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Processing of Thermoplastic Elastomers (TPE) by In-Situ Ground Tire Rubber (GTR) Vulcanization using Waste Ethylene-Vinyl-Acetate (wEVA) and Dicumyl Peroxide (DCP)

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Processing of Thermoplastic Elastomers (TPE) by In-Situ Ground Tire Rubber (GTR) Vulcanization using Waste Ethylene-Vinyl-Acetate (wEVA) and Dicumyl Peroxide (DCP)

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Abstract: Tire rubber waste (TRW) is a complex mixture of materials, such as rubbers, steel, textile fibers, carbon black, and other additives. Its polluting capacity is a severe environmental problem, especially in landfills and waste management processes. As a practical solution to mitigate TRW's environmental impact, thermoplastic elastomers (TPE) commonly reuse the ground tire rubber (GTR). This work presents an in-situ devulcanization of ground tire rubber (DGTR) and re-vulcanization of devulcanized ground tire rubber using dicumyl peroxide (DCP) and waste ethylene-vinyl-acetate (wEVA). The GTR was devulcanized through thermo-mechanical action and then blended with waste ethylene-vinyl-acetate (wEVA) and dicumyl peroxide (DCP) to produce the thermoplastic elastomer (TPE). This blending process was monitored using a torque rheometer and analyzed with differential scanning calorimetry (DSC) to evaluate the crosslinking reactions and kinetic behavior. The results indicated that in-situ vulcanization took place within the rheometer mixing chamber, evidenced by an increase in torque. DSC analysis of the DGTR-DCP-wEVA system confirmed the curing reaction prior to vulcanization. The resulting in-situ vulcanized TPE ensures improved component adhesion. This research offers practical insights into a scalable, non-advanced process for local plastics industries in developing countries to incorporate vulcanized TPEs, thereby enhancing their knowledge and understanding of this innovative approach.

Keywords: Thermoplastic Elastomers, Vulcanization, Waste Plastic, Ground Tire Rubber

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Introduction

Sustainable strategies focusing on developing plastic composites after their end-of-life cycle are crucial for the circular economy and pollution mitigation. Tire and plastic residues are ever-growing waste in developing countries, especially South America. This oversight prompts the exploration of a material derived from blending thermoplastic and tire waste, presenting a potential alternative to conventional practices. Thus, TPE are a common alternative to address these problems, employing recycled thermoplastic and elastomers. The main advantage of TPE is that they are easily produced using typical plastic processing methods (i.e., extrusion and injection molding) and the mechanical properties of a rubber [1].

TPE development methodologies from TRW usually use this material as it is received in a particle shape (GTR) without pretreatment. This causes a low interfacial adhesion and poor mechanical properties due to their limited compatibility and crosslinked structure [2]. Consequently, surface and structure modification of GTR can be achieved through chemical or physical methods. Reactive chemical techniques often involve peroxides, with common additives based on ethylene-octane copolymer (EOC), trans-polyoctenamer rubber (TOR), ethylene vinyl acetate (EVA), maleic acid grafted polyolefins (such as PE-g-MA), or ethylene propylene diene monomer (EPDM) [3-5].

This work presents a study of the processability, thermal, and kinetic properties of TPE blends composed from DGTR, wEVA, and DCP. This novel approach allows for the evaluation of the thermal and physical conditions of the devulcanization process by thermomechanical action and the synthesis of vulcanized TPE based on recycled and wasted materials.

Materials and Method

GTR with a particle size of 1 mm was used for the devulcanization process. wEVA with a 10% acetate content was employed as a binding agent. Additionally, DCP was utilized as a crosslinking agent for DGTR/wEVA blends [6]. The devulcanization process of GTR and the processability of composites were evaluated through a Brabender Plastograph® EC Plus torque rheometer at fixed conditions of velocity (90 rpm) and time (10 minutes). Thermal and kinetic analysis of composites was performed by a Differential Scanning Calorimeter (DSC) in non-isothermal conditions and a nitrogen atmosphere, from room temperature to 220°C at 20°C min^{1} to study the vulcanization reaction. The nomenclature of all samples was based on X parts of DGTR by Y parts of wEVA (XDGTR/YwEVA). All samples were mixed with 1.5%wt of DCP [6]. Table 1 depicts the nomenclature of the synthesized composites.

Table 1. Nomenclature and compositions of TPE.

Sample (DGTR:wEVA)	Nomenclature
0:1	wEVA
2:1	2DGTR/wEVA
4:1	4DGTR/wEVA
6:1	6DGTR/wEVA

GTR devulcanization

Devulcanization of GTR was investigated at temperatures ranging from 170°C to 200°C, with increments of 10°C. Subsequently, the DGTR samples were analyzed using the torque rheometer to evaluate the torque increase with the DCP addition. The devulcanization conditions for the DGTR were selected based on the highest torque obtained during re-vulcanization with DCP at 180°C.

TPE synthesis

The composites were prepared at temperatures of 110°C and 180°C. At 110°C, the objective was to obtain the TPE without inducing vulcanization. On the other hand, at 180°C, the aim was to produce in-situ vulcanization in the composites due to the decomposition of DCP.

The kinetic study of composites was conducted using the Borchardt and Daniels (B/D) method (equations 1 and 2) and the Arrhenius equation in this logarithmic form (equation 3) [7], as shown in Table 2.

Table 2. Employed equations for kinetic analysis.

Crosslinking conversion (α)	$\alpha(T) = \dfrac{\int_{T_0}^{T_i}(dH/dT)dT}{\int_{T_0}^{T_\infty}(dH/dT)dT}$	1)
Reaction rate constant described by B/D method (k)	$\ln k(T_i) = \ln\left(\dfrac{q_{T_i}}{\Delta H_d}\right) - n \cdot \ln(1-\alpha_{T_i})$	2)
Reaction rate constant described by Arrhenius (k)	$\ln k(T) = \ln(A) - \dfrac{E_a}{R}\left(\dfrac{1}{T}\right)$	3)

dH/dT is the reaction enthalpy at an infinitesimal temperature; T_0 is the onset reaction temperature; T_i is the reaction temperature on finishing the crosslinking process. q_{Ti} is the heat flow; n is the reaction order; and ΔH_d is the crosslinking energy. A is the pre-exponential factor; R is the universal gas; and E_a is the activation energy.

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Results and Discussion

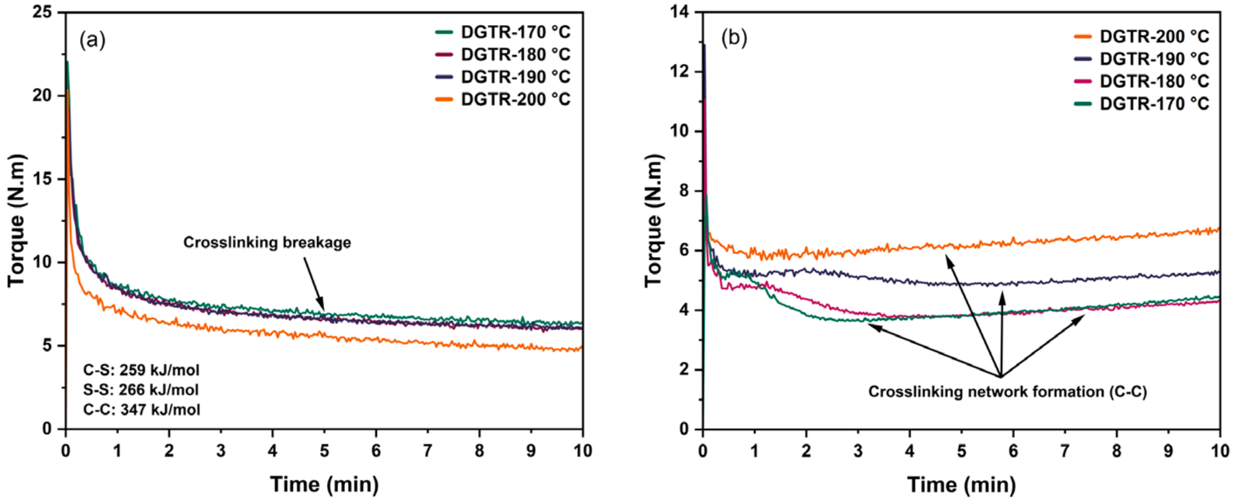

Figure 1. Devulcanization process by thermomechanical action at different temperatures. (b) In-situ re-vulcanization of DGTR by DCP decomposition in the Brabender mixing chamber at 180°C.

Figure 1(a) illustrates the torque-time profile of GTR devulcanization, while Figure 1(b) depicts its in-situ re-vulcanization process. Figure 1(a) shows a decreasing trend in torque values at elevated temperatures (i.e. 200°C). According to Ábel et al. [8], this reduction in torque values is due to the crosslinking breakage effect on carbon-sulfur (C-S), sulfur-sulfur (S-S), and carbon-carbon (C-C) bonds. Markl et al. [9], state that the devulcanization process by thermomechanical action is selective concerning bond breakage. Thus, C-S and S-S bonds are more likely to break in the devulcanized structure of GTR due to their lower bond energies than C-C bonds. Figure 1(b) presents the re-vulcanization torque-time curves measured when the temperature is set to 180°C in the presence of DCP. These results indicate an improved crosslinking behavior for DGTR when devulcanized at higher temperatures. Therefore, GTR devulcanized at 200°C (DGTR-200°C) was chosen as the base material for all compounds.

Figure 2(a) and (b) exhibit the rheological behavior of TPE composites at 110°C and 180°C, respectively. Figure 2(a) displays the processability of TPEs without DCP decomposition due to the lower process temperature to avoid any crosslinking reaction [10]. It can be observed that the torque values are related to the DGTR content in the composites. For example, a disturbance in the torque curve is predominant in 6DGTR/wEVA and 4DGTR/wEVA samples (in contrast to 2DGTR/EVA and EVA) due to DGTR particles in the molten wEVA, as these particles can alter the flow and viscoelastic properties of the polymer matrix, restricting the mobility of the chains [11]. Rigail et al. [12] mention that elevated torque levels are problematic in plastics manufacturing due to their complex processability. Figure 2(b) reveals the change in the torque profiles by vulcanization because of DCP decomposition in the DGTR/wEVA composites. This effect results from the increase in the molecular weight by the free radical polymerization between wEVA-wEVA, DGTR-DGTR, and wEVA-DGTR interfaces [13]. It is essential to highlight the different effects of DCP at different values of DGTR. For instance, wEVA and 2DGTR/wEVA samples show a torque stabilization curve after the polymerization, which, according to Dluzneski [10], is a synonym for a successful crosslinking reaction. Nonetheless, 4DGTR/wEVA and 6DGTR/wEVA composites expose a reversion in the vulcanization reaction. As indicated by Dluzneski [10], this phenomenon may be due to radical transfer and oxygenation due to the air presence in the mixing chamber. The first option is based on a possible stabilizing effect of the crosslinking reaction by wEVA molecules. Thus, at low DGTR contents, an equimolar reaction mechanism between DGTR and wEVA is presumed, which would explain the reversion in samples with higher DGTR content. This stabilizing effect is further enhanced by the abstraction of hydrogen from the methyl group of the acetate in wEVA [10,14,15].

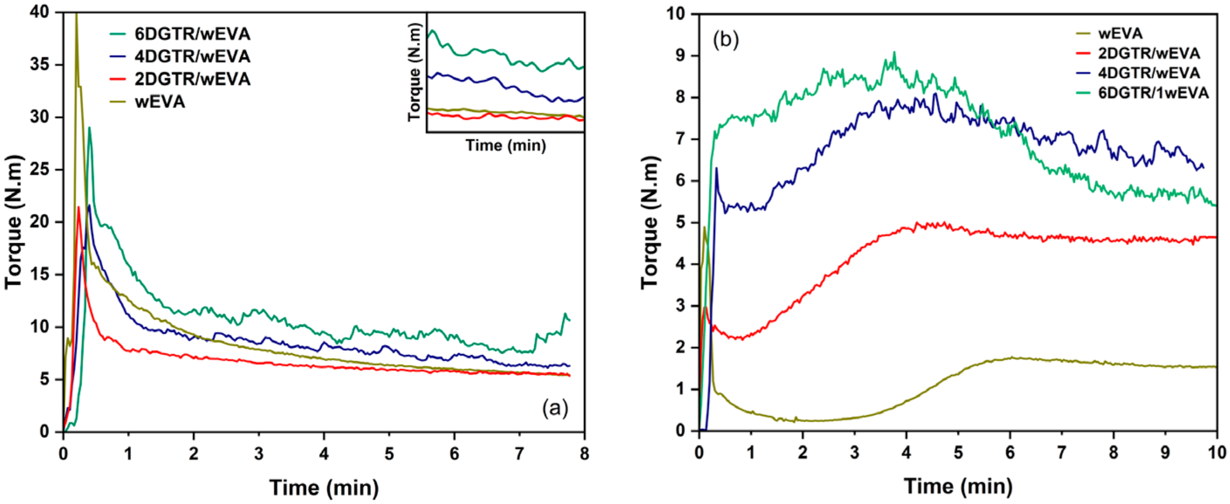

Figure 2. Processability of composites at different temperatures, (a) 110°C and (b) 180°C.

Figure 3(a) and (b) display the thermal behavior and crosslinking rate (α) of samples prepared in Table 1, respectively. Figure 3(a) shows two effects depending on the DGTR content. The first is based on the inverse proportional relation between the released energy and the DGTR content. This suggests that DGTR cannot correctly form free radicals in the presence of decomposed DCP, which supports the results obtained in torque rheometry at 180°C. The second effect is an elevation in the peak maximum temperature of the cross-linking reaction, which is related to the increase in activation energy, as shown in Table 3. The change in the crosslinking conversion rate or reaction order (n) states that crosslinking also occurs at the wEVA/DGTR interface, as Bianchi et al. [15] confirm in their study. From the DSC results, correlations from equations 1, 2, and 3 were employed to obtain crosslinking conversion versus temperature study (Figure 3[b]). These results state that samples containing increasing amounts of GTR showed longer times for the reaction induction, that is, a slower EVA crosslinking rate in the EVA/GTR blends [15], which is related to the higher values of activation energies. However, 6DGTR/wEVA is the only one that shows values of In(A),

E_a, and n different from the trend already discussed, which may be related to the predominance of DGTR, which could explain why these values are very similar to those of 4DGTR/wEVA. This hypothesis must be confirmed by an in-depth study at different DGTR grades up to 100 w/w.

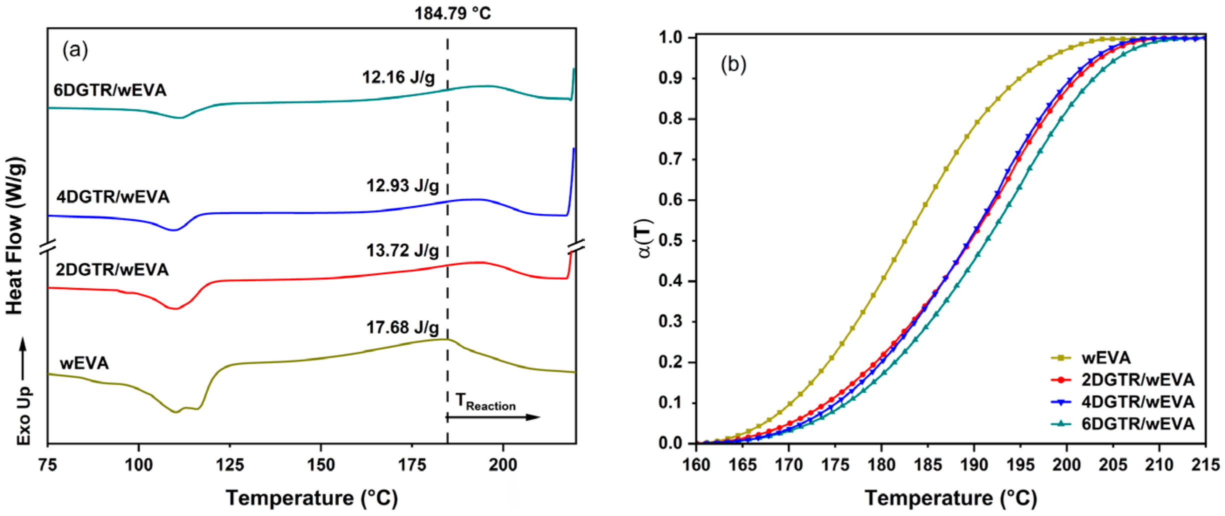

Figure 3. (a) DSC analysis for TPE composites at heating rate of 20°C min^{-1}, and (b) crosslinking conversion (α) of blends using B/D method.

Table 3. Kinetic parameters of DGTR/wEVA blends in DSC at 20°C min^{-1}.

DGTR:wEVA	In(A)	E_a($kJ\ mol^{-1}$)	n	R^2
0:1	63.62	251.20	2.007	0.999
2:1	68.27	273.88	1.860	1.00
4:1	72.16	288.63	1.840	0.999
6:1	70.66	284.07	1.899	1.000

These results provide information on the efficiency of the devulcanization of GTR by thermomechanical action and manufacturing of TPE from plastics and tires, using recycled wEVA, and DCP as a crosslinking agent from a processing, thermal, and kinetic perspective.

Conclusion

This study investigated the influence of DGTR content on the processability, thermal behavior, and kinetics of composites comprising wEVA and DCP (1.5 wt%). Torque rheometry analysis revealed that increasing DGTR content intensified mixing instability, resulting in higher disruptive torque effects. Notably, wEVA demonstrated a stabilizing effect on the vulcanization process of TPE composites. Lower DGTR contents facilitated successful crosslinking of the TPE, whereas higher DGTR contents induced a reversion reaction. Moreover, samples with higher DGTR content exhibited higher activation energy values and lower crosslinking rates. Future research should explore additional properties (mechanical, acoustic, thermal, etc.) to fully assess the potential applications of these composites derived from recycled materials.

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