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Graphene-filled natural rubber nanocomposites: Influence of the composition on curing, morphological, mechanical, and electrical properties

Thananya Siriwas¹^(b), Skulrat Pichaiyut¹^(b), Markus Susoff²^(b), Svea Petersen²^(b), Charoen Nakason¹^{*}^(b)

¹Faculty of Science and Industrial Technology, Prince of Songkla University, Surat Thani Campus, Surat Thani, Thailand ²Faculty of Engineering and Computer Science, University of Applied Sciences Osnabrück, Osnabrück, Germany

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Abstract. The properties of graphene (GP) filled rubber nanocomposites were investigated in functions of rubber type (unmodified natural rubber (NR) and epoxidized natural rubber with 25 mol% epoxides (ENR-25)) and filler content. The Fourier transform infrared spectroscopy (FTIR) spectrum indicated that GP surfaces contain polar hydroxyl and carbonyl functional groups. The ENR-25/GP compound exhibited higher maximum torque, torque difference, storage modulus, initial relaxation modulus, bound rubber, and degree of reinforcement with smaller GP aggregates dispersed in the rubber matrix than the NR/GP composites. Additionally, an increasing trend of tensile strength was observed in the ENR-25/GP composite, but the contrary trend was obviously seen in the NR/GP composites due to the interaction between polar functional groups in ENR-25 and GP surfaces. Furthermore, a higher Payne effect (filler-filler interaction) was found in the NR/GP composites, corresponding to larger GP agglomerates and voids dispersed in the NR matrix. Moreover, the ENR-25/GP composite had higher electrical conductivity and dielectric constant than the NR/GP composite due to the higher polarity of the ENR with the dipoles, leading to increasing orientation polarization and interfacial polarization.

Keywords: nanocomposites, epoxidized natural rubber, graphene, reinforcements, electrical properties

1. Introduction

Natural rubber (NR) is a biopolymer from *Hevea brasiliensis* trees that consist of *cis*-1,4-polyisoprene together with non-rubber contents including protein, lipids, and inorganic salts [1]. This specific isomerism of polyisoprene molecules together with non-isoprenyl components provides outstanding properties of NR, including high flexibility, high elasticity, and very low heat build-up during deformation [2]. However, natural rubber has some drawbacks in terms of poor weathering, aging, oil resistance, and poor electrical conductivity [3]. To promote the useful properties of NR and to extend the scope of NR applications, chemical modifications of NR molecules

*Corresponding author, e-mail: <u>charoen.nakason@gmail.com</u> © BME-PT to epoxidized natural rubber (ENR) [4–6] has been performed. ENR has higher oil resistance, weathering, and aging properties, whilst retaining many useful properties of NR [7]. Furthermore, the epoxide groups in ENR molecules promote higher polarity, resulting in higher compatibility with other polar polymers and/or fillers [8].

Graphene (GP) is a two-dimensional monolayer of carbon atoms composed of sp^2 hybridized carbon structure, which is the basic building block for graphitic materials, including carbon nanotube, graphite, and fullerene [9, 10]. In addition, the carbon-carbon bond angles in graphene can be mechanically distorted reversibly, and core electrons can act

as free electrons on GP surfaces. Thus, graphene has high mechanical strength with very high Young's modulus, tensile strength, and other related strength properties [11] with a high specific area, aspect ratio, and electrical conductivity [12]. Graphene has received enormous interest due to its potential in various applications, including modern chemistry, physics, materials science, and engineering [13]. However, the state of GP dispersion in the polymer matrix, interfacial interaction, and the formation of GP networks are very important for promoting the electrical conductivity and mechanical properties of graphene composites [14]. The GP-filled polystyrene nanocomposites with 0.9 wt% graphene nanosheets revealed 70 to 57% higher tensile strengths and Young's modulus [15]. Graphene oxide (GO) is another form of modified graphite, consisting of a single-atomic-layered material formed by the oxidation of graphite with high oxygen content that can be located at the edges or in the basal planes of the carbon sheets and conventionally, it is also called graphite oxide [16]. Graphene oxide has been synthesized using different chemical methods such as Hummer's method, modified Hummer's method, and Staudenmaier method [17]. Typically, the oxygen-containing functional groups on the GO layers are hydroxyl (-OH), aldehyde (-CO-H), carboxylic (-COOH), and carbonyl (-C=O) functional groups [18]. Therefore, GO exhibits good dispersibility and compatibility in the polar polymer matrix. In addition, reduced graphene oxide (rGO) is a material that is obtained by subjecting graphene oxide (GO) to a reduction process. This process involves the removal of some or all of the oxygen functional groups from GO, resulting in the restoration of the conjugated sp² carbon network of graphene. As a result, rGO exhibits improved electrical conductivity, mechanical strength, and thermal stability compared to GO. The unique properties of rGO make it a promising material for a variety of applications, including the development of advanced electronic devices, energy storage systems, sensors, and biomedical devices [19]. Graphene oxide (GO) and reduced graphene oxide (rGO) have been used as fillers in polar acrylonitrile-butadiene rubber (NBR) and nonpolar ethylene-propylenediene terpolymer rubber (EPDM). It was found that the polar NBR matrix had about 461 and 405% higher interaction parameters with GO and rGO than the EPDM composites [20]. In addition, the GO-filled hydrogenated carboxylated nitrile-butadiene rubber

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composites were prepared by a solution-blending method. It was found that the GO caused effective improvement of electrical, thermal, mechanical, and gas barrier properties of the polymer matrix [21]. Also, hybrid nanocomposites of polyurethane were prepared by in-situ polymerization of 4,4-diphenylmethane diisocyanate (MDI) with a mixture of graphene oxide and graphene nanoplatelet (GP) dispersed in poly(tetramethylene ether glycol) (PTMEG). It was found that the electrical conductivity and mechanical properties of the nanocomposites based on the GO/GP hybrid filler were superior compared to the nanocomposite based on solely GP [22]. The impact of graphene nanoplatelets and carbon black fillers on the dynamic mechanical and tensile properties of an epoxidized styrene-butadiene rubber (SBR) matrix was investigated. The results indicated an improvement in stress and torque with increasing filler loading, but at the cost of a decrease in curing time [23]. Furthermore, chemically reduced graphene oxide (crGO) was synthesized and mixed with roomtemperature-vulcanized silicone rubber (RTV-SR) and found that a crGO loading at 2 phr could effectively transform the rigid RTV-SR into a soft composite with high electrical properties [24].

In this study, the influence of natural rubber types (*i.e.*, NR and ENR-25) on the properties of GP-filled natural rubber nanocomposites was investigated. Cure characteristics, mechanical and electrical conductivity, and dynamic properties, together with stress relaxation of the nanocomposites, were studied.

2. Experimental 2.1. Materials

Two types of rubber were used in this work: two types of natural rubber (NR) were used in this work: unmodified NR (Ribbed Smoked Sheet, #RSS), manufactured by Na Bon Farmer Co-operative Co., Ltd., (Nakhon Si Thammarat, Thailand) and epoxidized natural rubber with epoxide content of 25 mol% (ENR-25), manufactured by Muang Mai Guthrie Public Company Limited (Surat Thani, Thailand). Graphene (GP) of the GS-030P grade was manufactured by Graphene Star Ltd., (London, England). It has a specific surface area ranging from 40 to 80 m^2/g , a thickness of up to 3 nm, and an average particle size of 10-30 µm with a purity level of approximately 99.8%. Other chemicals used in the rubber formulations are listed in Table 1. These are cure activators (zinc oxide and stearic acid), a cure accelerator

Table 1. Materials used and the compounding formulations.

Chemical	Supplier	Loading [phr]	
Natural rubber (NR), Ribb Smoked Sheet (#RSS)	Na Bon Farmer Co-operative Co., Ltd., (Nakhon Si Thammarat)	100	
Epoxidized natural rubber with 25 mol% epoxide (ENR-25)	Muangmai Guthrie Co., Ltd., (Surat Thani, Thailand)	100	
Stearic acid	Imperial Industry Chemical Co., Ltd., (Pathum Thani, Thailand)	1	
Zinc oxide (ZnO)	Global Chemical Co., Ltd., Samut Prakarn, Thailand)	5	
2,2-Dithiobis-(benzothiazole) (MBTs)	Flexsys, (Termoli, Italy)	1	
Sulfur (S)	Ajax Chemical Co., Ltd., (Samut Prakarn, Thailand)	2.5	
Graphene (GP)	Graphene Star., Ltd., (London, England)	1, 3, 5, 7	

(2,2'-dithiobis benzothiazole, MBTs), and sulfur curing agent.

2.2. Preparation of NR/GP and ENR/GP nanocomposites

Natural rubber (i.e., #RSS or ENR-25), the addition of GP together with various chemicals (Table 1) were firstly compounded by a tangential internal mixer (Brabender Plasticorder with Mixer 50 EHT model 835205, Duisburg, Germany) at 60 °C and a rotor speed of 60 rpm. In the compounding process, rubber was first masticated for about 1 min, and then cure activators (i.e., zinc oxide and stearic acid) were sequentially added and continuously mixed for about 2 min. Then, the GP was added, and mixing was continued for another 5 min. After that, the curing agents, *i.e.*, cure accelerator (MBTs) and sulfur, were added and continuously mixed for another 4 min to reach the total mixing time of 12 min and final mixing temperature of about 85-90 °C. The rubber compound was then sheeted out at room temperature through the 1 mm nip and a roller rotation speed ratio of 1:1.25 (front roller to back roller) of the tworoll mill (model YFCR 600, Yong Fong Machinery Co., Ltd. (Samut Sakorn, Thailand)). This process was repeated for several cycles to improve the dispersion of GP particles in the rubber matrix. The cure characteristics of the rubber compounds were then investigated by a moving die rheometer (MDR) (model MDR 2000, Alpha Technologies (Ohio, USA)) at 160 °C. Finally, rubber vulcanizate sheets were prepared by compression molding (model PR1DW400L450PM, Charoen Tut Co., Ltd. (Samut Prakarn, Thailand)) at 160 °C and the respective cure time based on the MDR test.

2.3. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was performed with a Thermo Nicolet Avatar 360 FTIR System, Thermo Electron Corporation, Thermo Nicolet (Madison, USA). The vulcanized rubber samples were prepared by cutting them to dimensions of approximately 3×3 cm before being installed in the ATR device of the FTIR instrument. The FTIR analysis was carried out over the wavenumber ranges of 2500–500 cm⁻¹ with a resolution of 2 cm⁻¹.

2.4. Cure characteristics

Cure characteristics of rubber compounds were determined at 160 °C by a moving die rheometer, model MDR 2000, Alpha Technologies, (Ohio, USA). The measurements were performed at the fixed oscillation frequency of 1.67 Hz with 1° arc amplitude at 160 °C. The optimum scorch time (t_{s1}), cure time (t_{c90}), minimum torque (M_L), maximum torque (M_H), and torque difference ($M_H - M_L$), were determined from the curing curves.

2.5. Tensile properties

The rubber vulcanizate specimens were first prepared by die cutting from the vulcanized rubber sheet to form a dumbbell shape specimen according to ISO 527 (Type 5A). The rubber samples were then clamped with the sample holders of the tensile testing machine, Zwick GmbH & Co., KG (Ulm, Germany). The test was then performed at room temperature by extending the samples with a crosshead speed of 200 mm/min according to ISO 527. Five specimens were replicated for each test.

2.6. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out by using Perkin Elmer DMA 8000, Perkin Elmer Inc. (Waltham, USA) in a tension mode in the temperature ranges from -100 to $80 \,^{\circ}$ C with a heating rate of $3 \,^{\circ}$ C/min and a fixed deformation frequency of 1 Hz.

2.7. Temperature scanning stress relaxation (TSSR)

The thermomechanical behavior of the rubber vulcanizate samples was characterized by temperature scanning stress relaxation (TSSR) using a TSSR meter, Brabender® GmbH & Co. KG, (Duisburg, Germany). Dumbbell-shaped specimens (type 5A) according to ISO 527 were firstly prepared and then annealed at 100 °C in hot air oven for 30 min to eliminate the storage-hardening effect of NR molecules [25]. The rubber samples were then placed in the sample holders in the test chamber of the TSSR meter. The sample was extended to about 50% elongation and conditioned at 23 °C for 2 h to allow the isothermal short-time relaxations [26]. Then, the non-isothermal condition was applied to the rubber sample by heating with a constant heating rate of 2 °C/min. The stress-temperature curve of each sample and relaxation spectra-temperature were eventually recorded. Also, the thermomechanical behaviors of the rubber samples were quantified. It is noted that the relaxation spectrum (H(T)) was determined by differentiating the non-isothermal relaxation modulus (E(T))and temperature (*T*), according to Equation (1) [27]:

$$H(T) = -T \left[\frac{\mathrm{d}E(T)}{\mathrm{d}T} \right]_{\mathrm{v}=\,\mathrm{const}} \tag{1}$$

2.8. Bound rubber contents

Bound rubber contents of the rubber composites were analyzed by the dissolution of the soluble parts of the unvulcanized rubber compounds in a suitable solvent. Firstly, the rubber samples were soaked in toluene and conditioned to the equilibrium state for at least 72 h at room temperature, and toluene was renewed every 24 h. The experiments were conducted either under normal conditions or in an ammonia atmosphere. After that, the samples were separated from the solvent and dried at 105 °C for at least 24 h. In the same manner, It is noted that the ammonia was used to disrupt the physical linkages between rubber molecules and filler surfaces. The bound rubber content was then determined by the following Equation (2) [28]:

Bound rubber content [%]
$$= \frac{W_{fg} - W_f}{W_p}$$
 (2)

where $W_{\rm f}$ and $W_{\rm p}$ are the weights of filler and rubber in the samples, respectively, and $W_{\rm fg}$ is the weight of filler with absorbed bound rubber after toluene extraction.

2.9. Payne effect

The Payne effect was estimated from the relationship between the storage moduli and strain amplitude, which was determined by a rubber process analyzer (RPA), Alpha Technologies (Akron, USA). The Payne effect is typically used to indicate the state of filler dispersion, filler-filler, and filler-rubber interactions [29]. The test was performed by measuring the storage shear modulus (G') of each filled unvulcanized rubber compound under shear deformation in a strain amplitude range of 0–100% at a fixed oscillating frequency of 1 Hz at 100 °C.

2.10. Electrical properties

Electrical properties in terms of dielectric constant (ε') and electrical conductivity (σ) of gum NR, gum ENR-25, and GP-filled rubber vulcanizates were measured at room temperature using an LCR meter, model Hioki IM 3533, Hioki E.E. Corporation, (Nagano, Japan). A sample with a thickness of about 2 mm was first placed between the plates, and then the test was performed over the frequency ranges from 1 to 10^5 Hz. The dielectric constant (ε') and electrical conductivity (σ) were calculated by the following Equations (3) [30] and (4) [31], respectively:

$$\mathbf{\varepsilon}' = \frac{C_{\mathrm{p}} \cdot d}{A \cdot \mathbf{\varepsilon}_0} \tag{3}$$

$$\sigma = \frac{1}{\rho} = \frac{d}{R_{\rm p} \cdot A} \tag{4}$$

where *d* and *A* refer to the sample thickness and the area of an electrode, respectively. The factor ρ is the

volume resistivity, the reciprocal of conductivity, and R_p is resistance. The parameter C_p is the parallel capacitance, and ε_0 is the dielectric constant of the free space, which is $8.854 \cdot 10^{-12}$ F/m.

2.11. Morphological characterization

The morphological properties of gum NR, gum ENR-25, and 5 phr-GP-filled NR and ENR vulcanizates were characterized by scanning electron microscopy (SEM), Quanta 250, FEI Company (Černovice, Czech Republic). Each specimen was first cryogenically cracked in liquid nitrogen to create a fresh cross-sectional surface. Then, the dried surface was gold coated and examined by SEM.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (ATR-FTIR)

The FTIR was used to determine the chemical structure and chemical interactions between rubber molecules (i.e., NR and ENR-25) and the polar functional groups on GP surfaces. Figure 1 represents the FTIR spectrum of pure GP particles. It can be seen that the infrared spectrum of GP shows the absorption bands of the oxygen-containing functional groups at wave numbers 1720, 1360, 1260, and 1030 cm⁻¹, which correspond to C=O stretching vibration of carbonyl groups, -OH bending vibration of phenol or tertiary alcohol, -OH in-plane bending vibrations, and C-O stretching vibration, respectively [32, 33]. This confirms the presence of polar hydroxyl and carbonyl groups linked to the GP particle surfaces. Figure 2 shows FTIR spectra of gum rubbers (i.e., gum NR (#RSS) and ENR-25) and GP-filled rubber vulcanizates with the FTIR peak assignments shown



Figure 1. FTIR spectrum of pure graphene.



Figure 2. ATR-FTIR spectra of gum NR (#RSS), gum ENR-25, NR/GP, and ENR/GP nanocomposites with 5 phr of GP.

in Table 2. Absorption peaks at 840 and 870 cm⁻¹, which are assigned to =C–H wagging vibrations of isoprene units in the NR molecules and the -C-O-stretching vibration of oxirane rings in the ENR molecules, are clearly seen in the FTIR spectra of gum NR and ENR-25 and their GP-filled vulcanizates, respectively. Therefore, the -C-O-bonds exist in the FTIR spectra of the gum ENR and the ENR-GP composite, but this bond is absent in the FTIR spectra of NR and the corresponding NR/GP composite. In addition, lower intensity of the =C–H wagging vibration

Table 2. Assignments of FTIR peak absorptions for gumrubber (*i.e.*, gum NR and ENR-25) and GP-filledNR and ENR-25 vulcanizates.

Wave number [cm ⁻¹]	Assignments		
490	-S-S stretching vibration in sulfidic bond [34]		
570	Aromatic ring [35]		
840	=CH wagging vibration [3]		
870	-C-O stretching vibration of the oxirane ring [33]		
1030	-C-O stretching vibration [32]		
1244	-C-O stretching of the interaction (C-O-C) [36]		
1260	-OH in-plane bending vibrations [33]		
1310	C–N stretching vibration [34]		
1360	-OH bending vibration of phenol or tertiary al- cohol [33]		
1375	-CH ₃ bending vibration [33]		
1445	-CH scissoring vibration [33]		
1536	C=O stretching vibration of zinc stearate [37]		
1575	C=C stretching vibration of the sp ² hybridized carbon atoms [32]		
1664	C=C bending vibration [33]		
1720	C=O stretching vibration of carboxyl groups [32]		

at a wavenumber of 840 cm⁻¹ is apparent in the spectra of ENR and ENR/GP composites compared to spectra of NR and NR/GP composites, respectively. In Figure 2, characteristic infrared absorption peaks associated with MBTs molecules are observed at wavenumbers 570 and 1310 cm⁻¹ (Table 2). These peaks are attributed to the aromatic ring and C–N stretching vibration, respectively. Additionally, the sulfidic bonds in cross-linked rubber display a characteristic peak at 490 cm⁻¹, corresponding to the S–S stretching vibration.

This is a hint for a lower number of -C=C- double bonds in isoprene units of ENR and ENR/GP composites. In addition, peak intensity ratios were quantified by using the symmetric CH₂ stretching vibration (2961 cm⁻¹) as the reference peak [37]. In Figure 2, it is clear that a peak intensity ratio between the peaks at 2961 and 870 cm⁻¹ (*i.e.*, C–O stretching vibration of the oxirane rings) in ENR-25/GP spectrum is 1.04, which is lower than the peak intensity ratio of the gum ENR at 1.14. This is mainly attributed to the ring-opening reaction of epoxirane rings in ENR

molecules at high temperatures [37]. These opened ring products are capable of reacting with the polar functional groups on GP surfaces, following the proposed interaction scheme in Figure 3. The creation of new links between ENR and filler can be readily observed through the absorption peak in the FTIR spectrum at a wavenumber of 1244 cm⁻¹, which corresponds to the C–O stretching vibration of these newly formed links [38]. This causes good dispersion and compatibilization of the GP particles are more likely in the ENR matrix due to the chemical interactions of polar functional groups in ENR and GP surfaces. That is, the high vulcanization temperature causes a ring-opening of epoxirane groups in ENR molecules to form diol groups (-OH) along ENR molecular chains that may further interact with the active -OH and -COOH groups on the GP surface. Therefore, strong chemical interactions between ENR molecules and GP surfaces are formed, resulting in good dispersion and distribution of the GP particles in the ENR matrix [39]. In Figure 2 and Table 2, characteristic infrared absorption peaks associated with



Figure 3. Possible chemical interaction between epoxidized natural rubber with functional groups on GP surfaces.

MBTs molecules are observed at wavenumbers 570 cm⁻¹ [35] and 1310 cm⁻¹ [34]. These peaks are attributed to the aromatic ring and C–N stretching vibration, respectively. Additionally, the sulfidic bonds in cross-linked rubber display a characteristic peak at 490 cm⁻¹ [34], corresponding to the S–S stretching vibration. Moreover, the peak observed at wavenumber 1536 cm⁻¹ indicates the C=O stretching vibration of zinc stearate resulting from the reaction between zinc oxide and stearic acid in the rubber compound [37].

3.2. Cure characteristics

Figure 4 shows curing curves of gum rubbers (*i.e.*, NR (#RSS) and ENR-25) and graphene-filled rubber compounds with different graphene loadings of 1, 3, 5, and 7 phr. Also, Table 3 summarizes the respective curing characteristics based on the cure curves in Figure 4. It can be clearly seen that the gum ENR-25



Figure 4. Cure curves of gum rubbers and their graphenefilled compounds with various GP loadings of 1–7 phr at 160 °C

exhibited much higher cure curves than that of the respective gum NR compound. This might be due to the self-crosslinked ENR molecular chains during vulcanization by chemical interactions among the opened oxirane rings. Furthermore, the ENR composites had largely higher cure curves than the unmodified NR composites. This is due to the synergistic effect of self-crosslinking ENR molecules and also higher interaction between polar functional groups in ENR molecules and polar groups in GP particles.

In addition, the curing curves of unmodified NR display a plateau curing curve, while the ENR-25 compound shows a reversion cure curve. This is attributed to more breakdown of polysulfidic and ether linkages with low bonding energy in the ENR crosslinked networks [40]. In Figure 4 and Table 3, it is also seen that the minimum torques $(M_{\rm L})$, maximum torques ($M_{\rm H}$), and torque differences ($M_{\rm H} - M_{\rm L}$) of both NR/GP and ENR/GP compounds increased with increasing GP loadings. This may be due to higher solid particulate contents and also higher interaction between graphene and rubber molecules, causing higher torques and hence crosslink density of the rubber vulcanizates. At a given GP loading, it is clear that the GP-filled ENR-25 shows higher maximum torque $(M_{\rm H})$, and torque difference $(M_{\rm H} - M_{\rm L})$ but lower minimum torque (M_L) , than its NR counterpart. This is attributed to higher chemical reactions between the functional groups on GP surfaces and the oxirane rings of ENR molecules, together with additional self-crosslinking of ENR compounds [3]. It is also seen that the incorporation of GP causes ac-

celeration of the curing reaction in both NR and

Table 3. Cure characteristics in terms of minimum torque (M_L), maximum torque (M_H), torque difference ($M_H - M_L$), scorch time (t_{s1}), cure time (t_{c90}), and cure rate index (*CRI*) of gum rubbers and their graphene-filled compounds with various GP loadings.

Compound	M _L [dN·m]	M _H [dN·m]	$\frac{M_{\rm H} - M_{\rm L}}{[\rm dN\cdot m]}$	t _{s1} [min]	<i>t</i> _{c90} [min]	<i>CRI</i> * [min ⁻¹]
Gum NR	1.30	5.19	3.89	5.90	15.23	10.72
NR/GP1	1.33	5.42	4.09	5.84	15.11	10.79
NR/GP ₃	1.36	5.52	4.16	5.77	14.95	10.89
NR/GP ₅	1.45	5.63	4.18	5.65	14.72	11.03
NR/GP ₇	1.51	6.08	4.57	4.96	13.28	12.02
Gum ENR-25	0.60	6.98	6.38	1.42	4.78	29.76
ENR-25/GP ₁	0.63	7.37	6.74	1.40	4.31	34.36
ENR-25/GP ₃	0.66	8.43	7.77	1.32	4.20	34.72
ENR-25/GP ₅	0.72	8.62	7.90	1.30	3.72	41.32
ENR-25/GP7	0.75	8.70	7.95	1.28	3.63	42.55

 $^{*}CRI = 100/(t_{c90} - t_{s1})$

ENR-25 compounds by decreasing scorch time (t_{s1}) and cure time (t_{c90}) along with increasing cure rate index (CRI), as clearly indicated in Table 3. This is attributed to the higher thermal conductivity of the rubber compound with the addition of graphene, which thereafter caused the acceleration of the curing reaction [41]. In addition, the ENR-25 compound shows much lower scorch time and cure time and much higher CRI as compared to the NR compound. Again, this is evidence of chemical interactions between ENR molecules and polar groups at the GP surfaces and the influence of self-crosslinking of ENR molecules. Furthermore, Table 4 and Figure 3 demonstrate that the scorch time is primarily affected by the epoxidation of ENR, while the impact of the graphene content is comparatively weaker. This could be due to the high reactivity of ENR, which possesses dual crosslink sites that can react via available double bonds to undergo sulfur-cured reactions, as well as self-crosslinking reactions via the epoxirane rings present in the ENR molecules. As a result, the latter reaction is more reactive than the effect of graphene on the curing reaction of ENR.

3.3. Mechanical properties

Effects of the rubber types (NR and ENR-25) without and with different loadings of GP at 1, 3, 5, and 7 phr on the stress-strain behaviors are shown in Figure 5, with the data summarized in Table 4.

It is clearly seen that the gum NR vulcanizate exposes a higher tensile strength and elongation at break but lower modulus than the gum ENR-25 vulcanizate. This might be due to the influence of molecular characteristics of ENR molecules and their chemical interaction among the molecular chains. On the one hand, this provokes higher chemical interaction



Figure 5. Stress-strain curves of gum rubbers and their graphene-filled vulcanizates with various GP load-ing of 1–7 phr.

among molecules but, on the other hand, poses lower strain-induced crystallization and hence lower strength properties [42]. Also, the chemical modifications of NR to ENR cause deterioration of the rubber molecular chains, molecular weight and hence strength properties [37]. Therefore, a lower tensile strength of graphene-filled unmodified NR (transparent symbol) is seen as compared to unmodified gum NR vulcanizates (Table 4). This might be due to poorer rubber–filler interaction in the unmodified NR (#RSS), causing heterogeneous dispersion of GP particles in NR matrix as large agglomerates and hence the deterioration of strength properties.

In Figure 5, it can also be seen that increased GP loading caused a lowering of tensile strength, fracture toughness and elongation at break but increased 100% moduli of the graphene-filled unmodified NR vulcanizates. On the other hand, in the GP-filled ENR-25 composites (solid symbol in Figure 5), increasing

 Table 4. Tensile properties in terms of tensile strength, elongation at break, 100% modulus and, fracture toughness of gum rubbers and their graphene-filled compounds with various GP loadings.

Material	Tensile strength [MPa]	Elongation at break [%]	100% modulus [MPa]	Fracture toughness [J·m ⁻³]
Gum NR	16.50±0.25	839.1±29.2	0.55±0.12	2715±30
NR/GP1	13.49±0.23	779.4±26.3	0.61±0.22	2513±29
NR/GP ₃	12.23±0.13	716.2±20.1	0.65±0.17	2326±31
NR/GP ₅	10.93±0.20	637.6±21.3	0.74±0.11	1860±26
NR/GP ₇	8.89±0.11	584.9±26.3	0.84±0.14	1446±25
Gum ENR-25	13.62±0.27	695.3±25.2	0.73±0.15	2045±21
ENR-25/GP ₁	15.38±0.15	667.3±22.1	0.80±0.13	2242±23
ENR-25/GP ₃	17.66±0.14	666.4±23.2	0.90±0.11	2315±23
ENR-25/GP ₅	20.56±0.23	617.4±20.2	1.12±0.15	3401±27
ENR-25/GP7	15.47±0.17	612.6±26.3	1.24±0.17	2274±26

GP loadings tend to have higher tensile strength and fracture toughness but lower elongation at break in the GP loading ranges 1 to 5 phr. This is due to the higher reinforcement because of higher ENRgraphene interactions. That is, the GP particles in the ENR-25 matrix had strong chemical and physical interactions between the filler particles and the ENR matrix [43], which can be described by the proposed chemical interactions of ENR and GP, as shown in Figure 3. However, increasing GP loading higher than 5 phr (*i.e.*, 7 phr) caused lowering tensile strength, fracture toughness, and elongation at the break of graphene-filled ENR, probably due to GP agglomerates. This may cause localized weakening of the rubber sample to break up during the tensile test. In Figure 5 and Table 4, it is also seen that both graphene-filled unmodified NR and ENR composites show an increasing trend of 100% moduli with higher GP loadings. This is due to an increasing amount of solid particulates in the rubber matrix, causing more GP agglomeration and hence fillerfiller interaction leading to more rigid materials [44]. Moreover, the 100% moduli of graphene-filled ENR composites are higher than that of the unmodified NR composite due to higher reinforcement and rubber-filler interaction in ENR composites by higher compatibility of graphene and ENR matrix due to their hydrophilic nature [45].

3.4. Dynamic mechanical analysis (DMA)

Figure 6 shows storage modulus and $\tan \delta$ as a function of temperature for the gum unmodified NR and ENR-25 compounds as well as their graphene-filled compounds. It can be seen that the storage modulus consists of three typically different regions: the glassy, glass transition, and rubbery regions. In the glassy region in the low-temperature ranges, the high storage modulus is seen due to the restriction of chain mobility. In Figure 6, it is clearly seen that the GPfilled NR composites show lower storage moduli than ENR composites in the glassy region due to poor filler-rubber interactions between GP and NR with strong GP agglomeration. This leads to weaker rubbery networks which are prone to crack propagation in the NR matrix during deformation [46]. In addition, the storage modulus increased significantly with increasing filler loadings in the glassy region in particularly of the GP-filled ENR composites. This might be due to higher solid particulate contents that caused higher intermolecular attractions between



Figure 6. Storage modulus (E') and $\tan \delta$ as a function of temperature for gum rubbers and their graphene-filled compounds.

ENR molecules and graphene surfaces together with higher chain entanglements of rubber molecules [47]. In addition, in the glass transition region, abruptly decreasing storage modulus is seen with increasing test temperature due to increased chain mobility of rubber molecules [48]. This region could also be observed in tan δ curves (Figure 6), where the tan δ peak indicates the glass transition temperature (T_g), as indicated in Table 5.

It is clearly seen that the addition of GP in gum NR and ENR-25 compounds shifts T_g towards higher temperatures due to more restrictions of rubber chain mobility. That is, the addition of GP caused the creation of free volumes (voids) and also large agglomeration in the rubber matrix that restricts the rubber chain mobility [49]. For ENR compounds, increasing T_g -s are more dominant compared to the unmodified NR (#RSS) counterpart (Table 5). This is attributed to higher interaction between GP surfaces and the epoxide groups in ENR molecules, causing

Table 5. Glass transition temperature (T_g) for gum rubbers and their graphene-filled compounds.

Materials	Glass transition temperature, <i>T</i> _g [°C]
Gum NR	-50.9
NR/GP ₁	-49.1
NR/GP ₃	-49.1
NR/GP ₅	-49.2
NR/GP ₇	-49.7
Gum ENR-25	-31.1
ENR-25/GP ₁	-29.1
ENR-25/GP ₃	-29.0
ENR-25/GP ₅	-27.7
ENR-25/GP ₇	-28.2

more restriction in molecular movement of the rubber molecular chains [50]. The rubbery region is the last region in Figure 6, where rubber molecules have more free chain mobility and lower storage moduli as the temperature increases [47].

3.5. Temperature scanning stress relaxation (TSSR)

The relaxation behavior of the gum rubbers and GPfilled rubber composites was measured by TSSR measurement. Figure 7 shows the relaxation modulus (Figure 7a) and relaxation spectra (Figure 7b) as a function of temperature for gum NR and ENR-25 and their graphene-filled compounds. It is noticed that the initial relaxation modulus (Figure 7a) can be used to indicate the level of crosslinked networks and also the reinforcement efficiency of the rubber compound. That is, the gum ENR-25 had a higher initial relaxation modulus than the gum NR compound due to its high capability of self-crosslinking reaction via oxirane rings together with the sulfur vulcanization, corresponding to higher torque difference (Table 3) and 100% modulus (Table 4). Furthermore, the incorporation of GP particles in ENR caused a significantly increasing of the initial relaxation moduli up to a GP loading of 5 phr; above this GP loading (i.e., 7 phr), the relaxation modulus was decreased. This is due to the higher rubber-filler interaction and hence reinforcing effect followed by the formation of large GP agglomerates at higher GP loading, causing weak locations in the ENR composite. This correlates well to the observed trend in tensile strength (Table 4). However, for the GP-filled NR, the highest initial modulus is already seen at 1 phr of GP, increased GP loadings caused a decreasing trend of the initial relaxation modulus due to strong GP agglomeration and void formation. These agglomerates and voids could act as weak locations to cause failure in the NR composites.

In Figure 7a, after the initial moduli, the relaxation modulus-temperature curves showed a slightly increasing slope before a decreasing trend is seen at about 85 °C in ENR and 115 °C in NR, respectively. This slope of the relaxation modulus-temperature curve typically represents the degree of crosslinking and, thereby, the reinforcing efficiency of rubber compounds. Therefore, the gum ENR and its nanocomposites are more sensitive to stress relaxation under heating conditions than their NR counterparts, as evidenced by the earlier decreasing trend of the relaxation modulus at about 85 °C. This is probably due to the presence of weaker linkages in crosslinked ENR vulcanizates that contain a higher level of chemical bonds with lower bonding energy, including –O–O– linkages (bonding energy ~146 kJ/mol) compared to polysulfidic linkages (bonding energy < 265 kJ/mol) [51]. This phenomenon has a close relation to the reversion cured behavior of ENR compound and plateau cure curves of NR compounds (Figure 4). The decreasing slopes in Figure 7a at higher temperatures is due to higher chain mobility and hence stress relaxation. Furthermore, the eventual reaching of the melting temperature of both gum rubbers and their composites is evidenced in the relaxation spectra in Figure 7b. It is noticed that the relaxation peak was typically formed due to the breakdown of weak linkages, such as sulfidic bonds and/or scission of the polymer main chains [51]. In Figure 7b it is clearly seen that the ENR compounds show the first shoulder peaks in the temperature



Figure 7. Relaxation modulus (a), and relaxation spectrum (b) as a function of temperature of gum rubber and their graphenefilled compounds.

ranges 85 to 140 °C and the second peaks at 150 to 200 °C. The first peaks should of relaxation peaks of ENR composites (solid line at 85 to 140 °C) associated to the breakage of weak physical cross-links, possibly hydrogen bonding between the oxirane rings and hydroxyl groups along the ENR molecular chains and other associated links [52], while the second peaks (at 150 to 200 °C) indicate the degradation of crosslinking networks or maybe some ENR main chains. These peaks were shifted towards higher temperature ranges as compared to the NR vulcanizates due to the thermal resistance improvement of ENR compounds with polar epoxirane rings [53]. On the other hand, the NR compounds exhibited the first sharp relaxation peaks at about 130 to 175 °C with small shoulder peaks in the temperature ranges from 180 to 190 °C. The first relaxation peak of the unmodified NR represents the breakdown of sulfidic linkages, while the second peak in the temperature range (at 180 to 190 °C) may arise from the scission of the polymer main chains [54].

3.6. Bound rubber contents

The rubber-filler interactions can be assessed from the bound rubber contents in the rubber compounds, as shown in Figure 8. It is clearly seen that the ENR-25/GP showed higher bound rubber contents than the NR/GP compounds. Also, the incorporation of 1 phr GP caused an abrupt increase of the bound rubber contents in both NR and ENR compounds. Then, a marginal increased bound rubber content of ENR compounds is seen with increasing GP loading ranging from 1 to 5 phr; above this, the bound rubber content decreases again. On the other hand, the bound rubber contents of NR compounds show a decreasing



Figure 8. Bound rubber contents of gum rubbers and their graphene-filled compounds.

trend for the whole range of investigated GP loadings 1 to 7 phr.

The increasing trend of bound rubber contents in ENR is due to high filler-rubber interactions between polar ENR molecules and polar groups on the GP surfaces. The decreasing trend of the bound rubber upon higher GP loadings than 5 phr may be due to excessive graphene contents, leading to the formation of large GP agglomerates with poorer filler-rubber interactions. In addition, the decreasing trend of bound rubber contents in NR compounds for all GP loadings is attributed to lower interaction between GP agglomeration and voids in the NR matrix. Therefore, the trend of bound rubber content has a close relation to the trend of tensile strength (Table 4), and the initial relaxation modulus (Figure 7a).

3.7. Payne effect

Filler networks or filler-filler interaction is commonly assessed by the Payne effect, which is typically determined from the difference in storage moduli at very low strain (G'_0) and very high strains (G'_∞) regimes, as Equation (5) [29]:

$$\Delta G' = G'_0 - G'_{\infty} \tag{5}$$

where G'_0 and G'_{∞} are the minimum and maximum storage moduli.

Figure 9 shows the storage modulus as a function of stran amplitude for gum NR and ENR-25 compounds and their graphene-filled compounds. In addition, Table 6 shows storage moduli at the low strain $(G'_{0.56})$ and the high strain (G'_{100}) , as well as the storage modulus difference ($\Delta G'$). It is clearly seen that the storage modulus is only slightly decreased in the low-strain regimes but dramatically reduced with increased strain amplitude higher than 10% for all rubber compounds. Additionally, the ENR composites showed a smaller decreasing trend in the lower strain deformation ranges (i.e., <10% strain) due to their stronger molecular network structures based on higher filler-rubber interaction as compared to the NR/GP composites. Increasing strain amplitude higher than 10% caused an abrupt decrease trend of the storage moduli in all rubber compounds. This phenomenon is caused by the destruction-reformation of filler-filler networks and the adsorption-deposition of polymeric chains at the filler interface of the rubber vulcanizates [55]. Therefore, the filler-filler



Figure 9. Storage modulus as a function of strain amplitude for gum rubbers and their graphene-filled compounds at 100 °C

interaction is essentially responsible for the decrease in the storage moduli. That is, the mechanical load for shear deformation of rubber compounds caused the breaking up of GP agglomerates (clusters), resulting in decreased stiffnesses and hence storage moduli. Typically, small particles of GP are capable of forming a filler-filler network within the rubber matrix, offering high resistance to the small amplitudes, but if the strain amplitude gets too large (*i.e.*, >10% strain), this network breaks down. As a result, the shear modulus decreases drastically.

In Table 6, it is seen that the shear modulus difference ($\Delta G'$) of both NR and ENR compounds increased with increasing GP loadings, indicating the stronger filler–filler interaction and hence the larger Payne effect [29]. In Figure 9, it is also clearly seen that the NR compound shows lower shear modulus

Table 6. Storage modulus at very low strain $(G'_{0.56})$ and at very high strain (G'_{100}) , and their difference $(\Delta G')$ for gum rubbers and their graphene-filled compounds at 100 °C.

Compound	G' _{0.56} [kPa]	<i>G</i> ' ₁₀₀ [kPa]	⊿G' [kPa]
Gum NR	74.28	36.25	38.03
NR/GP1	75.82	36.89	38.93
NR/GP ₃	83.56	38.10	45.46
NR/GP ₅	87.21	35.04	52.17
NR/GP ₇	92.75	35.33	57.42
Gum ENR-25	104.20	78.80	25.40
ENR-25/GP ₁	111.39	85.40	25.99
ENR-25/GP ₃	114.62	85.86	28.76
ENR-25/GP ₅	119.73	87.48	32.25
ENR-25/GP7	118.20	84.59	33.61

than the ENR compound, resulting from higher interaction between GP and ENR than the unmodified NR (#RSS). Also, in Table 6, the NR/GP composites have higher storage modulus difference ($\Delta G'$) and hence the Payne effect compared to ENR/GP composites, reflecting higher rubber-filler interaction with smaller GP aggregates in the ENR/GP composites. Therefore, a strong decrease in the storage modulusstrain curve and large storage modulus difference indicate higher filler-filler interaction of large filler agglomerates in unmodified NR composites [3]. In Figure 9, a slightly decreased storage modulus at high strain amplitude is also seen in the gum rubbers, arising from the release of chain entanglement or degradation of rubber molecular chains at the test temperature. That is, the higher strain amplitude caused dissociation in the rubber main chains due to the movement of the entangled rubber chains. Furthermore, the Payne effect results correlate to higher tensile properties (Figure 5), and bound rubber content (Figure 8) in ENR composites.

3.8. Morphological properties

Figure 10 shows SEM micrographs of GP-filled NR and ENR-25 composites with various GP loadings at 1, 3, 5, and 7 phr. It can be clearly seen that good dispersion and distribution of GP particles with smaller aggregates are seen in the ENR composites (Figure 10e–10g), apart from the composite with 7 phr GP (Figure 10h) where large agglomerates are seen. This is caused by strong chemical interactions between ENR molecules and GP surfaces (Figure 3), leading to enhanced dispersion and distribution of the GP particles in the ENR matrix. On the other hand, incompatibility between the NR matrix and GP is clearly evidenced by the existence of holes (voids) and large agglomeration (Figure 10a-10d). This is due to poorer and less interaction between unmodified NR molecules and GP particles. Therefore, the good GP dispersion and distribution in ENR composites caused improvement of various important properties, including torque difference (Table 3), tensile properties (Table 4), storage modulus (Figure 6), relaxation modulus and stress relaxation behavior (Figure 7), and rubber-filler interaction (Table 6).

3.9. Electrical properties

The electrical conductivity of different natural rubber types and their graphene-filled composites are shown in Figure 11. It is clearly seen that the electrical



Figure 10. SEM micrographs of graphene-filled rubbers compounds; a) NR/GP₁, b) NR/GP₃, c) NR/GP₅, d) NR/GP₇, e) ENR-25/GP₁, f) ENR-25/GP₃, g) ENR-25/GP₅, and h) ENR-25/GP₇.



Figure 11. Electrical conductivity of gum rubbers and their graphene-filled compounds.

conductivity of rubber compounds increased steadily with an increased frequency. Furthermore, the gum ENR-25 compound had much higher electrical conductivity than the gum unmodified NR (#RSS) compound due to the higher polarity of the ENR molecules. In addition, the electrical conductivity showed a linear increase with increasing GP loadings. Additionally, the GP-filled ENR-25 shows much higher electrical conductivities than the NR composites in the whole range of frequencies and investigated filler loadings. This is due to the high electric conductivity of GP from the free electron movement of the localization sp² hybridized atoms. In another study [56], the incorporation of graphene was found to increase electrical conductivity, and this effect was observed to be more pronounced with increasing graphene content.

Also, these electrons can be freely moved throughout the ENR matrix due to the polar nature of ENR molecules, causing synergistically enhanced electrical conductivity of ENR nanocomposites. In addition, the formation of continuous GP networks in the ENR matrix caused enhancement of the electrical conductivity. This is indicated by the finer GP dispersion with smaller GP aggregates (Figure 10).

Figure 12 shows the dielectric constant as a function of oscillating frequency for gum NR and gum ENR-25 compounds and their graphene-filled compounds. It is noted that the dielectric constant of a material is defined as the ratio of the electric permeability of the material and the electric permeability of free space (*i.e.*, vacuum), and it can be measured by appeal to a simplified capacitor model [57]. In addition, the dielectric behavior of the composite de-



Figure 12. Dielectric constant as a function of oscillating frequency for gum rubbers and their graphene-filled compounds.

pends on the dielectric properties of the matrix and filler, chemical composition, molecular structure, shape, morphology of particles, and filler dispersion in the composite [58]. In Figure 12, it can be seen that the dielectric constant of gum rubbers is low and has more or less frequency-independent properties but upon the incorporation of GP in both NR and ENR composites, the frequency-dependent dielectric constant with higher value is clearly seen. That is, the dielectric constant of composites significantly increased with increasing filler loadings. This is attributed to the space charge accumulation at the interface between the polymer and the filler or interfacial polarization, known as Maxwell-Wagner-Sillar (MWS) effect resulting in different dielectric systems [59]. Hence, increasing frequencies lead to a slightly decreased dielectric constant due to molecular movements arrested or decreased orientation polarization that leads to decreased dielectric constant [60]. Also, a higher dielectric constant was observed in the gum ENR-25 due to the higher polarity of the ENR and hence the dipoles, leading to increasing orientation polarization and interfacial polarization [61]. Moreover, much higher dielectric constant is seen in the GP-filled NR and ENR-25 composites as compared with the gum rubbers, especially in the GP-filled ENR-25. This may be attributed to the sp² hybridization electrons in the GP-filled ENR with various free electrons forming electric dipoles [3].

4. Conclusions

Graphene-filled unmodified natural rubber (#RSS) and epoxidized natural rubber with 25% mol epoxide

were successfully prepared with the investigation of various important properties. We found that the chemical interaction between rubber molecules and GP surfaces has a high influence on the dispersion and distribution of the GP particles in the rubber matrix, and it is crucial for the properties enhancement of the rubber composites. That is, the polar epoxirane rings in ENR molecules are capable of reacting with the hydroxyl and carbonyl groups on the GP surfaces to form a permanent linkage among them. This causes the ENR/GP nanocomposites with various GP loadings to have higher torque differences, tensile strength, modulus, relaxation modulus and bound rubber content than the NR/GP composites. This is attributed to higher filler-rubber interactions causing finer dispersion of GP particles with smaller aggregates in the ENR matrix. Also, the tensile strength and 100% modulus were significantly increased with increasing GP contents in ENR nanocomposites, but a contradicting trend was found in GP/NR composites. This is attributed to the chemical interaction between polar epoxirane rings of ENR molecules and polar groups at the GP surfaces while lacking interaction in the unmodified NR molecules (#RSS). In addition, the glass transition temperature (T_g) was slightly increased with the incorporation of GP loadings due to more restrictions on the rubber chain mobility. Moreover, enhancement of electrical conductivity and dielectric constant in ENR/GP nanocomposite was obvious due to the higher polarity and dipoles of the ENR and hence orientation polarization and interfacial polarization.

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