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Comparative study of three vulcanization kinetic models for natural rubber/leather wastes composites

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Abstract

In this article, the effect of leather residues from chrome tanning on the vulcanization kinetics and rheometric properties of a natural rubber composite was evaluated using three kinetic models proposed in the literature. Leather wastes were classified according to their size as fine (smaller than 0.6 mm) or coarse (between 0.84 and 2 mm). Subsequently, they were chemically treated with a sodium bicarbonate solution to neutralize their acidic nature derived from the tanning processes. The composites studied in this paper were obtained using a torque rheometer. Fine and coarse leather wastes were added to a natural rubber matrix in proportions of 20, 40, 60, 80, and 100 phr. The rheometric properties of all the composites were monitored during the curing process using a moving die rheometer. The addition of leather wastes increased the vulcanization time and stiffness of the composites; however, materials with fine leather wastes achieved lower vulcanization times than materials with coarse residues. The curves obtained during vulcanization rheometry were fitted to the three kinetic models, which made it possible to determine the kinetic parameters k and n. The fits for the three models were satisfactory based on the R-squared results. The values and trends of the kinetic parameters of each model were analyzed and related to the vulcanization phenomenon of each composite.

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Introduction

The incorporation of residues in an elastomeric material can produce different technical responses in the composites, which depend on several characteristics of the residues, such as size distribution, shape, and chemical nature. Therefore, to understand the effects of adding post-industrial leather waste to natural rubber composites, it is important to know their physicochemical nature and the processes used to obtain them.[1-6]

During the vulcanization reaction, rubber compounds undergo alterations in some mechanical properties, such as hardness, resistance, and elastic modulus. By understanding this principle, it is possible to measure the change in the torque generated in the rubber composites as the vulcanization reaction takes place, i.e., as a function of time and at a set temperature. The technique known as vulcanization rheometry is useful to monitor the vulcanization reaction due to the formation of elastically active bonds between the rubber chains.[7-11]

The strong acids used in the leather tanning process can influence the vulcanization reaction of natural rubber compounds. These chemical modifications must be taken into account when designing rubber/leather waste compounds.[3,8] Consequently, studies have been carried out to analyze post-industrial leather wastes after subjecting them to chemical neutralization treatments to reduce their acidic nature and minimize the effect of such acidity on the rubber vulcanization process.[2,12,13]

Vulcanization rheometry provides information on the times and torques generated before, during, and after the formation of crosslinks. At the end of the reaction, the torque can be stabilized, increased (marching curve), or decreased after having reached its maximum value; a phenomenon known as reversion, which is directly related to the desulfurization of the composites.[7,11,14]

Different kinetic models have been used to predict the behavior of rubber compounds during the curing process. They have also been useful to establish some parameters that improve the understanding of factors such as the kinetics of the curing process and the order of the reactions that take place during the curing of elastomeric and thermosetting polymers.[15-22] Likewise, kinetic models have been employed in curing processes occurring under both isothermal and non-isothermal conditions. Moreover, some of them have been implemented by fitting experimental data obtained during vulcanization rheometry or differential scanning calorimetry (DSC) tests.[15,16,18,21,22]

The kinetic models developed to predict the curing process of elastomers and thermosets can be classified into two main groups: empirical models and mechanistic models. The empirical models are based on regression models, where the experimental measurements obtained from different tests are fitted. The mechanistic models, for their part, are based on the construction of complex equations that represent the physical and chemical phenomena that occur during the vulcanization process.[17,20-22]

In this study, a comparative analysis of the rheological properties of vulcanization and the kinetic parameters obtained by fitting the kinetic models proposed by Isayev and Deng, Kamal and Sourour, and Rafei et al. was performed. The analysis considered the particle size and the leather waste content previously treated with a sodium bicarbonate solution.

Experimental Section

Materials

First, the post-industrial leather wastes were chemically treated for 2 h with a 1% w/v aqueous sodium bicarbonate solution, thus neutralizing the chromium salts from the tanning process. Subsequently, the wastes were dried at 105°C for 12 h. The natural rubber was not prepared before mixing the composites. The rest of the additives used in the formulation (i.e., zinc oxide, stearic acid, and *N*-t-butyl-2-benzothiazole sulfenamide-TBBS) were of commercial grade. The leather wastes were classified by size ranges as fine when the particles were smaller than 0.6 mm and as coarse when the particles were between 0.84 and 2 mm.

Microscopy and chemical analysis

The morphology and fiber structure of the fine and coarse leather wastes were analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) on a JEOL JSM-6490LV scanning electron microscope. In addition, wastes of different sizes were compared and the effect of the chemical treatment with sodium bicarbonate was evaluated.

Preparation of the composites

The composites were obtained by incorporating the different ingredients into the natural rubber matrix according to the formulation described in ASTM D3182 and using a torque rheometer with Banbury-type rotors (HAAKE PolyLab OS Rheodrive 7 internal mixer). Subsequently, the fine and coarse leather wastes were incorporated in proportions of 20, 40, 60, 80, and 100 phr. Afterwards, the activation system (*6-phr zinc oxide* and *0.5-phr stearic acid*) was added. The sulfur-based vulcanization system (*3.5-phr sulfur* and *0.7-phr TBBS*) was then incorporated using an open two-roll mill. Finally, the reaction and vulcanization kinetics of the composites were evaluated.

Rheometric test and fitting to the vulcanization kinetic models

The vulcanization reaction can be monitored using different methods, including isothermal rheometric tests carried out on vulcanization rheometers according to ASTM D5289.[23] Using this type of test, the induction and optimum vulcanization times (t_0 and t_{100}, respectively) of the rubber composites can be analyzed at isothermal temperatures that depend on their composition (the temperature used in the tests was 150°C). The data

obtained in the test were transformed into a degree of cure (θ), as a function of torque and time, using equation (1).

$$\theta = (M_t - M_i)/(M_h - M_i) \tag{1}$$

Where M_t is the torque as a function of time, M_h is the maximum torque, and M_i is the minimum torque. All these parameters were evaluated during vulcanization rheometry; therefore, the progress of the vulcanization reaction can be observed from the beginning to the end.

The kinetic parameters of the vulcanization reaction—which have been monitored by vulcanization rheometry—can be obtained from the evaluation of the degree of experimental cure (θ). To this end, vulcanization kinetic models proposed by different authors must be implemented.

For the present study, the experimental data of the degree of cure were fitted to the kinetic models by Isayev and Deng,[16] Kamal and Sourour,[15] and Rafei et al.[17] Similarly, the kinetic parameters of the reaction progress were obtained by fitting the experimental data to the isothermal curing models proposed by the same authors (Equations (2)-(4)). The model by Rafei et al. was also used under non-isothermal conditions. In addition, an optimization algorithm in Python was employed to achieve the fit of the degree of cure curves, and the function used a non-linear least squares method. Furthermore, the trust region reflective (TRR) method was proposed to solve problems that required limits, since it iteratively solves subproblems by means of a diagonal quadratic term.[24]

$$\theta_{model\ I\&D} = \frac{kt^n}{(1 + kt^n)} \tag{2}$$

$$\theta_{model\ K\&S} = \frac{[k(t - t_0)]^n}{1 + [k(t - t_0)]^n} \tag{3}$$

$$\theta_{model\ R\ et\ al.} = \frac{\theta_0 - b}{1 + \left[\frac{t - t_0}{k}\right]^n} + b \tag{4}$$

Where k is the reaction rate, n is the reaction order for all models, and t_0 is the induction time. In the model by Rafei et al., θ_0 is the degree of cross-linking at the beginning of the observation and b is the degree of cross-linking at the end of the observation. To fit the model, 0 and 1 were used, respectively.

Results and discussion

Microscopy and chemical analysis

The morphological tests revealed the structure of the leather wastes. A mainly fibrillar structure with partial agglomeration was observed. The fibers of the fine and coarse leather wastes analyzed at magnifications of ×500 and ×2500 did not present significant differences. Figure 1 shows the micrographs of the fine and coarse leather wastes. The leather fibers had white

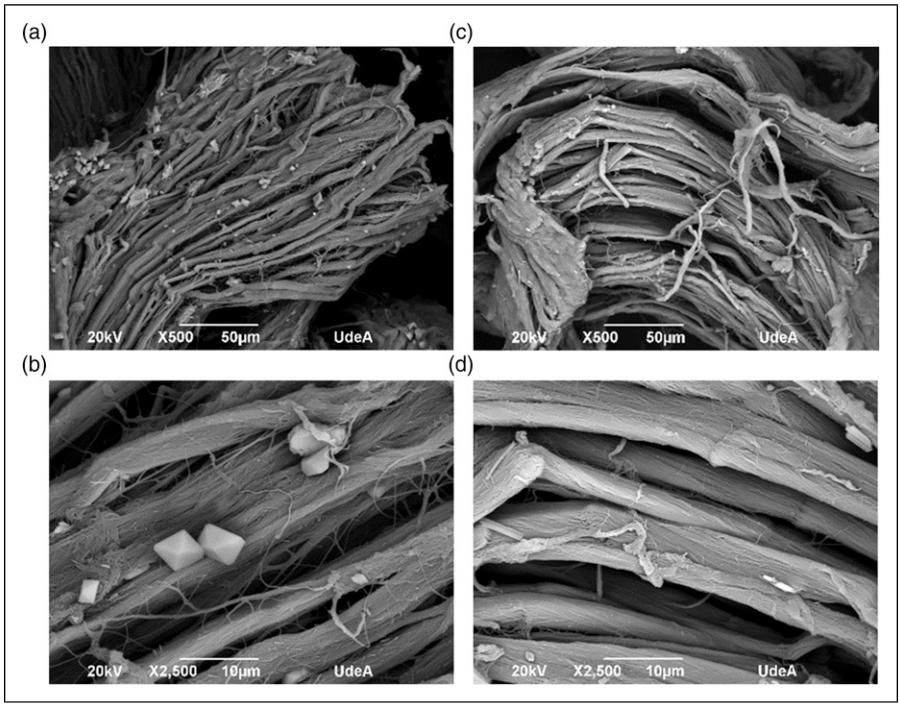

Figure 1. Micrographs at different magnifications (scanning electron microscopy). Untreated coarse (a,b) and fine (c,d) leather wastes.

particles that correspond to residues from the tanning process with chromium salts and that were later removed in the chemical treatment with sodium bicarbonate.[2,25]

The fibrillar structure of the leather residues remained after the neutralization process. In addition, the white particles associated with the tanning process decreased. In EDS spectra shown in previous studies,[2,25] a decrease in the peaks corresponding to Cl and Cr was observed, thus proving the effectiveness of the neutralization process.

Composite vulcanization times

Based on the results from the vulcanization rheometries of the different natural rubber/leather waste composites, the main parameters of the vulcanization process were identified. The induction (t_0) and vulcanization (t_{100}) times were influenced by the addition of different amounts of leather waste. Figure 2 shows the behavior of the induction and vulcanization times of the different composites. Note that, as the amount of fine and coarse leather wastes increased, t_0 decreased. Furthermore, coarse wastes caused an increase in t_0 with respect to the rubber composite without leather waste. In any case, coarse leather wastes led to a longer delay in the induction time compared to fine residues. In other words, by adding leather wastes, regardless of their size and quantity, the t_{100}

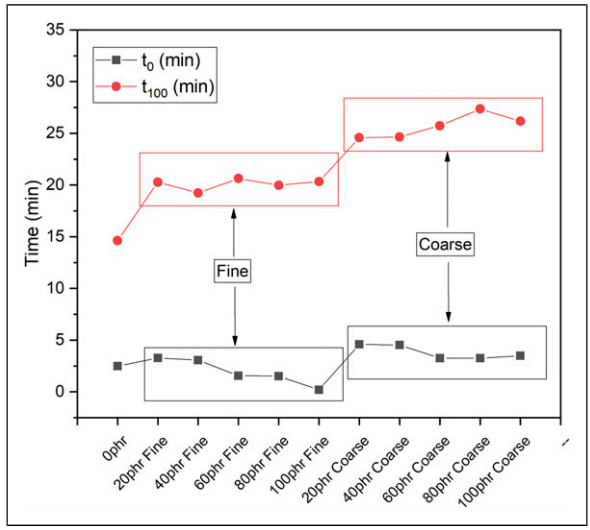

Figure 2. Induction (t_0) and vulcanization (t_{100}) times of natural rubber composites with fine and coarse leather wastes.

increased with respect to the composite without leather wastes. The effect, however, was more significant for composites with coarse leather residues.

The difference between the vulcanization (t_{100}) and induction times (t_0) obtained by vulcanization rheometry made it possible to determine the real time during which the vulcanization reactions that form elastically active bonds took place. Figure 3 shows the behavior of t_{100}-t_0 when different sizes and amounts of leather wastes were added. The addition of leather wastes increased the vulcanization times, the effect being stronger for the composites with coarse leather wastes. Moreover, an increasing trend towards the difference of t_{100}—t_0 was observed as the amount of leather wastes increased.

Fit of the vulcanization kinetic models

Initially, the degree of cure (θ) was calculated as a function of time for all the composites containing fine and coarse leather wastes. The curves of all the composites had an S-type behavior, which can be divided into three main zones: induction, vulcanization, and post-curing.[16,20] The values of the degree of cure started at 0 and ended at 1—which corresponds to the time in which the vulcanization reaction has already completely occurred. The vulcanization kinetic models proposed by Isayev and Deng, Kamal and Sourour, and Rafei et al. were fitted to the experimental data of the degree of cure employing Equations (2)-(4), respectively. The fit yielded the parameters k and n for all the composites. Figure 4 shows the fit of the three models with the experimental data of the degree of cure of the composite made with natural rubber and 40 phr of fine leather wastes. For all cases, the fit was

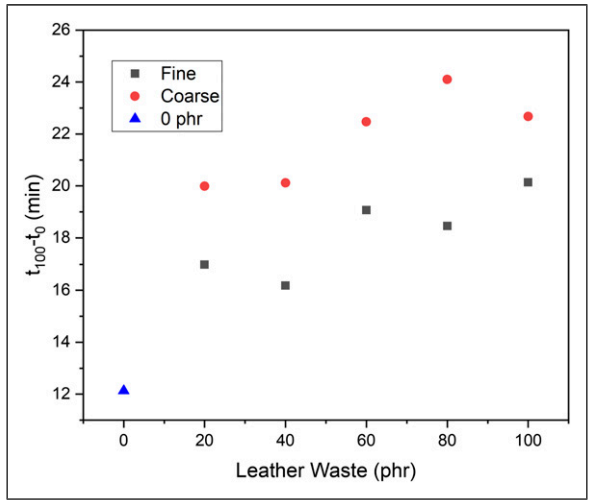

Figure 3. t_{100}-t_0 of natural rubber composites with fine and coarse leather wastes.

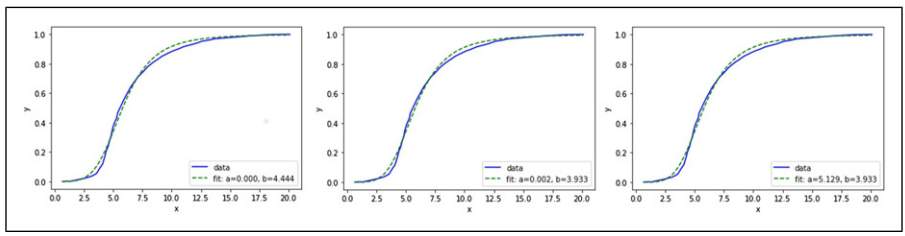

Figure 4. Fit of the three models with the experimental data of the degree of cure of the composite made with natural rubber and 40 phr of fine leather wastes.

satisfactory, evidencing an R-squared greater than 0.99. The data of parameters k, n, and R-squared are expressed with 15 significant units due to the small differences between the values of n and the R-squared of the models by Kamal and Sourour and Rafei et al.

Kinetic parameter n obtained by fitting the models for the natural rubber composite with 40 phr of fine leather wastes showed the same level or order in the three models. However, in the case of parameter k, the order was different in the model proposed by Rafei et al. Table 1 details the values of the kinetic parameters k and n obtained by fitting the three models analyzed. In all cases, the R-squared achieved by fitting the models was greater than 0.99. The use of the models and the Python script for this purpose was satisfactory. The trends of the kinetic parameters k and n obtained with the different models were studied independently and subsequently compared.

Table 1. Vulcanization kinetic parameters obtained by fitting the three models with the experimental data of the degree of cure of the composites evaluated.

Vulcanization kinetic models - Parameters k, n, and R-squared									
	Isayev-Deng model			Kamal-Sourour model			Rafei et al. model		
Mixtures	k (I-D)	n (I-D)	R-squared	k (K-S)	n (K-S)	R-squared	k (R et al.)	n (R et al.)	R-squared
0 phr	0.00125	4.32431	0.995	0.00632	3.68171	0.996	3.95668	3.68171	0.996
20 phr Fine	0.00048	4.31225	0.993	0.00135	3.93392	0.994	4.66315	3.42848	0.995
40 phr Fine	0.00040	4.44365	0.994	0.00161	3.93303	0.995	5.12894	3.93303	0.995
60 phr Fine	0.00740	3.13425	0.997	0.02291	2.69144	0.998	4.06697	2.69144	0.998
80 phr Fine	0.00603	3.26882	0.996	0.03269	2.60691	0.997	3.71381	2.60691	0.997
100 phr Fine	0.00608	3.28915	0.996	0.02592	2.71097	0.998	3.84688	2.71097	0.998
20 phr coarse	0.00005	4.86828	0.996	0.00035	4.23020	0.997	6.52517	4.23020	0.997
40 phr coarse	0.00001	5.06428	0.995	0.00086	3.80629	0.996	6.37915	3.80629	0.997
60 phr coarse	0.00018	4.22926	0.995	0.00250	3.34196	0.997	6.00438	3.34196	0.997
80 phr coarse	0.00029	3.97014	0.995	0.00071	3.67412	0.995	7.17115	3.67412	0.996
100 phr coarse	0.00001	5.26778	0.993	0.00018	4.47459	0.994	6.85069	4.47459	0.994

Isayev-Deng model fitting

Figure 5 shows the kinetic parameters k and n obtained by fitting the Isayev-Deng model with the experimental data of the degree of cure of natural rubber/leather waste composites. The model proposed by Isayev and Deng does not include the induction time (t_0) in the equation because, during the induction period, no chemical reaction associated with the vulcanization process takes place. Therefore, it is assumed that, in this period, the change in the vulcanization heat as a function of time is equal to zero ($\partial Q/\partial t = 0$) for $t \leq t_0$.[16]

Parameter k obtained by fitting the Isayev-Deng model displayed higher values for the composites with fine leather wastes than for the composites with coarse leather residues. This behavior is consistent with the results obtained in the total vulcanization times (t_{100}-t_0), where the composites with coarse residues took longer to vulcanize, that is, they presented higher values of t_{100}-t_0. However, the values of parameter k obtained with this model when evaluating the composites with 60, 80, and 100 phr of fine leather wastes did not show any trend, in contrast to what was reported at times t_0, t_{100}, and t_{100}-t_0, where the effect of both size and amount of leather wastes was clearly seen (Figures 2 and 3).

Parameter n obtained for the different composites did not show any trend related to the size or amount of leather residues. It is worth mentioning that the values of n were in a range between 3 and 5. The variation in these values could be influenced by the effect of the leather wastes. However, it was observed that the reaction order for some composites and for rubber without leather residues was similar; therefore, these results were not enough to determine in which of the vulcanization reaction stages the leather wastes participated.

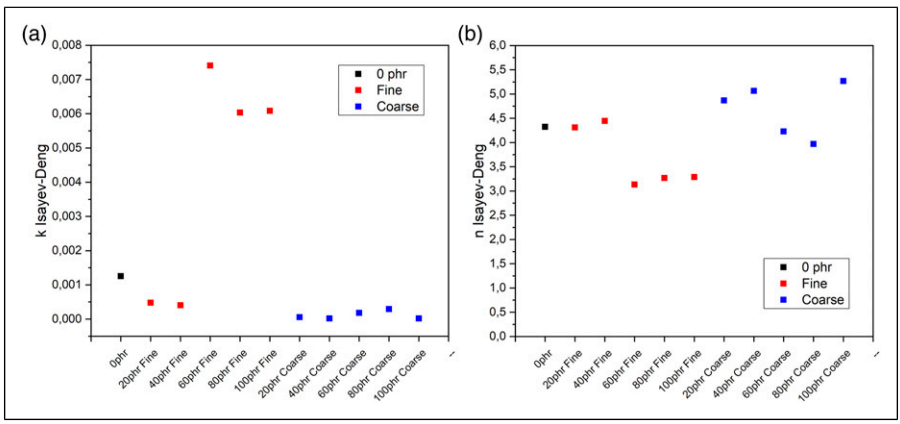

Figure 5. Kinetic parameters k (a) and n (b) obtained by fitting the Isayev-Deng model.

Kamal-Sourour model fitting

The behavior and scales of the kinetic parameters obtained by fitting the model proposed by Kamal and Sourour were similar to those of the parameters obtained using the Isayev-Deng model. Except for the parameters of the composites made with 60, 80, and 100 phr of leather wastes, the values of k were on a similar scale. Moreover, as in the parameters obtained by the Isayev-Deng model, lower values of k were observed in the composites with coarse leather wastes. Regarding the parameter n obtained by fitting the Kamal-Sourour model, it can be said that the scale is similar to that obtained with the Isayev-Deng model.

The values of n of the composites with coarse leather residues displayed a particular behavior. They initially decreased in the composites with 20 phr to 60 phr of leather wastes. However, they started to increase by adding 80 phr and 100 phr of leather residues.

In some studies reported in the literature, when the Kamal-Sourour model was fitted, some trends were observed in parameters k and n as a function of the composition and vulcanization temperature of the composites.[7,20-22] For example, the larger the amount of sulfur, the higher the parameters k and n, as a consequence of greater average vulcanization speeds, shorter induction times, and theoretically higher vulcanization reaction order.[7]

From the behavior of parameters k and n, illustrated in Figure 6, it can be concluded that the leather wastes had an effect on the vulcanization reaction rate constant (k) because it decreased in the composites with coarse leather residues. It is interesting to observe that the composites made with 60, 80, and 100 phr of fine leather wastes achieved values of k and n that were slightly out of trend. This behavior is presumed to be related to the decrease in the induction time of the three compounds (Figure 2), which leads to an increase in the speed in the initial period of the vulcanization reaction, where this effect causes a decrease in the reaction order and an increase in the values of k.

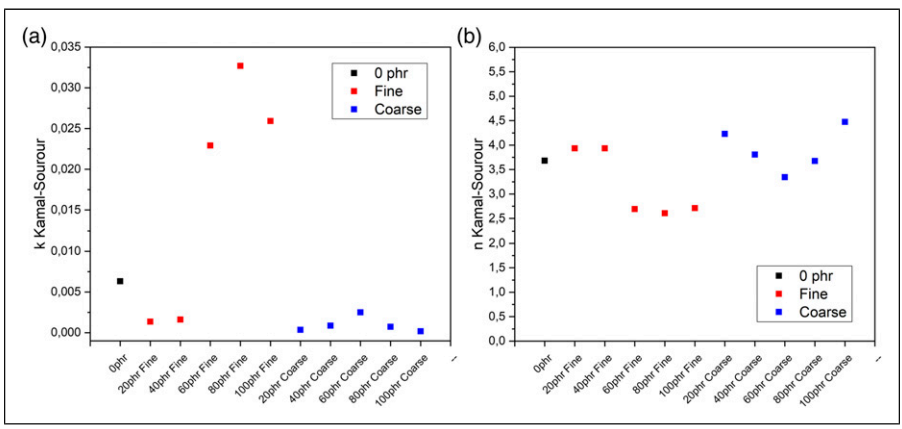

Figure 6. Kinetic parameters k (a) and n (b) obtained by fitting the Kamal-Sourour model.

Rafei et al. model fitting

Figure 7 shows the behavior of the kinetic parameters k and n obtained by fitting the Rafei et al. model. In the case of parameter k, a particular behavior was observed in the composites with leather residues, where it was possible to identify a block of composites with coarse wastes and another of composites with fine wastes. In addition, the block with fine residues displayed a higher degree of dispersion. The values of k obtained by fitting the Rafei et al. model were higher than those obtained in the Isayev-Deng and Kamal-Sourour models, so it was not possible to compare them. Furthermore, the trend of parameter n was very similar to the values obtained by fitting the degree of cure with the Kamal-Sourour model.

The value of parameter k—which is a function of the amount and size of leather particles—rose as the amount of leather wastes in the composites increased, the effect being stronger for the composites with coarse leather residues. Analyzing the equation proposed in the Rafei et al. model and assuming values of 0 for θ_0 and 1 for b, it was possible to determine that the model can be expressed using an alternative mathematical relationship, which is represented by the following equation

$$\theta_{model\ R\ et\ al.} = \frac{(t - t_0)^n}{k^n + (t - t_0)^n} \quad when\ \theta_0 = 0\ and\ b = 1 \tag{5}$$

Equation (5) shows an important aspect related to the location of parameter k in the mathematical expression. In this case, unlike what occurs in the Isayev-Deng and Kamal-Sourour models, parameter k is a term that is added to the time difference. Therefore, the value of k obtained by the Rafei et al. model was so high that it could not be compared with the k parameters of the other two models. Additionally, the trend of said parameter

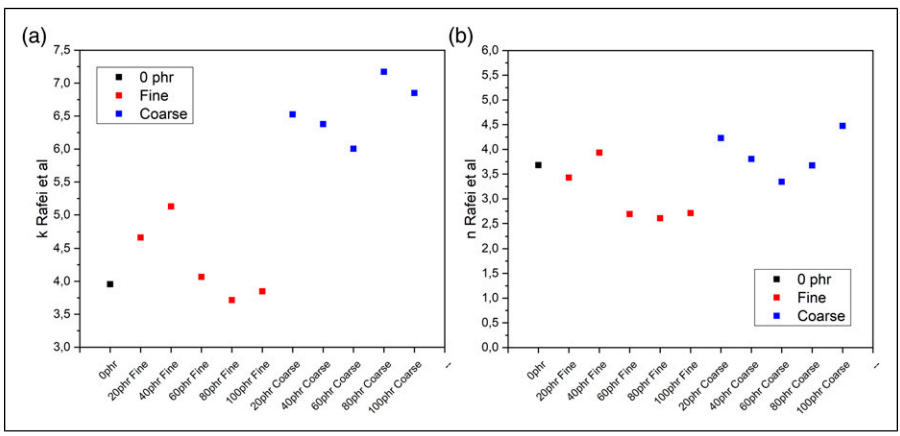

Figure 7. Kinetic parameters k (a) and n (b) obtained by fitting the Rafei et al. model.

was contrary to what was expected because coarse leather wastes delayed the vulcanization reaction. However, the composites made with these residues were the ones with the highest values of k obtained by fitting this model.

Comparative vulcanization kinetic models

In the previous section, the behavior of the parameter k obtained by fitting the Rafei et al. model was analyzed. However, when examining Figure 8, which compares the behavior of the parameters k obtained by fitting the three models, the difference in the value of the parameter obtained by the Rafei et al. model becomes evident. Consequently, the values of the kinetic parameter k obtained by fitting the Rafei et al. model could not be compared with those of the other two models used in this study.

The model by Rafei et al. emerged in response to the limitations of the model proposed by Kamal and Sourour to describe the curing process at the initial stage of the vulcanization process under non-isothermal curing conditions of rubber compounds.[17] Nevertheless, in this study that evaluated the effect of leather wastes on the vulcanization kinetic parameters obtained under isothermal conditions using a vulcanization rheometer, it was not possible to obtain values of k comparable to those obtained with the Isayev-Deng and Kamal-Sourour models.

Considering the values of k obtained by fitting the three kinetic models employed in this study (Figure 8) and that it was not possible to perform a comparative analysis of the three models, the kinetic parameters k of the vulcanization Isayev-Deng and Kamal-Sourour models were compared (Figure 9). A similar situation occurred with

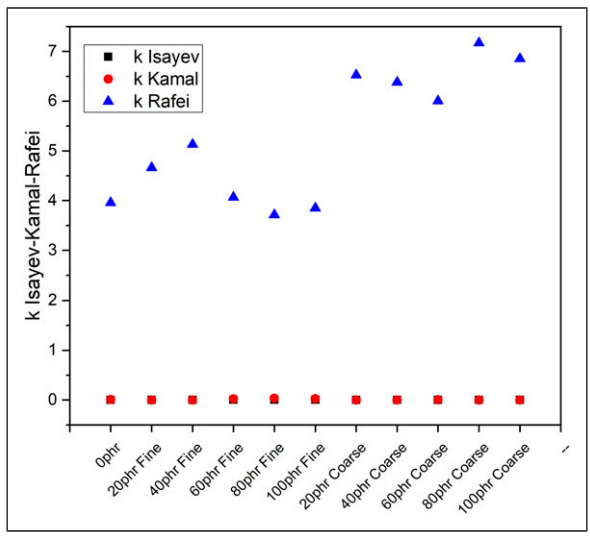

Figure 8. Comparison of the kinetic parameters k obtained by fitting the Isayev-Deng, Kamal-Sourour, and Rafei et al. models.

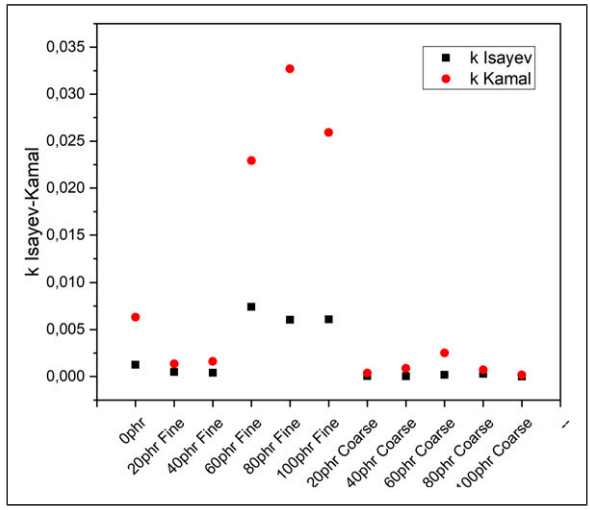

Figure 9. Comparison of the kinetic parameters k obtained by fitting the Isayev-Deng and Kamal-Sourour models.

the values of k obtained by fitting these two models, where the composites with coarse leather wastes displayed lower values because they delayed the curing speed. Similarly, as discussed in previous sections, the two models exhibited values of k with a certain degree of dispersion for the composites made with 60, 80 and 100 phr, suggesting a possible influence of decreasing induction times (Kamal-Sourour model) and initial vulcanization speed (Isayev-Deng and Kamal-Sourour models).

Lastly, Figure 10 shows the behavior of the parameter n (reaction order) obtained by fitting the three models based on the size and amount of leather wastes. It is interesting to note that the values of n were within the same scale of values and showed similar trends in the three models used in the study. In addition, the figure reveals three main zones. The first zone shows a block of composites with coarse leather wastes, where the reaction order is between 3 and 5 and the values and trends of n are similar for the Kamal-Sourour and Rafei et al. models. The second zone displays the behavior of the composites made with 60, 80, and 100 phr of fine leather wastes and reveals an atypical behavior in the values of k and n. It can be noted that, in the three models, the parameters n of the three compounds are the lowest values. This phenomenon is possibly related to the lower occurrence of chemical reactions associated with the formation of elastically active bonds. Finally, the third zone shows the composites with 20 and 40 phr of fine leather wastes and the natural rubber composite without leather residues. In this zone, the values of n obtained with the three models also show a similar trend, which demonstrates that these three

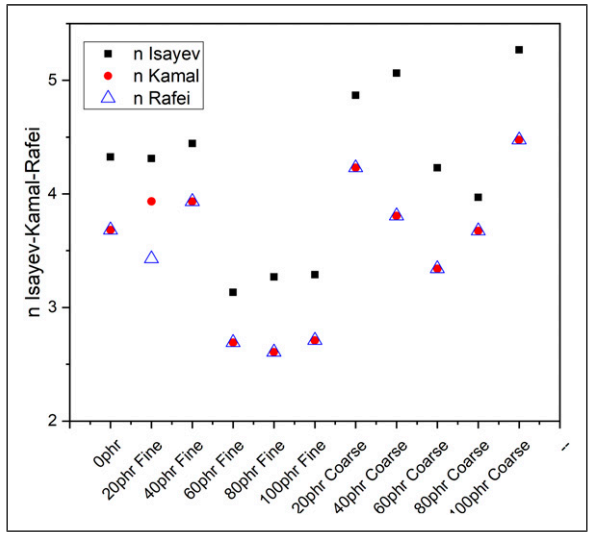

Figure 10. Comparison of the parameters n obtained by fitting the Isayev-Deng, Kamal-Sourour, and Rafei et al. models.

models predict, in a similar way, the values of parameter n related to the reaction order.

Conclusions

The addition of leather wastes to a natural rubber matrix modifies its vulcanization conditions, directly affecting variables such as induction and vulcanization times. This effect must be considered since several studies have shown that rubber composites mixed with leather residues have great scientific and technological potential; however, processing and vulcanization conditions must be monitored and controlled to avoid affecting product quality and process productivity.

The degree of cure of natural rubber compounds with leather residues calculated from the experimental data obtained by vulcanization rheometry was satisfactorily fitted to the kinetic models proposed by Isayev and Deng, Kamal and Sourour, and Rafei et al. Therefore, the kinetic parameters known as rate constant (k) and kinetic equation or reaction order (n) were obtained.

It was not possible to carry out a comparative analysis of the values of k obtained with the three models for the composites evaluated in this study because the model proposed by Rafei et al. yielded much higher values. However, the values of k obtained by fitting the Isayev-Deng and Kamal-Sourour models showed similar trends and seemed to be related to the behavior of vulcanization times, where coarse leather wastes delayed the vulcanization reaction; therefore, the values of k were lower.

In the case of parameter n, related to the order of the kinetic equation, the values obtained by fitting the three models displayed a similar behavior in the Kamal-Sourour and Rafei et al. models. In addition, the values of n obtained with the Isayev-Deng model also showed a similar trend, that is, these values were in the same scale or order.

Consequently, based on these models and the kinetic parameters obtained by fitting the experimental data, it is possible to predict the curing behavior of natural rubber compounds mixed with leather wastes of different sizes and in different proportions.

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