Cure Characteristics, Tensile and Morphological Properties of Graphene Nanoplatelets (GNPs) Filled NR/EPDM Composites

Juliana Yaakub, Noraiham Mohamad, Jefferie Abd Razak, Zanariah Jano, Mohammed Iqbal Shueb

Proper filler-matrix compatibility is a key factor in obtaining nano-composites with well-dispersed nanofillers displaying enhanced properties. Natural rubber/ethylene–propylene–diene rubber (NR/EPDM) blends reinforced with untreated and treated graphene nanoplatelets (GNPs) were prepared through melt compounding. The untreated and treated GNPs were varied from 0, 0.25, 0.50, 1, 3 and 5 wt% into the compounding recipes to determine the influences of filler loading to the cure characteristics, swelling and morphological properties of the nanocomposites. It was observed that the scorch time (Ts), cure time (T90), minimum (M1) and maximum torque (M0) increased as untreated and treated GNPs filled in NR/EPDM composites increased. However, M0 and M1 values of treated GNPs filled NR/EPDM composites exhibit decreased as compared to untreated GNPs filled NR/EPDM composites. These findings were further supported by swell behavior and morphological characterization of the nanocomposites.

Keywords: Elastomer, Graphene, Cure Characteristics, Swelling, Morphology

INTRODUCTION

Elastomers are a class of polymers with many valuable applications in engineering due to their exceptional properties. Nowadays, elastomers are highly demanded for a wide range of products such as tires, vibration mounts, seals and bearings [1, 2]. Various types of nanofillers are analyzed as most neat elastomers are not mechanically and thermally strong, including the well-known carbon nanotubes (CNTs). Starch and clay are analyzed recently to improve the physico-mechanical properties as well as to reduce cost of the vulcanizates [3, 4]. Due to CNTs high aspect ratio, they remain the dominant fillers especially for conductive polymer composites for their very low percolation thresholds [5]. However, it has not yet reached a situation where CNTs are ideal for reinforcing polymers because of high manufacturing costs and the high viscosity caused by the ‘bird’s nest’ structure of the entangled tubes [6].

In contrast, graphene, a monolayer of sp2-hybridized carbon atoms arranged in a two-dimensional lattice, has gained a tremendous interest in recent years owing to its novel mechanical, thermal and electrical properties [7]. Its parent graphite is abundant in nature and thus, cost effective as a raw material and it is the stiffest and strongest material ever measured [8]. On the other hand, graphene carries higher electrical and thermal conductivity than multi-walled CNTs [9]. To fully exploit these properties, homogenously dispersed graphene must be done judiciously, as delicate morphological organization, fine interface control, uniform dispersion and ease of processing are vital to the performance of the resulting composites [10]. In polymer composites, filler dispersion as well as interfacial interaction has been shown to be an

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important parameter for the enhancement of mechanical properties. In fact, one of the biggest challenges is to obtain a homogeneous dispersion of graphene in a polymer matrix because strong π–π stacking and van der Waals interactions between individual sheets often lead to significant aggregation or agglomeration, thus reducing the expected property improvements of the resulting composite [11]. Like many other nanomaterials, the prevention of agglomerations is important in the preparation and processing of graphene, which will assure the unique and novel properties of an individual graphene sheet.

The functionalization of graphene nanosheets can be achieved by noncovalent and covalent functionalization [12]. For covalent functionalization, the intrinsic electrical and thermal conductivity properties of graphene are severely demolished whereas the non-covalent functionalization is fascinating because it has less destruction on the structure and the electronic network of graphene, and subsequently the intrinsic properties of graphene can be preserved [13]. Nowadays, the biological applications of graphene have been widely analyzed. For example, Shan et al. [14] demonstrated a convenient method to prepare water dispersible graphene sheets functionalized by biocompatible poly-L-lysine as a linker through covalent amide bonds. However, the covalent functionalization can destroy the intrinsic properties of graphene. Herein, we report a noncovalent strategy for stabilizing aqueous dispersion of graphene by adding chitosan molecules. Then, the noncovalently functionalized graphene was utilized as reinforcing nanofillers to fabricate the NR/EPDM nanocomposites.

2. Objectives:

To date, there are just a few studies on graphene based elastomeric nanocomposites and there is almost no study found on cure characteristics, tensile and morphology properties of graphene-filled NR/EPDM nanocomposites [15]. Compatibilized NR/EPDM blends with the 70/30 blend ratio have shown their good performance in processability and physico-mechanical properties [16]. To evaluate the effect of untreated and treated GNPs contents, various contents of GNPs were varied from 0, 0.25, 0.5, 1, 3, 5 wt% with respect to the resultant of cure characteristics properties. The findings of good interaction of untreated and treated GNPs in NR/EPDM blends were further supported by swelling behavior and SEM. This observation later attributed to the improvement processability of graphene nanoplatelets (GNPs) filled NR/EPDM composites.

3. Experimental:

3.1 Materials and chemicals:

The compound formulation used in the present study is given in Table 1 and 2 respectively. Natural rubber, SMR 20 grade was supplied by Rubber Research Institute of Malaysia. Ethylene propylene diene monomer was supplied by EPDM Buna® EPT 9650, procured from Lanxess Corp. with ENB content of 6.5 ± 1.1 wt%; ethylene content = 53 ± 4 wt%; Mooney viscosity UML (1 + 8) at 150°C = 60 ± 6. Epoxidized natural rubbers (ENR) under the trade name ENR-50 with 53% epoxidation were supplied by Malaysian Rubber Board. The average Mooney viscosity measured at ML (1 ± 4) 100°C was 67, and the average specific gravity at approximately 25°C was 0.9366. Other compounding ingredients such as sulphur, zinc oxide, and stearic acid were purchased from System/Classic Chemical Sdn Bhd.; tetramethyl thiuram disulfide (Perkacit-TMTD) and 2,2-dithiobis (benzothiazole) (Perkacit-MBTS) were acquired from Perkacit; N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) was supplied by Flexsys America (United States).

Table 1. Typical formulations

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Loading (phr)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR (SMR 20)</td>
<td>70</td>
</tr>
<tr>
<td>EPDM</td>
<td>30</td>
</tr>
<tr>
<td>ENR-50</td>
<td>10</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
</tr>
<tr>
<td>MBTS</td>
<td>1.0</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.3</td>
</tr>
<tr>
<td>6PPD</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Parts per hundred rubber

Table 2: GNPs loadings.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Loading (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene nanoplatelets (GNPs)</td>
<td>0, 0.25, 0.50, 1, 3, 5</td>
</tr>
</tbody>
</table>

As for the treatment preparation of GNPs, commercialized graphene nanoplatelets, GNPs KNG-150 were supplied by Xiamen Graphene Technology Co. Ltd, China with true density of ~2.25 g/cm³ and
carbon content > 99.5 wt%. Chitosan with particle size between 1.320μm – 590.102μm were purchased from Sigma Aldrich. All other reagents were analytical grade and used as received.

3.2 Preparation of graphene nanoplatelets (GNPs):

A mixture of water/ethanol (25/75 by volume) was prepared by applying overall volume of 1000 ml. A quantity of 2g of GNPs was first introduced into the mixture of water/ethanol. The resultant suspension was then gradually added into an acidic aqueous solution of chitosan (3g in 0.5 M HCL) by applying ultrasound for another 2h to yield a uniform brown-colored dispersion. The suspension was then filtered through a Milipore hydrophilic (0.22μ) filter paper and washed with distilled water to eliminate unreacted chemicals; the filtration process took 2 hours. Functionalized graphene-chitosan was further dried in a vacuum oven at 70°C for 24 hours. The resultant product was ground and placed in a closed-sealed container.

3.3 Preparation of the nanocomposites and cure characteristics assessment:

Melt mixing. The melt compounding process was performed according to ASTM D-3192. NR, EPDM and ENR-50 were masticated using two-roll mill prior to nanocomposites blends preparation. On the mixing procedure, NR, EPDM and ENR-50 were firstly fed into the chamber. Then, after 1 min, compounding ingredients were added simultaneously with GNPs. Finally, sulphur and accelerators were added and mixed for 1 min before the mixture was dumped and left to cool down to room temperature. From this stock, sheets approximately 1 mm thickness were vulcanized with a semi-efficient vulcanization system with a hot press at 150°C at the respective cure times, t90 which was derived from a rheometer test in accordance with ASTM D 2084.

3.4 Measurement of swelling behavior:

The swelling test was carried out according to ISO 1817. The cured specimens, with dimensions of 30 mm x 5 mm x 2 mm, were weighed using an electric balance, followed by an immersion in a toluene for 72 hours at room temperature (25°C) in a dark environment. After the conditioning period, the swollen specimens were taken out and weighed again. The specimens were then dried in an oven at 60°C until constant weight was obtained. Swelling percentage (%) = \( \frac{W_1 - W_0}{W_0} \times 100 \)

Where \( W_1 \) is the mass of samples after the swelling while \( W_0 \) is the initial mass of samples before the immersion in toluene.

3.5 Scanning electron microscopy (SEM):

Scanning electron microscopy, model EVO-50 from Zeiss, was used to analyze the fracture surfaces concerning morphological properties of the blends. Samples were placed onto aluminum stubs and sputter coated with thin layer of gold, about 20 mm thickness; prior to scanning to avoid electrostatic charging and poor resolution during examination.

Results and Discussion

4.1 Cure characteristics:

Figure 1 (a) and 1 (b) depict the effect of untreated and treated GNPs loading on the scorch time (\( t_{92} \)) and cure time (\( t_{90} \)) of NR/EPDM nanocomposites. There was an increase in scorch and cure time with the addition of both untreated and treated GNPs contents. Longer scorch and cure time indicated that the onset for pre- and vulcanization process had been delayed. This is due to the fact that GNPs has a large specific surface area imparted by the very low thickness and platelet type morphology of graphene sheets whereby it is able to absorb certain curative ingredients especially accelerator into the GNPs sheets and hence, delaying the onset and optimum time for vulcanization process. As compared to untreated GNPs, the \( t_{92} \) and \( t_{90} \) values of treated GNPs were higher. This may be attributed to the presence of long polymer chain of the treated GNPs with chitosan along with the rubber matrix. Hence, a longer scorch and cure time for treated GNPs loaded samples was demonstrated compared to untreated GNPs samples.

Figure 1 (c) and 1 (d) shows the effect of untreated and treated GNPs on the minimum and maximum torque of NR/EPDM nanocomposites respectively. The minimum (\( M_L \)) and maximum torque (\( M_H \)) values for NR/EPDM composites increased as the untreated and treated GNPs loading increased respectively. Minimum torque (\( M_L \)) is regarded as an indirect measure of the viscosity of the compound [17]. Therefore, it can be considered as a measure of stiffness of the unvulcanized compound. Incorporation of untreated and treated GNPs (Figure 1c) slightly increased the minimum torque, thus increased the viscosity of the corresponding nanocomposites. The increment in viscosity with the addition of GNPs suggests a possibility that the GNPs are already crosslinked and do not easily flow. Hence, the crosslinked reduced mobility of the rubber chains caused by the incorporation of these fillers consequently increased the torque.
Fig. 1: The effect of untreated and treated GNP loading on the (a) scorch time ($t_{52}$); (b) cure time ($t_{90}$); (c) minimum torque ($M_L$) and (d) maximum torque ($M_H$) of NR/EPDM nanocomposites.
Meanwhile, the increment in the $M_{h}$ values indicates that the presence of GNP{s} in the compounds tends to reduce the mobility and flexibility of the chain on the rubber nanocomposites. This is in agreement with the observations work by Varghese et al. [18]. However, slightly lowered $M_{h}$ and $M_{w}$ values of treated GNP{s} filled NR/EPDM nanocomposites compared to untreated GNP{s} were observed. This behavior may be due to the presence of bulky side groups of functionalized graphene sheets within the rubber matrix, particularly when the GNP{s} are modified with chitosan polar functional groups (i.e., -COOH, -OH, -NH$_3$ groups in functionalized GNP{s} with chitosan). Hence, increasing the separation between chains and reduction of rubber viscosity.

4.2 Swelling assessment:

Swelling measurement was conducted to prove the crosslinking effectiveness of the nanocomposites as most elastomers have no commercial values unless properly crosslinked. Figure 2 depicts the relationship between the weights of toluene uptake per gram of rubber against filler loading. From the plots, it can be observed that the swelling (%) values of NR/EPDM blends filled untreated and treated GNP{s} were decreased with the increase of GNP{s} content until 3wt% and then slightly increased at 5wt% in the composites. It can be possibly explained by the presence of GNP{s} in the matrix which caused the increase of crosslinking which form networks in the nanocomposites. Therefore, it has reduced the capability of the nanocomposites to diffuse toluene since there is less open chain for the toluene to penetrate [19].

Sombatsompop [20] asserts that increasing interaction between filler and polymer matrix would lead to an increase in crosslink density and reduction in solvent uptake. This, hence, supports the argument that GNP{s} have helped for a better crosslinking and in turn, given a better swelling resistance. However, at 5 wt% of GNP{s} contents, it shows a slight increase in the swelling percentage. This may be due to the formation of filler agglomerations in the rubber matrix at a higher GNP{s} content which creates holes or free volume in the composites which causes the easy diffusion of toluene molecules. This result is in line with the maximum torque results discussed earlier.

Fig. 2: The effect of GNP{s} loading on the swelling behavior of NR/EPDM blends filled untreated and treated GNP{s}.

4.3 Morphological properties:

To observe the dispersion of GNP{s} microscopically concerning the interfacial interaction between rubber matrix and graphene sheets, the tensile fractured surfaces of the nanocomposites were further investigated by SEM. Figure 3 (a-g) depicts the tensile fracture surfaces of the neat elastomers and its nanocomposites at 0, 0.25, 3 and 5 wt% of untreated and treated GNP{s} content respectively. The neat NR/EPDM fracture surface is relatively smooth and shows no signs of matrix deformation (Figure 3a). In contrast, the fracture surfaces of all nanocomposites incorporated with GNP{s} are obviously greater matrix tearing and rougher surface, implying that GNP{s} play an important role in reinforcing the elastomer. At lower filler loading (refer Figure 3 (b) and (c)), the nanocomposites shows uniformly distributed of GNP{s} as there are no images of clustering and agglomerations. Meanwhile, at higher loading (Figure 4 (d-g) of GNP{s} in the nanocomposites, the surfaces became rougher with many matrix tearing lines and thick tearing ridges indicating that more energy was needed to break the sample compared to lower filler loading as observed in Figure 4(b, c). A broader tearing line was observed.
Fig. 3: SEM micrographs of the tensile fracture surfaces of the nanocomposites: (a) neat NR/EPDM; (b) rubber with 0.25 wt% untreated GNPs; (c) rubber with 0.25 wt% treated GNPs; (d) rubber with 3 wt% untreated GNPs; (e) rubber with 3 wt% treated GNPs; (f) rubber with 5 wt% untreated GNPs and (g) rubber with 5 wt% treated GNPs at 500x magnification.

From the microstructures observation, these thick tearing ridges were formed during shear yielding mechanism. The thickness of the ridges showed the difficulties for the material to fail under stress and represent the occurrence of plastic deformation in the material before failure [21]. From the micrographs, better blend homogeneity at 3 wt % for untreated and treated GNPs was shown which indicated the coherence of the two rubber phases and uniform dispersion of GNPs in the NR/EPDM matrix. On the other hand, it also altered the crack path, which led to increased resistance to crack propagation and thus improved their physico-mechanical properties. Meanwhile, at 5 wt% of both untreated and treated GNPs (Figure 4(h)), some white particles are found to coexist with many tiny particles that should be either GNPs or their clusters. This can be explained by the poor wettability and agglomerations of the nanofillers on the matrix when the ratio of the nanofillers is too high, hence initiating cracks in the composites under stress. Hence, it could be concluded that the reduction in swelling resistance with further increases of 5 wt% GNPs contents was in good agreement with the fractured surfaces observed. Overall, the micrographs reveals the fractured surface of treated GNPs exhibit
less well compared to untreated GNPs.

5. **Conclusion:**

In conclusion, this study shows that the incorporation of untreated and treated GNPs in NR/EPDM nanocomposites enhances the scorch time, cure time, minimum and maximum torque. However, a slightly lowered M<sub>c</sub> and M<sub>H</sub> values of treated GNPs filled NR/EPDM nanocomposites compared to untreated GNPs are observed due to increase separation between chains caused by the presence of bulky side groups in the nanocomposites. On the other hand, swelling percentage of both untreated and treated GNPs has decreased to 3 wt% as indicated by the enhancements of crosslink density in the nanocomposites. The comparison of the morphological studies of the tensile fractured of the nanocomposites reveals that uniformly distributed untreated and treated GNPs increases the stiffness of the nanocomposites as the filler loading increases, however, the effect reduces as the presence of chitosan in treated GNPs is added in the compound. In future study, further characterizations remain to be carried out in order to understand clearly the mechanism of reactions and demonstrate a new route to the development of graphene processing to broaden the area of interest towards this highly functional carbon material.

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**References**


