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Vulcanization Kinetic Study of Different Nitrile Rubber (NBR) Compounds

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Summary: The vulcanization process of rubber compounds comprises multiple chemical reactions and the investigation of this process can be carried out using several techniques. This paper aims at investigating the influence of acrylonitrile content (28, 33 and 45%) and the presence of a carboxyl group in the vulcanization process of nitrile rubber. A methodology that uses rheometric parameters to determinate the cure rate constant (k) and activation energy (E) was conducted. The results showed that there was a decrease in cure rate constant with increasing of acrylonitrile content in the rubber, for a given vulcanization temperature. Furthermore, a higher value of activation energy was obtained for the 33% of acrylonitrile compound.

Keywords: activation energy; crosslinking; cure rate constant; nitrile rubber; vulcanization

Introduction

Poly(acrylonitrile-co-butadiene), also known as nitrile rubber (NBR), is the most widely elastomer used in fat, oil and fuel applications. The reason why NBR is used in applications with non-polar or slightly polar fluids is because of the strong polar characteristic of acrylonitrile. Additionally, acrylonitrile content also affects the glass transition temperature, heat resistance and mechanical properties of the rubber. NBR grades are often produced with 18–51% of acrylonitrile content. Table 1 shows the effect of acrylonitrile content on the properties of the nitrile rubber.[1–4]

Crosslinking is an important topic in rubber science. It can be defined as a process of forming a three-dimensional network structure in the rubber by chemical or physical interaction. In rubber industry, when non-sulfur chemicals are used, this process generally is called curing. On the other hand, when sulfur chemicals are used, the process is often called vulcanization.[5]

Rubber based goods can be produced from different heat treatment methods. During curing process, significant changes occur in the physical properties of the rubber. As an example, the compound changes from a weak to a relatively strong viscoelastic solid. Vulcanization is the most used technology in rubber industry, with which it is possible to achieve different types of crosslink network, e.g., mono- (C–S–C), di- (C–S–S–C) and polysulfide (C–S_n–C) structures.[6]

The formulations, as well as, the process parameters have a strong influence on rubber products performance. The formulation comprises a combination of different components; usually they are divided into five categories: polymer, fillers, stabilizers, special materials and vulcanization system.[6] According to ISO1382:2013, fillers are a solid ingredient, which are added in large quantities to rubber or latex formulations for either technical or economic

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Table 1.
Effect of acrylonitrile content on nitrile rubber properties.[4]

Property	Content of acrylonitrile 18% ↔ 50%
Oil resistance improves	→
Tensile strength increases	→
Hardness increases	→
Abrasion resistance improves	→
Gas impermeability improves	→
Heat resistance improves	→
Low temperature resistance improves	←
Rebound resilience increases	←

reasons. As an example, carbon black is the most common filler used.

Kinetic studies of crosslinking are useful for understanding and modeling the curing behavior. In the literature, several techniques have been used to determinate the cure rate constant (k), order reaction (n) and activation energy (E), being the use of a moving die rheometer (MDR) one of them. This method is based on the rheometric parameters and considers that torque change can be directly related to crosslink formation. Additionally, knowing the time in which the cure rate is maximum, allows a more accurate assessment of the cure rate constant (k). This procedure is based on the decreasing reaction rate, which only the data obtained after the maximum cure rate point is taken into consideration.[7]

This work was motivated by huge interest in kinetic studies of rubber technology and the little information available on the effect of acrylonitrile content and reactive groups on nitrile rubber samples vulcanization kinetic. The purpose was to investigate the influence of acrylonitrile contents on the NBR vulcanization process, as well as the presence of reactive groups on the elastomer structure. Therefore, three commercial samples of nitrile rubber with different acrylonitrile content were used, in addition to a carboxylate nitrile rubber sample. The kinetic parameters were determined at three vulcanization temperatures and the results were compared.

Experimental Part

Compounding

Nitrile rubbers samples were kindly supplied by Nitriflex S/A Indústria e Comércio. The commercial grades rubbers used were: N615B (Mooney viscosity ML(1 + 4) at 100 °C: 40–52; acrylonitrile content: 31–34%), N216 (Mooney viscosity ML(1 + 4) at 100 °C: 50–70; acrylonitrile content: 43–48%) and Nitriclean N3350X (Mooney viscosity ML(1 + 4) at 100 °C: 40–55: 40–52; acrylonitrile content: 26–28%).

Carbon black SP6630 kindly supplied by Cabot Brasil Indústria e Comércio Ltda and commercial grades of sulfur; zinc oxide; stearic acid and N-tert-butyl-2-benzothiazole sulfenamide (TBBS) were used as received. Table 2 shows the compounds formulation according to ASTM D3182. The formulations were prepared in a roll mill (400 mm × 200 mm) at a friction rate 1:1.2.

Test Methods

The rheometric parameters were determined according to ASTM D2084 standard, under isothermal conditions, using the oscillating die rheometer, RheoTech MDPt Rheometer. Samples of all compounds were tested at the following temperatures: 140 °C (383 K), 150 °C (393 K) and 160 °C (403 K). The rheometric parameters obtained were: Maximum torque (M_H), minimum torque (M_L), scorch time (ts_1) and the optimum vulcanization time (t_{90}).

From the torque values, the conversion variable x can be obtained as a function of

Table 2.
Compounds formulation according ASTM D3182–amounts in part per hundred of rubber (phr).

Components	*XNBR*	*NBR 33*	*NBR 45*	*NBR 33/45*
N615B	–	100	–	50
N216	–	–	100	50
N3350X	100	–	–	–
Zinc oxide	3			
Stearic acid	1			
Sulfur	1.5			
TBBS	0.7			
Carbon black SP6630	40			

time, using the equation: $x_t = (M_t - M_L)/(M_H - M_L)$, where M_t is a torque at a given time t.[7]

The cure rate constant (k) and the order reaction (n) were determined from the conversion-*versus*-time curve for time values at/or superior to that for which the cure rate is maximum. The kinetic equation is given by the equation $dx/dt = k\ (1-x)^n$, where dx/dt is the conversion ratio, n is the reaction order, and t is the time.[7]

For first-order kinetic reactions, n is equal to 1. The integrated form of this kinetic equation resulting in $ln(1-x) = -k(t-ti)$, where t_i is the induction time. Then, by using linear regression, the cure rate constant (k) was determined.[7]

However, when the reaction order is different from 1 ($n \neq 1$), the integrated form is $(1-n)^{-1*}(1-x)^{(1-n)} = 1/(1-n) - k(t-ti)$.[7] Then, by using iterative methods, the cure rate constant (k) and reaction order (n) were determined. The criterion chosen was that the minimum value of correlation coefficient must be higher than 0.99.

As the reaction rate and the temperature have an exponential relation, Arrhenius equation $k = Ae^{(-E/RT)}$ could be employed to estimate the activation energy (E). In practice, the vulcanization reactions for the most thermoset systems can be adequately described in terms of these simple kinetic models.[8]

Results and Discussion

Table 3 shows the vulcanization rheometric parameters (M_L, M_H, ts_1 and t_{90}) obtained for all NBR compounds. These parameters are known to be strongly affected by the vulcanization system. Furthermore, the difference between the maximum and minimum torques is directly proportional to the total crosslink density.[9] However, because in this study, the same vulcanization system was employed in all compounds; the difference between the torques, and therefore between crosslink densities, comes from the difference of the elastomer structure, either acrylonitrile content or the presence of reactive groups.

From Table 3, it can be observed that the highest difference between maximum and minimum torques values was obtained for *XNBR* compound at all temperatures. The result indicates this compound achieved higher crosslink density than the other

Table 3.
Rheometric parameters of NBR compounds.

Components	*XNBR*	*NBR 33*	*NBR 33/45*	*NBR 45*
		Vulcanization temperature: 140 °C		
M_L dN.m (±0.03)	1.8	2.3	2.1	1.5
M_H dN.m (±0.1)	20.6	17.2	15.4	15.8
$(M_H - M_L)$ dN.m (±0.13)	18.8	14.9	13.3	14.3
ts_1, minute (±0.0)	4.9	11.8	7.5	7.7
t_{90}, minute (±0.4)	42.5	31.5	39.4	41.0
		Vulcanization temperature: 150 °C		
M_L dN.m (±0.03)	2.1	2.1	1.9	1.2
M_H dN.m (±0.1)	22.3	17.1	16.8	15.6
$(M_H - M_L)$ dN.m (±0.13)	20.2	15.0	14.9	14.4
ts_1, minute (±0.0)	2.9	11.8	4.0	4.0
t_{90}, minute (±0.4)	27.1	19,6	32.3	36.5
		Vulcanization temperature: 160 °C		
M_L dN.m (±0.03)	1.5	1.9	2.0	1.1
M_H dN.m (±0.1)	23.7	16.7	17.2	18.4
$(M_H - M_L)$ dN.m (±0.13)	22.2	14.8	15.2	17.3
ts_1, minute (±0.0)	1.5	3.3	2.5	2.2
t_{90}, minute (±0.4)	23.8	11.3	21.5	32.0

formulations. The obtained result can be related to the fact that in this rubber sample, N3350X, the crosslink formation occurs via both sulfur and carboxyl groups. The crosslink bonds via carboxyl groups occur by thermal activation and it is also dependent on zinc oxide amount.[10,11]

Table 4 presents the kinetic parameters (*k*, *n* and *E*). Based on the cure rate constant (*k*) and using the Arrhenius equation, above mentioned, the relation between *ln k* versus (1/T), was plotted on Figure 1, from which it was possible to calculate the activation energy (*E*) as the slope from each curve. In order to depict that the kinetic models were in agreement with their respective observed values, two graphs are also presented, as shown in Figure 2, for *NBR33* and *NBR45* compounds.

From Table 4, it is noticed that the reaction order values (*n*) were higher than 1.0 for all rubber compounds. Regarding non-carboxylate rubber compounds (*NBR 33, NBR 45 and NBR33/45*), it is observed that reaction order values were similar, suggesting that, among them, the cure process employed similar chemical species. However, different result was found for *XNBR* compound rubber, which showed comparatively lower order reaction values. One can infer that different chemical reactions were involved in the curing

Table 4.
Cure rate constant (*k*), order reaction (*n*) and activation energy (E).

Compound	Temperature °C	*n*	*K* (s^{-1}) *E-03*	*E* ($kJmol^{-1}$)
XNBR	140	1.1	1.06 ± 0.01	78 ± 5
	150	1.2	2.14 ± 0.02	
	160	1.5	3.02 ± 0.03	
NBR 33	140	1.4	3.54 ± 0.05	100 ± 6
	150	1.8	8.12 ± 0.09	
	160	1.8	13.49 ± 0.15	
NBR 33/45	140	1.4	1.88 ± 0.02	67 ± 3
	150	1.6	2.72 ± 0.03	
	160	1.7	4.61 ± 0.05	
NBR 45	140	1.3	1.57 ± 0.01	44 ± 4
	150	1.6	2.42 ± 0.02	
	160	1.7	2.82 ± 0.03	

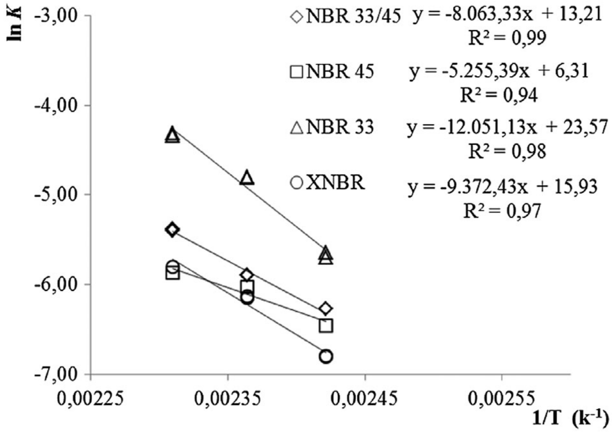

Figure 1.
ln *k versus* (1/T), from Arrhenius equation, at 140 °C (383 K), 150 °C (393 K) and 160 °C (403 K).

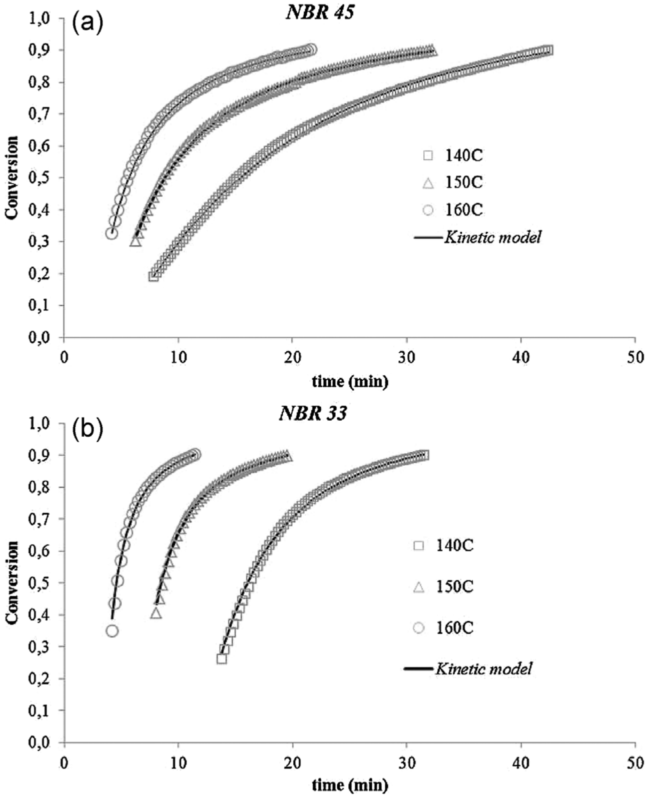

Figure 2.
Observed *versus* predicted vulcanization conversion as a function of time for: (a) NBR45 and (b) NBR33 compounds.

process. This result implies that, at lower temperatures, the crosslink reactions happened preferably via carboxyl groups. Increasing the temperature, however, other chemicals species started to engage in curing formation.

Regarding the cure rate constant (k) and activation energy (E) for non-carboxylate rubber compounds, it is observed a correlation between the results and the NBR grade. That is, an increase in butadiene content in the rubber, which has reactive sites (allylic hydrogen atoms), produces higher values of k. It can be visualized by the comparison of the cure conversion graphics of *NBR33* and *NBR45*, as shown in Figure 2. In addition, as acrylonitrile content is increased, lowers values of activation energy was necessary for the vulcanization process. This result shows that acrylonitrile groups increase the reactivity of the vicinal carbons, contributing for the reaction.

Furthermore, comparing the results of rubber compounds with similar butadiene content (N3350X and N615B), the lower values of k observed for *XNBR* compound may be attributed to the fact that the zinc oxide participates in the two parallel curing processes. Finally, the results of blend rubber compound were in accordance with the amount of each rubber in the composition.

Conclusion

This paper shows a kinetic study for the investigation of the influence of the nitrile rubber acrylonitrile contents on the vulcanization process, using three commercial nitrile rubbers with different acrylonitrile contents. From the results, it is possible to verify the influence of rubber structure on the vulcanization process.

Regarding the rheometric parameters, the higher difference between maximum and minimum torque was observed for the carboxylate rubber, indicating that *XNBR* compounds had a tendency to present higher crosslink density. This result corroborated to the kinetic cure evaluation, that indicated that different chemical species are present in the carboxylate and non-carboxylate rubber compounds, even though the same system cure were used. In addition, it was also observed that rubber composition affects kinetic parameters (k e n) and activation energy (E).

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