PERFORMANCE OF POLYCHLOROPRENE ADHESIVE CONTAINING AN ENVIRONMENTALLY FRIENDLY CURING SYSTEM

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ABSTRACT

Elastomeric adhesives are crucial in extreme conditions, and polychloroprene adhesives are commonly used. Traditional formulas often include harmful components like toluene and zinc oxide. This study explored alternatives, using ferric acetylacetonate as the vulcanizing agent and methyl ethyl ketone as the solvent, while testing fumed silica (2 to 6 phr) as a filler. A reference compound with 10 phr of precipitated silica, ZnO, and toluene was used for comparison. Results showed that ferric acetylacetonate-based adhesives had higher torque values, indicating better cross-linking than ZnO-based ones. Increasing silica content improved torque and peeling resistance. The best peeling resistance was found at higher silica levels. Despite these advancements, ZnO-based compounds still outperformed others in peeling resistance. DSC analysis revealed a more pronounced crystalline phase with higher silica content. Overall, the new formulations performed nearly as well as the traditional ZnO-toluene adhesives.

Keywords: Polychloroprene, Ferric acetylacetonate, Zinc oxide, Adhesive.

INTRODUCTION

Polychloroprene, commonly known by the trade name Neoprene, is a versatile synthetic rubber and adhesive. Its unique chemical structure, characterized by the presence of chlorine atoms, imparts superior properties such as exceptional resistance to oil, chemicals, and weathering. This makes polychloroprene an ideal material for a wide range of applications, from wetsuits and orthopedic braces to automotive belts and aerospace industry [1]. In its adhesive form, polychloroprene offers strong bonding capabilities, especially with metals, woods, and various plastics. It is widely used in the construction, automotive, and footwear industries due to its excellent adhesive properties, which include high initial strength and good heat and solvent resistance [2]. A critical component in the formulation of polychloroprene products is zinc oxide. This compound serves multiple purposes, including acting as an activator for the curing process, enhancing the heat resistance of the final product, and improving overall material properties. Zinc oxide helps in cross-linking during the vulcanization of polychloroprene rubber, contributing to the robustness and durability of the end products.However, the use of zinc oxide is not without environmental concerns. When polychloroprene products degrade or during the manufacturing process, zinc oxide can be released into water bodies. Zinc oxide is highly toxic to aquatic life, causing significant ecological damage. It can disrupt aquatic ecosystems by impairing the reproductive and growth capabilities of fish and other marine organisms. Moreover, it can accumulate in the food chain, posing risks to both aquatic species and human health. The environmental impact of zinc oxide underscores the need for careful management and innovative approaches to mitigate its release into the environment [3].

Ferric acetylacetonate is emerging as an innovative alternative to zinc oxide as a curing agent in polychloroprene adhesives [4, 5]. Its effectiveness as a curing agent for polychloroprene is based on its ability to facilitate cross-linking during the vulcanization process. This cross-linking enhances the mechanical properties, heat resistance, and durability of the adhesive. Ferric compounds do not bioaccumulate in the same way as zinc compounds, thereby mitigating the long-term environmental risks associated with their use [4]. The use of ferric acetylacetonate can enhance the thermal and oxidative stability of the adhesive. Its ability to maintain high-performance standards while offering environmental benefits makes it anattractive alternative for manufacturers seeking to adopt more sustainable practices [5].

Toluene, a solvent widely used in the production of this adhesive, is also being replaced to reduce environmental impacts and hazards to human health.Methyl ethyl ketone (MEK) is a possible alternative, with its faster evaporation rate enhancing production efficiency. The lower toxicity levels of MEK significantly reduce health hazards, creating a safer working environment [6].These benefits make MEK an excellent choice for CR-based adhesives.With this in mind, the aim of this work was to minimize environmental and human hazards by maintaining a high-quality adhesive material

EXPERIMENTAL

The CR compounds were prepared using a W-type neoprene (Denka); fumed silica (Cab-osil–M5, CABOT); triethanolamine (TEOA, NEON); methyl ethyl ketone (MEK, NEON); toluene (Química Moderna). Ferric acetylacetonate was synthesized from the dissolution of ferric chloride in water, followed by the addition of ammonium hydroxide. This solution was kept under stirring for 2 h. Then acetylacetone was added, and the solution was stirred for another 3 h. After that, the product was filtered, washed, and vacuum dried at 60°C for 24 h. CR compounds (CR-FeAc) were prepared directly in solvent, first dissolving the rubber in a mixture MEK/toluene (90/10) vol%., adding silica in their specific proportions, and then TEOA and FeAc under stirring. CR-ZnO compounds were also prepared directly in solvent, adding all the fillers under stirring.Part of the compound was dried at room temperature to evaporate the solvent for 48 hours to carry out the mechanical and thermal tests that require the solid material for analysis. The CR-FeAc compounds contained 100phr of CR, 0.1phr of FeAc, and 4phr of TEOA. Furthermore, the CR-FeAc compounds were differentiated based on the amount in phr of fumed silica in their composition (2; 4; 6). The naming of these compounds included the fumed silica amounts added in brackets after the acronym, CR-FeAc(x). The CR-ZnO compound was used as a reference, and it contained about 53% inorganic filler, with approximately 10% of precipitated silica. This compound cannot have its composition detailed for reasons of confidentiality.

All the compounds were cured in a Premier MDR equipment rheometer (Alpha Technologies) to monitor their mooney viscosity (high and low) and vulcanization parameters. All the analysis was conducted at a temperature of 145°C for 90 minutes.

Differential exploratory calorimetry analysis (DSC) was conducted to follow events involving heat variation, measuring temperature and enthalpy associated with the thermal transitions of the materials analyzed. The properties measured include the melting enthalpy (∆Hm) of the crystalline CR phase and the glass transition temperature (Tg) of the CR amorphous phase.DSC analyses were carried out on the DSC Q100, TA Instruments. The elastomeric compounds were cooled to -90°C and heated at 10 $°C.min^{-1}$ to 250°C. The analyses were carried out in duplicate, using each previously formulated CR compound, all kept at 20±5°C for at least one week to allow the crystallization of part of the CR chains.

The T-peel test was carried out following ASTM D1876-08 to assess the effectiveness of CR adhesives. The test was carried out using two unvulcanized NBR (acrylonitrile-co-butadiene) rubber laminate panels as a substrate, with the respective adhesive spread on both surfaces and then bonded. The specimens were then vulcanized inan autoclave for 6 hours at 145°C and 5 kgf/cm^2, sothey could be subjected to the T-Peel test, which was carried out on the ZWICK 1474 equipment, starting in traction mode with a speed of 256 mm/min and a load cell of 5 kN.

RESULTS AND DISCUSSION

The rheometry test is one of the most important tests for evaluating the behavior of the solid adhesive (rubber).It allows investigating the effectiveness of the curing agent and the interactions between the elastomer and its fillers [7]. Figure 1 and Table 1 show the rheometric profiles of the CR compounds. At first, comparing the compounds formulated with FeAc and ZnO, it is possible to notice the difference in torque (lb-in) of the materials. This fact can be explained by the effectiveness of the metal complex in creating a higher density of cross-links in the elastomer matrix. The Mooney viscosity difference (M_H-M_L) can also be used to evaluate the crosslink density of the material [4]. The CR-ZnO compound presented the lowest M_H-$M_L$indicating the lowest crosslink density. Another consideration about this result is that the compound containing ZnO has around 50% chloroprene rubber compared to the ~90% rubber present in the FeAc composition, which can result in a lower torque value and make the material "softer".Among the CR-FeAc compounds, the torque value increases as the amount of silica in the formulation increases. Therefore, when combined with the high density of crosslinks and the increase in reinforcement filler, the torque consequently increases in the CR compounds, with the exception of CR-ZnO.As far as vulcanization times are concerned (t_{50} and t_{90}), the fillers used seem to be quite decisive.The greater the amount of fillers in the elastomer matrix, the longer the vulcanization time.

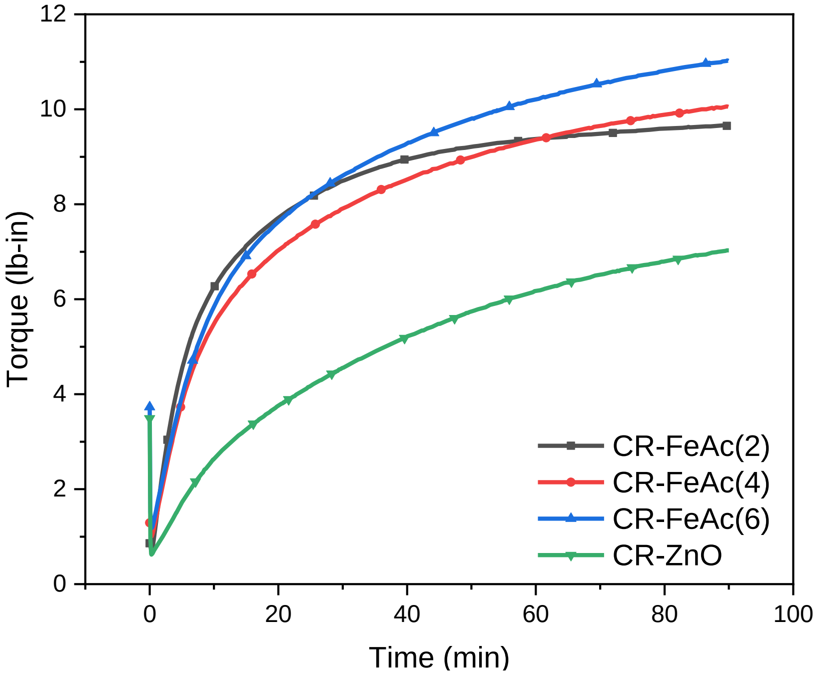

Figure 1: Rheometric curves obtained at 145°C for the CR compounds containing the vulcanization system based on FeAc or ZnO.

Table 1: Rheometric data obtained for CR compounds.

CR Compound (145°C)	M_L (±0,01 dN.m)	M_H (±0,01 dN.m)	t_{50} (min)	t_{90} (min)	M_H-M_L
CR-FeAc(2)	0.68	9.67	6.39	35.52	8.99
CR-FeAc(4)	1.01	10.07	10.24	54.05	9.06
CR-FeAc(6)	1.18	11.03	10.98	55.63	9.85
CR-ZnO	0.63	7.31	21.62	67.56	6.68

M_L: Mooney low; M_H: Mooney high; t_{50}: time taken to 50% vulcanization; t_{90}: time taken to 90% vulcanization.

Fig. 2 and Table 2 show the results of the DSC analysis. The CR Tg is expected to occur at approximately -45 °C [8]. In this study, all the CR compounds ranged from -37°C to -33°C (Fig. 2). Polychloroprene has a tendency to crystallize, favored by the presence of the polar -Cl group, resulting in the organization of part of the CR chains. Melting is a first-order transition, and will be recorded as an endothermic peak in the DSC curve [9, 10]. In Fig. 2 an endothermic peak due to the melting of CR crystalline phase occur at around 40°C (Table 2). The melting temperature (Tm) of the CR crystalline phase, obtained by the minimum of the endothermic DSC peak, showed a slight shift towards higher temperatures with the addition of silica. This result was expected since the silica particles act as crystallization nuclei. The melting enthalpy of the CR-ZnO compound was approximately half that observed for the CR-FeAc compounds, even after correcting it about the CR weight. This behavior is in accordance with the increasing in the CR crystalline phase up to 6 phr silica. This behavior can be explained considering that the smaller the amount of silica, the less chance of it creating agglomerates, thus having a larger surface area to interact with the elastomer chains. This interaction significantly increases the nucleation and, consequently, the crystalline phase. The lower enthalpy of melting of CR-ZnO compared to CR-FeAc compounds may be associated with the high filler content added to this compound, making crystallization of the CR chains more difficult. The crystalline phase is an important factor in increasing the mechanical strength of the adhesive [11].

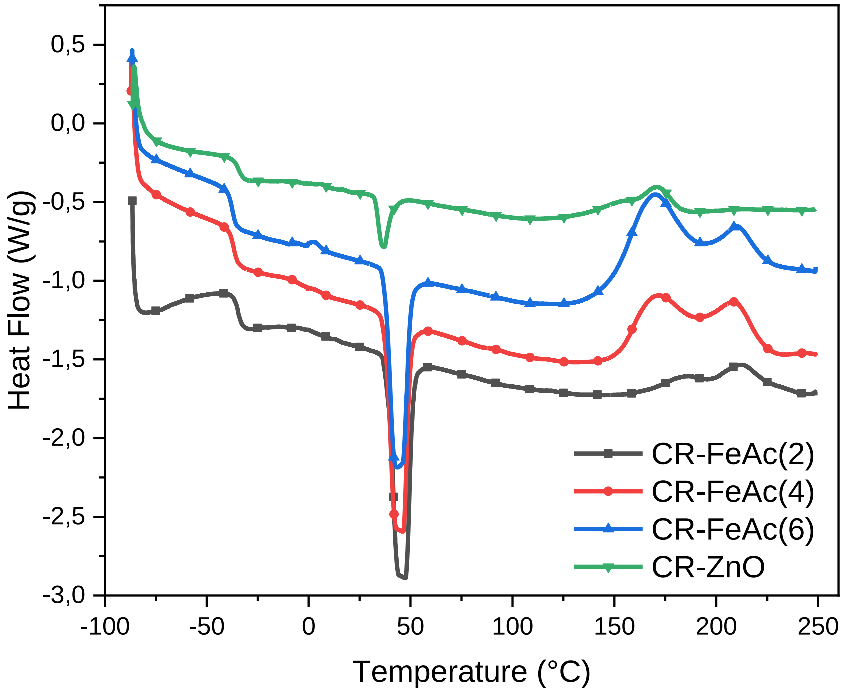

Figure 2: DSC curves of CR compounds in inert atmosphere.

Table 2: Glass transition temperature (Tg), melting temperature (Tm) and enthalpy of melting (ΔHm) obtained by DSC.

Compound	**Tg (±1°C)**	**Tm (±1°C)**	ΔHm**(J/g)**[a]	ΔHmc**(J/g)**[a,b]
CR-ZnO	-33	42	3,5	8,5
CR-FeAc(2)	-35	47	15,6	16,6
CR-FeAc(4)	-37	43	14,7	16,0
CR-FeAc(6)	-37	43	13,8	15,2

[a] ΔHm deviation ≤ 10%

[b] ΔHmc: enthalpy of melting considering only the polymer weight

The t-peel test was carried out in order to evaluate the adhesive strength of the CRadhesives, which were used to bond two NBR blankets. The peeling should be symmetrical and the failure should preferably propagate towards the center of the adhesive bond line [10]. Figure 3 shows the results of the peeling test, where the CR-ZnO adhesive showed the highest resistance to peeling, being very consistent throughout the test. The FeAc compounds, on the other hand, shows that the greater the amount of silica, the greater their resistance to peeling. However, it is worth noting how close the CR-FeAc(6) sample comes in terms of resistance to peeling to the CR-ZnO compound, which is commonly used in this type of adhesive, showing that a composition with far fewer additives, being even less aggressive to nature, can come close to what would be the standard used on the market. Still, on the FeAc composites, the oscillation in the force vs. displacement values (Figure 3) may be related to the non-continuous application of the adhesive on the surface of the NBR blanket, which can be easily adjusted at the adhesive application stage.

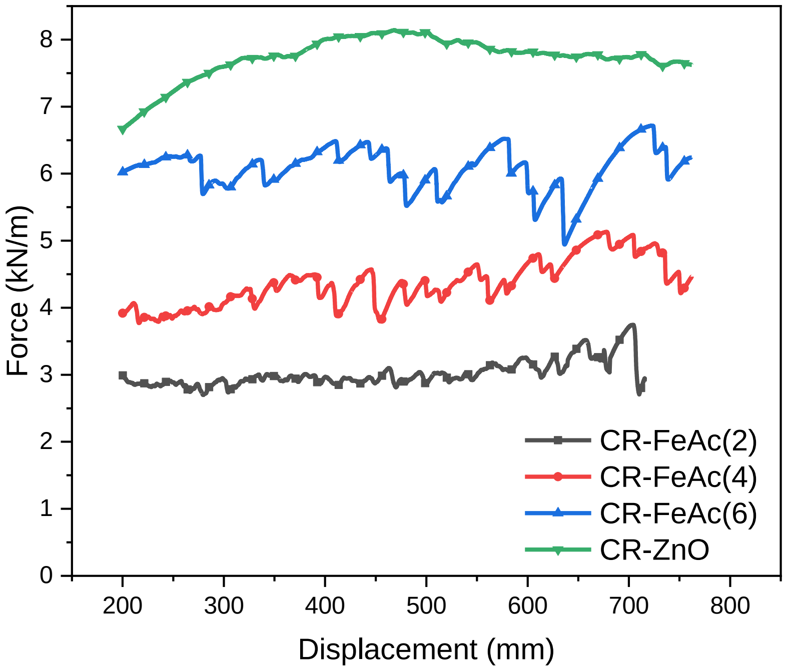

Figure 3: Curves obtained in the T-Peel test for NBR specimens containing CR-ZnO and CR-FeAc(x) adhesives.

CONCLUSION

The CR-FeAc compounds have a higher torque and a higher density of cross-links than the CR-ZnO compound. The addition of low levels of silica practically doubled the melting enthalpy of the crystalline phase of CR-FeAc compounds compared to CR-ZnO, causing a slight shift of the peak minimum towards higher temperatures due to the nucleating effect of the silica particles at lower levels. In the peeling resistance tests, the CR-ZnO adhesive showed the best result compared to the FeAc compounds, while the CR-FeAc(6) adhesive was very close to the CR-ZnO compound. Considering the smaller number of components in the formulation and the impact on nature and human health, compounds containing the metal complex are promising for replacing zinc oxide adhesives.

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