



ALTERNATIVE CROSSLINKING SYSTEM FOR POLYCHLOROPRENE

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ABSTRACT

Polychloroprene (CR) has been applied in different areas due to its chemical nature, polarity, and crystallinity characteristics. For this reason, CR has distinct properties from other elastomers, such as higher heat, flame, and oil resistance. Hence, its applications are broad and range from the aerospace and automotive segments to the footwear industry. Vulcanization systems based on zinc oxide are commonly used in halogenated rubbers. Recently, this inorganic oxide has been pointed out as responsible for causing severe environmental impacts, mainly on aquatic life. Therefore, alternative and more environmentally friendly curing agents have been studied. Among them, ferric acetylacetonate (FeAc) stands out due to its performance as a crosslinking promoter and low toxicity. In this study, polychloroprene compounds containing FeAc as a crosslinking promoter with different contents of fumed silica, 7phr (CR-7F) and 30phr (CR-30), were developed for use as a solvent-borne adhesive. A compound of polychloroprene and zinc oxide (CR-ZnO) was used as reference material. An oscillating disc rheometer monitored crosslink bond formation. The profiles of the vulcanization curves of the CR containing FeAc and CR-ZnO were similar. After vulcanization, the crosslinking density of CR compounds was obtained by swelling test. The CR-7F and CR-30F showed crosslinking density values between 2.5 and 4 times higher than that observed for the CR-ZnO compound. The alternative vulcanization system employed practically did not affect the CR compounds' glass transition temperature (T_g), which was approximately -38 °C for both systems. These results indicate that ferric acetylacetonate is a vulcanizing agent in polychloroprene rubber. It is an excellent substitute for ZnO in the vulcanization process, reducing the environmental risk associated with CR during its disposal.

Keywords: Polychloroprene, alternative crosslink system, crosslink density

INTRODUCTION

Polychloroprene is a versatile polymer present in several constantly evolving industries, such as aerospace and automotive. In addition, it is widely used as adhesive, due to its high polarity and crystallinity. Polychloroprene is obtained by emulsion polymerization, which results in two types of isomers, the most commercially available variation being

trans-1,4-polychloroprene. This type of configuration associated with regular tacticity, together with the presence of the chlorine (Cl) atom, results in better mechanical properties and a tendency to crystallize, which is not common in elastomers^(1,2). Vulcanization systems based on zinc oxide are commonly used in halogenated rubbers. However, its use in polymers has raised awareness about the environmental impact caused by the release of metallic oxide from materials discarded in nature, especially in aquatic life^(3,4). To mitigate this environmental impact and the risk to human health, alternative and eco-friendly vulcanizing agents, such as metal complexes, have been proposed⁽⁵⁾. In the present study, the ZnO-based vulcanization system was replaced by ferric acetylacetonate in polychloroprene compounds. In addition, triethanolamine (TEA) was added to the alternative vulcanization system to ensure the alkaline environment of the reaction, thus regenerating the catalyst during the process⁽⁵⁾. In this study, compounds based on CR were developed and evaluated for application as adhesive, containing components with a lower degree of toxicity and more sustainable.

MATERIALS AND METHODS

CR compounds were prepared in a two-roll rubber open mixing Mill Lab 350, COPE, using neoprene W type (100 phr), FeAc (0.1 phr), and triethanolamine (4 phr). Fumed silica was added to the adhesives as a reinforcing filler at 7 phr (CR-7F) and 30 phr (CR-30F). A compound of polychloroprene and zinc oxide (CR-ZnO) was used as reference material, containing about 54wt% solid filler. Rubber crosslinking reactions were monitored by rheometric test using an MDR rheometer, *Alpha Technologies*, at 145°C for 90 min. The crosslinking density of the CR compounds was obtained by a swelling test based on the ASTM D6814 standard. About 5 g of the adhesive film were vulcanized for 6 h in an autoclave at 145°C and 5 kgf/cm². Then, the CR compounds were put in acetone for 16 h, oven dried, and subjected to the swelling process in toluene for 72 h. The CR compounds crosslinking reaction was followed using a DSC Q100, TA Instruments. Adhesive films were cooled to -90 C and heated at 10 C.min⁻¹ up to 200 C in an inert N₂ atmosphere.

RESULTS AND DISCUSSION

Rheometry

Figure 1 shows the rheological profile of the different CR compounds and the NBR rubber. The main rheometric parameters are shown in Table 1.

Table 1 – CR compounds rheometric parameters.

CR compounds	ML (± 0,01dN.m)	MH (± 0,01dN.m)	t ₅₀ (min)	t ₉₀ (min)
CR-ZnO	0,30	3,30	23,99	65,39
CR-7F	0,77	9,21	15,02	56,60
CR-30F	4,87	27,43	16,55	62,81
NBR	3,78	16,89	8,78	49,87

ML, minimum torque; MH, maximum torque; t₅₀ and t₉₀ refer to the time required for crosslinking at 50 % and 90 %, respectively.

The minimum torque (ML) values correspond to the lowest torque recorded during the test, and it is measured before vulcanization begins, corresponding to the viscosity of the rubber^(6,7). The torque increase is associated with the rubber crosslinking processes. As the crosslinking agents and the active sites for bonds are consumed, the vulcanization reactions decrease, and a plateau is reached in the torque curves. The maximum torque (MH) is recorded⁽⁸⁾. According to the rheometric curves (Figure 1) and the parameters presented in Table 1, it is possible to verify higher ML values for the CR compounds containing FeAc/TEA system. At the beginning of the curve (ML), before the crosslinking reactions, it is noted that the silica content significantly increases the viscosity of CR. This should occur due to the interaction of the polar groups on the surface of the silica particles with the chlorine present in CR. The addition of silica also causes an increase in the MH values. In this case, there is the contribution of the crosslinking reactions of the CR chains, which should cause an additional increase in the stiffness of the CR compounds. The torque curves show that the crosslinking reaction in CR compounds containing FeAc/TEA system and NBR occurs simultaneously at 145 °C (Figure 1). This result shows that the CR compounds containing FeAc/TEA system are suitable for bonding NBR-based substrates. The filler content influenced the torque curves (Figure 1), as can be seen by comparing the curves of the CR compounds with 7 phr and 30 phr of silica.

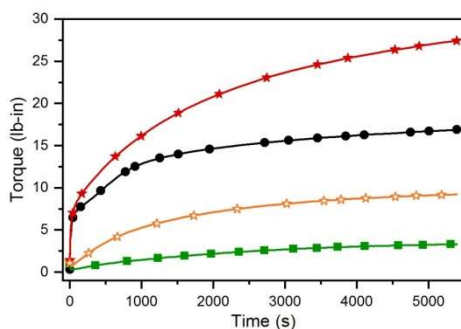


Figure 1 – Rheometric curves obtained at 145° C for: CR-ZnO (-■-), CR-7F (-★-), CR-30F(-★-) and NBR (-●-).

The difference between the maximum and minimum torques can be used as an indication of the crosslinking density of the vulcanized rubbers (Table 2)⁽⁹⁾. The filler effect on the torque values obtained must be mitigated when discounting the ML value, considering that vulcanization has not yet occurred in this region, and the torque values are relative to the presence of filler in the compound. CR compound containing 30 phr silica showed the highest $\Delta_{(MH - ML)}$ values, suggesting that higher crosslinking densities occur in the presence of higher silica contents.

Table 2 – Difference between the maximum and minimum torques for CR compounds.

CR compound	$\Delta_{(MH - ML)}$ (dN.m)
CR-ZnO	3.0
CR-7F	8.4
CR-30F	22.6

Crosslinking Density (Flory-Rehner)

The crosslink density (V_e) of the CR compounds was obtained according to the Flory-Rehner theory⁽¹⁰⁾ (Table 3).

Table 3 - Crosslinking density obtained by swelling test.

Rubber	Density in methanol (g.cm ⁻³)	Solvent _{absorbed mass} (g)	Crosslinking density - V _e (10 ⁻⁴ .mol.cm ⁻³)
CR-ZnO	1.6857	11.67	1.5
CR-7F	1.2672	12.09	3.8
CR-30F	1.3603	8.81	6.3

The CR compounds containing FeAc/TEA system presented the highest cross-linking density values by swelling test, following the previous results from rheometry. In addition, the CR-30F showed the highest V_e values, indicating a tendency for the crosslinking density to rise with increasing silica content. Khabiri et al.⁽¹¹⁾ observed a similar effect in their study, attributing the reduction of swelling to a solid filler that occupies a part of the composite volume. Soriano-Luna et al.⁽¹²⁾ obtained similar results and reported that the filler does not produce chemical crosslinking. However, its dispersion competes with crosslinking, leading to a physical effect that reduces the penetration of solvent molecules into the polymer matrix, which is reflected in the values of crosslinking density obtained from the Flory-Rehner equation. Although the CR-ZnO compound has the highest content of inorganic fillers, about 54 %, it presented the lowest value of V_e, even though it has 5-15 wt % precipitated silica. This behavior allows one to state that, despite the influence of the filler content on the crosslinking density obtained by swelling test, the FeAc/TEA system used as a crosslinking promoter for polychloroprene was effective and resulted in higher crosslinking densities compared to the CR compound based on zinc oxide. The swelling test results were influenced by both the surface area of the particles and the functional groups present on their surface. However, it is possible to state that the vulcanization system based on FeAc caused an increase in the chemical crosslinking density of the polymer when compared to the system involving zinc oxide.

DSC

The crosslinking reaction of CR compounds was followed using a DSC (Table 4 and Figure 2).

Table 4 – Glass transition temperature(T_g), melting temperature (T_m), enthalpy of melting (ΔH_m), and enthalpy of crosslinking reaction (ΔH_{cr}) for CR compounds.

Adesivo	T _g (± 1°C) ^a	T _g (± 1°C) ^b	T _m (± 1°C)	ΔH _m (J/g) ^{c,d}	ΔH _{cr} (J/g) ^{c,d}
CR	-39	-39	42	12	-
CR-ZnO	-38	-37	40	11	18
CR-7F	-40	-38	41	17	48
CR-30F	-40	-38	41	15	50

^aT_g values obtained in the DSC first heating (before the crosslinking reaction)

^bT_g values obtained in the DSC second heating (after the crosslinking reaction)

^c Up to 10 % deviation

^d Corrected value relatively to polymer mass

Typically, the polychloroprene T_g is approximately -45 °C⁽¹³⁾. All CR compounds presented T_g close to -40 °C in the first heating, observing a reduction of approximately 2 °C in the second heating (Table 4). This behavior can be attributed to the presence of the crystalline phase of the CR before the DSC first scan (Figure 2-a). In the DSC analysis, the melting

relative to the crystalline phase of the CR was observed only at the first heating and occurred at around 41 °C. Due to the cooling rate, there was insufficient time to crystallize the chains. Thus only the glass transition was observed at the second heating (Figure 2-b).

In Figure 2-a, for all CR compounds, there is an exothermic variation of the baseline occurring between 150 °C and 250 °C due to the CR crosslinking reaction. CR compounds containing FeAc showed the highest enthalpy values, 166–177% superior to that observed for CR-ZnO. This result indicates a higher degree of crosslinking of the polychloroprene in the presence of FeAc compared to that obtained using the system containing zinc oxide. It has also been noted that in the CR-ZnO compound, the vulcanization reaction occurs between 100 °C and 220 °C, while in the adhesive films containing FeAc, the reaction is shifted to higher temperatures, starting at around 130-140 °C.

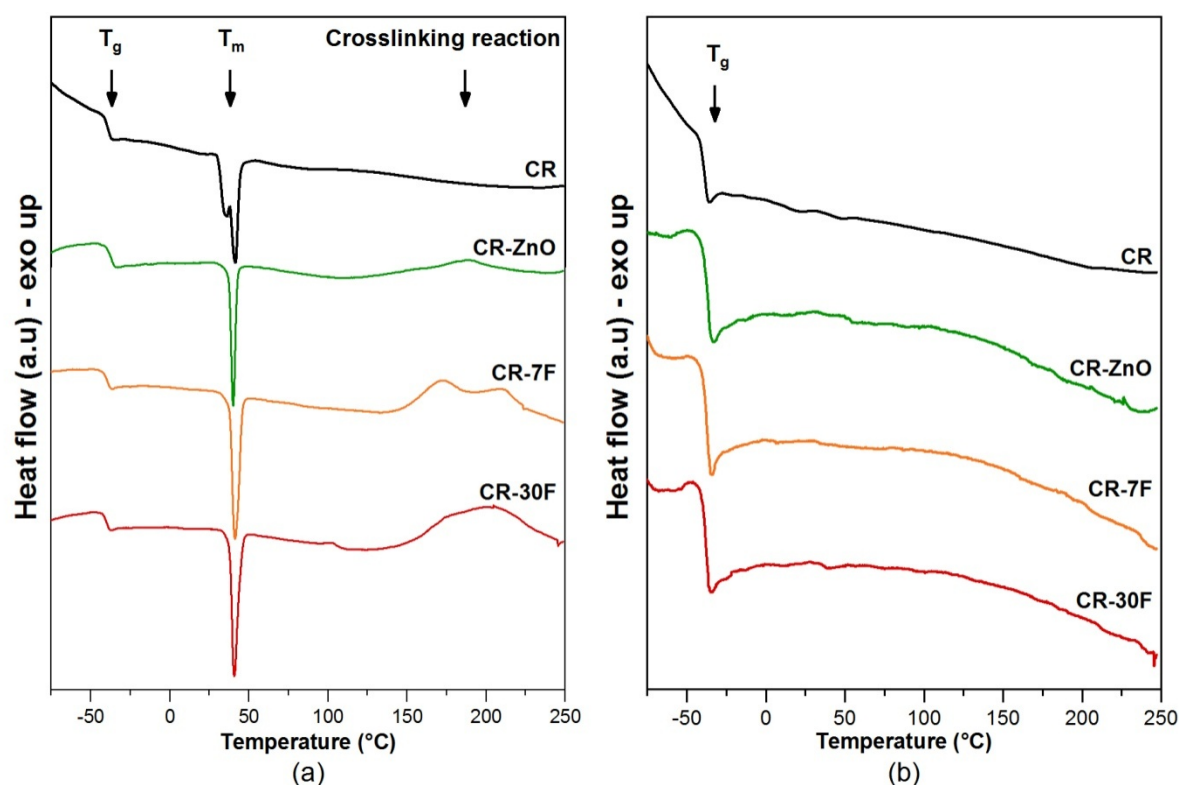


Figure 2 – DSC curves: (a) first heating; (b) second heating.

The enthalpy of crosslinking of the CR-FeAc/TEA compounds is almost three times higher than the enthalpy observed for the CR-ZnO compound, indicating a higher crosslinking density of CR in the presence of the FeAc/TEA system. Tchallaet *al.*⁽¹⁴⁾ and Sae-ouiet *al.*⁽¹⁵⁾ suggest that in the specific case of silica filler in polychloroprene rubbers, a strong interaction via hydrogen bonding occurs between the silanol group present on the silica surface and the chlorine atom of the CR, which can explain the increase in crosslinking density observed by different techniques used in this study.

CONCLUSIONS

CR compounds containing the FeAc/TEA system as a crosslinking system showed, by different techniques, a tendency to increase at least two times the values of crosslinking density when compared to the conventional CR-ZnO compound. Higher levels of silica caused the increase of crosslinking in tests such as rheometry and swelling tests (Flory-Rehner). These results suggest that silica particles act as a physical crosslinker, which has

been attributed to the presence of hydrogen bonds between silanol groups of the silica and the chlorine atom of the CR. The environmentally friendly AcFe/TEA system proved to be a superior vulcanization-promoting agent for polychloroprene compounds compared to a system based on zinc oxide.

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