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Research

Evaluation of Acetylglycerols as Process Oils in Natural Rubber Composites

Evaluación de acetil gliceroles como aceites de proceso en compuestos de caucho natural

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Abstract

Context: In this study, technical-grade glycerin from the biodiesel industry was chemically modified to obtain mono-, di-, and triacetylglycerols (MDTAG). The main objective was to use MDTAG to partially replace naphthenic and aromatic oils, which are actively used as plasticizers in the natural rubber industry.

Method: The synthesis of MDTAG was carried out by mixing glycerin with acetic acid in the presence of an ion-exchange resin as a catalyst. Compounds were prepared by mixing 100 parts of natural rubber with 60 parts of carbon black and adding MDTAG at concentrations of 0, 10, 20, and 30 parts by weight. Curing was performed using a sulfur-based acceleration system. Rheometric properties were evaluated before vulcanization, followed by measurements of tensile strength, elongation at break, tear resistance, abrasion resistance, and compression properties on vulcanized specimens.

Results: Rheometric analyses showed that the addition of MDTAG influenced the curing parameters and the mechanical properties of the compounds. At a dosage of 30 phr, compared with the compound without MDTAG, the maximum torque (MH) decreased by 58.3% when reducing the degree of crosslinking. Tensile strength decreased by 38.2%, elongation at break by 42.1%, tear strength by 24.35%, and comprehensive strength by 27.5%. At a dosage of 10 phr the maximum torque MH was not affected, and tensile strength, elongation at break, and compressive strength were preserved, while the tear resistance decreased by only 5.8%.

Conclusions: The addition of 30 parts by weight of acetylglycerols caused a significant deterioration in the mechanical properties and curing behavior, which may be attributed to the low compatibility between the MDTAG mixture and the NR natural rubber. These results were confirmed by the ANOVA statistical analysis, leading to the conclusion that the MDTAG dosage should be limited to a maximum of 10 phr when used as a partial substitute for naphthenic and aromatic oils in natural rubber mixtures.

Keywords: acetylation, composites, glycerol, MDTAG, natural rubber, vulcanization.

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Resumen

Contexto: En este estudio se modificó químicamente la glicerina de grado técnico proveniente de la industria del biodiesel para obtener mono, di, tri acetil gliceroles (MDTAG). El objetivo principal fue usar MDTAG para reemplazar parcialmente aceites nafténicos y aromáticos, los cuales se usan activamente como plastificantes en la industria del caucho natural.

Método: La síntesis de MDTAG se realizó mediante la mezcla de glicerina con ácido acético en presencia de una resina de intercambio iónico como catalizador. Se prepararon compuestos mezclando 100 partes de caucho natural y 60 partes de negro de humo, agregando MDTAG en concentraciones de 0, 10, 20 y 30 partes en peso. El proceso de curado se realizó con un sistema de aceleración a base de azufre. Se evaluaron propiedades reométricas antes de la vulcanización y, posteriormente, se midieron resistencia a la tracción, la elongación a la rotura, la resistencia al desgarro, la resistencia a la abrasión y las propiedades de compresión en probetas vulcanizadas.

Resultados: Los análisis reométricos mostraron que la adición de MDTAG influyó en los parámetros de curado y en las propiedades mecánicas de los compuestos. Con una dosificación de 30 phr, en comparación con el compuesto sin MDTAG, se obtuvo una disminución del torque máximo (MH) en 58.3%, lo que indica una reducción en el grado de entrecruzamiento. Asimismo, se observó una reducción del 38.2% en la resistencia a la tracción, del 42.1% en la elongación a la rotura, del 24.35% en la resistencia al desgarro y del 27.5% en la resistencia a la compresión.

Con una dosificación del 10 phr, el torque máximo (MH) no se vio afectado significativamente, y se conservaron la resistencia a la tracción, la elongación a la rotura y la resistencia a la compresión, mientras que la resistencia al desgarro disminuyó solo en un 5.8%.

Conclusiones: La adición de 30 partes en peso de acetil gliceroles provocó una degradación significativa de las propiedades mecánicas y del comportamiento de curado, lo que puede atribuirse a la baja compatibilidad entre la mezcla del MDTAG y el caucho natural (NR). Estos resultados fueron confirmados mediante el análisis estadístico ANOVA, lo que permite concluir que la dosificación de MDTAG debe limitarse a un máximo de 10 phr cuando se utiliza para su uso como sustituto parcial de aceites nafténicos y aromáticos en mezclas de caucho natural.

***Palabras clave*:** acetilación, caucho natural, compuestos, glicerol, MDTAG, vulcanización.

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1. Introduction

The international market is experiencing an oversupply of glycerin driven by the increase in global biodiesel production. Crude glycerin is generated as a by-product of the transesterification of palm oil with methanol in the presence of a basic catalyst, generally sodium hydroxide [1]. It is also obtained during biodiesel production from oleaginous crops and other biomass-derived oils, accounting for approximately 10% of the total conversion output [2]. The large quantities generated, together with the presence of impurities, pose challenges for its purification and commercialization for use in biorefineries [3]. The starting point for recovering glycerin consists of purifying it to remove methanol, soaps, salts, and water, thereby obtaining technical grade glycerin (GT) with a purity of 97% [4]. Glycerol carbonate is the dominant product used to maximize glycerol profitability [3]. Various valorization alternatives for GT have been studied, including its use as a raw material for the production of alkyd resins, biodegradable polyurethanes, 1,3-propanediol, succinic acid, fertilizers [5], [1], glycerol carbonate [6], and solketal, which can enhance fuel octane number and oxidation stability [7]. Other applications include oxygenated fuel additives, polymer precursors and other industrial bio-based chemicals [8]. Additional purification of GT to obtain USP-grade glycerin (with purity >99.7%) proves to be more costly than the synthesis itself [9].

One of the chemical modification routes for glycerin consists of transforming acetyl glycerol esters (mono-, di- and triacetin) [10] it into MDTAG mixtures [11], [12]. This process uses acetic acid (AA) at a molar ratio (GT:AA 1:6), adding toluene and employing ion-exchange resin as a catalyst [13]. The reaction is can be carried out by mixing glycerin with glacial acetic acid in the presence of a heterogeneous catalyst, generally an ion-exchange resin [14], [15], [16]. In [17], a renewable bio-based solid acid (LFuS) was obtained and used as a catalyst for the selective esterification of glycerol (GL), generating a fuel bio-additive with mixture of glycerol diacetates (DAG) and glycerol triacetate (TAG). A GL conversion of 98.0% conversion was achieved, with a selectivity of 94.1% toward DAG + TAG. In the past, concentrated sulfuric acid was used as a catalyst on an industrial scale; however, due to industrial safety and environmental considerations, it has been practically abolished [18]. MDTAG are also known as acetins; they have a high boiling point (258–280 °C) and a density higher than water (1.16–1.21 g/cm^3). MDTAG are used as coolants and oxygenated fuel additives, and are also employed in the cosmetics, pharmaceutical, and plastics industries [19]. Recent studies have investigated glycerol derivatives such as versatile glycerol trilevulinate plasticizer, which creates a plasticization effect on both amorphous and semicrystalline polymers, reducing their glass transition temperature and stiffness [20].

In this research, an alternative application of MDTAG in the rubber industry is investigated. Therefore, its behavior as process oil in compounds made with natural rubber (NR), carbon black (CB), and a sulfur curing system is analyzed. The objective is to partially replace the aromatic and naphthenic oils traditionally used as plasticizers in NR and synthetic styrene-butadiene rubber compounds. Both oils are petroleum derivatives, and aromatic oils, in particular, has adverse effects on human health. Plasticizers are incorporated into rubber compounds to improve load dispersion, reduce viscosity,

decrease hardness, and lower costs. However, the addition of plasticizers can cause a loss of mechanical properties, particularly tensile strength and tear resistance [21].

Natural rubber was selected because it is a polymer obtained from a renewable source, the *Hevea brasiliensis* tree. NR is an isoprene whose vulcanizates have high mechanical strength and excellent elasticity. Therefore, NR is an indispensable raw material in all rubber industries, including tire manufacturing, footwear, bridge bearings, conveyor belts, among others. [21]. However, compared to synthetic elastomers, NR has lower resistance to environmental conditions, ultraviolet radiation, and ozone [22].

2. Materials and methods

2.2 Materials

Crude glycerol from the biodiesel industry contains approximately 80% glycerol, approximately 10% NaCl, approximately 10% water, and less than 1% methanol [23], whereas synthetic glycerol is produced from propene [2]. The synthesized acetylglycerols consists of a mixture of 1- and 2-acetylglycerol, 1,2- and 1,3-diacetylglycerol, and triacetin [24], obtained through the chemical modification of technical grade glycerin. Glycerol can also be converted into di- and tri-*tert*-butyl ethers (h-GTBE), which can be used to produce fuel additives than improve diesel combustion efficiency of diesel combustion [23].

The reagents used for the synthesis of MDTAG were technical grade glycerin (GT, 97.5%), toluene (99.6%), and glacial acetic acid (99%), which were purchased from El Alquimista® store in Bogotá, Colombia. Amberlyst15® ion-exchange resin was acquired from Sigma-Aldrich®, USA. The ingredients used to prepare the compounds were SMRL, natural rubber, carbon black (Cabot® 330), double-pressed stearic acid, gold-seal zinc oxide, staining antioxidant TMQ (Flexys®), accelerator DPG (Flexys®), and sulfur. These materials were purchased from Gomafina® Ltda., Bogotá, Colombia.

2.2. Methods

2.2.1 MDTAG synthesis

The reaction was carried out in a 500 cm^3 glass reactor with three necks, equipped with a heating mantle, magnetic stirring, oil thermal bath, mercury bulb thermometer, Vigreux-type fractionating column, Dean-Stark apparatus for removing the water produced during the reaction, and a condenser with cooling water (Fig. 1). The flask was charged with 35 g of glycerin, + 117.5 g of acetic acid, and + 135 g of toluene. When the system reached 95 °C, 2.5 g of Amberlyst®15 catalyst were added. The reaction conditions were an initial temperature of 95 °C, a final temperature of 110 °C, a system pressure of 560 mmHg, and a reaction time of 4.5 h. Toluene was used as a drag agent to remove the water produced by the reaction and the excess acetic acid at the end of the process.

The MDTAG product was washed with water and then subjected to rotary evaporation for 2 h to remove moisture residual acetic acid.



Figure 1. Synthesis of MDTAG

2.2.2 NR/MDTAG formulation design

Four formulations were developed according to a one-factor experimental design with three levels, in which the factor was the concentration of MDTAG in the compound. The concentrations of MDTAG are expressed in parts per hundred rubber (phr). The response variables were the following: a) rheometric parameters of the compounds before vulcanization and b) mechanical properties of the vulcanized compound.

Table I. NR/MDTAG compound formulations

Ingredients (phr)	NR/ 0MDTAG	NR/10MDTAG	NR/20MDTAG	NR/30MDTAG
Natural rubber	100	100	100	100
Carbon black 330	60	60	60	60
MDTAG	0	10	20	30
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
Antioxidant TMQ	1	1	1	1
DPG	1.6	1.6	1.6	1.6
Sulfur	1.2	1.2	1.2	1.2

Glycerol used as a processing oil has higher viscosity than paraffinic and aromatic oils due to the high polarity and solubility parameters of the former [25]. When employed as a plasticizer, glycerol reduces the viscosity of rubber compounds, improving the dispersion and distribution of the filler in the rubber matrices, indicating that it has a high plasticizing effect [26]. Compared to oleic acid, glycerol is more effective as a plasticizer, resulting in a deformation of up to 70% and greater elongation at break [27].

2.2.3 Preparation of compounds

NR + CB + MDTAG + sulfur curing-system compounds were prepared in a laboratory mill with a mixing capacity of 1000 cm^3, equipped with two rolls of 14 cm in diameter and 32 cm in length, with a friction ratio between the rolls of 1.42. The natural rubber was masticated in the mill until a band was formed. The antioxidant was then added, followed by the gradual addition of CB and AGs. Subsequently, stearic acid, zinc oxide, DPG, and sulfur were added. Finally, the compound was homogenized by mixing in various directions, and the material was removed from the mill in the form of a band.

Vulcanization of the NR/MDTAG compounds was carried out in a laboratory-scale vulcanizing press. All specimens were cured at 160 °C. Sheets used to determine tear strength, tensile strength, and elongation were vulcanized in a mold measuring of 5 × 15 cm of area with a thickness of 3 mm for 8 minutes. Specimens used to determine abrasion resistance were obtained by pressing the compounds in a rectangular mold measuring 6 × 6 cm with a thickness of 8 mm for 12 minutes. The cylinders for measuring compression were vulcanized in a four-cavity mold with a diameter of 28 mm and a height of 14.2 mm for 20 minutes.

2.2.4 Rheometry of NR/MDTAG compounds

The cure state parameters for the compounds prior to vulcanization were determined according to ASTM D2084-17 standard. A Monsanto® MDR 2000™ (USA) oscillating-disc rheometer was used. Rheometric curves were obtained at 160 °C with a test duration of 6 minutes. The compound samples prior to testing were kept at rest at 23 °C for 24 hours.

2.2.5 Determination of mechanical properties of NR/MDTAG vulcanizates

Tensile strength and tear resistance of the vulcanized compounds were determined according to ASTM D412-06A and ASTM D624-00 standards, respectively. Type I (Tensile) and Type B (Tear) dies were used. A KJ 1065B tensile testing machine (Kejian Instruments®, China) was employed. The test parameters were the following: crosshead speed 80 mm/min, temperature 23 °C, relative humidity 50%. Three specimens were tested for each property and for each compound.

Abrasion resistance was measured according to ISO 4649-10 standard, Method B, using a Kejian® 3025 abrasion tester. The specimens were die-cut to a diameter of 16.0 mm and a height of 6 mm. The

test parameters were: test length 40 m (84 revolutions), cylinder rotation 42 rpm, vertical force 10 N, and grade-60 abrasive paper. The temperature was 23 °C, and the relative humidity was 50%. Three specimens were tested for each formulation.

Abrasion resistance was calculated by applying equation (1):

$$Loss\ of\ volume\left(mm^3\right) = (\Delta m * S_0) / (\rho * S) \quad (1)$$

where Δm is the mass loss (mg), ρ is the density of the rubber sample (mg/mm³), S_0 is the nominal abrasive value (200 mg), and S is the average abrasive value of the sandpaper (mg), which was determined by standardizing the sandpaper using a standard rubber sheet which is tested on the sandpaper.

Compression under constant deflection was measured according to ASTM D395, Method B. The vulcanized cylinders had a resting period longer than 24 h at 23 ºC and then were placed in a mold made of two rectangular steel plates separated by two spacer bars. The plates had cavities at the ends to fix the screws and apply closing pressure between them. The cylinders were placed on the base plate, after which the spacer bars were positioned at two opposite ends. The second plate was then placed over the specimens, and the mold was closed, applying pressure to compress the cylinders to the limit or height defined by the spacer bars.

According to the standard, the cylinders were compressed 25% of their original height. The mold containing the samples was placed in a laboratory oven with forced convection at 75 ºC for 22 hours. At the end of the compression period, the specimens were released and allowed to recover for 30 minutes, the height of each cylinder was measured. Three cylinders were used for each compound. Compression was calculated using equation (2):

$$Compression\ set\,(\%) = \left[\left(t_0 - t_f\right) / \left(t_0 - t_n\right)\right] * 100 \quad (2)$$

where: t_o and t_f are the initial and final height of the cylinder (compound), respectively, and tn is the thickness of the spacer bar.

3. Results

3.1 Cure state of NR/MDTAG compounds

Unlike those of synthetic origin, natural rubber can be vulcanized using a single primary accelerator because of its chemical structure. The rheometric curves are shown in Fig 2.

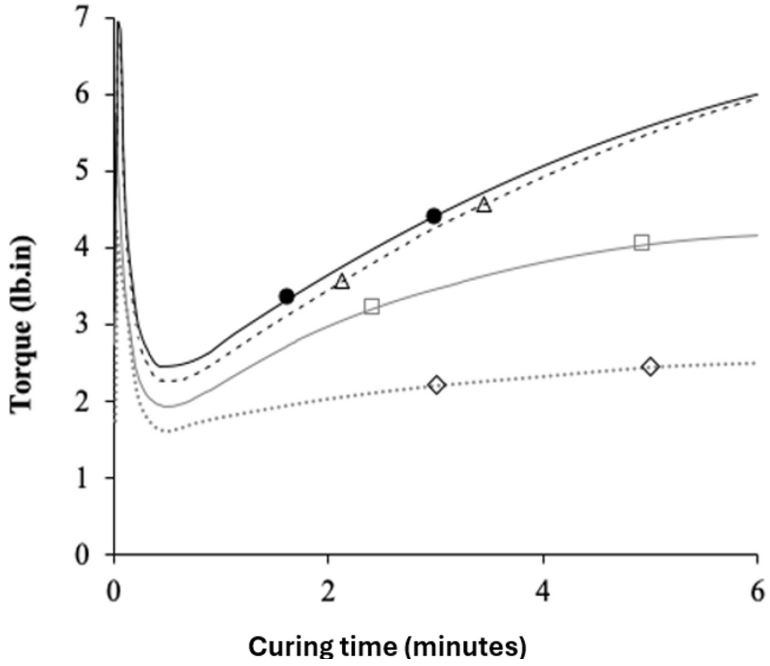


Figure 2. Rheometric curves: –●–NR/0MDTAG --△- -NR/10MDTAG – □–NR/20MDTAG --◇--NR/30MDTAG

The rheometric parameters are shown in Table II. Scorch time (t_{S2}) is the point at which the crosslinking reaction begins through the formation of sulfur bonds that form a three-dimensional network. This parameter is important because enables the establishment of the time available for the compound to flow into the cavities of a mold and fill them before vulcanization begins. Cure time (t_{90}) represents the time required to vulcanize the compound; during this period, the material should be placed in the mold. The remaining 10% of vulcanization is achieved with the residual heat of the vulcanized material when leaving the mold. The minimum torque (M_L) refers to the viscosity of the compound before starting vulcanization and therefore provides an indication of its processability (flowability) of the compound during preform production and mold filling. The maximum torque (M_H) is proportional to the degree of crosslinking reached during vulcanization [28].

Table II. Rheometric parameters of NR/MDTAG compounds

Composite	Minimum torque M_L (N.m)	Maximum torque M_H (N.m)	Scorch time t_{S2} (min)	Cure time t_{90} (min)
NR/0MDTAG	2.46	6.00	0.65	5.90
NR/10MDTAG	2.26	5.96	0.72	5.86
NR/20MDTAG	1.94	4.17	0.67	5.40
NR/30MDTAG	1.62	2.50	0.60	5.60

The compound without acetylglycerols (NR/0MDTAG) exhibited the highest M_H value. The addition of 10 phr of MDTAG did not significantly affect the M_H value. However, dosages of 20 and 30 phr significantly decreased the maximum torque value by 30.5% and 58.3%, respectively, compared with the NR/0MDTAG compound. Regarding the minimum torque (M_L), the incorporation of MDTAG improved the flowability of the compound; that is M_L decreased as the MDTAG increased.

No significant variations in the scorch time t_{S2} were observed because of the addition of MDTAG. Similarly, no significant differences were observed in the cure time (t90) reported by the software. This behavior may be attributed to the geometric shape of the curves, which does not allow clear differences to be established between the curing times.

3.2. Evaluation of mechanical properties NR/MDTAG

Fig 3. shows the tensile strength and elongation at break of the NR/MDTAG compounds. In general, carbon blacks of type 330 or 220 have high reinforcing power and therefore they impart high mechanical strength values to rubber compounds [29]. The highest value reported for tensile strength was given by the compound without MDTAG, at 8.61 MPa. The addition of MDTAG in amounts of 10 phr did not significantly affect the tensile value which was 8.47 MPa. However, the compound with 30 phr showed a significant decrease in tensile strength, with a value of 5.32 MPa for the NR/30MDTAG compound, representing a 38.2% reduction compared to the compound without MDTAG (Fig 3).

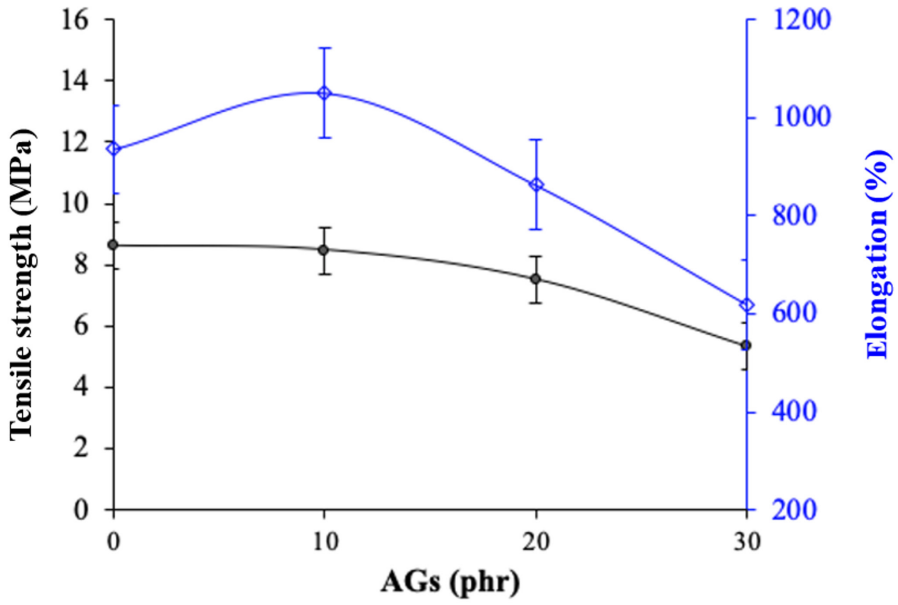


Figure 3. Tensile strength and elongation properties of NR/MDTAG

Elongation is the ability of a rubber compound to stretch several times its original length and it is an important property of these materials. Elongation at break is the maximum stretching that the compound can withstand before breaking [22]. In this study, the addition of MDTAG in amounts up to 20 phr did not

significantly affect this property, as shown in Fig 6, with elongation values close to 1000% being achieved. An increase in ductility was expected with the incorporation of MDTAG; however, at a concentration of 30 phr the compound lost ductility, with elongation decreasing drastically to 617.8%. This value represents a loss of approximately 41.2% compared with the compound containing 10 phr of MDTAG.

3.3. Tear strength of NR/MDTAG vulcanizates

Tear strength measures the ability of the rubber compound to resist propagation of a cut or crack. The tear, abrasion, and compression results are shown in Table III.

Table III. Mechanical properties of NR/MDTAG compounds

Composite	Tearing (KN/m)	Abrasion (mm^3)	Compression (%)
NR/0MDTAG	35.23 ± 0.6	166 ± 6.2	38.2 ± 0.6
NR/10MDTAG	33.16 ± 0.6	164 ± 8.4	37.3 ± 0.5
NR/20MDTAG	32.18 ± 0.5	189 ± 9.5	41.5 ± 0.5
NR/30MDTAG	26.66 ± 0.5	214 ± 7.7	48.7 ± 0.4

Carbon blacks of type 330 offer high tear strength in rubber compounds [29]. The highest value was observed for the compound formulated without MDTAG. The compound containing 10 phr showed a 5.8% decrease in tear strength compared to the compound without MDTAG. However, the addition of 30 phr of MDTAG caused a drastic decrease of 24.3% in tear strength compared with the compound without MDTAG.

3.4. Abrasion resistance of NR/MDTAG vulcanizates

According to ISO 4649, abrasion resistance is related to the volume loss of a vulcanized rubber specimen subjected to testing. A compound has greater abrasion resistance when it loses less volume. Carbon black 330 is a filler used in the rubber industry to improve this property [29]. Table III shows that the compounds with highest abrasion resistance are NR/20MDTAG and NR/30MDTAG.

3.5. Resistance to permanent deformation of vulcanizates NR/MDTAG

Compression under permanent deformation conditions measures the ability of a vulcanizate to recover its original dimension after compression has ceased. Unlike the properties discussed previously, carbon black type 330 does not have a dominant effect on this property [29]. The degree of crosslinking primarily influences the compression values. According to equation (2), low values of this property indicate that the material has good resilience. The compound with the lowest performance was NR/30MDTAG, which exhibited a 27.5% decrease in compression resistance compared with the compound formulated without MDTAG.

3.6 Statistical analysis

The rheometric parameters of the NR/MDTAG compounds were analyzed using one-way ANOVA at a significance level of α=0.05, based on 10 measurements. F-statistic values of 362.38 and 778.85 were obtained for the minimum torque (ML) and maximum torque (MH), respectively. These values are greater than the critical value of 2.86, indicating that the addition of MDTAG to NR results in significant differences in the rheometric parameters, evidencing changes in viscosity before vulcanization and the formation of the cross-linking of the network during vulcanization.

The variations in scorch time (t_{S2}) remain practically unchanged, indicating that the addition of MDTAG does not affect the time taken to fill the cavities to initiate vulcanization. Meanwhile the cure time (t_{90}) shows slight variations, signifying that the vulcanization kinetics of NR are slightly affected by the addition of MDTAG.

A one-way ANOVA was also performed to determine whether there were significant variations in the mechanical properties among the samples. 10 measurements were taken, and the following hypotheses were proposed:

H_0:*There are no significant differences between the samples*

H_1:*There are significant differences between at least two of the samples*

After performing the analysis at a significance level of α=0.05, the following F-statistic values were obtained (Table IV).

Table IV. ANOVA statistical analysis for Mechanical properties

	Tearing	**Abrasion**	**Compression**
F-statistic	439.11	84.93	1050.29

These values fall within the rejection zone of the null hypothesis since they exceed the critical value of F=2.86. The results were further corroborated by the Tukey test. Therefore, significant differences exist between the mechanical properties of at least two of the samples, meaning that the increased concentration of the MDTAG compound significantly influences the mechanical properties of the composites.

4. Discussion

Based on the results obtained from rheometric and mechanical property tests, the effect of adding MDTAG on the behavior of carbon black–reinforced natural rubber was analyzed. This analysis was used to interpret the observed variations and determine the optimal levels of MDTAG addition that do not adversely affect these properties.

The addition of up to 10 phr of MDTAG does not significantly affect the maximum torque (M_H) compared to the general compound; however, at levels of 20 and 30 phr, reductions of 30.5% and 58.3%, respectively, were observed. This behavior is directly related to the intrinsic effect caused by the addition of acetylglycerols. Because of their liquid nature, acetylglycerols tend to decrease the hardness of the compounds, affecting the degree of vulcanization, diluting the polymer network, and interfering with crosslink formation [28], [29]. Regarding the minimum torque (M_L), a decrease is observed as the MDTAG concentration increased, exhibiting greater fluidity. This effect is attributed to the intrinsic effect of oils or plasticizers, which penetrate the polymer matrix and extend or separate the chains, reducing the initial viscosity and facilitating their displacement [29]. Meanwhile, scorch time (t_{S2}) and cure time (t_{90}) do not show significant variations. Therefore, vulcanization is not altered by the incorporation of MDTAG; it is maintained despite the addition of plasticizers [28].

With respect to the mechanical properties, tensile strength was maintained at up to 10 phr of MDTAG; however, a decrease in this property was observed as the MDTAG concentration increased. The decrease in tensile strength may be a consequence of the curing state (low MH) and low compatibility between NR and MDTAG. Excess oil in elastomeric blends can reduce the reinforcing efficiency provided by carbon black, as indicated by [29], [28]. Regarding elongation, an increase in ductility close to 1000% was observed with levels up to 20 phr, whereas a drastic decrease of 41.2% was observed at 30 phr. This may be attributed to the low compatibility between MDTAG and NR and to the formation of microcavities that reduce network cohesion [30].

As for abrasion resistance, the compounds with 20 and 30 phr of MDTAG showed volume losses, indicating that at these levels the wear resistance decreases; this occurs due to the softening of the matrix and the reduction of internal cohesion [28]. Regarding compression, the NR/30MDTAG compound exhibited poor performance, with a decrease of 27.5%. The addition of MDTAG in amounts equal to 30 phr causes a loss of this property due to the low compatibility between natural rubber and MDTAG, leading to less efficient absorption of elastic energy and reduced elastic recovery [30], [28].

5. Conclusion

Natural rubber compounds can be formulated with carbon black by adding mono-, di-, and tri-acetylglycerols at concentrations of up to 10 phr. Higher concentrations deteriorate the quality of the compound due to the lack of compatibility between MDTAG and natural rubber, as evidenced by the loss of curing characteristics, a decrease in mechanical properties, and the appearance of exuded liquid on the surface of the vulcanizate, primarily in the compound formulated with 30 phr of MDTAG.

Statistical analysis indicates that the mechanical properties of the compound decrease significantly when the MDTAG content exceeds 10 phr, suggesting that the structure of the vulcanized material is affected at high concentrations.

Based on the results obtained, it is concluded that natural rubber reinforced with carbon black can incorporate MDTAG at concentrations of up to 10 phr. This value represents maximum recommended level for glycerol addition, at which the mechanical and vulcanization properties are preserved. Above this threshold, deterioration and a decrease in tensile strength, elongation, and tear resistance are observed, due to the low compatibility between natural rubber and MDTAG, as well as the reduction in the degree of crosslinking.

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Author contributions

E. Delgado T: Idea and conceptualization, research and investigation, original draft preparation.

E. Rodríguez C: Original draft preparation, research, review and editing.

Statement on Conflicts of Interest

Authors state no conflict of interest.

Statement on Artificial Intelligence

AI was not used during the preparation of this work.

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