swelling. The differences between the swollen and the dry weights yields the weight of *n*-heptane absorbed during swelling. The SBR/*n*-heptane interaction parameter was taken as 0.59 and *n*-heptane's molar volume as 147.47 $cm^3 mol^{-1}$ [26]. The volume of the fillers was deducted from the samples to find the rubber volume. The relationship between the volume of swollen rubber and the initial volume of the rubber yields υ_r. Each swelling experiment was repeated, and an average value of [*X*] was obtained.

Results and discussions

Cure characteristics

Figure 1 shows the variation of torque values for SBR-r composites as a function of SBR-r content. In the ODR analysis, the measured torque is proportional to the system viscosity and elasticity, and the crosslinking formation is expected to increase the torque with time [14, 27]. The minimum torque is a measure of stock viscosity, and the maximum torque is related to the crosslink density.

The torque values obtained by ODR indicated that the addition of SBR-r to the composites did not significantly affect these characteristics up to 80 phr of SBR-r (Fig. 1). Minimum torque values presented only a small variation in the stock viscosity with the increase in SBR-r content. Considering that all formulations were prepared with the same mill mixing time and temperature conditions, this result indicates that the addition of SBR-r had no significantly adverse effect on processing of the compounds [8]. The same behavior was observed for the maximum torque values, which presented a slight decrease with the addition of SBR-r up to 60 phr. The ΔM values, which are related to the influence of the residue on the composites, corroborated these findings.

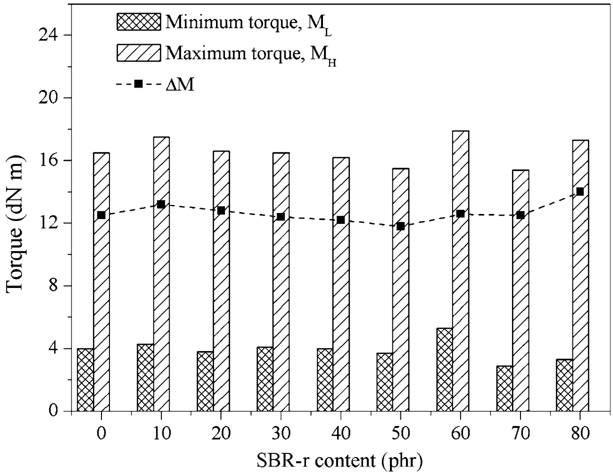

Fig. 1 Torque values of the SBR-r composites

According to Gibala and Hamed [7], sulfur added to the mixture can migrate from the matrix into the ground scrap rubber, resulting in further crosslinking of the particles (increasing modulus), as well as reducing the concentration of sulfur in the rubber matrix, thus reducing its cure state (decreasing the modulus). In addition, the lower level of crosslinks on the rubber matrix may be attributed to the relatively fewer reaction sites available for further crosslinking upon the addition of the vulcanized rubber scraps [10]. Thus, the similar torque values observed for the SBR-r composites can be related to the occurrence of both reactions. The same behavior was corroborated by DSC analysis and is discussed later.

Figure 2 shows the cure characteristics of SBR-r composites. Scorch time is the time taken for the minimum torque value to increase by one unit. It is a measure of the premature vulcanization of the material [28]. In this study, the scorch safety of the SBR-r composites did not change with the increase in SBR-r content. The optimum cure time (t_{90}) presented only a small variation with the addition of SBR-r up to 60 phr of SBR-r. For higher SBR-r content, an increase in the t_{90} values was observed. Considering that the weight of curatives was proportional to the virgin matrix, it is possible that for higher volumes of rubber, the rate of diffusion of the curatives within the matrix decreases, resulting in an increase in the t_{90} [11].

Investigations involving the cure characteristics of rubber compounds containing vulcanized rubber powder revealed that sulfur can migrate from the matrix into the rubber powder. Alternatively, it was suggested that accelerator fragments are not irreversibly bound to the scraps and might be available for subsequent crosslinking of the matrix [7, 15]. This accelerator fragment availability could lead to a faster vulcanization process. In our previous study [16], the ground rubber scraps were characterized and the DSC results showed no exothermic peak in the region of 200 °C, indicating that the amount of residual unreacted curatives was not sufficient to cause additional sample vulcanization. The absence of this exothermic peak can be attributed to heating of the samples during the grinding process, during which it

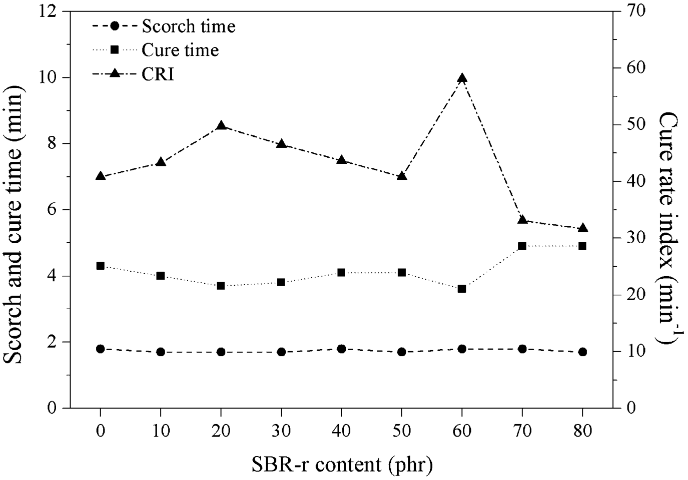

Fig. 2 Scorch time and optimum cure time of the SBR-r composites

is possible that further sample vulcanization has occurred [19]. Thus, similar scorch times and optimum vulcanization times were observed.

Relating these two characteristic times in terms of cure rate index values, a slight increase by the addition of SBR-r up to 60 phr was observed, which can be interesting for rubber processing. For higher SBR-r contents, the CRI values decreased, indicating an influence of the residue in the cure reaction. It is possible that the already crosslinked SBR-r phase acted as a physical barrier, slowing down the SBR matrix crosslink rate.

The observations on the rheometric characteristics made here are in contrast to the results obtained by several other studies in the literature [7–13]. It was found that the presence of residual sulfur and accelerators in the rubber powder caused a decrease in the scorch time and cure time, due to the migration of these curatives into the matrix. In this study, only a possible migration of the sulfur from the matrix to the SBR-r particles was observed.

Cure kinetics

The exothermic peaks in the range of 80 to 200 °C obtained by DSC (Fig. 3) are related to the crosslink reactions. From these curves, the crosslink enthalpies were determined to be proportional to the area below the exothermic peak of each sample. After the curing test, each sample was submitted to another scan in order to check for the presence of uncrosslinked material. In all cases, no thermal variation was observed, which indicates that the vulcanization reaction was completed in the first heating cycle.

The crosslink enthalpies (ΔH) along with the onset (T_o) and end set (T_e) crosslink reaction temperatures, and the maximum peak temperature (T_p), obtained by DSC are reported in Table 1.

The exothermic peak temperatures indicated that the reactions occurred at similar temperatures (Fig. 3 and Table 1). However, the onset and end set temperatures of

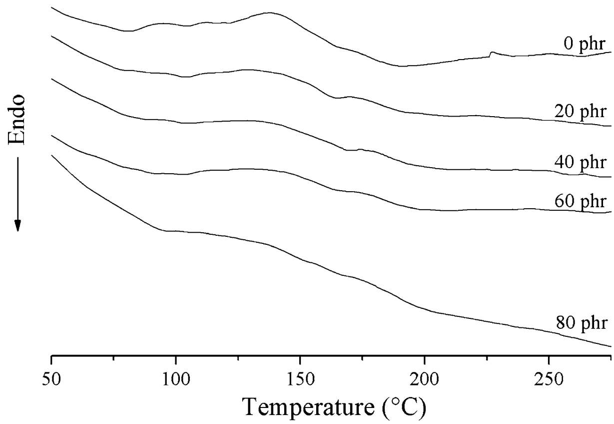

Fig. 3 DSC scans of SBR-r composites with 0, 20, 40, 60, and 80 phr of SBR-r (first run)

Table 1 Onset, peak, and end set temperatures of crosslink reactions, and enthalpy of reaction for the SBR-r composites

SBR-r (phr)	Temperature (°C)			Enthalpy ΔH (J g^{-1})
	T_o	T_p	T_e	
0	82	139	188	9.3
10	81	136	200	5.6
20	83	140	194	5.2
30	92	140	200	5.0
40	88	139	200	4.9
50	90	136	200	4.9
60	101	143	200	4.9
70	98	134	204	5.6
80	94	137	205	5.9

T_o onset reaction temperature, T_p peak temperature, T_e end set reaction temperature

SBR-r composites showed that as the SBR-r content increased, the crosslink reactions occurred at higher temperatures. The addition of SBR-r led to a general decrease in the reaction enthalpy values. It is possible to attribute this to the sulfur and accelerators incorporated during the compounding, which could enhance the crosslink reactions in the particles. Another factor that can contribute to this relationship is agglomeration and hence particle–particle interaction, which can cause the confinement of sulfur/curatives within the residues, leading to the decrease in rubber matrix vulcanization.

The crosslink conversion curves as a function of temperature ($\alpha(T)$) for SBR-r composites containing 0, 20, 40, 60, and 80 phr of SBR-r are presented in Fig. 4. All curves showed a sigmoidal shape, indicating fast crosslink processes during the initial stages. As described above, for higher SBR-r contents, the reaction occurred at higher temperatures. Also, the samples containing higher amounts of SBR-r showed longer times for the reaction induction, that is, a slower crosslinking rate in the SBR-r composites.

The kinetic parameters of SBR-r composites obtained by Eq. 4 are presented in Table 2. It was observed that, in general, the nonlinear predictions and the experimental results presented a close agreement up to 60 phr of SBR-r.

The kinetic parameters showed an increase in the parameter A, which is related to the crosslink rate. The same trend was observed for the activation energy (E_a) and reaction order (n) values, which slightly increased with the increase in SBR-r content up to 70 phr, except for the samples containing 30 and 40 phr of SBR-r, which presented similar values to the control sample. In this reaction, the activation energy reflects the energetic barrier of the reaction, as well as the diffusion of the reactants in the bulk [6, 14]. The increase in the bulk viscosity and consequently the reduced mobility of the elastomeric matrix during the reaction can hinder the crosslink growth, thereby increasing the E_a values [6]. Therefore, more energy is required for the curing of SBR-r composites. Moreover, the increase in the reaction order values indicated a change in the mechanism of reaction, which is related to the higher complexity of the crosslink reaction due to the scrap rubber.

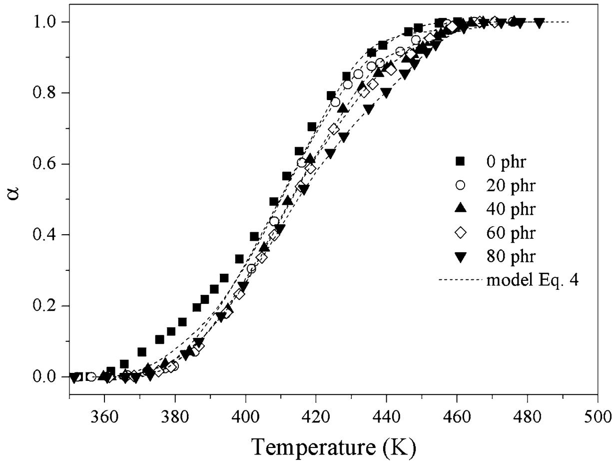

Fig. 4 Crosslink conversion (α) of SBR-r composites as a function of temperature. The *scattered points* correspond to the experimental data and the *dotted line* corresponds to the regression fitting, according to model Eq. 4

Table 2 Kinetic parameters of SBR-r composites

SBR-r (phr)	A (s^{-1})	E_a (kJ mol^{-1})	*n*	*r*
0	1.63×10^{9}	72.7	1.18	0.9913
10	8.98×10^{9}	78.0	1.71	0.9606
20	1.56×10^{11}	87.4	1.40	0.9745
30	5.73×10^{8}	69.2	1.25	0.9781
40	4.28×10^{8}	68.8	1.23	0.9097
50	1.14×10^{12}	93.2	1.68	0.9910
60	7.77×10^{10}	85.6	1.69	0.9899
70	1.52×10^{11}	87.3	1.94	0.9279
80	3.70×10^{6}	53.8	1.13	0.9058

Crosslink density

The most important structural property of vulcanized rubber is the number of moles of the sulfur crosslinks per unit volume of the rubber, namely, crosslink density. Crosslinking generally restricts the degree of swelling in polymers. Therefore, its determination is based on the absorption of a proper solvent and subsequent swelling of the rubber [18, 27]. Table 3 reports the variations of crosslink density of SBR-r composites as a function of the SBR-r content.

The incorporation of rubber scraps slightly decreased the crosslink density up to 60 phr of SBR-r (Table 3). For higher SBR-r content, the values were similar to the control sample. These findings corroborate the torque values obtained by the rheometric analysis and by the DSC results. This finding suggested that the change in crosslink density was more dependent on the vulcanizing recipe, which was kept constant, rather than on the SBR-r content.

Table 3 Crosslink density of the SBR-r composites

SBR-r content (phr)	Crosslink density ($\times 10^{-4}$) (mol cm^{-3})
0	1.13 ± 0.018
10	1.12 ± 0.042
20	1.06 ± 0.008
30	1.07 ± 0.003
40	1.09 ± 0.051
50	1.14 ± 0.039
60	1.02 ± 0.047
70	1.15 ± 0.050
80	1.13 ± 0.024

Conclusions

In this study, the cure reaction of composites with SBR scraps was studied by ODR and DSC analysis. The ODR results indicated that incorporation of rubber powder did not significantly affect the cure characteristics of the composites. Scorch and cure time were only affected at higher SBR-r content. DSC analysis indicated that the SBR-r altered the crosslinking kinetics of SBR-r composites. The samples with higher SBR-r content reacted at elevated temperatures. This can be related to the reduced mobility of rubber chains with the addition of SBR-r. The partially crosslinked SBR-r phase acted as a physical barrier, increasing the complexity of the cure reaction. Nonlinear adjustment was successfully applied for fitting the cure reaction curve up to 60 phr of SBR-r, and may be used to assess the best conditions for vulcanization of the developed compounds.

Acknowledgments The authors are grateful to Ciaflex Indústria de Borrachas Ltda. for supplying the SBR rubber scraps, additives, and the control sample, and to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), to Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS—PqG 06/2010 1006663), and to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for their financial support.

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