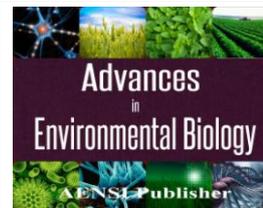




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The Effects of Covalent Treated Graphene Nanoplatelets Surface Modification to Cure Characteristic, Mechanical, Physical and Morphological Properties of NR/EPDM Rubber Blend Nanocomposites

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ABSTRACT

Functionalization of graphene nanoplatelets (GNPs) could be done through either covalent or non covalent method. In this study, a facile approach of covalent treatment using aminopropyltriethoxysilane (ATPS) was introduced by a combination method of ultrasonication and high shear mechanical stirring procedure. Covalent surface modification of GNPs caused their uniform incorporation into NR/EPDM matrix with improved compatibility since a strong interlayer cohesive energy of GNPs made the dispersion of this nanofiller are challenging. Strong vibration in Raman peak at 2081.11 cm^{-1} indicates a possible strong vibration due to formation of covalent bonds of C=C between the GNPs and ATPS, while disappearance of 821.08 cm^{-1} in IR spectra, confirmed the treatment mechanism through dehydration. In this study, the effects of covalent treated GNPs at 1.00wt.% addition to the NR/EPDM rubber blend cure characteristic, physical, mechanical tensile properties and the fracture morphology are evaluated. Blend with similar loading of untreated GNPs and unfilled NR/EPDM blend were also prepared through melt blending procedure for a comparison purposes. For cure characteristic, an addition of 1.00 wt.% GNPs-ATPS decreased the t_{s2} , T_{c90} , M_H - M_L but increased the CRI and both M_H and M_L torque, indicating improves blend processability. On rubber-filler interaction, lower value of Lorentz and Park ratio of Q_f/Q_g at 0.940 for covalent treated GNPs filled NR/EPDM blend confirmed the improvement in interface interaction between the covalent treated GNPs and rubber matrix, while reduced toluene uptake Q value and percentage of swelling provides hints for increased crosslinking behavior of the blend. It is also found that, the tensile strength was improved at about 59.81% over the unfilled blend system and yields the different about 2.84% of improvement as compared to untreated GNPs filled NR/EPDM blend. The M100, M300 and M500 for covalent treated filled blend experienced a significant increased at about 28.67%, 37.98% and 95.08%, respectively, over the untreated GNPs filled NR/EPDM blend system. As for conclusion, the improvement in tensile strength, %E, Shore-A hardness and modulus at various elongation with addition of 1.00 wt.% covalent treated GNPs-ATPS as well as noticeable morphological change in the fractured samples, confirmed the surface activity due to covalent treatment on GNPs that are successfully in controlling the resulted properties of NR/EPDM rubber blend nanocomposites.

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INTRODUCTION

Polymer blend is prepared to meet performance requirement that cannot be satisfied by the current available commodity polymer or properties lacking in the component polymers [4,24,26]. Blending of rubbers also enhance the physical properties of the final vulcanized product [1]. Polymer blending is one of the new approaches for the preparation of inexpensive new materials with good processability [16,38]. The properties of

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polymer blends can be controlled by regulating blend morphology, blend compositions and processing condition [27].

Previously, many researchers have employed natural rubber (NR) and ethylene-propylene-diene-monomer (EPDM) synthetic rubber for the preparation of elastomeric blends [3,7,9,24,25,29,30-32,40]. Vulcanized NR/EPDM blend systems have been extensively studied because of their superior performance in tire application, as well as significant improvement in heat and ozone resistance [24].

NR is a natural biosynthesis polymer having an attractive range of properties, excellent elasticity and mechanical strength, and good processing characteristics [8,33]. However, NR is highly unsaturated and it is chemically reactive [30] that make it susceptible to degradation due to environmental factors such as ozone, light, moisture, humidity and radiation [4,8,33]. The improvement in poor ozone resistance of NR can be achieved by blending it with low-unsaturation rubbers of highly saturated and non-reactive EPDM rubber [4]. EPDM imparts good resistance to aging, weathering, oxidation and chemical resistance which is suit for excellent outdoor applications [1,7,26]. EPDM is obtained by polymerizing ethylene and propylene with a small amount of a nonconjugated diene (3-9 %) [1,7,8,20] and is highly saturated [20]. The saturated backbone of EPDM results in high mechanical, dynamic and electrical properties [1], good resistance to aging, heat and oxidation and low temperature flexibility, with high chemical and swelling resistance. Blending of high cost EPDM with low cost NR suit the economic reasons since appreciable price difference is balanced with outstanding results that are normally in practice for various applications such as automotive sealing systems, wire and cable insulation, building profiles, roofing sheets and under-the-bonnet applications [20]. To further increase the added-value of rubber blend, many functional nanofiller has been added to the system for various intended applications.

Presence of various functional fillers in NR/EPDM blends enhances the engineering properties and its functionalities. Up to now, limited references are available and only Motaung *et al.* [24] and Alipour *et al.* [3,5] has been reported the use of TiO₂ and organoclay nanofiller in their studies of NR/EPDM blend nanocomposites. Previous studies by [3,5,24] had just reporting the effect of nanofiller content and variation of matrix or blend ratio to the resulted properties without highlighting to the effect of specific surface treatment to the nanofiller used. In addition, to the best of our knowledge, the references dealing with graphene nanoplatelets (GNPs) addition to the rubber blend, especially for NR/EPDM blend system are really scarce. Thus, this study is intended to report the characterization of unfilled NR/EPDM elastomeric rubber blend and blend with filled ATPS covalent treated and untreated GNPs nanofiller.

For this study, NR/EPDM blend was incorporated with versatile carbon nanomaterials of GNPs that basically are one-atom thick two-dimensional (2D) layers of sp²-bonded carbon atoms that arranged in a honeycomb hexagonal lattice structure. GNPs is emerging advanced materials due to its prominent intrinsic properties and its potential application in various areas [11,12,15,17,18,23,21,34,35,40]. The density of GNPs is ~2 g/cm³ and the reported stiffness of the order of 300-400 N/m, with a breaking strength of 42 N/m, represents the intrinsic strength of a defect-free graphene sheet. The estimates of the Young's modulus yielded approximately 0.5 – 1.0 TPa which is very close to the accepted value for bulk graphite [35] with breaking strength to be approximately 40 N/m [40]. The platelet thickness is in the range of 0.3 – 100 nm and high aspect ratio combined with the extraordinary properties make GNPs ideal reinforcing fillers in polymer nanocomposites [11,28,33]. Graphene has combined benefits of layered silicates and carbon nanotubes, and is considered as the most promising reinforcing and functional filler of polymers coupled with inexpensive economical sources from graphite [13].

Direct addition of nanofiller often creates common problem of agglomeration, worst filler dispersion and weak matrix-filler interaction which later diminish the resulted properties of produced nanocomposites. Surface treatment either covalent or non-covalent is employed to the nanofiller before their incorporation with polymer matrices. Thus, this study explored the potential of GNPs in improving the mechanical, physical, processability and morphological behavior of the common NR/EPDM blend, coupled with the role justification of adding about 1.00 wt.% ATPS-covalent treated and untreated GNPs for filled and unfilled NR/EPDM blend system observed throughout the overall experimental output.

Experimentation:

GNPs were used as received for untreated filled NR/EPDM nanocomposites blend and undergone facile approach of covalent treatment prior incorporation with rubber for NR/EPDM filled treated GNPs-ATPS blend preparation. GNPs KNG-150 was supplied by Xiamen Graphene Technology Co. Ltd, China in a black and gray powder form with bulk density of ~ 0.3g/cm³; true density of ~ 2.25 g/cm³; specific surface area of 40-60 m²/g and carbon content > 99.5 wt.%. Covalent GNPs surface treatment performed in this study was adapted from Ganguli *et al.*, 2008 that previously deal with chemical modification of the exfoliated graphite flakes. Mixture of solvent at ratio 25:75 of water: ethanol was prepared for the treatment using overall volume of 1000 ml for every 2 gram GNPs and 3 gram ATPS treatment mixture. The mechanical stirring (WiseStir HT50DX) at 1000 rpm was performed for 5 hours with combination of ultrasonication effect using ultrasonic bath set-up

(JE10Tech UC-02) at 60°C. Next, treated GNPs drying were performed using hot-plate magnetic stirring for 100 rpm, 100°C for 45 minutes. Then, GNPs were washing using distilled water as to eliminate unreacted chemicals. Further oven heating at 150°C was performed for complete drying at 5 hrs. The dried product was grinded using agate mortar and placed in a close-sealed container. The commercial grade SMR 20 supplied by Mentari Equipment and Project Sdn. Bhd. has 0.16 max. %wt. dirty retained on 44 apertures, 1.00 max. % wt. ash content, 0.60 max. %wt. nitrogen, 0.80 max. %wt. volatile matter, 30 min Wallace rapid plasticity (P_{30}) and 40 min. % of plasticity retention index (PFU). Ethylene propylene diene rubber (EPDM) grade BUNA EP T 9650 is supplied by LANXESS, Pittsburgh, USA. The Mooney viscosity UML (1+8) at 150°C is 60 ± 6 MU, ethylene content 53 ± 4 wt%, ENB content 6.5 ± 1.1 wt% with volatile matter ≤ 0.75 wt%, specific gravity 0.86 and total ash ≤ 0.50 wt% with non-staining stabilizer. Both rubber were masticated with two-roll mill prior of their use. Other compounding ingredients such as sulphur, zinc oxide and stearic acid were purchased from System/Classic Chemical Sdn. Bhd., and tetramethylthiuram disulfide (TMTD) from Aldrich Chemistry; N-cyclohexylbenthiazolyl sulphenimide (CBS) and N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) were supplied by Flexyx America, USA and all are used as received without further purification. The compounding process was performed in accordance to ASTM D-3192. The formulations recipes were summarized as in the Table 1 for all NR/EPDM blend. Both treated and untreated filled NR/EPDM nanocomposites blend are loaded with 1.00 wt.% GNPs while unfilled NR/EPDM blend are also prepared as for comparison purposes. The cure characteristic testing was conducted in accordance to ISO 3417 for maximum cure time t_{c90} . The compounded NR/EPDM nanocomposites blend were vulcanized using a semi EV system and formulation in a hot press on a three piece preheated die placed on 46 cm x 46 cm platen using an electrically heated press maintained at the temperature of 150°C with 150 kgf of the molding pressure at specified molding time taken from the cure characteristic testing.

Table 1: Compounding formulation used in NR/EPDM blend preparation

| NR/EPDM System | EPDM-g-MAH | ZnO | Stearic acid | 6-PPD | CBS | TMTD | Sulphur |
|-----------------|------------|------|--------------|-------|------|------|---------|
| 70 NR / 30 EPDM | 1.30 | 5.00 | 2.00 | 2.00 | 1.00 | 0.30 | 1.50 |

Morphological and Spectroscopy Characterization of GNPs:

Morphological inspection of treated and untreated as-received GNPs used in this study is done by using the transmission electron microscopy (TEM) model Zeiss Libra 200 FE at 100 000x magnifications and field-emission electron microscopy (FESEM) model Hitachi SU8000 at 2000x magnification and 2.0kV accelerating voltage. For spectroscopy evaluation on the covalent treatment, the success of surface treatment was confirmed through Raman and FTIR spectroscopy studies. Raman spectra were obtained using a Horiba JobinYvon model HR800, employing a laser wavelength of 514.53 nm (laser power at sample = 10 mW; microscope objective = 100x; exposition = 3; accumulation = 5 and multi-spectro) with a focal length of 800 mm and drift amount of < 0.015 nm/sec. FTIR analysis were performed using JASCO FT/IR 6100 setup at 0.5 cm^{-1} resolution in the range of $4000 - 400 \text{ cm}^{-1}$ for 50 times scan laser type-II with data interval about 0.120529 cm^{-1} .

Processability Evaluation by Cure Characterization:

The cure characteristics of the blend were studied using Monsanto moving die rheometer MDR 2000 according to ISO 3417 at 160°C. Vulcanizates blend were conditioned for 24 hour in a closed container at control room temperature before testing. In addition to curing characteristics, the MDR 2000 gives digital output of cure properties such as cure time t_{c90} , scorch time, t_{S2} , minimum torque, M_L , and maximum torque, M_H . Cure rate index (CRI) or the speed of curing reaction is calculated using the following relation [1]:

$$CRI = \frac{100}{\text{cure time} - \text{scorch time}}$$

Swelling and Rubber-Filler Interaction Studies:

Swelling tests were performed using cured samples in toluene under dark environment until equilibrium was achieved in accordance with ISO 1817 for 72 hours at 25°C [26]. The samples (dimension: 20 mm length x 20 mm width x 2mm thickness) were dried in an oven at 60°C until a constant weight was obtained. The change in mass is referred as the percentage of swelling and is given as follows:

$$\text{Swelling (\%)} = \frac{(W_2 - W_1)}{W_1} \times 100$$

where W_1 is the initial mass (g) and W_2 is the mass (g) after immersion in toluene. For rubber-filler interaction, the Lorenz and Park equation was applied.

$$\frac{Qf}{Qg} = a e^{-z} + b$$

where subscripts f and g refer to filled and gum vulcanizates, respectively and z is the ratio by weight of the filler to the rubber matrix in the vulcanizates, and a and b are constants. The higher the Q_f/Q_g values, the lower the extent of interaction will be between the filler and the matrix. In this study, the weight of toluene uptake per gram of rubber matrix (Q) as follows:

$$Q = (Ws - Wd) / Wi \times 100(\%)$$

where Ws is the swollen weight, Wd is the dried weight and Wi is the original weight.

Mechanical Tensile Properties and Shore A Hardness:

Tensile tests were carried out according to ASTM D1822 on a testometric tensometer Toyoseiki Strograph-R1. Dumb-bell shaped specimens of ~2 mm thickness were cut from the molded sheet with a Wallace die cutter. The specimens were tested at a crosshead speed of 500 mm/min and the tests were performed at $23 \pm 2^\circ\text{C}$ of at least 7 samples for averaging purposes. The tensile properties like tensile strength (TS), modulus at 100%, 300% and 500% of elongation (M100, M300 and M500) and the percentage of elongation are determined in this study (%E). The following equation is used for %E determination [1]:

$$\%E = \frac{\text{Displacement at failure}}{\text{Effective gauge length}} \times 100$$

The hardness measurements of the NR/EPDM blend samples were done according to ISO 7691-1 by using a manual durometer type Shore A.

Fracture Morphologies Observation via SEM Observation:

Tensile fractured sample from each formulation was adhered on the aluminum stub with carbon tape and later was sputter coated with a thin layer of gold by using the Polaron E-1500 sputter coater. The morphologies of NR/EPDM was then observed at 1000x magnification by using the variable pressure scanning electron microscope model Zeiss Evo VPSEM operated at 15 kV accelerating voltage with secondary electron (SE) mode signal detector.

RESULT AND DISCUSSION

Morphological and Spectroscopy Characterization of GNPs:

Raman inspection for covalent treated and untreated GNPs is reported as in Figure 1a. It is found that there are basically three characteristic peaks presence at $\sim 1370\text{-}1375\text{ cm}^{-1}$, $\sim 1600\text{-}1610\text{ cm}^{-1}$ and $\sim 2710\text{-}2740\text{ cm}^{-1}$ which representing D band, G band and 2D band, respectively. Another peak at $\sim 2460\text{-}2485\text{ cm}^{-1}$ is referred as another second-order 2D peaks that indicates a layering nature of GNPs platelets and uGNPs sample at this peak are more intense than GNPs-ATPS peak. Strong vibration peak at 2081.11 cm^{-1} for covalent treated GNPs indicates a possible strong vibration due to formation of covalent bonds of C=C bond between the GNPs and ATPS. Besides, the ratio of D band and G band intensity (I_D/I_G) for GNPs-ATPS sample is markedly increase than uGNPs sample indicate the formation of some sp^3 carbon by functionalization and wrinkled formation of GNPs after the treatment. Higher G mode of treated GNPs than untreated GNPs confirmed the higher level of disorder for GNPs-ATPS sample which relates to random arrangement of platelets. Both of these situations might open wide possibilities for molecular chain of rubber to intercalate the interlayer space of treated GNPs and improved the mechanical interlocking between the surface of GNPs and the rubber blend for better interfacial interaction.

FTIR spectra for uGNPs and GNPs-ATPS are presented in Figure 1b for comparison. The presence of new characteristic peak and changes in the peak intensities for treated GNPs sample spectra confirmed the success of covalent treatment applies in this work. Basically, the absorption band at below $\sim 1000\text{ cm}^{-1}$ for uGNPs is due to the presence of trace acid group that intercalates between the graphite planes. The disappearance of 821.08 cm^{-1} for GNPs-ATPS sample in comparison to uGNPs tells the possibility of covalent treatment by ATPS is occurred through dehydration mechanisms which hinder the minor functional groups of -C-O. In addition, shifting of C-C stretching of ethyl group at $1060\text{-}1070\text{ cm}^{-1}$ for GNPs-ATPS indicates the asymmetric Si-O-C doublet stretching vibration.

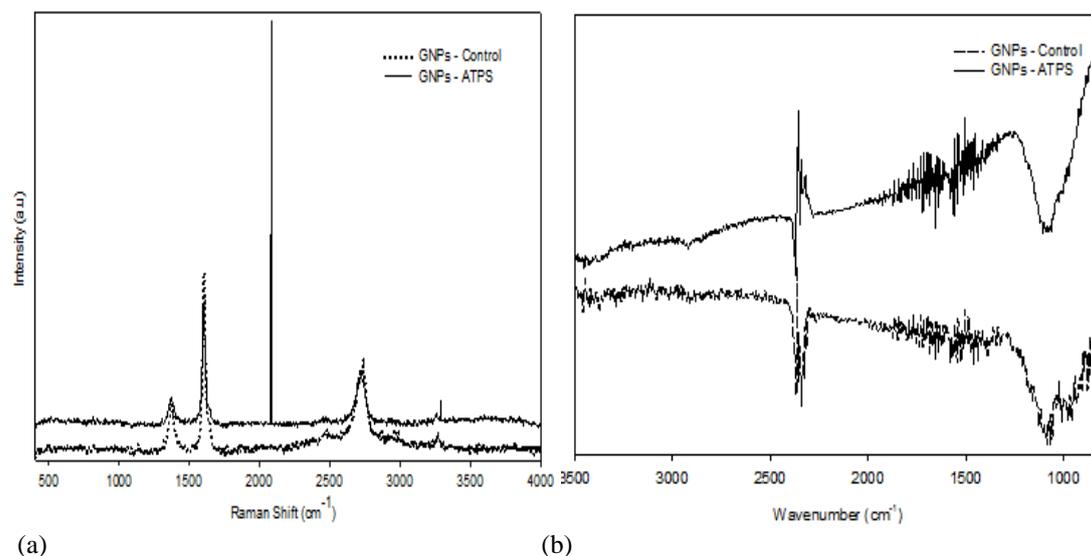


Fig. 1: (a) Raman spectra for untreated and covalent treated GNPs; (b) FTIR spectra for untreated and covalent treated GNPs

FESEM images of as-supplied and covalent treated GNPs are depicted as in the Figure 2a-b. Clear separation and increased interlayer spacing between platelets for covalent treated GNPs-ATPS confirmed the exfoliation nature of treated GNPs after undergone the sonication and shearing treatment. The covalent treatment also caused reduction on platelets size and inconsistency in lateral dimension as compared than uGNPs. Further dimensional analysis applying Zeta-nanosizer for size distribution found that the platelets size of uGNPs and GNPs-ATPS are varied about ~ 1220.67 d.Nm and ~ 448.10 d.Nm, respectively. Reduction in lateral diameter at about four-fold for GNPs-ATPS, significantly reduced their aspect ratio that may affect the reinforcement but may enhance the dispersibility of GNPs. TEM observation at 5000x magnification for both uGNPs and covalent treated GNPs-ATPS sample are depicted as in Figure 2c and Figure 2d, respectively. It is obviously found that the uGNPs micrograph is a bit darker than GNPs-ATPS indicating the reduced stacking and platelets thickness for covalent treated sample which beneficial for good dispersion and platelets exfoliation while incorporation with the rubber blends. The darker spot at uGNPs sample represent closely spaced of layer stacked that provide many possible spot of platelets agglomeration and thick GNPs layers stacking (Figure 2c). For both uGNPs and GNPs-ATPS, the presence of folding edge, crumple and wrinkled nature of GNPs surface indicates flexible nature of GNPs which is good to improve the elasticity behavior of filled composites.

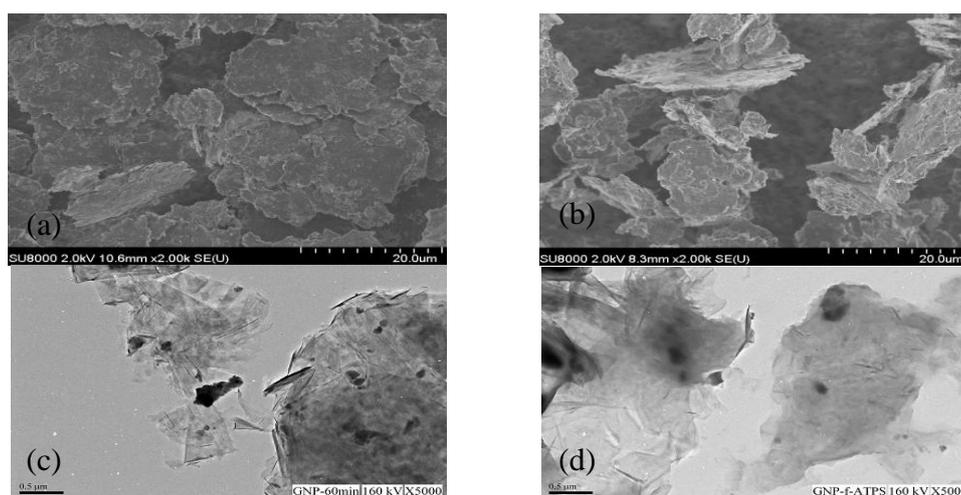


Fig. 2: FESEM and TEM observation for untreated and covalent treated GNPs morphologies; (a) uGNPs; (b) GNPs-ATPS; (c) uGNPs on TEM at 5000x mag. and (d) GNPs-ATPS on TEM at 5000x mag.

Processability and Physical Properties Evaluation by Cure Characterization, Swelling and Rubber-Filler Interaction Studies:

The processability for three blend system of unfilled NR/EPDM and NR/EPDM blend filled ATPS covalent treated and untreated GNPs at 1.00 wt.% filler addition is studied by understanding the cure characteristic data (Table 1). It is found that, with addition of GNPs, it reduced the scorch time (t_{s2}), maximum cure time (T_{c90}) and torques different (M_H-M_L) of covalent treated GNPs filled blend system which significantly lower than untreated GNPs filled blend nanocomposites. However, this reduction pattern is opposed for minimum torque (M_L) and the cure rate index (CRI) attributes. Maximum torque data for covalent treated blend is larger than other system while untreated filled blend system possessed a lower M_H value among others. The decreased in t_{s2} with addition of covalent treated GNPs tells that the ATPS functionalized into GNPs surface tend to promote the fast curing of NR/EPDM blend due to improved interaction between rubber-filler interface. High thermal conductivity nature of GNPs is basically dissipates the heat effectively during the scorch delay period when majority chemistry and accelerator reaction are took place. Bad interface interaction between untreated GNPs with the blend caused delays in the time required for the state of cure to increase to two torque units above the minimum at 160°C of curing temperature.

It is believed that the active silane functional group attached to the surface of GNPs provides an additional site for curing to take place during blend vulcanization. This phenomenon was confirmed by similar reduction pattern for T_{c90} . Addition of covalent treated GNPs seems like able to eliminate the interaction hindrance between the rubber blend and nanofiller due to improved filler solubility in the rubber blend. Reduced lateral dimension size of GNPs and presence of ATPS active site in the GNPs accelerate the cross-linking or polysulfide formation. This finding well agreed with previous works done by other researcher working with different blend system [8,31]. The cure rate index, CRI for covalent treated GNPs-ATPS filled NR/EPDM blend are increased than other blend system indicating that an addition of treated filler enhanced the curing rate due to reduce activation energy for crosslink formation [37]. The functional site covalently attached to the GNPs surface may enhance the cross-linking formation in the blend. For processing torque, increase pattern of M_H and M_L value for treated filled blend as compared than unfilled NR/EPDM blend, confirmed an adequate filler surface wetting and strong filler interaction between the binary phases of rubber molecules in the network containing covalent treated GNPs. This results is further confirmed by the calculated Lorentz and Park equation which found smaller number of Q_f/Q_g ratio for NR/EPDM blend with 1.00 wt.% GNPs-ATPS nanofiller addition (Table 2). Theoretically, the lower the number of calculated Lorentz-Park ratio, the higher the rubber-filler interaction will be. M_H indicates vulcanizates strength of rubber blend compound [22], while M_L is a representative of the uncured stock's elastic modulus that also provides valuable information about a compound processability [26]. Thus, from the obtained results, it can be said that, addition of GNPs-ATPS could enhanced the mechanical strength of the blend produced with little drawback in their processability advantages due to increase processing load caused by smaller size of treated GNPs (Figure 1b). The flow resistance that obstructs the mobility of NR/EPDM macromolecular chain is also due to another additional factor introduced by added GNPs-ATPS that initiate extra crosslinking sites from the silane functionalization on the GNPs surfaces. M_H-M_L is a measure of shear dynamic modulus which indirectly relates to the crosslink density of the nanocomposites blend of NR/EPDM [3,30]. It is also the extent of vulcanization and attainment of characteristic network chains (Konar *et al.*, 2010). Lower torque different of GNPs-ATPS filled blend than untreated filled and unfilled blend explained the less crosslink density for this blend as compared to other blend studied. The swelling data at 72 hours of blend immersion in the toluene is not in line with the torque different findings. The lower the swelling percentages, the higher crosslinking density or curing of the blend will be. It is found that, NR/EPDM blend filled with GNPs-ATPS covalent treated nanofiller, possessed more crosslinking than other and inferiority in torque different results could be explained by the possibility of curing mismatch between the unsaturated NR and highly saturated EPDM that cause in an uneven crosslink density distribution and hence inferior mechanical properties (Nabil *et al.*, 2013a). Lower toluene uptake value (Q) and also lower percentage of swelling for covalent treated GNPs filled NR/EPDM blend, further confirmed on the improvement of crosslinking density which improves resulted physical and mechanical properties of the prepared blend. For this case, the roles of treated GNPs in assisting the curing are more obvious for treated GNPs than untreated one.

Table 2: Cure characteristic data, swelling and rubber-filler interaction data for NR/EPDM blend filled uGNPs, GNPs-ATPS and unfilled blend

| Blend / Characteristics | t_{s2} | T_{c90} | CRI | M_L | M_H | M_H-M_L | Swelling | Q | Q_f/Q_g^E |
|----------------------------|----------|-----------|---------|-------|--------|-----------|----------|-------|-------------|
| Unfilled NR/EPDM | 2.460 | 3.200 | 135.135 | 6.590 | 20.055 | 13.465 | 193.260 | 2.180 | - |
| NR/EPDM-1.00wt.% uGNPs | 2.355 | 3.035 | 147.059 | 6.665 | 19.845 | 13.180 | 208.140 | 2.280 | 1.045 |
| NR/EPDM-1.00wt.% GNPs-ATPS | 1.509 | 2.042 | 187.617 | 8.060 | 21.105 | 13.045 | 194.940 | 2.050 | 0.940 |

Mechanical Tensile Properties and Shore A Hardness:

Improvement in all tensile performance attributes was occurred when either treated or untreated GNPs are added to the NR/EPDM blend at about 1.00 wt.% addition. However, it is interesting to note that the covalent

treatment introduced to the GNPs gives an extra further improvement for its tensile strength and modulus at 100, 300 and 500% elongation as compared to untreated GNPs filled blend and unfilled blend. Tensile strength was increased about 59.81% than unfilled blend when GNPs-ATPS is used and yield the difference about 2.84% improvements as compared to untreated GNPs filled blend. In this case, GNPs surface treatment using covalent method with ATPS are considered successful in improving the reinforcing behavior of platelets when incorporates with NR/EPDM rubber blend. Silane covalent treated GNPs are caused presence of some Si-alkyl groups that ensures low surface tension and good wetting properties. Commonly, GNPs is easily attracted to each other due to their high specific surface area and high surface energy. Covalent treated GNPs-ATPS assist the separation and intercalation between filler surface which may further assist the adsorption of binary NR/EPDM blend in the platelets spacing area that increase surface wetting which at the end improve the tensile performance of produced samples. In addition, interaction between EPDM-g-MAH with oxygen functionalities presence on GNPs may enhance the interfacial adhesion between the NR and EPDM matrix. This provides an added advantage of GNPs for reinforcing the blend. Percentages of elongation (%E) for both GNPs filled system are higher than unfilled rubber blend at 1057.269 % and 999.855% for untreated and treated GNPs filled blend, respectively. Increase in %E for both GNPs filled NR/EPDM blend is due to interesting phenomena of platelets slippage which assist the macromolecular mobility during the stress loading. It is believed that when sample was mechanically loaded, the weak van der Waals bonding between the GNPs platelets will loosen their stack between them and tend to separate the GNPs layers from the matrix if the interfacial bonding between them is weak or no perfect wetting by rubber matrix is available. It is interesting to note that %E for covalent treated filled blend are a bit lesser than untreated filled blend. This gives a strong indication of improved rubber-filler interaction between the covalent treated GNPs with NR/EPDM rubber matrix due to the presence of silane functional group which provide an anchoring nature in the treated nanofiller surface to the matrix for further stiffness improvement that indirectly lowering the %E value. Stiffness representation through M100, M300 and M500 data confirmed the reinforcing capability of covalent treated GNPs when incorporated with the NR/EPDM rubber blend. Lamellar structure of the graphene allows for better wettability and enhanced polymer-matrix interactions between the nanofiller and rubber matrix, thereby leading to better stress transfer and stiffness behavior [33]. This could be further confirmed through the fracture morphological observation as depicted in the Figure 3. The result and explanation on the improvement of tensile properties for covalent treated GNPs filled blend is in agreement and well supported by the rubber-filler interaction findings as available at Table 2. Shore A hardness value draw a similar pattern like %E whereby covalent treated filled blend hardness value is lower than the untreated GNPs filled blend hardness. Using 1.00 wt.% GNPs-ATPS improved the blend hardness at only 4.39% as compared to unfilled blend system. This situation could be explained as similar explanation of %E. In this case, addition of GNPs either untreated or covalent treated is able to improve the mechanical reinforcement, ductility as well as local resistance into failure or deformation.

Table 3: Tensile properties and Shore-A hardness data for NR/EPDM blend filled uGNPs, GNPs-ATPS and unfilled blend

| Blend / Characteristics | TS | %E | M100 | M300 | M500 | Shore A |
|----------------------------|--------|----------|-------|-------|--------|---------|
| Unfilled NR/EPDM | 7.322 | 824.687 | 1.080 | 2.046 | 4.375 | 45.550 |
| NR/EPDM-1.00wt.% uGNPs | 11.378 | 1057.269 | 1.172 | 2.313 | 5.289 | 48.000 |
| NR/EPDM-1.00wt.% GNPs-ATPS | 11.701 | 999.855 | 1.508 | 3.122 | 10.318 | 47.550 |

Fracture Morphologies Observation via SEM Observation:

SEM observation of the fractured surface for three blend systems is depicted as in the Figure 3(a-c). For unfilled blend (Figure 3a), it can be clearly seen that the minor phase of EPDM are well distributed and embedded within the major phase of NR. It is believe that a good anchorage between the matrix phases is promoted by the reaction between the anhydride groups along the EPDM backbone and the double bonds of the NR diene rubber [33]. Good wetting between both phases represent good compatibility and processability between both rubbers that could yield good resulted end properties. Addition of GNPs either untreated or covalent treated GNPs was then changes the morphological appearance of the fractured surface. Distribution of covalent treated GNPs can be clearly seen well attached to the rubber blend matrix (Figure 3c) as homogeneously white entities while rough nature of the fractured surface explained the strong interaction between NR/EPDM rubber blend to the covalent treated GNPs nanofiller inclusion. Strong interaction between EPDM-g-MAH with oxygen functionalities that presence in GNPs surface may enhance the interfacial adhesion between NR and EPDM matrix. Obvious rubber matrix tearing line for treated GNPs filled blend confirmed strong matrix-filler pull-out during stress loading before failure while formation of dimple and voids in the micrographs provides indication of filler debonding or matrix detachment. Presence of rough fracture surface and formation of matrix yielding line as can be seen in Figure 3c confirmed the characteristic of ductile failure mode. However, this can be less spotted in the fractured surface for untreated GNPs filled blend (Figure 3b) as well as the unfilled blend (Figure 3a). The clearer view of clean GNPs surface embedded in the matrix at Figure 3b indicates poor rubber wetting to the filler that reflect less performance in tensile properties for untreated GNPs filled NR/EPDM nanocomposites blend as compared to treated filled blend counterparts. Bad adherence

in the filler-matrix would give rise to the formation of voids in the interphase, which would decrease the mechanical properties of filled rubber [8]. Voids in the untreated filled blend was formed when GNPs platelets are not well wetted with the rubber whereby the multilayer GNPs nanofillers protrude cleanly from the fracture surface during the tensile stress loading. From the micrographs as depicted shown in Figure 3, it could be said that the treatment done to GNPs are significantly play its role in enhancing the interfacial characteristic which inducing many proof of reinforcement mechanism by GNPs within the NR/EPDM rubber blend nanocomposites.

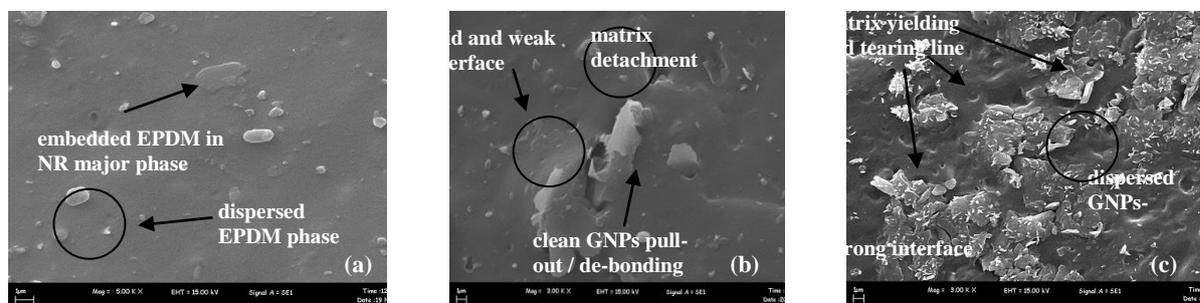


Fig. 3: SEM observation of tensile fractured morphologies for; (a) unfilled NR/EPDM blend at 5000x mag.; (b) NR/EPDM filled 1.00wt.% uGNPs at 3000x mag. and (c) NR/EPDM filled 1.00wt.% GNPs-ATPS at 3000x mag.

Conclusion:

The covalent treatment of GNPs, the cure characteristics, physical, mechanical and fracture morphologies of NR/EPDM blend containing 1.00 wt.% of treated and untreated GNPs has been evaluated in this study. The success of GNPs treatment was confirmed by the spectroscopy observation using Raman and FTIR spectra on the presence of new peak and other characteristic band. The rubber blend was then blended within the confined space of high shearing banbury rotor internal mixer with semi-EV vulcanization and formulation strategy. The effect of covalent treatment on tensile properties was correlated with the nanocomposites fracture morphologies and cure characteristics of the blend. The tensile strength was improved about 59.81% over the unfilled blend system and yields the different about 2.84% of improvement as compared to untreated GNPs filled blend. The M100, M300 and M500 for covalent treated filled blend experienced a significant increased about 28.67%, 37.98% and 95.08%, respectively, over the untreated GNPs filled NR/EPDM blend system. Using 1.00 wt.% GNPs-ATPS also improved the Shore-A hardness at about 4.39% over the unfilled blend system. As for conclusion, from the mechanical tensile properties, the improvement of tensile strength, %E and modulus at various elongation with addition of 1.00 wt.% covalent treated GNPs-ATPS confirmed that the surface activity due to covalent treatment on GNPs are successfully control the resulted properties of NR/EPDM rubber blend. Silane treated GNPs able to perform its function as coupling agent and compatibilizer between filler and both matrix rubber. This was further confirmed by Lorentz and Park calculation which found that the utilization of covalent treated GNPs was significantly improved the rubber filler interaction with the lowest value of Q_f/Q_g ratio at 0.940. Besides, all attributes from the cure characteristic studies found that the treatment done into GNPs is greatly effects the processability of NR/EPDM rubber blend and the noticeable morphological differences captured from the SEM observation tells the role of ATPS silane covalent treated GNPs in influencing the performances and failure characteristic of the rubber blend nanocomposites.

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