

Hybrid Graphene Oxide/Carbon Black Reinforcement in Natural Rubber: A Sustainable Approach for Multifunctional Tire Tread Compounds

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Carbon black (CB) is the primary reinforcing filler in tire tread elastomers; however, high filler loadings increase hysteresis and accelerate aging. In this context, hybrid reinforcement strategies incorporating graphene oxide (GO) have attracted considerable attention due to the unique mechanical and thermal properties of this nanomaterial. This study evaluates a laboratory-scale, industrially compatible approach for GO incorporation through conventional two-roll-mill mixing, using processing oil as the dispersion medium. Elastomeric formulations with GO loadings of 0.5–1.25 parts per hundred rubber (phr) were prepared and evaluated for rheological, mechanical, dynamic mechanical, morphological, and thermal conductivity properties. Overall, GO incorporation did not significantly alter the cure characteristics or conventional mechanical properties of the compounds. Nevertheless, NR/CB/GO_{0.75} showed the highest retention of tensile strength after thermo-oxidative aging and a 10.6% increase in thermal conductivity, whereas NR/CB/GO_{1.25} exhibited a favorable $\tan \delta$ profile. The latter formulation showed higher $\tan \delta$ at low temperature and lower values at elevated temperatures, suggesting potential improvements in wet-grip-related response and reduced hysteretic losses, respectively. Although the oil-assisted incorporation route did not produce substantial mechanical reinforcement under the investigated conditions, it showed potential for selectively modifying dynamic behavior, thermal transport, and the retention of mechanical properties after aging using conventional rubber-processing equipment. Further optimization of GO purity, dispersion stability, and filler-matrix compatibility is required before the practical and economic feasibility of this approach can be established.

Keywords: Graphene oxide, mechanical mixing, tire tread, dynamic-mechanical properties, linear thermal conductivity.

1. Introduction

The tire industry has historically relied on carbon black (CB) as the primary reinforcing filler for elastomeric compounds used in tread formulations. Although CB provides effective mechanical reinforcement and abrasion resistance, its high loading levels increase hysteresis and heat build-up, thereby accelerating fatigue and reducing tire service life. To address these limitations, hybrid reinforcement strategies incorporating nanomaterials have emerged as a promising approach to enhance the dynamic-mechanical performance and durability of elastomeric compounds^{1,2}.

Among carbon-based nanomaterials, graphene oxide (GO) has attracted considerable attention due to its high specific surface area, tunable surface chemistry, and potential for scalable production via graphite oxidation^{3,4}. The incorporation of GO into natural rubber (NR) matrices has been reported to improve tensile strength, tear resistance, and thermal stability under appropriately controlled processing and dispersion conditions^{5,6}. Nevertheless, achieving homogeneous dispersion of GO within the elastomeric matrix remains challenging due to the strong tendency of graphene-based sheets to restack through van der Waals interactions. Conventional approaches, including solution mixing⁷, latex mixing³, and in situ polymerization⁸, have been explored to improve filler dispersion and interfacial interactions; however, these

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methods often involve additional processing steps and may present limitations in terms of industrial scalability.

Beyond single-filler approaches, hybrid systems combining CB, silica, and GO have shown synergistic effects on stress transfer, crack resistance, and fatigue performance. For example, Cao et al.⁹ reported that silanized silica combined with GO promoted a more effective reinforcing network and improved filler dispersion. Using only 10 phr of an unvulcanized green composite containing 1% GO in the tread formulation, those authors reported a 44.5% increase in wear resistance based on real-tire running tests, along with favorable changes in dynamic mechanical analysis (DMA)-derived indicators of rolling resistance and wet-skid resistance.

Nanocarbons such as carbon nanotubes (CNTs) and GO have also been investigated in green tire technologies aimed at reducing energy consumption and improving rolling efficiency. Campini et al.¹⁰ investigated NR/butadiene rubber (BR) systems containing CNTs and silica and reported significant improvements in electrical conductivity, rolling-resistance-related response, and dynamic properties. These results illustrate the multifunctional role of nanocarbon fillers in elastomeric composites and support further investigation of GO as a complementary component in conventional filler systems.

Mechanical mixing is the standard compounding method used in rubber-processing plants and avoids the solvent-removal or coagulation steps required by solution- and latex-based routes. However, the high shear forces generated during mixing may fragment graphene-based platelets or fail to disrupt persistent agglomerates, thereby limiting reinforcement efficiency. One strategy proposed to facilitate nanofiller incorporation is pre-dispersion in processing aids already used in rubber formulations¹¹. Processing oils, in particular, have been evaluated as entry vehicles for carbon nanotubes and graphene nanoplatelets in rubber compounds^{11,12}. Despite these precedents, the use of processing oil as a direct incorporation vehicle for GO in conventional CB-reinforced NR formulations remains insufficiently investigated.

Previous studies have explored the partial replacement of CB with graphene derivatives in tire compounds; however, important questions remain regarding the incorporation of low GO contents into conventional NR/CB formulations without replacing the primary reinforcing filler. Rajan et al.¹ employed an NR/BR blend in which CB was partially replaced with 1–5 phr of modified multilayer graphene while the total filler loading was maintained at 55 phr. In contrast, the present study maintains the CB content at 40 phr and introduces 0.5–1.25 phr of GO as a complementary component in an NR-based formulation. This experimental design enables evaluation of whether small amounts of GO can modify the behavior of an established CB-reinforced system without substantially changing its conventional formulation.

Another distinguishing feature of the present study is the use of processing oil already included in the formulation as the GO incorporation vehicle. Although processing oils have previously been investigated as entry media for other carbonaceous nanofillers^{11,12}, their performance and limitations as incorporation vehicles for GO remain insufficiently understood, particularly because the high polarity of GO hinders its stabilization in nonpolar naphthenic oil. Against

this background, the present study evaluates an oil-assisted, solvent-free incorporation route followed by conventional two-roll-mill mixing, without requiring latex coagulation or additional solvent-removal steps. The effects of this strategy were assessed through rheological, crosslink-density, bound-rubber, mechanical, aging, dynamic-mechanical, thermal-conductivity, morphological, and macrodispersion analyses. Therefore, the contribution of this work lies not only in evaluating the functional response of NR/CB/GO compounds but also in critically establishing the capabilities and limitations of an industrially compatible laboratory-scale route for incorporating GO into tire-tread formulations.

2. Experimental Section

2.1. Materials

GO was obtained from BoomaTech Company (São Marcos, RS, Brazil) and used as received, except for the drying procedure described below. It should be noted that the authors performed no additional purification or chemical functionalization, and no metals or other elements were intentionally introduced into the commercial material.

The remaining raw materials were generously supplied by Rinaldi S/A Indústria de Pneumáticos (Bento Gonçalves, RS, Brazil) and are described as follows: NR grade GEB-10, supplied by ASK Trading (Mirassol, SP, Brazil); N-220 CB, manufactured by Birla Carbon (Cubatão, SP, Brazil); zinc oxide (ZnO), supplied by Nexa (Três Marias, MG, Brazil); octadecanoic acid (stearic acid), obtained from SimEstearina (Curitiba, PR, Brazil); naphthenic process oil, supplied by Ergon (Jackson, MS, USA); pre-dispersed sulfur, provided by Rhein Chemie (Porto Feliz, SP, Brazil); and the accelerator *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), pre-dispersed in styrene-butadiene rubber (SBR), also supplied by Rhein Chemie (Porto Feliz, SP, Brazil).

2.2. Characterization of GO

GO characterization was performed by UCSGRAPHENE® (Embrapii Research and Development Unit). Before analysis, the sample was dried in an oven at 105 °C for 24 h to remove residual moisture. Field-emission gun scanning electron microscopy (FEG-SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) was performed using a TESCAN MIRA 3 microscope (Brno, Czech Republic). EDS was used for semi-quantitative elemental screening rather than for precise stoichiometric determination.

Raman spectroscopy was conducted using a Horiba LabRAM HR Evolution spectrometer (Kyoto, Japan), in accordance with ABNT ISO/TS 21356-1¹³, over the spectral range of 3000–500 cm⁻¹, with an acquisition time of 10 s. Fourier transform infrared spectroscopy (FTIR) was performed using a PerkinElmer Spectrum 400 spectrometer (Waltham, MA, USA) after mixing the dried GO with potassium bromide (KBr, spectroscopic grade, Sigma-Aldrich, St. Louis, MO, USA) and pressing the mixture into a pellet. The spectrum was then recorded in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹.

Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449 F3 analyzer (Selb, Germany),

following procedures adapted from ASTM C561-16¹⁴ and ABNT ISO/TS 11308¹⁵. For ash content determination, the GO sample was heated from room temperature to 910 °C under air in an alumina crucible, using heating rates of 8 °C min⁻¹ up to 500 °C, 2 °C min⁻¹ up to 750 °C, and 3 °C min⁻¹ up to 910 °C, with a 1 min isothermal hold at the final temperature. For carbon purity evaluation, the sample was heated from room temperature to 1010 °C at a rate of 5 °C min⁻¹ under air, also in an alumina crucible.

2.3. Preparation of GO dispersion in processing oil

GO was dispersed in the processing oil by BoomaTech Company using a 400 W ultrasonic bath (CTA do Brasil, Campanha, MG) for 36.8 h. A single dispersion containing 12.5 wt% GO was prepared and used in all GO-containing formulations. The naphthenic processing oil employed in the rubber compounds served as the dispersion medium. The amount of dispersion added to each formulation was calculated so that the total processing-oil content remained constant at 10 phr. Thus, the oil functioned as the GO incorporation vehicle without introducing oil-content differences among the formulations.

Before incorporation into the rubber compounds, the GO/oil dispersion was maintained at approximately 60 °C under manual stirring to facilitate dosing and handling. Table 1 presents the dispersion composition and the distribution of the processing oil between the different stages of the compounding process.

2.4. Preparation of the elastomeric compounds

At the laboratory scale, compound mixing and homogenization processes were performed using an open two-roll mill (EEMCO, Erie, Pennsylvania, USA), with a batch mass of

0.3 kg and a roll-speed ratio of 1:1.35. For comparison in the RPA strain-sweep analysis, an unfilled NR was separately masticated for 90 s under the same two-roll-mill conditions.

The raw materials were added in the following sequence: NR, followed by the GO/oil dispersion, activators, CB, and the remaining processing oil. Four GO concentrations were investigated (0.5, 0.75, 1.0, and 1.25 phr), designated as NR/CB/GO_0.5, NR/CB/GO_0.75, NR/CB/GO_1.0, and NR/CB/GO_1.25, respectively. The total mixing time ranged from 14 to 20 min, depending on the formulation. After resting for 18 h, the curing agent and accelerator were incorporated using the same mill for approximately 180 s. The compounds were sheeted to a thickness of approximately 4 mm and conditioned for at least 16 h at 23 ± 2 °C before characterization. Table 2 presents the composition of the studied formulations.

2.5. Characterization of the elastomeric compounds

2.5.1. Rheological properties

Vulcanization characteristics were evaluated using a moving-die rheometer (MDR, model MD 2002/E, Indústria HP, Lanús Oeste, Buenos Aires Province, Argentina), in accordance with ASTM D5289-12¹⁶. Mooney viscosity was determined using a Mooney viscometer (VM1000, Indústria HP, Lanús Oeste, Buenos Aires Province, Argentina), following ASTM D1646-07¹⁷, at 100 °C under ML(1+4) conditions.

Strain-sweep measurements were performed using an RPA 2000 rubber process analyzer (Alpha Technologies, Hudson, OH, USA) at 60 °C and 1 Hz over a strain-amplitude range of 0.09–12.5%.

Table 1. Composition of the GO dispersion and distribution of processing oil at each stage of the compounding process.

Raw material	NR/CB	NR/CB/GO_0.5	NR/CB/GO_0.75	NR/CB/GO_1.0	NR/CB/GO_1.25
<i>Stage 1: Preparation of the dispersion</i>					
GO	0	0.5	0.75	1.0	1.25
Naphthenic oil	0	3.5	5.25	7.0	8.75
GO dispersion in oil (phr)	0	4.0	6.0	8.0	10.0
<i>Stage 2: Preparation of the formulations</i>					
Oil from dispersion (phr)	0	3.5	5.25	7.0	8.75
Oil added during mixing stage (phr)	10	6.5	4.75	3	1.25
Total oil content (phr)	10	10	10	10	10

Table 2. Formulation of the elastomeric compounds (values expressed in phr).

Raw material	NR/CB	NR/CB/GO_0.5	NR/CB/GO_0.75	NR/CB/GO_1.0	NR/CB/GO_1.25
NR	100	100	100	100	100
CB N220	40	40	40	40	40
Oil	10	6.5	4.75	3	1.25
GO dispersion in oil	0	4	6	8	10
ZnO	4	4	4	4	4
Octadecanoic acid	2	2	2	2	2
Sulfur	2	2	2	2	2
CBS accelerator	1.5	1.5	1.5	1.5	1.5

2.5.2. Bound rubber content

The bound rubber content (BdRC) was determined in triplicate by extracting approximately 1.5 g of each unvulcanized compound with toluene using a Soxhlet apparatus¹⁸. After 60 h of continuous extraction, the insoluble residue was dried in an oven at 100 °C for 6 h and subsequently analyzed by TGA.

Thermogravimetric measurements were performed using a TA Instruments Q-5000 analyzer (New Castle, DE, USA) at a heating rate of 10 °C min⁻¹, first under nitrogen from room temperature to 500 °C and then under an oxidative atmosphere from 500 to 750 °C. BdRC was calculated from the polymer fraction retained after extraction, considering the total polymer content of the corresponding unextracted compound and the polymer mass loss determined by TGA.

2.5.3. Mechanical properties

Tensile and tear properties were determined using a universal testing machine (EMIC 23-5D, Instron, São José dos Pinhais, PR, Brazil), in accordance with ASTM D412-06¹⁹ and ASTM D624-00²⁰, respectively.

Abrasion resistance was evaluated according to DIN ISO 4649:2006 (*Method A*)²¹ using a MAQTEST abrasion tester (A188, Franca, SP, Brazil). Hardness was measured in accordance with ASTM D2240-05²² using a Shore A durometer (HP series, Bareiss, Germany).

2.5.4. Aging

Accelerated thermo-oxidative aging was conducted in a laboratory oven without air circulation at 100 °C for 72 h. After exposure, the specimens were subjected to tensile testing under the conditions described in Section 2.5.3. The retention of tensile strength, elongation at break, and modulus at 300% elongation was used to compare the aging response of the compounds.

2.5.5. Swelling test

Crosslink density $[X]$ was estimated from equilibrium-swelling measurements using the Flory–Rehner theory²³. Rectangular specimens (20 × 20 × 2 mm) were first extracted with acetone in a Soxhlet apparatus to remove soluble polar components. After 24 h of continuous extraction, the specimens were dried in an oven at 70 °C for 6 h and subsequently immersed in heptane for 120 h at 23 ± 2 °C, protected from light. Crosslink density was calculated using Equation 1:

$$[X] = \frac{-\left[\ln(1 - v_r) + v_r + \chi v_r^2\right]}{V_o \left(\frac{1}{v_r^3} - \frac{v_r}{2}\right)} \quad (1)$$

where $[X]$ is the estimated crosslink density (mol cm⁻³), v_r is the rubber volume fraction in the swollen specimen, χ is the rubber-solvent interaction parameter, and V_o is the molar volume of the solvent (cm³ mol⁻¹).

The amount of absorbed solvent was obtained from the mass difference between the swollen and dried specimens. The combined filler volume (CB + GO) was excluded when calculating the effective rubber volume. The value of v_r

was then calculated as the ratio between the initial rubber volume and the total volume of the solvent-swollen rubber phase. The calculations were performed using $\chi = 0.50$ and $V_o = 147.47$ cm³ mol⁻¹ for heptane. All measurements were performed in triplicate, and the results are reported as mean values.

2.5.6. Dynamic-mechanical properties

Dynamic-mechanical properties were measured from -120 to 110 °C using a DMA Q800 analyzer (TA Instruments, New Castle, DE, USA) in tension mode, at a strain amplitude of 0.06%, a frequency of 10 Hz, and a heating rate of 2 °C min⁻¹. Rectangular specimens measuring 30 × 6.3 × 2 mm were used in the analysis¹⁸.

2.5.7. Thermal conductivity

The linear thermal conductivity (k) of the compounds was determined using an H111A heat-transfer unit (P.A. Hilton Ltd., Hampshire, United Kingdom). The apparatus comprises heated and cooled cylindrical brass plates arranged in parallel, with the specimen positioned between them under compressive loading. Two thermocouples embedded in each plate were used to determine the temperature gradients (Figure 1). Disc-shaped specimens measuring 25 mm in diameter and 2 mm in thickness were placed between the brass plates. A voltage of 80 V and a current of 0.109 A were applied to the upper plate, corresponding to a theoretical heating power of 8.72 W. The lower plate was continuously cooled with circulating water at room temperature at a flow rate of 1.5 L min⁻¹.

The temperatures at the hot and cold plate-specimen interfaces, T_{hot} and T_{cold} , respectively, were estimated according to the manufacturer's guidelines using Equations 2 and 3:

$$T_{hot} = T_2 - \frac{T_1 - T_2}{2} \quad (2)$$

$$T_{cold} = T_3 + \frac{T_3 - T_4}{2} \quad (3)$$

Finally, k was calculated based on Fourier's unidirectional heat transfer law, as expressed in Equation 4:

$$k = \frac{Qx}{A(T_{hot} - T_{cold})} \quad (4)$$

where Q is the theoretical heating power (W), x is the specimen thickness (m), and A is the cross-sectional area of the specimen (m²).

2.5.8. FEG-SEM analysis

FEG-SEM analysis was performed using a TESCAN MIRA 3 microscope (Brno, Czech Republic). Micrographs of the elastomeric compounds were obtained from surfaces produced by cryogenic fracture after immersion in liquid nitrogen and from fracture surfaces generated during tensile testing. The GO powder was also examined. Before imaging, all specimens were sputter-coated with gold using a Desk V metallizer (Denton Vacuum, Moorestown, NJ, USA).

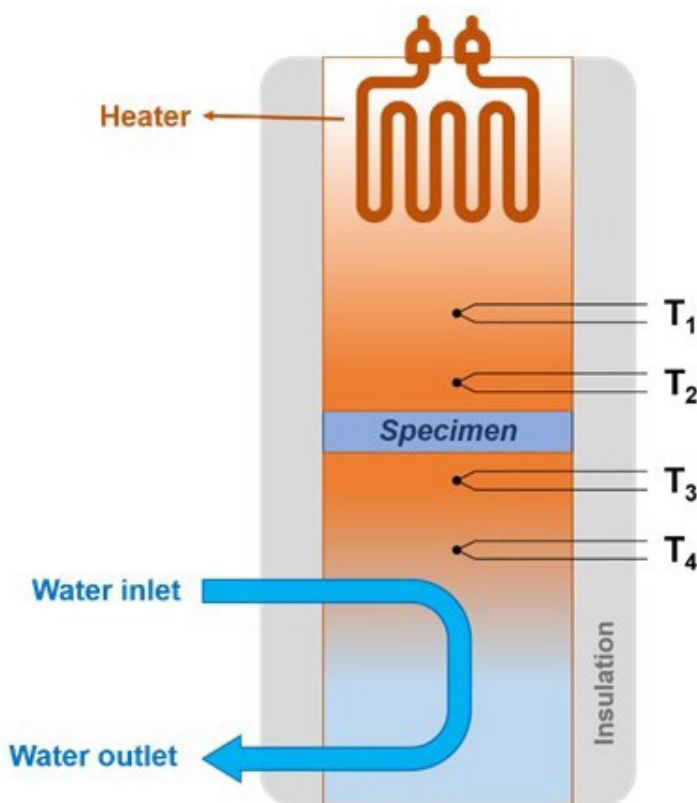


Figure 1. Schematic representation of the linear thermal conductivity measurement setup.

Macrodispersion of optically detectable filler agglomerates was additionally evaluated using a reflected-light microscope (Dispergrader+, Dynisco Instruments LLC, Franklin, MA, USA), following the general sample-inspection principles described in ISO 11345²⁴. The dispersion index (%) was calculated by the instrument image-analysis software from the surface area associated with optically detected agglomerates. This analysis does not chemically distinguish CB from GO or determine the nanoscale spatial distribution of the fillers.

2.5.9. Statistical analysis

Statistical differences among the formulations were evaluated by one-way analysis of variance (ANOVA) at a 95% confidence level ($p < 0.05$). When differences among the means were detected, Tukey's post hoc test was applied for pairwise comparisons. Statistical analyses were performed using OriginPro software (OriginLab Corporation, Northampton, MA, USA).

3. Results And Discussion

3.1. GO characterization

The FEG-SEM micrographs of the GO are presented in Figures 2a–c. At low magnification (Figure 2a), the dried powder exhibits extensive agglomeration and irregular domains composed of stacked lamellar structures. This morphology is consistent with the tendency of GO sheets to restack during

drying as a result of intersheet interactions involving the graphitic domains and oxygen-containing surface groups²⁵.

At higher magnifications (Figures 2b and 2c), overlapping sheets with irregular contours, folded edges, and pronounced surface corrugations become evident. Such features are commonly reported for oxidized graphene derivatives and have been associated with structural distortions produced during graphite oxidation²⁶. Stacked platelets and micrometric agglomerates were observed, whereas isolated monolayers could not be identified by FEG-SEM. Accordingly, the micrographs demonstrate a lamellar and strongly agglomerated morphology but do not establish the number of layers or degree of exfoliation of the commercial material.

EDS analysis (Figures 2d–i) was used to obtain semi-quantitative information on the elemental composition of the GO. The analyzed region yielded approximate atomic fractions of 47.5% carbon (Figure 2e) and 27.0% oxygen (Figure 2f), consistent with an oxidized carbonaceous material²⁷. Signals assigned to sodium (12.2%, Figure 2g), sulfur (6.2%, Figure 2h), and chlorine (5.9%, Figure 2i) were also detected. These elements may originate from chemicals or washing and neutralization steps used during GO production²⁸. However, because the material was commercially supplied and EDS does not determine chemical speciation, their sources and chemical forms cannot be established from the available data. Moreover, the reported atomic fractions represent semi-quantitative estimates for the analyzed region and should not be interpreted as precise bulk composition,

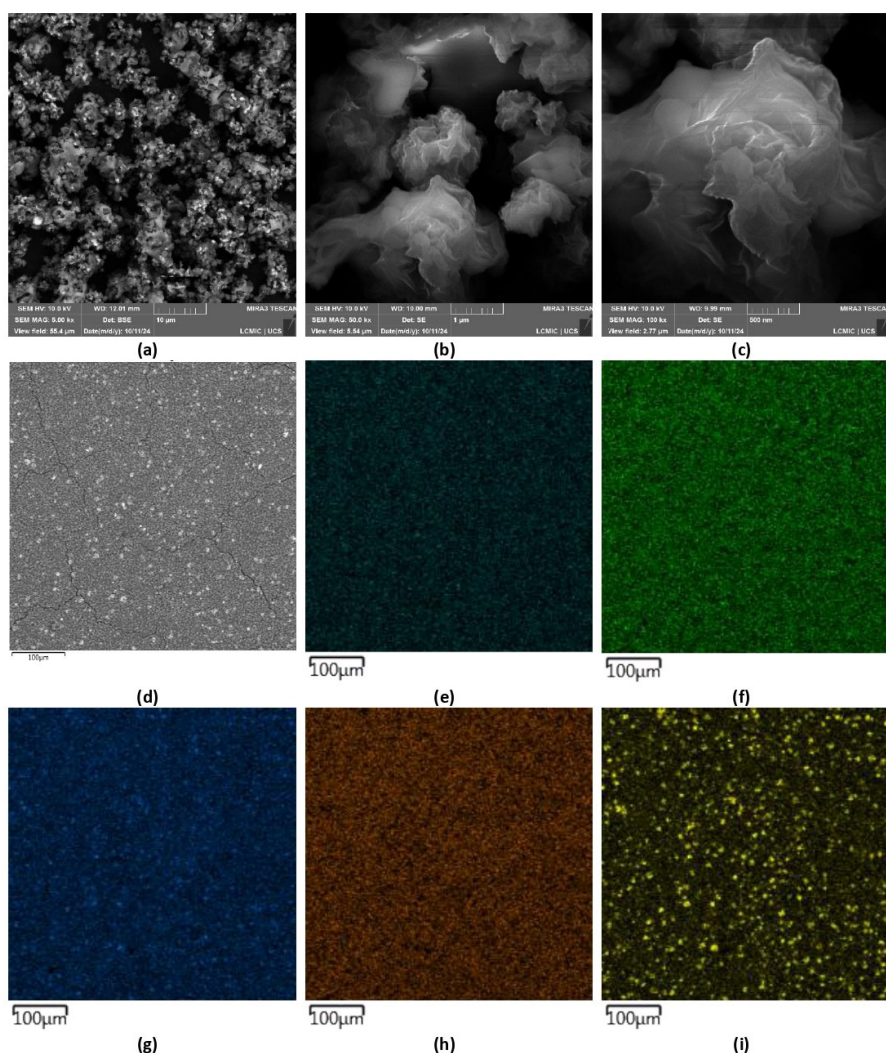


Figure 2. FEG-SEM micrographs of the GO at magnifications of (a) 5 k $\times$, (b) 50 k $\times$, and (c) 100 k $\times$. Secondary electron images of the GO sample at 250 $\times$ magnification are shown in (d). EDS elemental maps showing signals assigned to (e) carbon, (f) oxygen, (g) sodium, (h) sulfur, and (i) chlorine.

exact stoichiometry, or an accurately determined C/O ratio. Nevertheless, the comparatively intense Na, S, and Cl signals indicate that inorganic residues were present in the commercial material.

Raman spectroscopy (Figure 3a) was subsequently employed to further evaluate the structural organization and defect density of the GO. The spectrum exhibits peaks at 1339, 1580 and 2670 cm^{-1} , corresponding to the D, G, and 2D bands, respectively. According to ABNT ISO/TS 21356-1¹³, the presence of these bands is consistent with the graphitic structure of the material. The D band, commonly referred to as the disorder band, is activated by defects and disruptions in the sp^2 carbon lattice. The G band corresponds to the in-plane vibration of sp^2 -hybridized carbon atoms, while the 2D band is widely used for the identification of graphene-based materials^{29,30}. The intensity ratio between the D and G bands (I_D/I_G) provides information on the structural disorder of carbonaceous materials³¹. The measured I_D/I_G

ratio for the GO sample was 0.68, indicating the coexistence of ordered sp^2 domains and defect-containing regions. However, this ratio alone does not permit an unambiguous determination of the oxidation degree, defect density, or lateral dimensions of the GO sheets.

While Raman spectroscopy provides insight into structural disorder, FTIR analysis (Figure 3b) offers complementary information concerning surface chemistry and functional groups. The FTIR spectrum exhibits distinct absorption bands corresponding to O–H stretching vibrations at 3413 cm^{-1} and bending vibrations at 1637 cm^{-1} , C=C stretching at 1618 cm^{-1} , C–O vibrations at 1115 cm^{-1} , and a low-wavenumber band at 616 cm^{-1} , assigned to C–S vibrations. The broad O–H band and its associated bending mode are indicative of hydroxyl groups and adsorbed water, commonly observed in oxidized carbon materials^{31–33}. The band at 1618 cm^{-1} is consistent with aromatic C=C stretching, indicating partial preservation of the sp^2 -hybridized carbon network within

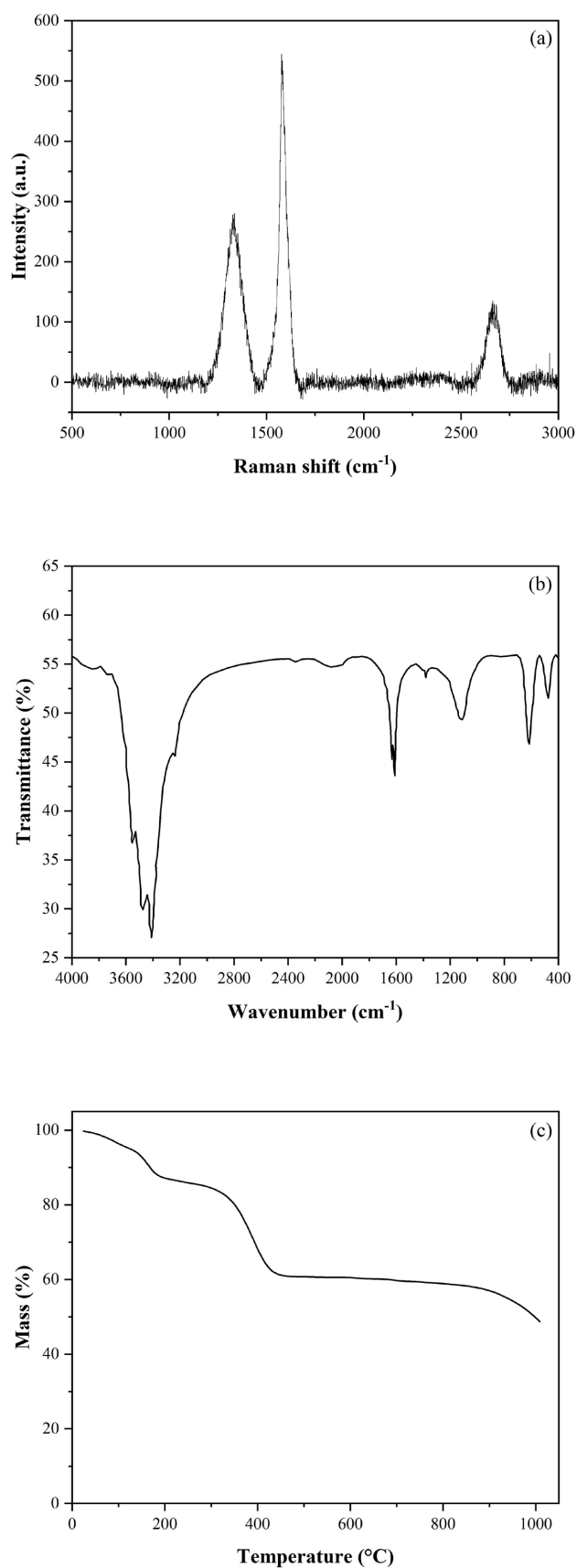


Figure 3. (a) Raman spectrum, (b) FTIR spectrum, and (c) TGA curve of the GO.

the GO structure^{31,33}. The C–O vibration at 1115 cm⁻¹ is typically attributed to epoxy or alkoxy functional groups, confirming the presence of oxygen-containing functionalities introduced during oxidation^{32,33}. Considering the sulfur signal detected by EDS, the band at 616 cm⁻¹ may be associated with sulfur-containing species remaining from GO production. However, this tentative assignment does not demonstrate covalent incorporation of sulfur into the GO structure. Compared with literature reports, which frequently show intense bands in the 1700–1725 cm⁻¹ region assigned to carboxylic C=O groups, the absence of this feature in the present sample suggests a comparatively low abundance of such groups under the measurement conditions, which may influence the material's reactivity and compatibility with further functionalization.

TGA analysis (Figure 3c) was performed to further assess the thermal stability, ash content, and carbon purity of the GO. The mass loss occurred in three main temperature ranges: up to 100 °C, attributed to water evaporation; between 100 and 360 °C, corresponding to the decomposition of oxygenated functional groups; and from 360 to 1000 °C, associated with oxidative pyrolysis of the carbon framework³⁴. Following the procedure adapted from ASTM C561-16¹⁴, the measured ash content was 41.6%, indicating a substantial noncombustible fraction. The carbon-purity calculation adapted from ABNT ISO/TS 11308:2020¹⁵ yielded a value of 49.8%. Because ISO/TS 11308 was developed for the thermogravimetric characterization of single-wall carbon nanotubes rather than GO, this value should be regarded as an operational estimate based on the adapted procedure, not as a formal classification of GO purity under that standard.

The combined characterization results indicate that the commercial material exhibits structural and chemical features consistent with GO. Nevertheless, its high inorganic fraction, low carbon purity, and heterogeneous composition must be considered when interpreting the behavior of the elastomeric compounds. These characteristics may influence GO surface chemistry, dispersion stability, interactions with curing species, and the organization of the hybrid filler network. Therefore, the structure–property relationships observed in the composites cannot be attributed exclusively to the intrinsic characteristics of GO, because the possible contribution of the detected inorganic residues cannot be separated using the available data.

3.2. Stability of GO dispersion in processing oil

The homogeneous distribution of nanofillers within the elastomeric matrix is essential for properly assessing their reinforcing effect on the developed material. In this context, several strategies have explored the dispersion of graphene derivatives in different media as a means of facilitating their incorporation into elastomeric compounds. Gheller and Zanchet¹¹, for example, investigated the dispersion of graphite nanoflakes (GNf) in paraffinic oil, followed by their incorporation into SBR and BR composites through mechanical mixing. Different GNf loadings (0.1, 0.5, and 1.0 phr) were evaluated, and the dispersions were subjected to 20 min of ultrasonic treatment in an ice bath. However, when compared with the direct addition of the nanofiller, no significant improvement in the physico-mechanical

properties was observed, suggesting that either higher GNf contents or longer ultrasonication times would be required. Therefore, nanofiller dispersibility, as well as dispersion stability and homogeneity, remain critical factors governing nanocomposite performance.

In the present study, the dispersion of GO in naphthenic oil exhibited sedimentation, even after prolonged ultrasonication for 36.8 h, during which temperatures neared 60 °C. The presence of oxygen-containing functional groups on GO nanosheets imparts high polarity to the material, thereby favoring dispersion in polar solvents. Konios et al.³⁵ reported long-term stability of GO dispersions in water, ethylene glycol, and *N*-methyl-2-pyrrolidone, all characterized by high dipole moments. In contrast, the low polarity of naphthenic oil likely contributed to the instability observed in the present dispersion system. Interestingly, the same authors observed low stability of GO in *o*-dichlorobenzene, a relatively polar solvent, and high stability in toluene, a nonpolar solvent³⁵. These findings suggest that GO dispersion stability is not exclusively governed by solvent polarity but also depends on additional factors such as surface tension, interfacial interactions, and viscosity.

To overcome the limited affinity of GO for nonpolar media, several approaches have been proposed, including the use of dispersing agents. Passero et al.³⁶ recently employed a solvent-free copolymer with high deflocculating capacity, originally recommended for CB dispersion, to stabilize 1.0 wt% GO in naphthenic oil. Although the dispersant proved effective in improving dispersion stability, laser diffraction results indicated a tendency toward particle re-agglomeration. Other studies have proposed the chemical functionalization of GO nanosheets with hydrophobic groups to reduce surface polarity and consequently enhance compatibility with nonpolar materials such as naphthenic oil³⁷. The lower oil viscosity at approximately 60 °C facilitated dosing and mixing, although complete dispersion stability was not achieved.

It is also worth noting that ultrasonication, widely employed for graphene layer exfoliation and dispersion, may induce structural modifications in GO^{38,39}. Studies indicate that ultrasonic bath treatment is less aggressive than probe ultrasonication, resulting in fewer alterations to the lamellar structure and morphology³⁹. Moreover, ultrasonic power and exposure time have been correlated with changes in interlayer spacing and in the atomic C/O ratio³⁸, highlighting the importance of carefully controlling processing conditions to avoid unintended structural modification of the nanofiller.

Based on the limited colloidal stability observed in the present study, improving GO incorporation into nonpolar rubber compounds requires strategies beyond extending the duration of bath ultrasonication. Potential approaches include the use of dispersing or compatibilizing agents specifically designed for carbonaceous fillers, surface modification of GO to reduce its polarity, and preparation of a concentrated GO/oil masterbatch under controlled high-shear conditions. A combination of mechanical pre-dispersion and shorter, carefully controlled ultrasonication could also be evaluated as a means of improving dispersion stability while limiting sonication-induced damage to the nanosheets. These alternatives were not experimentally evaluated in the present study and are therefore proposed as directions for optimizing the oil-assisted incorporation route.

3.3. Rheological properties and crosslink density

The rheometric parameters and Mooney viscosity values are summarized in Table 3. The most pronounced variation was observed for NR/CB/GO_0.75, with increases of approximately 30% in ML and 24% in Mooney viscosity compared with the NR/CB compound. This behavior indicates greater resistance to flow at this composition but does not, by itself, demonstrate enhanced filler-matrix interactions. In a related study, Zhang et al.⁴⁰ reported a similar increase in torque upon incorporating 1 phr of GO into NR via latex mixing, attributing this effect to reduced molecular mobility and an improved reinforcing contribution.

Despite the increase in ML observed for NR/CB/GO_0.75, MH remained essentially unchanged across the formulations, in agreement with the findings of Rajan et al.¹, who investigated the partial substitution of N330 CB with HOOC-functionalized graphene. Those authors associated the absence of significant variation in M_H with nanosheet self-aggregation and limited dispersion within the elastomeric matrix, factors that constrain effective stress transfer and network development. Consistently, ANOVA performed in the present study did not reveal statistically significant differences in these rheometric parameters.

The ΔM values and corresponding crosslink densities are presented in Table 4. GO incorporation did not produce a consistent increase in crosslink density, and a slight tendency toward lower values was observed at the higher GO contents. NR/CB/GO_0.5 was the only compound showing a small increase of approximately 2% relative to NR/CB; given the magnitude of this variation, however, it should not be interpreted as evidence of a distinct reinforcing effect. As described by the Flory-Rehner equation²³ (Equation 1), the equilibrium swelling behavior reflects the molecular architecture of the crosslinked network and may consequently influence the macroscopic mechanical response.

Several mechanisms reported in the literature may help contextualize the tendency toward lower crosslink density observed in some GO-containing compounds. Xie et al.⁴¹ proposed that oxygen-containing groups on GO can adsorb

reactive species derived from sulfur-based curing systems, thereby reducing their effective availability during vulcanization. Restricted transport of curing agents through hybrid filler domains has also been suggested for graphene-containing elastomeric systems⁴², while Raef et al.⁴³ associated changes in vulcanization kinetics with filler-induced restriction of polymer-chain and reactive-species mobility. However, adsorption of curing agents and their diffusion through the compounds were not directly measured in the present study. Moreover, the differences in curing times were not statistically significant. These mechanisms should therefore be regarded as literature-supported hypotheses that may contribute to the observed tendencies rather than as experimentally demonstrated explanations.

Similar reductions in cure rate have been associated in the literature with adsorption of accelerator-derived species onto oxygen-containing groups of GO⁴⁰. Conversely, increases in CRI have also been reported for graphene-containing rubber compounds^{1,7}, and have been discussed in terms of interactions among graphene surface groups, elastomer chains, and curing-system components¹. The different trends reported in the literature indicate that GO may either retard or promote vulcanization depending on its surface chemistry, purity, dispersion, and the curing formulation. In the present study, the small and non-monotonic CRI variations do not allow either mechanism to be identified conclusively.

Finally, the inorganic species detected by EDS may have contributed to the vulcanization behavior of the compounds. However, EDS does not provide information on chemical speciation and therefore cannot establish whether sodium, sulfur, and chlorine were present as free ions, residual salts, surface-bound species, or other compounds. Consequently, their specific interactions with sulfuring intermediates or accelerators cannot be determined from the present data. The reduction in crosslink density observed at the highest GO loading may reflect the combined effects of curing-agent adsorption by oxygen-containing groups, restricted diffusion of reactive species, GO aggregation, and the presence of inorganic residues. Accordingly, the contribution of these

Table 3. Mooney viscosity, minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}), curing time (t_{90}), and cure rate index (CRI) of the elastomeric compounds.

Sample	Mooney viscosity (ML 1 + 4 at 100 °C)	M_L (dN m)	M_H (dN m)	t_{s2} (min)	t_{90} (min)	CRI (min ⁻¹)
NR/CB	24.0 ± 0.95	0.72 ± 0.06	11.8 ± 0.30	2.92 ± 0.02	4.35 ± 0.05	1.17 ± 2.3
NR/CB/GO_0.5	22.4 ± 2.61	0.65 ± 0.15	11.7 ± 0.60	2.99 ± 0.05	4.48 ± 0.03	1.11 ± 1.3
NR/CB/GO_0.75	29.8 ± 1.90	0.93 ± 0.14	11.9 ± 0.34	2.98 ± 0.08	4.44 ± 0.07	1.15 ± 1.0
NR/CB/GO_1.0	24.3 ± 2.71	0.72 ± 0.13	11.6 ± 0.28	2.96 ± 0.04	4.36 ± 0.08	6.76 ± 1.4
NR/CB/GO_1.25	23.3 ± 2.40	0.60 ± 0.14	11.5 ± 0.40	2.96 ± 0.06	4.40 ± 0.06	7.62 ± 1.2

Table 4. ΔM and crosslink density of the elastomeric compounds.

Sample	ΔM (dN m)	Crosslink density [X] ($\times 10^{-4}$ mol cm ⁻³)
NR/CB	11.1 ± 0.23	2.12 ± 0.05
NR/CB/GO_0.5	11.1 ± 0.45	2.16 ± 0.02
NR/CB/GO_0.75	10.9 ± 0.20	2.12 ± 0.02
NR/CB/GO_1.0	10.9 ± 0.14	2.09 ± 0.02
NR/CB/GO_1.25	10.9 ± 0.26	1.97 ± 0.04

mechanisms should be regarded as a plausible interpretation rather than a directly demonstrated causal relationship.

Additional purification of GO by repeated washing, dialysis, or membrane-assisted filtration could reduce soluble ionic contaminants and residual synthesis-derived species. Previous studies have demonstrated that purification procedures can effectively remove contaminants such as Na^+ , Cl^- , SO_4^{2-} , and other residual ions from GO dispersions^{44,45}. Because the GO employed in the present study was obtained commercially and used without additional purification, the extent to which the observed vulcanization behavior arose from the intrinsic surface chemistry of GO or from inorganic residues cannot be established. A more highly purified GO would be expected to reduce the possible contribution of these contaminants and could therefore alter vulcanization kinetics and crosslink density. Nevertheless, the direction and magnitude of this change cannot be predicted from the present results, because the oxygen-containing functional groups intrinsic to GO may still adsorb curing species or restrict their diffusion. A direct comparison between GO samples with different purification levels would be required to distinguish these effects.

3.4. Dynamic mechanical-rheological properties

The strain-dependent rheological behavior of the compounds and the Payne effect ($\Delta G'$) were evaluated using an RPA. Figure 4 presents the variation of the storage modulus (G') as a function of the applied strain amplitude. The masticated unfilled NR exhibited lower G' values and a less pronounced strain dependence than the filled compounds, reflecting the absence of the reinforcing filler network present in the NR/CB and NR/CB/GO formulations. The NR/CB/GO_0.75, NR/CB/GO_1.0, and NR/CB/GO_1.25 exhibited G'_0 values that were, respectively, 24%, 14%, and 7.6% higher than that of the NR/CB compound. Higher G' values at low strain are commonly associated with a more

pronounced contribution from filler-filler organization and the resulting physical filler network^{46,47}.

In their investigation of the synergistic effect of GO, CNTs, and N330 CB in an NR matrix, Wei et al.⁴⁸ attributed the increase in G'_0 to the development of a hybrid filler network with enhanced structural organization and improved filler connectivity. However, the RPA strain-sweep response does not independently distinguish among CB-CB, GO-GO, and GO-CB contacts. The pronounced decrease in G' with increasing strain observed in Figure 4 corresponds to the progressive strain-induced disruption of the physical filler network, commonly described as the Payne effect. Thus, a larger $\Delta G'$ indicates the presence of a more developed but highly strain-sensitive filler network; it does not, by itself, demonstrate that the interactions between GO and CB are intrinsically weak. In the present system, the simultaneous increase in G'_0 and $\Delta G'$ for NR/CB/GO_0.75, NR/CB/GO_1.0, and NR/CB/GO_1.25 indicates that GO modified the organization and strain sensitivity of the filler network. In conjunction with the comparatively low BdRC values and the morphological heterogeneity discussed in the following sections, this response is consistent with a greater contribution from physical filler-filler organization and localized aggregation than from enhanced filler-rubber coupling. As emphasized by Yang et al.⁴⁹, the strain stability of the filler network, rather than the absolute G' value alone, should therefore be considered when evaluating its structural development.

Quantitatively, NR/CB/GO_0.75, NR/CB/GO_1.0, and NR/CB/GO_1.25 exhibited increases of 28.6%, 18.5%, and 11.8% in $\Delta G'$, respectively, compared with NR/CB. These trends support the interpretation of a more developed but strain-sensitive filler network, potentially intensified by non-uniform filler distribution and localized aggregation. Similar behavior has been associated with the polarity mismatch between the nonpolar NR matrix and the oxygen-containing functional groups of GO in composites prepared by mechanical mixing⁵⁰. In contrast, NR/CB/GO_0.5

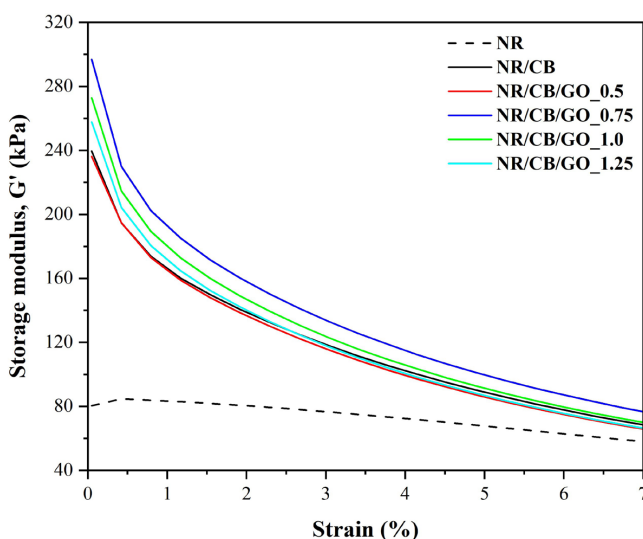


Figure 4. Storage modulus (G') as a function of strain amplitude for the masticated unfilled NR and the NR/CB and NR/CB/GO compounds, as determined by rubber process analysis.

exhibited only a slight reduction of 0.3% in $\Delta G'$ compared with NR/CB; however, this variation was not statistically significant according to ANOVA.

3.5. Bound rubber content

The mass-loss values and calculated BdRC are summarized in Table 5. Numerically, GO incorporation resulted in formulation-dependent changes in BdRC. NR/CB/GO_0.75 displayed the lowest value, 17.2% lower than that of NR/CB, while also exhibiting the highest G'_0 and $\Delta G'$ values. This combination is consistent with a greater contribution from physical filler-filler organization than from increased polymer immobilization at the filler interface.

Yang et al.⁴⁷ observed a strong negative linear correlation between G'_0 and BdRC ($R^2 = 0.882$) for NR/BR/trans-1,4-poly(isoprene-butadiene) rubber (TBIR) blended composites containing GO and different grades of CB. A qualitatively similar inverse tendency is apparent in the present results, particularly for NR/CB/GO_0.75; however, no correlation analysis was performed for the investigated formulations.

BdRC includes not only polymer segments strongly adsorbed onto the filler surface but also rubber occluded or physically trapped within filler aggregates^{51,52}. Consequently, BdRC should not be interpreted as an exclusive measure of chemical filler-rubber interaction. In the present study, the generally lower BdRC values indicate that GO addition did not consistently increase polymer immobilization at the filler interface. The higher value obtained for NR/CB/GO_1.25, in contrast, may reflect either increased interfacial association or greater physical entrapment within filler-rich domains. Because ANOVA revealed no statistically significant differences among the formulations, these alternatives cannot be distinguished from BdRC alone.

Rajan et al.¹ reported an 18% increase in BdRC accompanied by an approximately 5% reduction in ΔM after partial replacement of CB with functionalized graphene, attributing this behavior to enhanced polymer–filler interactions. However, because BdRC may include physically entrapped rubber and a reduction in ΔM may reflect lower cure-network stiffness, neither parameter alone provides conclusive evidence of improved interfacial adhesion.

3.6. Physico-mechanical properties

Figure 5a presents the tensile strength, elongation at break, and modulus at 300% strain of the investigated compounds. No statistically significant differences were observed between NR/CB and the GO-containing compounds, indicating that nanofiller incorporation did not result in substantial reinforcement. The absence of substantial reinforcement

may be related to the dispersion limitations of the adopted processing route, because localized filler agglomerates can reduce stress-transfer efficiency and act as stress-concentration or crack-initiation sites⁵³.

An increase in modulus accompanied by a decrease in elongation at break does not necessarily represent contradictory behavior. Both responses may arise from restriction of polymer-chain mobility: filler-matrix interactions and physical filler networks can increase resistance to deformation while simultaneously reducing the ability of the chains to extend before failure. Conversely, weak interfacial coupling or filler aggregation may limit stress transfer and cause premature failure, thereby reducing strength or elongation without producing effective reinforcement. The final mechanical response therefore reflects competition among chain immobilization, filler-filler networking, filler-matrix coupling, aggregation, and strain-induced crystallization. In the present study, the absence of statistically significant differences and the lack of monotonic variation with GO content indicate that no single interaction mechanism can be inferred from the mechanical properties alone.

In this regard, Berki et al.⁵⁴ compared conventional mechanical mixing and latex compounding methods for producing NR/GO composites and demonstrated that mechanical mixing reduced both tensile strength and elongation at break. Similarly, Mao et al.³ reported a reduction in mechanical properties even when latex mixing was employed. In their study, incorporating GO into the NR matrix caused tensile strength and elongation at break to decrease, which was associated with strain-induced crystallization (SIC), an intrinsic characteristic of NR. According to the authors, the addition of GO interferes with SIC by hindering the onset of crystallization, thereby reducing elongation at break. Nevertheless, they emphasized that the structural anisotropy of GO sheets may contribute to reinforcement during deformation due to sheet alignment under strain³.

Figure 5b presents the results for tear strength, abrasion resistance, and hardness (Shore A). NR/CB/GO_0.75 and NR/CB/GO_1.25 exhibited numerical increases of 4.7% and 6.2%, respectively, in tear strength compared with NR/CB; however, these variations were not statistically significant. Similar trends were reported by Guo et al.⁶, who observed a 22.6% improvement in tear resistance, and by Zhang et al.⁴⁰, who attributed enhanced performance to the reinforcing capability of GO. However, in the present study, these increases were not accompanied by consistent improvements in other mechanical properties, indicating that they do not independently demonstrate effective structural reinforcement. Furthermore, the addition of GO did not significantly affect hardness or abrasion wear behavior.

Table 5. Mass losses and BdRC of the elastomeric compounds.

Sample	First mass loss (%)	Second mass loss (%)	Final residue (%)	BdRC (%)
NR/CB	23.8	67.4	7.32	10.1 ± 0.02
NR/CB/GO_0.5	24.8	65.5	7.99	8.72 ± 0.01
NR/CB/GO_0.75	18.4	71.6	8.37	8.35 ± 0.01
NR/CB/GO_1.0	21.5	68.9	8.40	8.36 ± 0.03
NR/CB/GO_1.25	26.4	64.3	8.12	10.8 ± 0.06

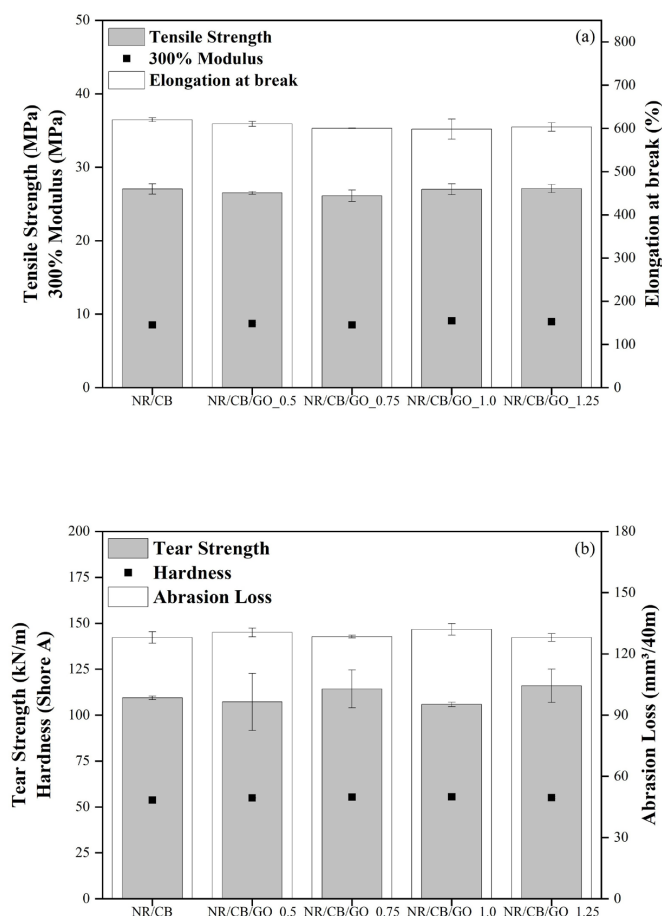


Figure 5. (a) Tensile strength, elongation at break, and modulus at 300% strain; (b) tear strength, hardness (Shore A), and abrasion resistance of the elastomeric compounds.

Yang et al.⁴⁷ correlated BdRC with abrasion resistance in NR, BR, and TBIR composites. Linear regression analysis revealed a strong positive correlation between these parameters, with higher BdRC values being associated with improved abrasion resistance and lower rubber volume loss during testing. Although several GO-containing formulations exhibited lower BdRC values, a proportional decrease in abrasion resistance was not observed. Thus, the strong linear relationship reported by those authors was not reproduced across the formulations investigated in the present study.

Overall, the mechanical results demonstrate that the adopted processing conditions did not produce consistent GO-induced reinforcement. Within the classical framework proposed by Coran⁵⁵, the tendency toward lower crosslink density in some GO-containing formulations may be qualitatively consistent with the modest increases in tear strength observed for NR/CB/GO_0.75 and NR/CB/GO_1.25. Nevertheless, this tendency should not be regarded as evidence of a definitive trade-off between tear and tensile properties.

3.7. Effect of aging on mechanical properties

Table 6 summarizes the retention of tensile strength, elongation at break, and modulus at 300% strain after thermo-oxidative aging at 100 °C for 72 h. The GO-containing

compounds generally showed higher retention of tensile strength after thermo-oxidative aging than NR/CB, although the magnitude of the response depended on GO content. In particular, NR/CB/GO_0.75 exhibited retention values of 64.3% for tensile strength and 65.6% for elongation at break, both higher than those of NR/CB. The same formulation also exhibited a 38.7% increase in modulus at 300% strain relative to its corresponding unaged value. Wang et al.⁵⁶ proposed that graphene-containing structures may delay oxidative degradation through radical-scavenging and oxygen-diffusion barrier effects. Furthermore, degradation studies conducted by Mensah et al.⁷ on NBR/GO composites suggested that improved thermal stability results from a combination of mechanisms. According to those authors, not only the physical barrier effect of the nanosheets but also strong filler-matrix interactions and homogeneous nanofiller dispersion contribute to enhanced resistance to thermal degradation.

In the present study, NR/CB/GO_0.75 showed the highest retention of tensile strength and elongation at break but also the lowest BdRC. This combination does not support stronger filler-rubber coupling as the primary explanation for its aging response. A physical barrier effect associated with lamellar graphene-derived structures, radical-scavenging activity,

Table 6. Retention of tensile properties after thermo-oxidative aging of the elastomeric compounds.

Sample	Tensile strength (%)	Elongation at break (%)	300% modulus (%)
NR/CB	56.0 ± 3.61	64.1 ± 1.04	127 ± 2.93
NR/CB/GO_0.5	61.0 ± 2.41	63.5 ± 0.44	135 ± 0.82
NR/CB/GO_0.75	64.3 ± 2.32	65.6 ± 0.39	139 ± 2.52
NR/CB/GO_1.0	61.5 ± 5.72	62.6 ± 3.87	137 ± 1.39
NR/CB/GO_1.25	60.3 ± 3.49	61.4 ± 1.57	137 ± 1.59

and changes in filler-network organization are possible mechanisms based on previous studies^{56–58}. However, oxygen permeability, oxidative induction time, radical-scavenging activity, and chemical degradation products were not evaluated. Therefore, the present results demonstrate improved retention of mechanical properties under the selected aging conditions but do not identify the molecular mechanism responsible for this behavior.

3.8. Dynamic mechanical properties

Figure 6a shows the temperature dependence of the storage modulus (E') and loss modulus (E'') of the formulations in the range from -120 to 100 °C. Below the glass transition temperature (T_g), no clear relationship between E' and GO content is observed. At -115 °C, the NR/CB/GO_0.75, NR/CB/GO_1.0, and NR/CB/GO_1.25 exhibited reductions of different magnitudes in E' , whereas NR/CB/GO_0.5 showed a slight increase (2.74%) compared with the NR/CB compound. The storage modulus reflects the elastic energy stored during deformation and provides an indication of the dynamic stiffness of the material. However, the variations observed among the formulations indicate that the influence of GO on low-temperature stiffness is relatively modest and depends on the dispersion state and physical organization of the fillers within the elastomeric matrix.

Above T_g , only NR/CB/GO_1.25 maintained lower E' values over the evaluated temperature range. At 25 °C, NR/CB/GO_0.5, NR/CB/GO_0.75, and NR/CB/GO_1.0 exhibited increases in E' of 1.7%, 5.2%, and 1.3%, respectively, compared with NR/CB. These modest and non-monotonic variations indicate that GO produced only limited changes in dynamic stiffness and do not independently demonstrate the formation of an interconnected GO-containing network. The influence of graphene–CB hybrid organization on the viscoelastic and fatigue behavior of NR composites under alternating loading has also been reported by Xue et al.⁵⁹ Figure 6a also reveals distinct behavior for E'' . At -115 °C, a general tendency toward increasing E'' with GO concentration was observed, except for NR/CB/GO_0.75, which showed the smallest variation. At 25 °C, NR/CB/GO_0.5, NR/CB/GO_0.75, and NR/CB/GO_1.0 exhibited increases of 6.1%, 7.6%, and 7.3%, respectively, compared with NR/CB, whereas NR/CB/GO_1.25 showed a reduction. These results further indicate that the dynamic response depended on the formulation and physical organization of the fillers rather than exclusively on GO content.

Figure 6b presents the loss factor ($\tan \delta$) curves from -120 to 110 °C. The $\tan \delta$ peak provides an estimate of T_g , whereas $\tan \delta$ at 0 and 60 °C are commonly used as laboratory indicators associated with wet-grip and rolling-resistance responses,

respectively⁵⁶. GO incorporation induced slight reductions in the $\tan \delta$ peak for NR/CB/GO_0.5, NR/CB/GO_0.75, and NR/CB/GO_1.0 (0.2%, 0.8%, and 1%, respectively), which may be considered in relation to the mechanism proposed by Xue et al.⁵⁹ for hybrid systems, in which GO partially isolates CB particles and reduces dissipative pathways.

$\tan \delta$ reflects the combined contribution of polymer-segment mobility, filler–matrix friction, and friction among filler particles under cyclic deformation^{59,60}. Therefore, the relatively small changes observed after GO incorporation cannot be assigned uniquely to isolation of CB particles or to a specific filler-network mechanism. Instead, they indicate that GO modified the balance among elastic storage, interfacial friction, and energy dissipation within the compounds. All GO-containing formulations showed increased $\tan \delta$ at 0 °C, representing favorable changes in the laboratory indicator commonly associated with wet-grip performance: NR/CB/GO_0.5, NR/CB/GO_0.75, NR/CB/GO_1.0, and NR/CB/GO_1.25 exhibited increases of 8.8%, 5.7%, 10%, and 4.1%, respectively, compared with the NR/CB compound. At 60 °C, however, only NR/CB/GO_1.25 showed a reduction of 16.2% compared with NR/CB, suggesting lower hysteretic losses in the temperature range commonly used as a laboratory indicator of rolling resistance. Based on these $\tan \delta$ indicators, this formulation presented the most favorable balance between the responses associated with wet grip and rolling resistance; however, direct tire-performance tests were not conducted.

These laboratory indicators are relevant to the environmental performance of tires because a substantial portion of their life-cycle impact arises during service, primarily from fuel consumption⁶¹. If translated into lower rolling resistance at the tire level, reduced hysteretic losses could contribute to improved fuel efficiency and lower associated CO₂ emissions. The $\tan \delta$ response at temperatures approaching 100 °C is also relevant because it provides information on hysteretic energy dissipation under the selected dynamic conditions. Recent reviews⁶⁰ indicate that the energy dissipated under cyclic deformation is proportional to both E' and $\tan \delta$. Consequently, high $\tan \delta$ values may lead to significant internal heating at elevated frequencies. This phenomenon, commonly referred to as heat build-up (HBU), is critical in tire applications, as it compromises durability by altering crosslink density, reducing fatigue life, accelerating aging, and increasing rolling resistance.

As shown in Figure 6b, the increase in $\tan \delta$ at 95 °C observed for NR/CB/GO_0.5, NR/CB/GO_0.75, and NR/CB/GO_1.0 does not follow a direct correlation with GO content. In particular, the addition of 0.75 phr GO resulted in an increase greater than 15%, indicating higher hysteretic dissipation under the selected DMA conditions. Frictional

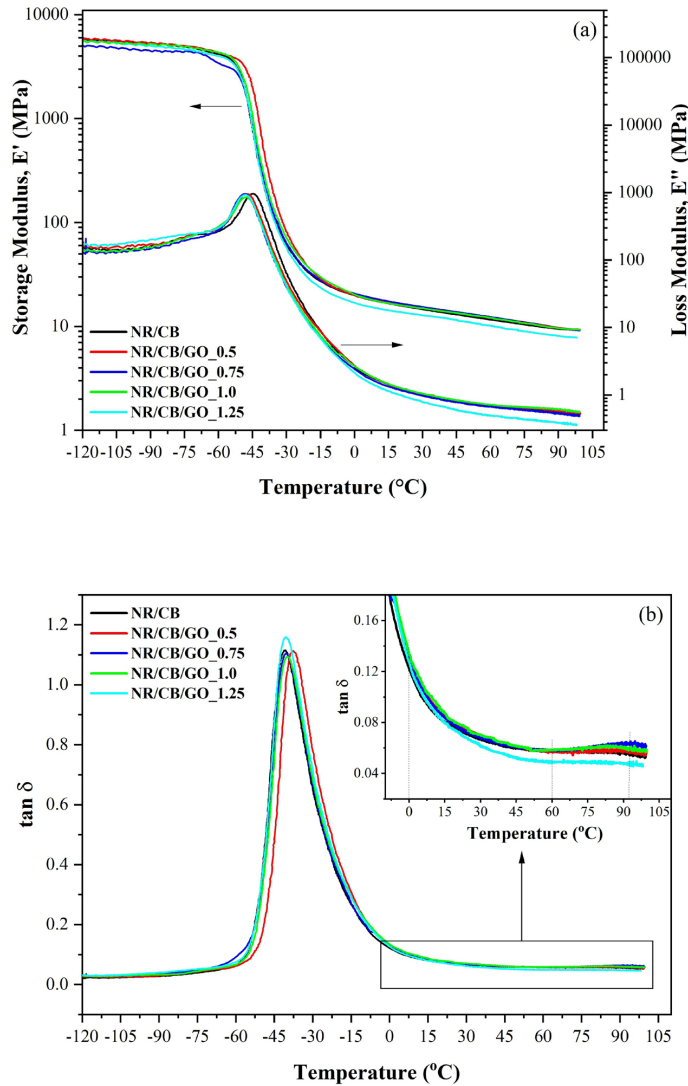


Figure 6. (a) Temperature dependence of the storage modulus (E') and loss modulus (E'') of the elastomeric compounds from -120 to 110 °C; (b) loss factor ($\tan \delta$) curves of the elastomeric compounds from -120 to 110 °C. Insert: detailed view of the loss factor ($\tan \delta$) curves from 0 to 100 °C.

processes involving polymer chains and filler interfaces may convert part of the stored mechanical energy into heat and thereby contribute to internal temperature rise under cyclic loading⁶⁰.

In contrast, NR/CB/GO_1.25 exhibited a 13.5% reduction in $\tan \delta$ at 95 °C compared with NR/CB, directly demonstrating lower viscoelastic energy dissipation. This response may be associated with changes in polymer mobility and filler-network organization at the highest GO content, but the underlying mechanism cannot be determined from $\tan \delta$ alone. Accordingly, NR/CB/GO_1.25 showed the most favorable high-temperature dissipation response among the investigated formulations, rather than a directly demonstrated reduction in tire heat build-up. Because the net thermal response of a tread compound depends on both heat generation and heat transfer, thermal conductivity was also evaluated as a complementary material property.

3.9. Linear thermal conductivity

The inherently low heat conduction capacity of rubber compounds contributes to temperature build-up and the premature failure of components such as tire treads and sidewalls. As an alternative to mitigate this limitation, the incorporation of thermally conductive nanofillers into hybrid reinforcement systems has been proposed as a strategy to create preferential heat-transfer pathways within the matrix, thereby improving thermal conductivity⁶². Figure 7 presents the linear thermal conductivity of the investigated elastomeric formulations.

The results reveal a non-linear dependence on GO content. The highest value was observed for NR/CB/GO_0.75, which exhibited a 10.6% increase in linear thermal conductivity compared with the NR/CB compound; this improvement was statistically significant relative to the other compositions

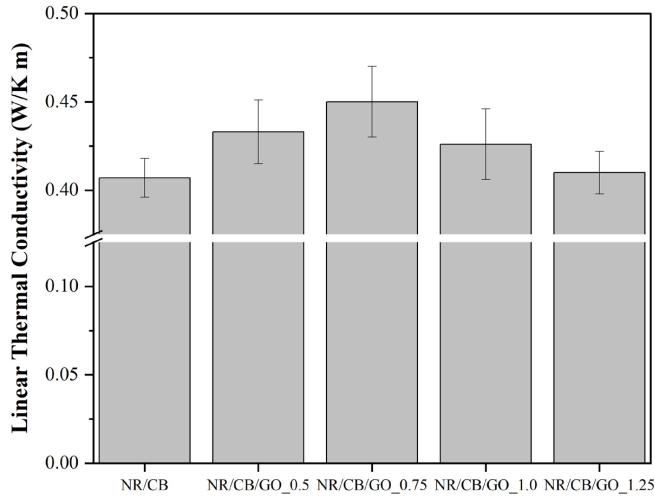


Figure 7. Linear thermal conductivity of the elastomeric compounds.

(ANOVA, $p < 0.05$). This behavior is consistent with the rheological findings, as NR/CB/GO_0.75 showed higher G'_0 and $\Delta G'$ values accompanied by a lower numerical BdRC value, suggesting a more pronounced contribution from strain-sensitive filler-filler organization than from filler-rubber coupling. Such organization may have contributed to the formation of preferential heat-transfer pathways across the composite; however, the continuity and composition of these pathways were not directly determined.

It is important to emphasize that, although NR/CB/GO_0.75 exhibited higher $\tan \delta$ at 95 °C, which is typically associated with greater hysteretic heat generation, its higher linear thermal conductivity may favor heat transfer away from regions subjected to dynamic energy dissipation. Therefore, the thermal response of the compound would be expected to depend on the balance between hysteretic heat generation and heat-transfer capacity. Nevertheless, because internal temperature rise under cyclic loading was not directly measured, the net effect of the increased thermal conductivity on heat build-up cannot be established from the present data. In this context, previous studies have shown that conductive carbonaceous fillers can promote preferential heat-transfer pathways in polymer matrices^{47,63}.

Kodal et al.⁶³ reported a 62.5% increase in thermal conductivity upon incorporating 7 phr of multiwalled CNTs into an N330 CB-reinforced NR/SBR blend. Similarly, Yang et al.⁴⁷ observed a 12.2% enhancement in hybrid systems containing N134 CB and GO. Although the two studies reported different trends in BdRC and G'_0 , the conductivity improvements were attributed to the formation of thermally conductive filler networks.

The non-monotonic dependence of thermal conductivity on GO content indicates that filler concentration alone did not control heat-transfer behavior. The higher value obtained for NR/CB/GO_0.75 is consistent with a favorable local organization of thermally conductive filler domains, whereas aggregation or restacking may have limited further improvement at higher GO loadings. However, the continuity, composition, and spatial distribution of the proposed heat-transfer pathways were not directly characterized. Therefore, the network-based

interpretation should be considered a hypothesis consistent with the combined thermal, rheological, and morphological observations rather than direct evidence of a continuous thermally conductive GO-CB network.

3.10. Field-emission gun scanning electron microscopy (FEG-SEM)

Figure 8 presents FEG-SEM micrographs of the cryogenic fracture surfaces and provides a localized morphological comparison among the compounds. The NR/CB compound exhibited a rough fracture surface with a comparatively uniform appearance within the analyzed field (Figure 8a). The GO-containing compounds displayed localized lamellar-like protrusions and irregular surface features, particularly NR/CB/GO_0.5 (Figure 8b). These features are morphologically consistent with graphene-derived platelets embedded in or detached from the elastomeric matrix. However, because phase-resolved elemental mapping was not performed on the fracture surfaces, their chemical identity cannot be established unequivocally, and not all lamellar-like features can be assigned exclusively to GO.

For NR/CB/GO_1.0 and NR/CB/GO_1.25, discrete lamellar-like features were less evident in the analyzed fields (Figures 8d and 8e). This observation could be associated with platelets embedded within the matrix, differences in platelet orientation, localized aggregation, or partial restacking at higher GO contents. Nevertheless, these possibilities cannot be distinguished from FEG-SEM morphology alone. Similarly, the protruding structures observed in some regions may be consistent with localized filler pull-out and limited interfacial adhesion, as reported for NR composites containing graphene derivatives⁵⁴, but this interpretation remains qualitative.

The micrographs of the GO-containing compounds (Figures 8b–8e) also reveal localized differences in fracture-surface morphology and in the apparent spatial organization of filler-rich features relative to NR/CB. Evgin et al.⁵⁷ similarly reported changes in filler distribution and interparticle spacing in hybrid systems containing N550 CB

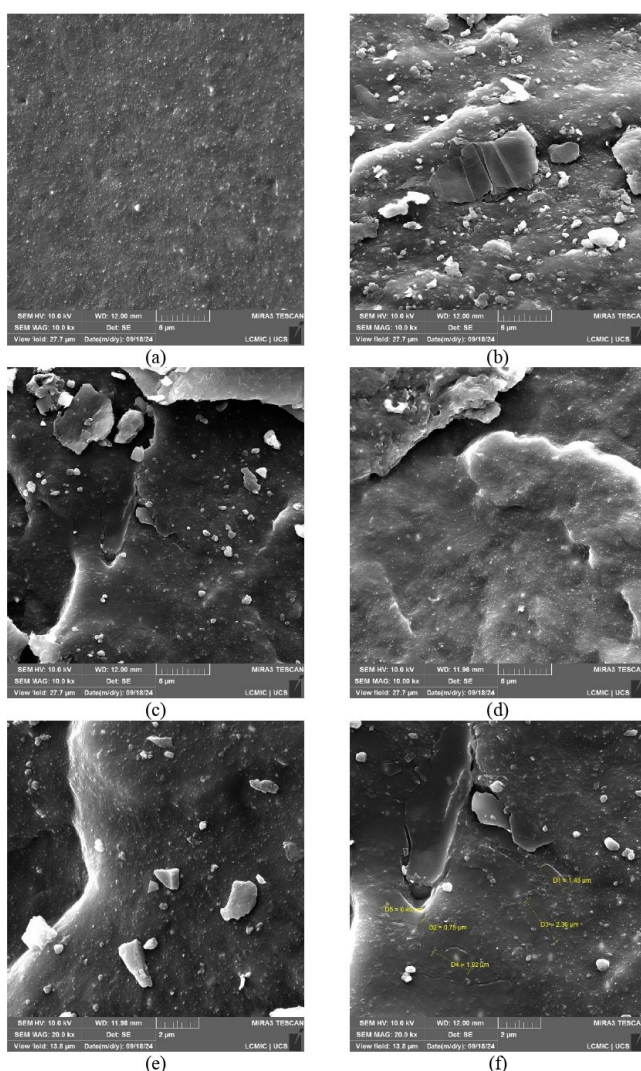


Figure 8. FEG-SEM micrographs of cryogenic fracture surfaces at 10,000 $\times$ magnification: (a) NR/CB, (b) NR/CB/GO_0.5, (c) NR/CB/GO_0.75, (d) NR/CB/GO_1.0, and (e) NR/CB/GO_1.25. Panel (f) shows a higher-magnification view (20,000 $\times$) of NR/CB/GO_0.75, displaying localized interconnected surface features tentatively associated with the filler-rich morphology.

and graphene nanoplatelets in an ethylene–propylene–diene monomer matrix. In the present study, the observed morphological heterogeneity may reflect local differences in filler organization; however, the micrographs do not chemically distinguish CB-rich regions from GO-containing domains. Therefore, the apparent variations in interparticle spacing should not be interpreted as direct evidence that GO induced separation between CB aggregates or reduced the overall homogeneity of CB distribution.

NR/CB/GO_0.75 exhibited regions with more interconnected surface features in the fields shown in Figures 8c and 8f. Figure 8f also shows comparatively fewer clearly discernible pull-out features within the selected field. In conjunction with the higher G'_0 and $\Delta G'$ values and thermal conductivity of this formulation, this morphology is consistent with more pronounced local filler-filler organization. However, the micrographs do not demonstrate a continuous GO-CB

network throughout the composite or establish synergistic reinforcement. Furthermore, the BdRC results do not indicate stronger filler-rubber coupling for this formulation. Therefore, the observed morphology should be interpreted as localized qualitative evidence that supports, but does not independently confirm, the filler-network interpretation derived from the rheological and thermal results.

The spatial representativeness of Figure 8 is limited by the number and dimensions of the analyzed fields and by the absence of phase-specific high-resolution mapping. Consequently, these micrographs cannot establish the homogeneous nanoscale distribution of GO and CB. In the present study, the FEG-SEM observations were therefore evaluated alongside the RPA, BdRC, mechanical, thermal-conductivity, and dispergrader results to provide complementary information across different length scales. Transmission electron microscopy (TEM), scanning

transmission electron microscopy (STEM), or spatially resolved elemental and spectroscopic mapping would be required to directly determine the nanoscale distribution and interfacial organization of the individual reinforcing phases.

3.11. Dispersion analysis

Table 7 summarizes the instrument-derived macrodispersion indices obtained by reflected-light microscopy. These values represent the percentage of the analyzed surface classified by the instrument software as adequately dispersed based on optically detectable defects associated with filler agglomerates. The method provides information at the macrodispersion scale but does not identify the chemical composition of individual features, distinguish CB agglomerates from GO-containing domains, or resolve the nanoscale distribution of the fillers. Accordingly, the indices should not be interpreted as direct evidence of homogeneous GO dispersion.

The NR/CB compound exhibited the highest macrodispersion index, whereas slightly lower values were obtained for the GO-containing formulations. All compounds showed indices above 90%, indicating a low proportion of optically resolved agglomerates under the conditions of the method. Nevertheless, the lower indices of the GO-containing compounds, in conjunction with sedimentation in the GO/oil dispersion and the localized morphological heterogeneity observed by FEG-SEM, suggest that the processing route did not completely prevent aggregation or spatial variations in filler organization. Therefore, satisfactory macrodispersion coexisted with unresolved heterogeneity at smaller length scales, which may have contributed to the non-monotonic rheological, mechanical, dynamic-mechanical, and thermal responses of the compounds.

To improve filler distribution across different length scales, alternative processing strategies have been described in the literature. Kodal et al.⁶³ proposed a modified mixing approach employing a high-torque micromixer to produce NR and SBR compounds reinforced with N330 CB and multiwalled CNTs. Dispersion levels above 80% were achieved, which the authors attributed to the distinct shear conditions generated by the micromixer, differing substantially from those provided by conventional Banbury-type internal mixers. However, the absolute dispersion indices reported for different filler systems and analytical procedures should not be compared directly.

Overall, the dispergrader results demonstrate satisfactory macrodispersion but do not establish homogeneous nanoscale distribution of GO and CB. When interpreted alongside the sedimentation observed in the GO/oil dispersion, the localized morphological heterogeneity detected by FEG-SEM, and the non-monotonic property changes among the formulations, the results indicate that the conventional processing route

enabled GO incorporation but did not completely overcome its tendency toward agglomeration and restacking. Under the investigated conditions, the main contribution of GO therefore lies not in generalized mechanical reinforcement but in formulation-dependent functional responses, particularly the improved retention of tensile properties after aging, the 10.6% increase in thermal conductivity obtained with 0.75 phr GO, and the favorable $\tan \delta$ profile observed with 1.25 phr GO.

4. Conclusions

In this study, the influence of GO incorporation on the mechanical, thermal, and dynamic-mechanical properties of an N220 CB-reinforced NR tread formulation was systematically investigated. The compounds were prepared at the laboratory scale using conventional two-roll-mill mixing, with processing oil as the GO incorporation vehicle. Although this approach employs equipment and formulation components representative of conventional rubber compounding, the present study did not include pilot-scale production, industrial process validation, or tire-level performance testing. Therefore, its industrial relevance is based on processing compatibility rather than demonstrated scalability. Four GO concentrations (0.5–1.25 phr) were evaluated to determine the capabilities and limitations of this oil-assisted incorporation strategy.

The commercial material exhibited morphological, spectroscopic, and thermal features consistent with GO; however, its measured ash content of 41.6% and estimated carbon purity of 49.8% indicated a substantial inorganic fraction and comparatively low carbon content. EDS additionally detected sodium, sulfur, and chlorine, although the corresponding atomic percentages are semiquantitative and do not establish the chemical forms of these elements. These characteristics represent an important limitation of the investigated material because the inorganic residues may have influenced dispersion stability, vulcanization, filler-network organization, and the resulting composite properties. Consequently, the observed responses cannot be attributed exclusively to the intrinsic structure and surface chemistry of GO. Moreover, the oil-assisted dispersion strategy provided limited colloidal stability of GO particles, as sedimentation was observed even after ultrasonication. Mechanical mixing in a two-roll mill did not overcome the colloidal instability observed in the GO/oil dispersion or establish homogeneous nanoscale distribution of the reinforcing phases. Although dispergrader analysis indicated satisfactory macrodispersion, the slightly lower indices of the GO-containing compounds and the localized morphological heterogeneity observed by FEG-SEM suggest that aggregation and spatial variations in filler

Table 7. Instrument-derived macrodispersion indices of the elastomeric compounds.

Sample	Macrodispersion index (%)
NR/CB	97.3 ± 0.6
NR/CB/GO_0.5	92.7 ± 0.9
NR/CB/GO_0.75	94.2 ± 1.2
NR/CB/GO_1.0	95.0 ± 2.5
NR/CB/GO_1.25	93.7 ± 1.8

organization remained present. Accordingly, no consistent increases were observed in crosslink density, vulcanization time, or tensile properties. The hybrid reinforcement did not translate into consistent improvements in tensile strength, modulus, or elongation at break, a tendency also consistent with the formulation-dependent BdRC response. These observations suggest that the adopted dispersion route had limited effectiveness in promoting strong filler-matrix interactions under the investigated processing conditions.

Despite the absence of substantial mechanical reinforcement, the GO-containing compounds exhibited formulation-dependent functional responses. All GO-containing formulations showed higher retention of tensile strength after thermo-oxidative aging than NR/CB, with NR/CB/GO_0.75 exhibiting the highest retention of tensile strength (64.3%) and elongation at break (65.6%). The same formulation showed a 10.6% increase in linear thermal conductivity and a more pronounced strain-sensitive filler response, as indicated by its higher G'_0 and $\Delta G'$ values. In contrast, NR/CB/GO_1.25 exhibited the most favorable $\tan \delta$ profile, with a 4.1% increase at 0 °C and reductions of 16.2% and 13.5% at 60 and 95 °C, respectively. These results show that GO incorporation selectively modified the aging response, heat-transfer capacity, and dynamic behavior under the investigated conditions, even though conventional mechanical properties remained essentially unchanged. Because the most favorable responses were obtained at different GO concentrations, however, the results do not identify a single optimized formulation.

The main contribution of this study is therefore not the demonstration of generalized GO-induced reinforcement, but the critical evaluation of an oil-assisted incorporation approach based on conventional rubber-processing equipment. The results identify both the functional potential and the limitations of this strategy under laboratory-scale conditions. In particular, the use of GO with higher and more consistent carbon purity, lower inorganic residue content, improved colloidal stability, and greater compatibility with the nonpolar elastomeric matrix would help distinguish the intrinsic contribution of GO and more fully assess its reinforcing potential. Further validation under industrial-scale processing and tire-relevant service conditions is also necessary before practical and economic advantages can be established.

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6. Data Availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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