NATURAL RUBBER COMPOSITES WITH HYDROCHAR AS A PARTIAL FILLER: INVESTIGATION OF KINETIC PARAMETERS

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ABSTRACT:
Reducing the environmental impact of the rubber industry has emerged as a major challenge, and one potential solution that has garnered significant attention is incorporating hydrochar as a partial filler in natural rubber composites. Hydrochar was obtained through hydrothermal carbonization treatment of hardwood waste biomass, and it has been found to have potential as a sustainable alternative to traditional filler carbon black. The aim of this study was to investigate the effect of varying hydrochar and carbon black content in natural rubber composites, while keeping the total filler amount constant at 50 phr. The study's findings indicated that higher hydrochar content resulted in a greater curing activation energy, facilitating the manufacture of larger natural rubber vulcanizates that required extended curing periods at reduced temperatures. The rubber industry's stringent environmental regulations have created a pressing need for sustainable alternatives, and incorporating hydrochar as a partial filler could offer a promising solution by repurposing waste materials into a valuable component for rubber composites.

KEYWORDS: hydrochar, hydrothermal carbonization, natural rubber composites, kinetic parameters

INTRODUCTION

The fossil fuels increasing consumption and huge dependence on them have become the pressing issues of 21st century [1]. The measures are taken in order to reduce the dependence on fossil fuels, where the first one is exploring renewable industrial products, and second is recycling and reusing waste. Products made from natural rubber find widespread use in a diverse range of applications, and typically, they are strengthened using nanofillers, with carbon black being a common choice [2]-[5]. Carbon black is widely used in rubber products due to its high purity and low cost, although its production is highly dependent on fossil fuels [6], [7]. As public awareness and pressure to reduce reliance on fossil fuels has intensified in recent decades, bio-sourced materials have gained attention as eco-friendly substitutes for petroleum-based reinforcing fillers [8]-[11]. Using waste as a source for production of hydrochar obtained by hydrothermal carbonization (HTC), for partially replacing the carbon black, as a traditionally used filler in rubber composites, is preferred. HTC presents a means of carbonizing biomass with high water content at lower temperatures than pyrolysis, resulting in the production of hydrochar, which is similar to carbon black in its properties and structure. Hydrothermal carbonization has emerged as a green, non-toxic, cheap, and environmentally benign process, which is simple to implement and does not require pre-treatment of biomass. Hydrochar is expected to degrade the rubber products properties since it has larger particles and there is a necessity for its milling [12]. Based on literature review, it was revealed that hardwood waste was most used for obtaining hydrochar, due to lower ash and higher carbon content, comparing to other feedstocks [13], [14].

In this study, the natural rubber samples with different hydrochar and carbon black content were prepared, and the total amount of the filler was 50 phr, while the amount of other additives was kept constant. Rheological curves of all prepared samples were obtained, in order to investigate the samples' kinetic parameters. The fitting procedure from previously published paper enabled calculating the kinetic parameters of all prepared samples, i.e., curing and reversion energy activation, Arrhenius pre-exponential factor and curing and reversion rate constants. The kinetic parameters provided valuable insights into the potential applications of the prepared samples in the production of large-scale natural rubber composites.

MATERIALS AND METHODS

MATERIALS

Natural rubber, standard Vietnamese rubber SVR CV60, crosslinking agent sulfur (S), carbon black (CB) and hydrochar (HC) as fillers, N-cyclohexylbenzothiazol-2-sulfenamide (CBS) as accelerator, crosslinking activators zinc oxide (ZnO) and stearic acid, as well as antioxidant N-isopropyl-N’-phenyl-p-phenylenediamine (IPPD), were obtained from Edos (Zrenjanin, Republic of Serbia). All raw materials used in the work, except for hydrochar, are commercially used in the rubber industry.

Hydrochar was obtained by hydrothermal carbonization of waste biomass from hardwood, which was conducted at 300 °C and 86.6 bar, during 30 min [15]. The obtained hydrochar was milled in a Fritch planetary mill at 200 revolutions per minute, for 5 min. The ground biochar particles were sieved from 500 to 800 μm, and washed with warm deionized water, until the dark leachate stopped separating [16]. In the rubber industry, the relative composition of the rubber mixture is expressed by considering that the basic ingredient of the mixture is the amount of natural rubber and is denoted by 100, while the amount of other components is represented in relation to the amount of rubber, and thus, obtained unit is denoted by phr (parts per hundred rubber).

In order to examine the possibility of partially replacing carbon black with an environmentally friendly filler, carbon black and hydrochar were mixed together in the rubber mixture, and the content of the two fillers was varied, where the total filler content was 50 phr. The content of the other components was not varied, and the samples were labelled as presented in Table 1.

Table 1. Samples labelling

Samples label	Description
VCB10	Vulcanized sample with 10 phr carbon black and 40 phr hydrochar
VCB20	Vulcanized sample with 20 phr carbon black and 30 phr hydrochar
VCB30	Vulcanized sample with 30 phr carbon black and 20 phr hydrochar
VCB40	Vulcanized sample with 40 phr carbon black and 10 phr hydrochar
VCB50	Vulcanized sample with 50 phr carbon black and 0 phr hydrochar

The recipe for obtaining samples of the rubber mixture is shown in Table 2, as explained in detail in previously published work [15]. The presented values of components are determined ensuring that the filling factor of the mixing chamber is 0.75, where the filling factor of the chamber represents the ratio of the volume of the mixture to the volume of the empty mixer chamber.

Table 2. Recipe for obtaining rubber mixture samples

Components	phr
NR	100
CB/HC	50*
ZnO	4
Stearin	1
IPPD	1
Sulphur	2.5
CBS	0.5

* The amount of CB and HC was varied according to Table 1, and the total amount of the filler was 50 phr.

The components shown in Table 2 are usually divided into inactive and active, where carbon black, hydrochar, ZnO, stearic acid and IPPD are inactive, and sulphur and CBS are active components.

RUBBER MIXING COMPOUND

A HAAKE Rheomix mixer (model 600) with a Rheocord EU-5 drive unit and "CAM" type mixers, manufactured by HAAKE, Germany, was used to mix the components of the rubber mixture. In order to ensure isothermal mixing, it was necessary to heat the mixer for 10 minutes, before adding the components, as well as a constant temperature of 90 °C in all zones, with the included air supply that ensures cooling and temperature maintenance.

Mixing was described in detail in previously published paper [17]. The first phase is idle, i.e., the mixer is set on rotation mixer rotor speed of 30 s^{-1}. After first part, the measured natural rubber is added to the chamber, the rotor speed is increased to 100 s^{-1} during three minutes, then the speed is reduced to 60 s^{-1} during three minutes. During the second and third phase, when only the rubber is mixed, its mastication occurs, which enables a greater dispersion of the mixture components during the following stages. In the fourth phase, at the same rotor speed, inactive components of the rubber mixture are added, i.e., fillers (CB and HC), zinc oxide, stearin and IPPD, and mixed for five minutes. In the last mixing phase, the active components, sulphur and CBS, are added and mixed for 2 min, at the same rotor speed. The specified mixing procedure enables optimal dispersion of all components and distribution of fillers in the polymer matrix. The resulting mixture is cooled and stored in a cold place until vulcanization is performed, at least 24 h, in order to ensure conditioning [18].

RHEOLOGICAL PROPERTIES

The rheological properties of the rubber mixtures were monitored using an oscillatory rheometer MDR-A Rotorless Rheometer, manufactured by Beijing Rade Instrument co., Ltd. The rheological properties of prepared samples were tested at 130-180 °C, with a step of 10 °C, in order to examine samples reversion phenomena. An oscillatory rheometer enables vulcanization monitoring by placing a rubber mixture sample between two disks, which oscillate with a small rotational amplitude causing material shear deformation. The torque that is necessary for the oscillation of the disc depends on the resistance to deformation, i.e., of the rubber shear modulus, and is monitored by an oscillating rheometer as a function of time.

FITTING PROCEDURE

The fitting procedure was explained in detail in research [19]. Crosslinking and reversion are considered as two parallel phenomena of complex vulcanization, where curing and reversion degree are calculated as following:

$$\alpha_c = 1 - \frac{1}{1+(k_c t)^n} \tag{1}$$

$$\alpha_r = x(1-e^{-k_r t}) \tag{2}$$

Where α_c and α_r are the curing and reversion degree, k_c and k_r are curing and reversion constants (s^{-1}), respectively, n is the reaction order, t is vulcanization time and x is the maximal reversion degree, temperature-dependent parameter. The curing and reversion constants have an Arrhenius dependence on temperature, whereas the temperature increases, the rate of the chemical reaction also increases, as shown by the following equation:

$$k_{c,r} = A_{c,r} \exp\left(\frac{-E_{ac,r}}{R_g T}\right) \tag{3}$$

Where $A_{c,r}$ represents the pre-exponential factor, $E_{ac,r}$ is the activation energy ($Jmol^{-1}$), for curing and revesion, respectively, R_g is the universal gas constant ($8.314\ Jmol^{-1}K^{-1}$) and T is the absolute temperature (K).

Experimentally obtained rheological data of the torque depending on time are available, for the purposes of fitting the experimental data, there is a necessity to define the form for calculating curing and reversion degree, as presented:

$$\alpha_c = \frac{M_c - M_0}{M_{Max} - M_0} \tag{4}$$

$$\alpha_r = \frac{M_{Max} - M_r}{M_{Max} - M_0} \tag{5}$$

Where M_c and M_r are the curing and reversion torques (dNm), respectively. Equation (5) is an indication that the rubber mixture vulcanization is defined as partially reversible, due to M_r not equal to M_0.

When the Equations (4) and (5) are included in (1) and (2), respectively, the integral forms of the model, modified for fitting the rheological data, can be obtained:

$$M_c = M_{Max} - \frac{M_{Max} - M_0}{1+(k_c t)^n} \tag{6}$$

$$M_r = M_{Max} - (M_{Max} - M_{Rev})(1 - e^{-k_r t}) \tag{7}$$

As curing and reversion reactions take place simultaneously, and the following general equation can be written for the vulcanization reaction:

$$M = M_c - M_r \tag{8}$$

Where M is the vulcanization torque (dNm). In order to define the final dependence of the torque on time, the Equations (6) and (7) were included in the Equation (8), and the following integral form of the equation describing the complete vulcanization can be obtained:

$$M = M_{Max} - \frac{M_{Max} - M_0}{1+(k_c t)^n} - (M_{Max} - M_{Rev})(1 - e^{-k_r t}) \tag{9}$$

The vulcanization data was divided into two separate fitting sets, where curing include part before experimentally obtained maximal torque and reversion part after it. The first step represented fitting the reversion with the Equation (6), which resulted in three parameters, i.e., maximal model torque (M_{Max}), model torque asymptote (M_{Rev}) and reversion rate constant (k_r). The initial values for the fitting parameters M_{Max}, M_{Rev}, and k_r were M_{MaxExp}, M_{RevExp}, and $\ln\left(\frac{1}{2}\right)/t_{hr}$, respectively. The initial fitting parameters were selected as experimentally obtained values, where M_{RevExp} was the experimentally obtained final torque, M_{MaxExp} was experimental maximal torque and t_{hr} was the time required to reach half of the experimentally obtained reversion value. After fitting the reversion and determining the model maximal torque, the model was fitted using Equation (5), where the reaction order (n) was the only adjustable fitted parameter, and the value 1 was taken as its initial value, while the initial torque (M_0) and the curing rate constant (k_c) were fixed parameters, obtained directly from experimental data [19]. The fitting of the vulcanization curve was performed by the least squares method.

DATA ANALYSIS AND PROCESSING

The collection, processing, analysis and display of results were performed using the computer program MATLAB (The Math Works Inc. License number 1108951). The quality of fitting is determined by statistical methods, i.e., using two methods, the mean absolute percentage error (*MAPE*), and coefficient of determination (R^2). The mean absolute percentage error and the coefficient of determination are calculated according to the equations:

$$MAPE = \frac{1}{m}\sum_{i=1}^{m}\left|\frac{y-\hat{y}}{2}\right| \qquad (10)$$

$$R^2 = 1 - \frac{\sum(y-\hat{y})^2}{\sum(y-\bar{y})^2} \qquad (11)$$

Where m is the number of fitted points, y is the actual (experimental) value, $\hat{y}$ is the predicted value, and $\bar{y}$ is equal to $\frac{\sum y}{m}$.

RESULTS AND DISCUSSION

RHEOLOGICAL PROPERTIES OF RUBBER MIXTURES WITH HYDROCHAR AS A FILLER

Rheometric vulcanization curves are presented at 160 °C for 2 h, in order to compare the effect of hydrochar on crosslinking and reversion (Figure 1).

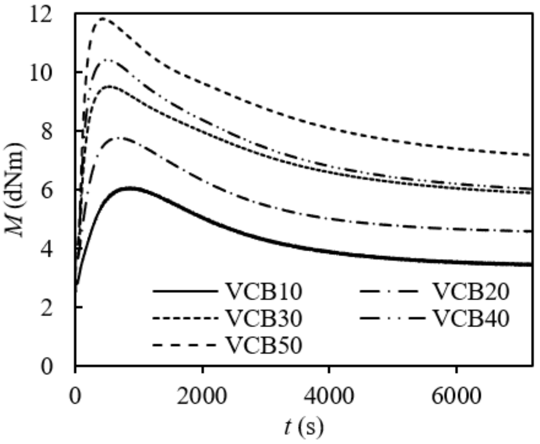

Figure 1. Vulcanization rheometric curves of rubber samples at 160 °C

Slower crosslinking with a higher hydrochar content can be seen in Figure 1. Sample VCB10, which consists 40 phr of hydrochar, reaches a maximum torque of 6.37 dNm, while in contrast, the sample without hydrochar (VCB50) reaches a value of 12.31 dNm, which is almost twice as high. Additionally, it can be noted that the filler type does not significantly affect the reversion of rubber compounds. The rheometric curves for samples containing hydrochar were recorded at all tested vulcanization temperatures for a duration of 2 hours to determine the kinetic parameters. However, only at 160 °C were presented for simplified explanation.

FITTING OF RUBBER COMPOUNDS WITH HYDROCHAR AS A FILLER

The described fitting procedure for rubber compounds was applied to determine the vulcanization parameters of rubber compounds with the addition of different hydrochar content, and the results and quality of fitting are presented in Table 3-

Table 3. Fitting quality

Sample	Parameter	*A*	R^2	*MAPE*
VCB10	k_u	2.653E08	0.9998	6.173
	k_r	7.86E14	0.9874	10.281
VCB20	k_u	1.75E8	0.998	4.819
	k_r	5.705E14	0.9985	9.581
VCB30	$\mathrm{k_u}$	2.281E8	0.9997	2.18
	k_r	4.625E14	0.9997	3.918
VCB40	k_u	1.56E8	0.9998	1.994
	k_r	4.463E14	0.9784	7.971
VCB50	k_u	2.357E8	0.9997	2.004
	k_r	5.166E8	0.9796	7.653

The curing and reversion activation energies of prepared samples with different hydrochar content are presented in Figures 2 and 3.

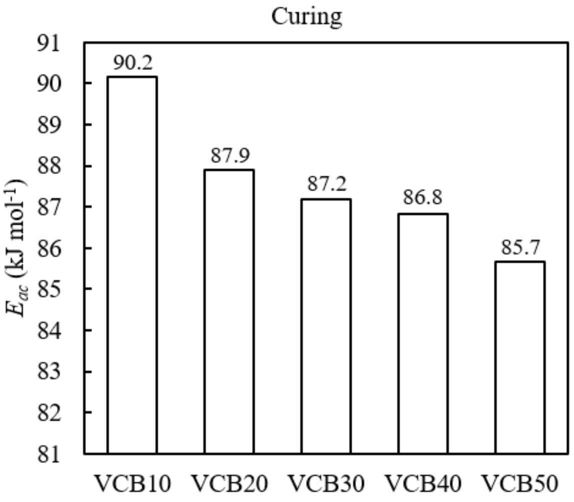

Figure 2. Effect of hydrochar content on curing activation energy

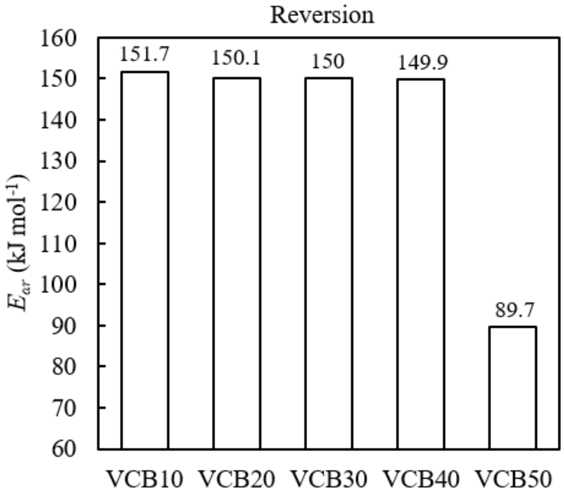

Figure 3. Effect of hydrochar content on reversion activation energy

The crosslinking and reversion rate constants were obtained by fitting Equation 7. As a high quality of crosslinking and reversion parameters was obtained, the results for all tested samples are shown in Figures 4-8.

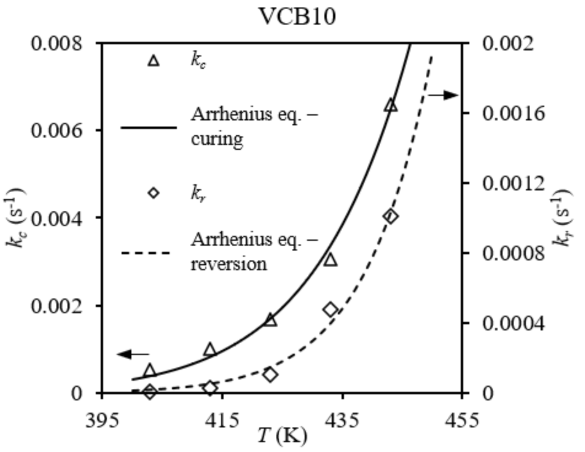

Figure 4. Dependence of curing and reversion rate constants on temperature, for the sample VCB10

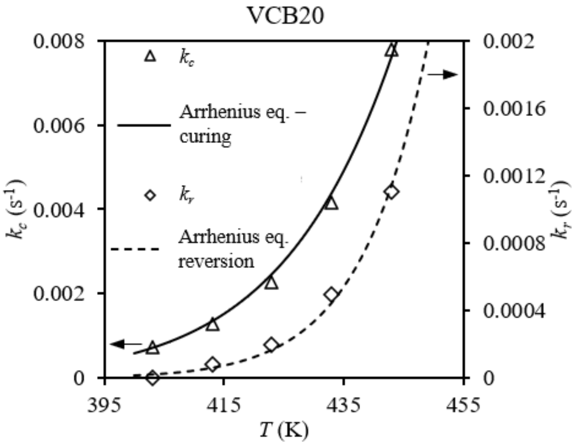

Figure 5. Dependence of curing and reversion rate constants on temperature, for the sample VCB20

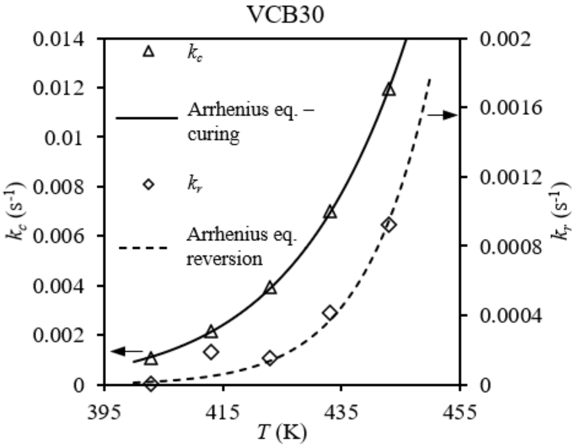

Figure 6. Dependence of curing and reversion rate constants on temperature, for the sample VCB30

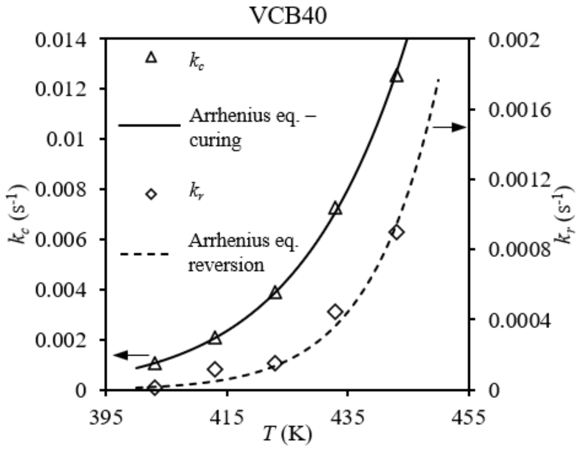

Figure 7. Dependence of curing and reversion rate constants on temperature, for the sample VCB40

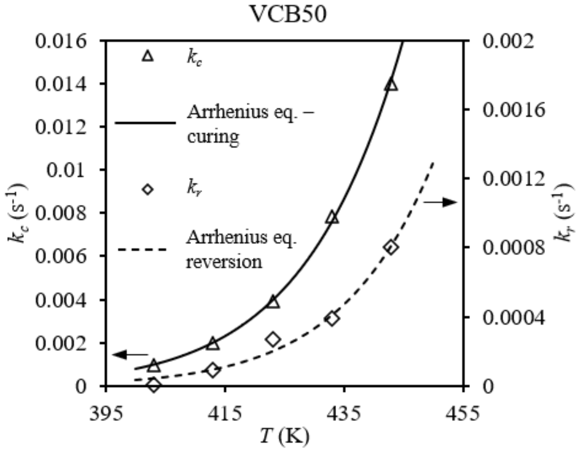

Figure 8. Dependence of curing and reversion rate constants on temperature, for the sample VCB50

Commercially available fillers used in the rubber industry reduce the amount of rubber necessary to obtain quality products, and therefore lower the price of final products. Fillers can be used to affect the course of vulcanization and the properties of the final product, and these are called active fillers, due to the functional groups on the surface of their particles. Active fillers increase the vulcanization rate and reduce the curing activation energy, thereby reducing the energy barrier for the beginning of the process [20]. Therefore, active fillers participate in the creation of polysulfide bridges in the rubber structure, contributing to the formation of a three-dimensional network. Inactive fillers can have the opposite effect on vulcanization, by increasing the activation energy and reducing the vulcanization rate, which can also be a consequence of the filler particles size [21]. In this research, a commercially available filler, activated carbon black and hydrochar obtained by hydrothermal carbonization of hardwood waste biomass were used. Observing the rate constants of products with different hydrochar content, it can be seen that the hydrochar addition reduces the curing rate constant, while it has no significant effect on the reversion rate constant. The curing activation energy increases with increasing hydrochar content, where the product without hydrochar has the lowest curing activation energy (Figure 2). The reversion activation energy is significantly lower for the rubber mixture without hydrochar, compared to products containing bio-filler (Figure 3). It is observed that the curing activation energy values are lower than the reversion activation energy for the same rubber samples, which is in accordance with literature data [21]. The lower curing activation energy of rubber compounds with the addition of hydrochar does not necessarily represent their negative property. Early start of vulcanization is often a problem in the rubber industry, which occurs even before the rubber mixture is distributed in the mould. Higher activation energy values delay the vulcanization beginning, and the hydrochar addition to the rubber mixture can reduce the risk of beginning the curing reaction before the mixture has the proper form in the mould, for which curing retarders are used. Postponing the beginning of curing is especially important for large-sized products, where curing of the surface next to the mould occurs, as well as reversion, while the interior is not yet cured [20]. A delayed start of vulcanization and a "stretched" shape of the process S-curve was observed in the sample with the highest hydrochar content (Figure 1), which makes this sample suitable for the production of large rubber products. The possibility of using hydrochar as a partial filler in the rubber mixture opens up the possibility of a gradual transition to bio-fillers, which can lead to a reduction of the problem of gases with the greenhouse effect, but at the same time the dependence on fossil fuels is also reduced, using sustainable bio-fillers.

CONCLUSIONS

Hydrochar and carbon black-based natural rubber mixtures were prepared, to investigate the influence of filler type and content on the kinetic parameters. A comparison of vulcanization parameters revealed that the bio-filler has impact on the vulcanization kinetic, in the way to lower the maximal vulcanization torque, while does not affect reversion phenomena. Furthermore, the increment of hydrochar content led to higher curing activation energy, presenting the products with hydrochar suitable composite material for production of large rubber products that needs longer time at low temperatures to be cured. On the other hand, an increase in the curing activation energy with the addition of hydrochar as a filler would represent a negative property during the production of rubber products of smaller dimensions.

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