EVALUATION OF VULCANIZATION PARAMETERS OF NR/CIIR/BENTONITE BLENDS

Baruel, A.F.[1,2]; Petroni, S. L. G. [2]; Dutra, J. C. N. [1]; Mello, S. A. C. [2]; Cassu, S. N. [1,2]

1. Instituto Tecnológico de Aeronáutica (ITA), São José dos Campos, SP, Brazil
2.Instituto de Aeronáutica e Espaço (IAE), São José dos Campos, SP, Brazil

e-mail: amanda.baruel.85296@ga.ita.br

ABSTRACT

Polymeric blends have been widely utilized in a variety of applications. Blending two different materials can lead to materials with enhanced properties. Adding Chlorobutyl rubber (CIIR) to Natural Rubber (NR) can improve degradation resistance and enhance damping and barrier properties. In recent years, nanomaterials such as bentonite clay have gained significant attention due to their ability to enhance properties at very low concentrations. In this study, the vulcanization process of a NR/CIIR blends containing a commercial bentonite clay was evaluated by MDR and DSC. The proportion of NR/CIIR varied between 100/0 phr and50/50 phr. The effects of increasing CIIR and clay contents were evaluated. A decrease in reversion was observed for NR/CIIR/Clay blends compared to NR rubber. Clay addition accelerated the vulcanization process, while CIIR addition slowed it. Clay addition also increased the Maximum Torque (M_H), which is related to the viscosity of the rubber, while CIIR decreased it.

Keywords: (3 a 5) Clay, Accelerating effect, Reversion

INDRODUÇÃO

Natural rubber (NR) is widely used in several areas and applications due to its unique properties, which are not achieved by synthetic rubbers. NR presents high abrasion resistance, good hysteresis properties, and high tear and tensile strength. However, it has inherent limitations, such as low fatigue resistance and low resistance to degradation (1).Modifications and reinforcement techniques have been extensively researched to overcome these limitations and enhance the performance of NR. Polymeric blends have the potential to combine the properties of different materials, thereby creating composites with enhanced performance characteristics. Chlorobutyl rubber (CIIR), known for its superior resistance to heat, oxidation, and weathering, offers potential benefits when blended with NR, resulting in improved durability and performance of the rubber. Halogenated butyl rubbers have a significant advantage over butyl rubber: increased compatibility with diene rubbers (2), thus being able to be mixed with NR.

Vulcanization is a critical process in rubber, and can be influenced by various factors, including the type of rubber, the presence of fillers, and the specific vulcanization conditions. CIIR has a low degree of unsaturation. Therefore, conventional vulcanization systems, with sulfur, provide a low degree of crosslink. It can also be vulcanized using only zinc oxide (ZnO) by the active chlorine present in the polymer chain (3).

In addition to blending, the incorporation of nanofillers such as clay has shown substantial potential in reinforcing rubber matrix. The layered structure of clay contributes to enhanced barrier properties, increased mechanical strength, and improved thermal stability of the rubber compounds. However, this improvement is highly dependent on good dispersion and exfoliation of the clay in the rubber matrix (4).Due to the low compatibility between NR and bentonite clay, an organic modification of the clay is needed to improve the affinity and, therefore, obtain a dispersion in a nanometric scale (5).

Understanding how these additives interact and influence the vulcanization process of NR and NR/CIIR blends is crucial for the development of advanced rubber materials with enhanced performance. The main goal of this study is to evaluate the effect on the vulcanization profile of adding a commercial organoclay to natural rubber (NR) and NR/CIIR blends, as well as to analyze the effect of CIIR addition.

MATERIALS

Chlorobutyl Rubber CIIR-1301 was purchased from Zhejiang Cenway Materials Co. Ltda, which contains a small quantity of calcium stearate to improve stability. Natural RubberGEB01 and Sulfur powder were purchased from Fragon Produtos para Indústria de Borracha Ltda. Claytone HY, a montmorillonite modified with ditallo dimethyl ammonium salt, was purchased from BYK Additives &

Instruments. Tetramethyl thiuram monosulfide (TMTM), N-Cyclohexylbenzo thiazol-2-sulfenamide (CBS), Stearin, and Peptizer were provided by NewBor Indústria e Comércio de Borracha Ltda. Zinc Oxide (ZnO) and Carbon Black N330 were provided by Orion S.A. Aromatic Oil was provided by Zanaflex Borrachas Ltda.

METHODS

Preparation of compounds

NR (100 phr) was mixed with peptizer (3 phr) in a two-roll mixing mill, LUXDOR, at 30°C. Then, the peptized NR and CIIR were dissolved in 1.2 L of chloroform under continuous stirring for 8 hours. In the meantime, Claytone HY was dispersed in chloroform at a ratio of 1:10 (w/v) using a high-power ultrasound device (Hielscher, model UP 200S, with an output power of 200 W and equipped with sonotrode S14 probe) stirring at 50% amplitude and 0.5 cycle for 15 min. The Claytone dispersion was subsequently poured into the rubber/chloroform solution and maintained under stirring for1 hour. The Rubber/Clay mixture was then dried in a vacuum oven at 40 °C for 24 hours. After evaporating the solvent, other additives were added to the Rubber/Clay mixture in a two-roll mixing mill. The amount of fillers added was the same for all compounds as shown in Table 1. Compounds were named according to the NR and Claytone HY fractions, e.g., N50H8 refers to the compound containing 50 phr of NR, 50 phr of CIIR, and 8 phr of Claytone HY.

Table1. Amount of fillers used in the rubber compounds.

Rubber compounds (phr)	
ZnO	5
CB N330	12
Aromatic Oil	12
Stearin	1
Sulfur	1
TMTM	0.3
CBS	1.5

Characterization

Rheometry analyses were conducted in a moving die rheometer (MDR) from ALPHA Technologies, model PREMIER MDR, at 145 °C for 60 minutes with a frequency of 100 cpm (1.67Hz) and a 1° rotation angle, according to ASTM D5289 (6).

Dynamic scanning calorimetry (DSC) analyses were carried out on a TA Instruments DSC Q-100. Approximately 5mg of each material were sealed in aluminum pans, and the analyses were conducted in a nitrogen gas flow of 100mL/min, with a temperature range from -90 °C to 250 °C and a heating rate of 10°C/min. The width of the exothermic peak, ΔT, was calculated using TA Universal Analysis 2000 software at half-height with linear peak integration.

Tensile properties were measured according to the ASTM D412 (7) with a dumbbell sample shape type C (115 x 25 x 2) mm. Tear strength was determined according to the ASTM D624 (8)type C (102 x 19 x 2) mm. Mechanical properties (tensile and tear strength) were measured at 25ºC using the Zwick 1474 test machine at 500 mm/min speed, and the strain was measured with an optical extensometer. Five specimens were analyzed to calculate average and standard deviation. The Shore A hardness test was carried out on an Instron Shore A hardness tester, model S1, according to ASTM D2240 (9).

The swelling method based on the ASTM D68147 (10) determined the crosslink density. First, the rubbers were vulcanized in a press according to t_{90}, which was found in the rheometry of each composition. Approximately 5g of the rubber, cut into small pieces, was kept under reflux in a Soxhlet apparatus in acetone for 24 hours until no residue was observed and then dried in a Brasimet-Heraeus oven, type B-UT 5050, with forced air ventilation for 16 hours at 70°C. After drying, rubbers were kept in reflux in a Soxhlet apparatus in toluene for 24 hours to remove residual rubber that did not vulcanize and subsequently dried using the same previous parameters. Afterward, rubber compounds were submitted to the swelling process in toluene for 72h, renewing the solvent every 24 hours. After swelling, the excess solvent was removed, and the swollen rubber was weighed. Then, the rubber was dried using the same previous parameters and subsequently weighed. The Flory-Rehner equation was used to calculate the cross-linking density. The density of dry rubber was obtained using a Mettler analytical balance, model XPE205.

RESULTS AND DISCUSSION

The vulcanization process was monitored by rheometric analysis, during which torque is expected to increase as the vulcanization progresses. In the rheometric curves, three stages can be observed. The first stage is known as scorch or induction, in which the cross-links are starting to form. The second stage corresponds to the main vulcanization, where the cross-links are formed to create a three-dimensional network. In the third stage, rubbers can present three different behaviors: a plateau, indicating the end of the cross-linking reactions; marching modulus, meaning the cross-linking reactions continue indefinitely; reversion, due to the cross-links break over a specific time, decreasing the torque (11). The percentage of reversion (R) at any time is defined as shown in Equation 1.

$$R = \frac{M_H - M_t}{M_H - M_L} \, x \, 100 \qquad (1)$$

Where M_H is the maximum torque, M_L is the minimum torque, and M_t is torque at any cure time (12).In this study, the reversion was analyzed at 60 min.

By rheometric analysis (Figure 1 and Table 2), it can be seen that the clay addition presented an accelerating effect, decreasing the scorch time (ts_1) of the compounds. This effect can be attributed to the ammonium groups of the quaternary salt present in the organoclay (2). It can also be observed through DSC analysis by the reduction in the onset temperature (T_0) and the peak temperature (T_{peak}), shown in Figure 2 and Table 3. In the literature, it is reported that the ammonium groups act as an accelerator participating in the cure reaction by forming a complex with Zinc and Sulfur (13,14). The vulcanization mechanism with sulfur is not well known and is proposed in the literature to be divided into steps as in Figure 3: (i) formation of active complex between accelerator and activator; (ii) formation of sulfurating agent due to the reaction between sulfur and the previously complex formed; (iii) formation of crosslinking intermediates due to the reaction of the sulfurating agent and the polymer chain; (iv) formation of polysufide crosslinking (15-17). Since there is no significant change in the cure rate index (CRI), which reflects how fast the vulcanization occurs after the scorch period, and is related to the slope of the curve, this behavior indicates that the ammonium salt accelerates the vulcanization on the initial steps (I and ii) (18), and presents no significant effect in the crosslinking reaction (step iii and iv). This behavior can also be observed by DSC analyses, with the width of the exothermic peak ($\Delta T_{half\text{-}height}$) showing almost no change. When comparing the neat NR with the rubber blend, the addition of CIIR caused a retardant effect, increasing ts_1as seen by rheometric analysis and confirmed by DSC analysis, shifting T_0 and T_{peak} to higher temperatures. This behavior can be attributed to a lower overall unsaturation of the blend compared to the pure NR and, therefore, lower efficiency to vulcanize with sulfur, delaying the vulcanization time (19). The same effect was reported by Shi *et al.* 2022(20),and the authors explained this behavior by stating that a vulcanization precursor is formed in the rubber when vulcanizing with sulfur (step iii).This precursor can be easily formed with higher NR content, facilitating the vulcanization.

Figure 1. Rheometric curves of NR/CIIR blends.

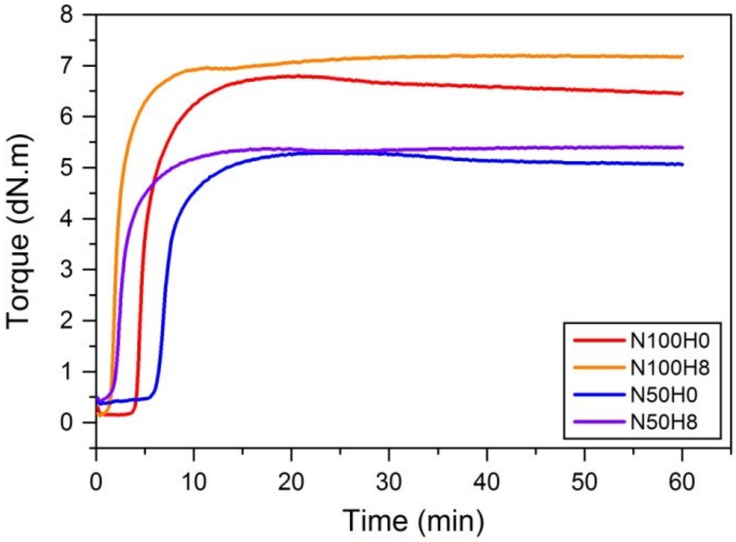

Table 2. Rheometric parameters obtained at 145 °C for NR/CIIR blends.

	M_L (*dN.m*±0.01)	M_H (*dN.m*±0.05)	R[a] (%±0.1)	ts_1 (*min*±0.05)	t_{90} (*min*±1)	ΔM (M_H-M_L)	CRI[b]
NR100H0	0.15	6.80	5.4	4.50	9.45	6.65	20.2
NR100H8	0.14	7.21	0.3	1.76	5.86	7.07	24.4
NR50H0	0.35	5.31	4.9	6.71	11.62	4.96	20.4
NR50H8	0.43	5.41	0.4	2.24	7.16	4.98	20.3

[a] R - Reversion percentage

[b] CRI–Cure rate index100/(t_{90}-ts_1)

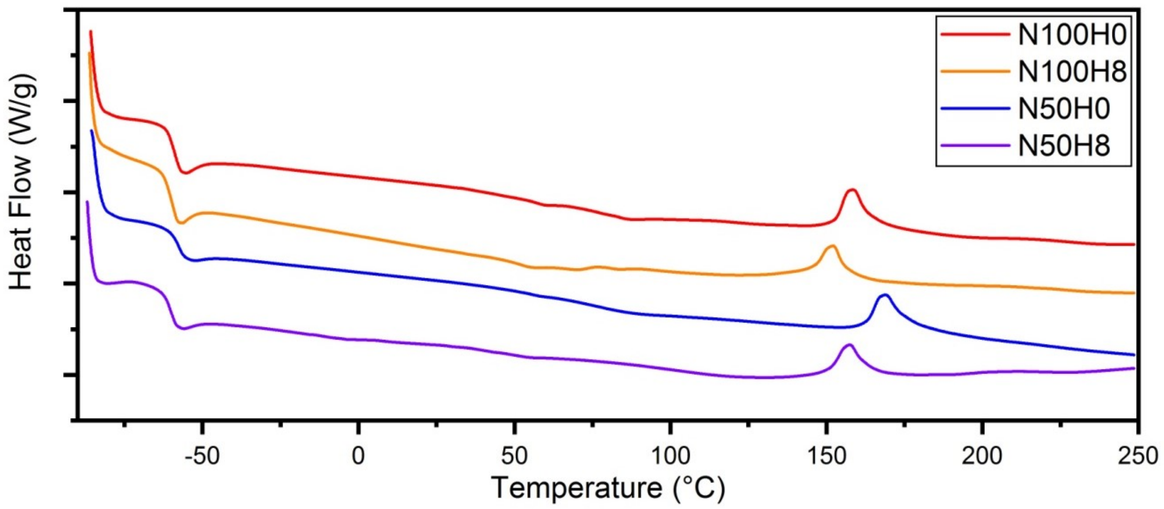

Figure 2. DSC curves of NR/CIIR blends.

Table 3. DSC parameters of NR/CIIR blends.

	Tg 1st heat [°C±0.5]	Tg 2nd heat [°C±0.5]	ΔH_{EXO} [J/g±0.3]	$\Delta T_{(half-height)}$ [°C± 0.5]	T_0 [°C±0.5]	T_{max} [°C±0.5]
N100H0	−58.8	−57.8	5.40	7.6	152.3	158.9
N100H8	−59.5	−57.8	6.36	7.9	145.0	152.5
N50H0	−58.1	−55.6	5.79	8.4	162.2	168.5
N50H8	−60.3	−57.1	5.45	8.7	150.5	157.4

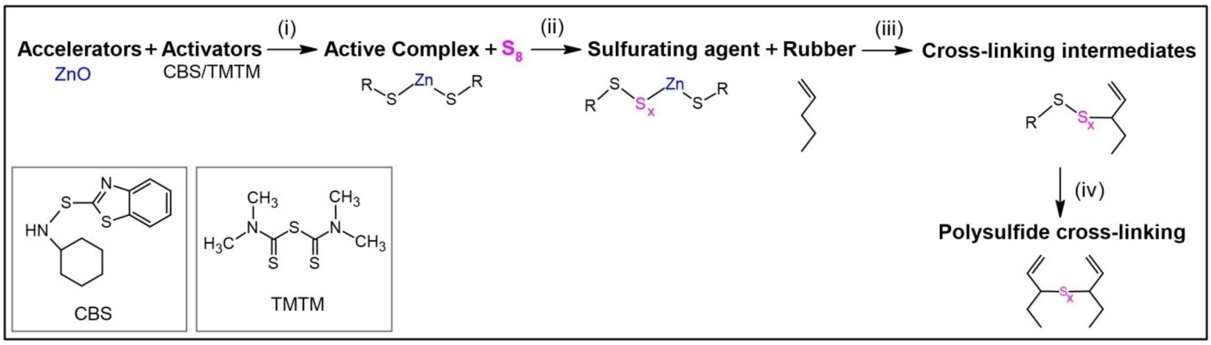

Figure 3. Reaction steps of rubber sulfur vulcanization (15-17).

For the compounds without clay, a decrease in the torque value, known as reversion, is observed over time. This indicates a degradation of the compound due to the breaking of crosslinking bonds, likely the polysulfide ones. With the addition of clay, reversion is no longer observed, indicating improved thermal resistance when clay is incorporated into the system. A slight decrease in the reversion is observed when CIIR is added. This may be due to the vulcanization of CIIR with ZnO, forming crosslinking bonds with better thermal resistance than polysulfide bonds.

Furthermore, for pure NR, M_H, and ΔM increased with the clay addition, indicating a reinforced effect of this filler, by the filler/polymer interaction (21). Although, for the NR/CIIR blend, the clay addition did not affect these parameters. This can be related to a poor interaction between the clay and the CIIR matrix (22).

Usually, the Tg can be used to study the miscibility in a blend. A single Tg or a well-separated Tg indicates a miscible or an immiscible system, respectively (23). However, in this case, the Tg of NR and CIIR are similar and, therefore, cannot predict miscibility (24). In Figure 2, a single Tg can be observed for all blend compositions, presenting values very close to each other. For all samples, the Tg in the second heating shifted to a higher temperature, which can be related to the vulcanization process (Table 3). The addition of clay shifted the Tg to slightly lower temperatures.

For the mechanical properties (Figure 4 and Table 4), the addition of clay slightly increased the tear strength, rubber hardness, and the elastic modulus, which shows a reinforcement effect of the clay, probably due to filler/polymer interaction as seen by rheometric analysis (25). For the NR, the clay decreased the tensile strength at break which might be due to clay agglomerate creating fragile points in the rubber (2), and for the blend, it caused an increased in the elongation at break.

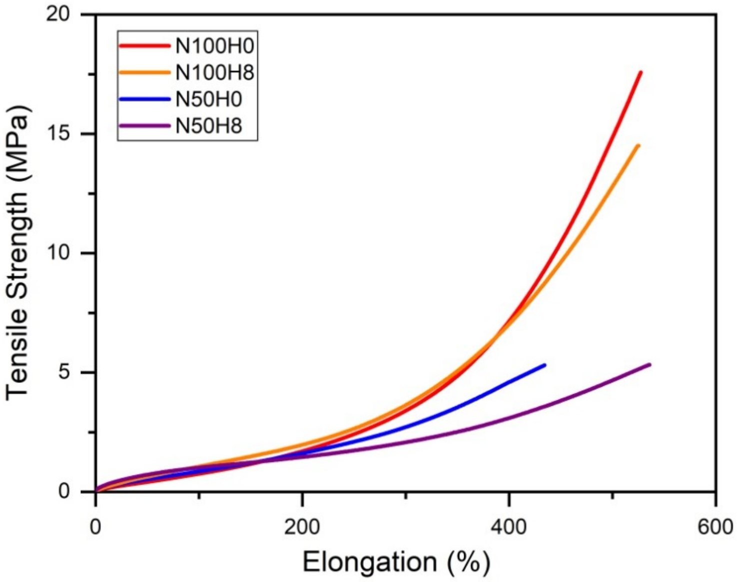

Figure 4: Mechanical properties of NR/CIIR blends.

Table 4: Values of mechanical properties of NR/CIIR.

	Tear strength (kN/m)	Elongation at break (%)	Tensile strength at break (MPa)	Modulus at 100% (MPa)	Shore A
NR100H0	28±6	527±15	17±1	0.75±0.01	33±1
NR100H8	31±6	525±27	15±1	1.08±0.03	42±0
NR50H0	16±2	434±32	5±1	0.85±0.03	37±1
NR50H8	17±1	533±16	5±1	1.01±0.01	41±1

CONCLUSION

On the other hand, the incorporation of CIIR into NR presented a retardant effect on vulcanization, increasing the scorch time and shifting the T_0 and T_{max} to higher values. This behavior is related to the lower overall unsaturation of the NR/CIIR blend, which delays the formation of cross-links during vulcanization.

The clay addition influenced the vulcanization acting as an accelerator, as evidenced by the decreased scorch time and shifting of onset (T_0) temperatures and the maximum temperature (T_{max}) of the exothermic peak related to the vulcanization reactions followed by DSC. This acceleration was attributed to the ammonium groups in the organoclay, which catalyzes the initial steps of the vulcanization. Even though it did not show any effect in the later steps of the vulcanization process, as showed by the CRI, that was practically constant .

Clay addition also caused a reinforcement effect, decreased the reversion, and increased the tear strength, the rubber hardness, and the elastic modulus.

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