CHARACTERIZATION ON THERMAL AND MECHANICAL PROPERTIES OF NON-COVALENT POLYETHYLENEIMINE WRAPPED ON GRAPHENE NANOPLATELETS WITHIN NR/EPDM RUBBER BLEND NANOCOMPOSITES

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ABSTRACT: This study focused on the characterization of Natural Rubber (NR)/Ethylene Propylene Diene Monomer (EPDM) filled Graphene Nanoplatelets (GNPs) nanocomposites. The effects of GNPs non-covalent surface treatment using polyethyleneimine (PEI) and different loading of filler addition (0.25-5.00 wt. %) to cure characteristics, thermo-mechanical and thermal degradation properties of produced NR/EPDM rubber blends nanocomposites were analyzed and inter-correlated with their fracture morphologies. The surface treatment of GNPs was found to enhance the filler-matrices interaction in the NR/EPDM blend nanocomposites compared with unfilled and untreated GNPs filled NR/EPDM systems at similar loadings. The nanocomposites with 3.00 wt. % of PEI-treated GNPs possessed outstanding mechanical properties compared with unfilled NR/EPDM blends and filled nanocomposites without treatment (tensile strength of 27.78 MPa, 19.65 MPa and 23.34 MPa; respectively). The results were supported with thermal and dynamic analyses. Highly homogeneous dispersion of GNPs nanofillers and the presence of strong interfacial interaction between the matrix and reinforcement nanofiller resulted in an excellent thermal-mechanical properties of nanocomposites filled with 3.00 wt. % PEI treated GNPs. Obvious fractured morphological changes due to the noncovalent treatment provided hints on the role of GNPs treatment in improving the NR/EPDM blends mechanical and thermal properties.

KEYWORDS: *Surface modification, rubber-filler interaction, noncovalent, GNPs, thermal properties*

1.0 INTRODUCTION

Graphene is a single-atom-thick sheet of *sp*^{2} bonded carbon atoms packed in a hexagonal honeycomb pattern, with a carbon-carbon distance of 0.142 nm. Meanwhile graphene nanoplatelets or GNPs refer to the short stacks of platelets shaped graphene sheets that are identical to those found in the walls of carbon nanotubes, but in planar form [1, 2]. Graphene is a naturally abundant material that is the thinnest, strongest and stiffest among other nano-structured materials. With estimated Youngs modulus of 1 TPa and ultimate strength of 130 Gpa, graphene was labelled as "the strongest material ever" [3]. Its mechanical strength is 200 times greater than the strength of steel at a sixth of the weight which is comparable to 1-dimensional carbon nanotubes. Breaking strength of graphene is 42 N/m which is much greater than that of steel which is in the range of 250-1200 MPa [4]. Graphene comes with high specific area, electrical, thermal, and chemical stability properties [2, 5]. Large specific surface area of the platelets is up to 2630 m^2/g due to the platelets consist of very fine graphene of 0.34 nm in thickness and ~1 μm in the lateral dimension [4, 5]. Graphene platelets are electrically conductive of 6000 S/cm and thermally conductive of 5000 W/mK at room temperature which is greater than that of diamond and cooper [3].

Graphene can be employed in polymer composites to lower the coefficient of thermal expansion (CTE) and increase ultimate use temperature (T_{ult}) values of most polymers. Dimensional stability and operating temperature range are also increased, making polymers modified with graphene are excellent for dimensionally critical parts in thermally demanding environments [6, 7-8]. Above all, these unique properties of GNPs have qualified them to advance the properties of a wide range of polymeric materials. However, hydrophobic graphene surface may not be compatible with many polymers. Dispersion of graphene nanoplatelets in polymer host materials are challenging due to their strong interlayer cohesive energy and surface inertia. Graphene reaggregation and restacking into graphite through π- π stacking and van der Waals interactions cause the fillers could hardly be found localized selectively in one of the polymer components [9-10].

Modification of graphene via noncovalent surface functionalisation has been attempted for a good dispersibility of GNPs in the composites.

Modifying the surface of GNPs by noncovalent functionalisation is achieved by attachment of reactive surfactant molecules to nanofillers surface by which the reactions between surfactant and matrix functional groups can afford nanofiller/matrix interfaces of high integrity. Noncovalent treatment is critical for solving chemical inertness of nanofillers by developing the surface-bound functional group which can enhance the wettability and surface reactivity of nanofillers. In this study, GNPs surface modification throuh noncovalent treatment is achieved by utilising a polymeric-based surfactant of polyethyleneimine (PEI). PEI effectively interacts with GNPs through both physisorption and electrostatic adsorption on the nanofillers surface in the aqueous solution. The graphene sheets are able to assemble the active amino groups in PEI to further enhance the functionalisation with some active groups, that further extends its application [9].

Generally, rubber blend nanocomposites intend to overcome the drawbacks of rubbers through reinforcing effects of the nanofillers while maintaining the natural advantages of the main rubbers matrix [11]. NR/EPDM blends is a good approach for the preparation of high-performance rubber materials with better resistance towards thermal oxidative aging due to the EPDM that has excellent resistance to heat, oxygen and ozone. High temperature attack is of most concern for NR based products that are subjected to static and dynamic loading in service because dynamic loading such as damping causes the rubber part to develop heat internally,resulting in damage [8, 12-14]. The build of internal heat is basically resulted by the low thermal conductivity of NR (~0.2 W/mK) [8] and therefore incorporation of GNPs into rubber blends is intended to impart high thermal conductivities into the polymeric materials. In this study, NR/EPDM blends filled with untreated and noncovalent treated GNPs at various loadings were tested for their cure characteristic and thermomechanical properties. The correlation between the surface treatment and GNPs loading with the thermal properties and the resulted fracture morphologies was established.

2.0 METHODOLOGY

Surface treatment of GNPs using PEI was performed using a mixture of solvent at ratio 25:75 of water: ethanol for 2 g GNPs and 3 g PEI. Mechanical stirring using WiseStir HT-50DX at 1000 rpm assisted with the ultrasonication effect using JE10Tech UC-02 ultrasonic bath set-up was performed for 5 hours in the temperature of 60°C. The treated GNPs were freeze dried using Labconco freeze dry system 4.5 over a period of 24 hours to obtain dry sample before being ground into fluffy powders using an agate mortar.

NR/EPDM filled GNPs nanocomposites compounding formulation is tabulated in Table 1. The NR, SMR 20 Grade was supplied by RRIM. EPDM used was EPDM Buna®EPT 9650, procured from Lanxess Corp. with ENB content of 6.5±1.1 wt. %; ethylene content = 53±4 wt %; Mooney viscosity (1 + 8) at 150°C = 60±6 UML. Graft copolymer (Maleic Anhydride grafted Ethylene Propylene Copolymer, MAH grafted EPM) was synthesised in UTeM laboratory. Other materials such as sulphur, zinc oxide, and stearic acid were purchased from System/Classic Chemicals; tetramethyl thiuram disulfide (Perkacit-TMTD) and 2,20-dithiobis(benzothiazole) (Perkacit-MBTS) were received from Perkacit (United States); *N*-(1,3-dimethylbutyl)- *N′*-phenyl-*p*-phenylenediamine (6PPD) was supplied by Flexsys America (United States). GNPs KNG-150 was obtained from Xiamen Graphene Technology Co. Ltd., China. The GNPs are in gray powder form with a bulk density of ~0.3 g/cm^3; true density of ~2.25g/cm^3; specific surface area of 40-60 m^2/g and carbon content of > 99.5%.

Table 1: Typical formulation

Chemicals	Loading [phr]
NR	70
EPDM	30
MAH-g-EPM	10
Zinc Oxide	5.0
Stearic Acid	2.0
6PPD	2.0
Sulphur	1.5
MBTS	1.0
TMTD	0.3

NR/EPDM filled GNPs nanocomposites with different loadings of GNPs were prepared according to ASTM D 3192 using a Rheomix OS, Haake internal mixer operating at temperature of 110 °C, rotor speed of 40 *rpm* and mixing time of 5 *mins*. The treated and untreated GNPs were added to the blend compounds at a percentage of 0.00, 0.25, 0.50, 1.00, 3.00, 5.00 *wt.* % according to 50 grams of overall blend.

The unvulcanised compounds were tested at 160°C for cure characteristic according to ASTM D 2084 using an oscillating rotorless rheometer U-CAN Dynatex UR2010 (U-Can Incorporation, Taiwan). The compound were then compression moulded at 160 °C and pressure of 110 kg/force at the respective cure times, t_{90} to produce 2 mm thick sheet of nanocomposites for tensile testing [7]. The tensile strength (TS), were measured using TOYOSEIKI Universal Test Machine (UTM) machine, with a load cell of 1 kN and crosshead speed of 500 mm/min.

Dynamic properties testing using dynamic mechanical analysis (DMA) was performed using a Perkin Elmer DMA-7e in the temperature scan mode with a parallel plate. The measurement was carried out at a heating rate of 10°C min^{-1} over a temperature range of -100°C to 150°C on a 2 mm thick sample. Heat degradation study by thermogravimetric analysis (TGA) was carried out in a Perkin Elmer Pyrist 6 TGA analyser. The samples were scanned from 25°C to 600°C at a heating rate of 20°C min^{-1} in nitrogen atmosphere. Morphological inspection of the fracture surface was done by field emission electron microscopy (FESEM) model Hitachi SU8000 at magnification of 20 K and accelerating voltage of 2.0 kV.

3. RESULTS AND DISCUSSION

Cure characteristics studies provide information on scorch time (t_{s2}), maximum molding time (t_{c90}) and maximum torque (*MH*). The processability of NR/EPDM filled GNPs nanocomposites is summarized in Table 2. The t_{s2} is the time required for the cure state to increase to two torque units above the minimum at a given cure temperature, and often correlates well with the Mooney scorch time [15]. For t_{s2}, the scorch safety of NR/EPDM blends filled with pure GNPs and PEI treated GNPs experienced a stable decreasing pattern with an increase in GNPs loadings. The NR/EPDM blends with PEI treated GNPs experienced a shorter scorch time compared than NR/EPDM blends filled with pure GNPs. It is understood that during the scorch delay period, the majority of the accelerator chemistry reaction took place [17]. At this point, it is believed that the addition of PEI treated GNPs encouraged fast curing to NR/EPDM blends due to high thermal conductivity properties of GNPs. In addition, the polymeric layer of PEI adsorbed on the GNPs surface made better rubber-filler interactions. Therefore, the lower scorch time following the addition of PEI treated GNPs resulted by active surface chemistry of PEI treated GNPs as compared to NR/EPDM blend filled with pure GNPs.

Table 2: Cure characteristic studies for NR/EPDM rubber blends filled with various loading of untreated GNPs and PEI treated GNPs (A: NR/EPDM filled untreated GNPs nanocomposites; B: NR/EPDM filled non-covalent PEI treated GNPs nanocomposites)

Result	System	GNPs loading (wt. %)					
		0.00	0.25	0.50	1.00	3.00	5.00
t_{s2} (min.sec)	A	2.37	2.06	2.06	2.01	1.56	1.54
	B	2.37	1.53	1.40	1.33	1.10	0.35
t_{c90} (min.sec)	A	3.32	2.46	2.45	2.38	2.31	2.25
	B	3.32	2.32	2.18	2.06	1.42	1.04

t_{c90} is the time required to reach 90% of complete cure, and this is normally the state of cure at which most physical properties reach their optimum [7]. From the study, it was found that the t_{c90} decreased with the increased of GNPs loading for both NR/EPDM blends, either filled with pure GNPs or PEI treated GNPs. However, the NR/EPDM blends filled with PEI treated GNPs possessed lower t_{c90} values in respect to all loading amounts compared to blends filled with untreated GNPs. This indicated that modifications to the GNPs had eliminated the barrier to interactions between the rubber blends and nanofillers, due to improved solubility of PEI treated GNPs. The PEI treated GNPs experienced a reduction in their lateral dimension size together with additional surface chemistry on GNPs by PEI. Both situations have assisted crosslink formation during the vulcanisation by promoting the accelerator systems to interact to each other for polysulfide formation [15]. After all, adding the PEI treated GNPs in NR/EPDM blends tends to lessen t_{c90} and t_{s2} or accelerate the vulcanisation process, but still efficiently cures the blends [16-19].

The tensile strength (TS) values are represented in Figure 1. The plots clearly showed that TS increased with an increase in both untreated GNPs and PEI treated GNPs loading. The nanocomposites filled with PEI treated GNPs exhibited higher tensile properties compared to the unfilled NR/EPDM and NR/EPDM filled with pure GNPs. The TS are drastically increased to 41% when up to 3.00 wt. % of PEI treated GNPs was added. However, a reduction in TS was encountered for composites filled with the highest content of pure GNPs. This was due to agglomeration and aggregation of platelets that resulted in premature failure, as meticulously observed in Figure 7. Morever, NR/EPDM filled with pure GNPs showed similar optimal GNPs loading of 3.00 wt. % with TS improvement up to 19% compared than unfilled NR/EPDM blends. Surface treatment of GNPs using PEI succeeded in improving the mechanical performance of NR/EPDM blends. The polymeric layer of PEI adsorbed on the GNPs surface created retention effects among GNPs and enhanced the separation between them. Polar interactions between GNPs and PEI sheets and polar polymer matrices were introduced by oxygen-containing groups in the platelets. On the other hand, limited functional groups on GNPs surfaces caused selective distribution of GNPs into high-polarity phases of NR instead of EPDM phase at higher loading of GNPs. This created an uneven tensile loading and finally caused a reduction in TS at 5.00 wt. % of pure or untreated GNPs loading in NR/EPDM matrix.

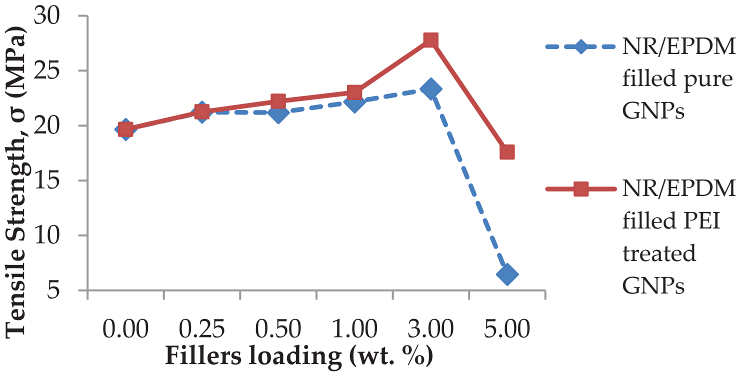

Figure 1: The effect of GNPs loading on the tensile strength of NR/EPDM blends filled with pure GNPs and PEI treated GNPs (A: NR/EPDM filled pure GNPs nanocomposites; B: NR/EPDM filled PEI treated GNPs nanocomposites)

DMA was done to determine the transition behaviour and compatibility of the NR/EPDM filled GNPs nanocomposites. The storage modulus (E'), loss modulus (E'') and *tan δ* factor of the unfilled NR/EPDM blends and the selected loading of NR/EPDM filled with pure GNPs and PEI treated GNPs are plotted in Figure 2, 3 and 4, respectively. Figure 2 shows the storage modulus-temperature profile of the unfilled NR/EPDM blends, NR/EPDM filled 3.00 wt. % of pure GNPs and NR/EPDM filled 3.00 wt. % of PEI treated GNPs. Storage modulus is a measure of the maximum energy stored in the material during one cycle of oscillation [20]. From Figure 2, NR/EPDM filled with 3.00 wt. % PEI treated GNPs loading demonstrated higher storage modulus value compared to the other blend systems. This revealed a larger surface area of intercalated and exfoliated surface-treated GNPs which had resulted in the formation of strong rubber-filler interactions that make the nanocomposites able to store more energy [20]. Herein, PEI treated GNPs had stiffened the polymer matrix, which was due to the high resistance of the treated nanofillers against the deformation.

Figure 3 shows the loss modulus-temperature profile of the unfilled NR/EPDM blends, NR/EPDM filled with 3.00 wt. % of pure GNPs and NR/EPDM filled with 3.00 wt. % PEI treated GNPs in relation to energy dissipation to friction as heat and internal motions reflecting viscous behaviour. From the profile, it was shown that there was remarkably more heat dissipation for NR/EPDM filled with 3.00 wt. % PEI treated GNPs compared to other samples, as shown by the increase in the loss modulus. The loss modulus peaks of unfilled NR/EPDM blends and NR/EPDM filled with 3.00 wt. % pure GNPs became broad due to the hindrance of the molecular motion and the reduction in energy dissipation.

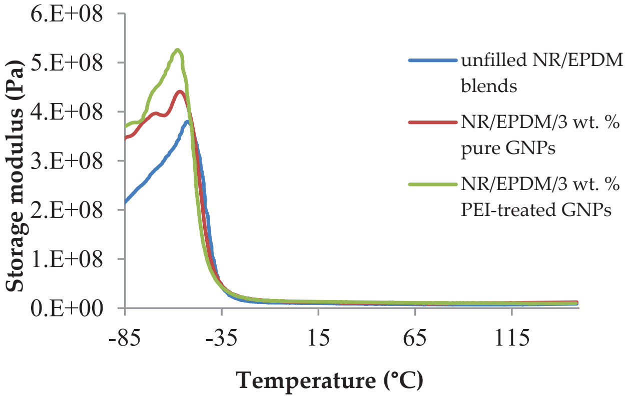

Figure 2: Storage modulus of unfilled NR/EPDM blends and NR/EPDM filled GNPs nanocomposites

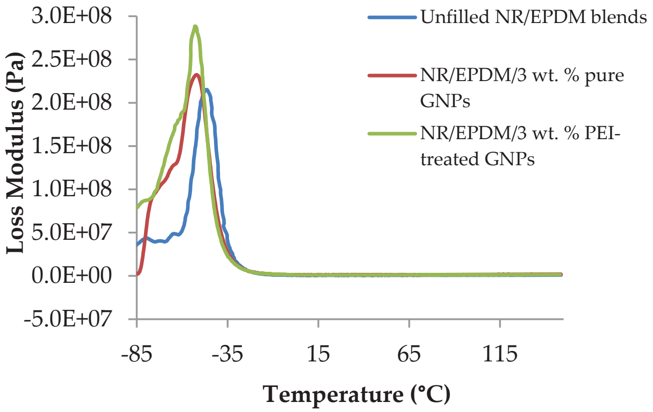

Figure 3: Loss modulus of unfilled NR/EPDM blends and NR/EPDM filled GNPs nanocomposites

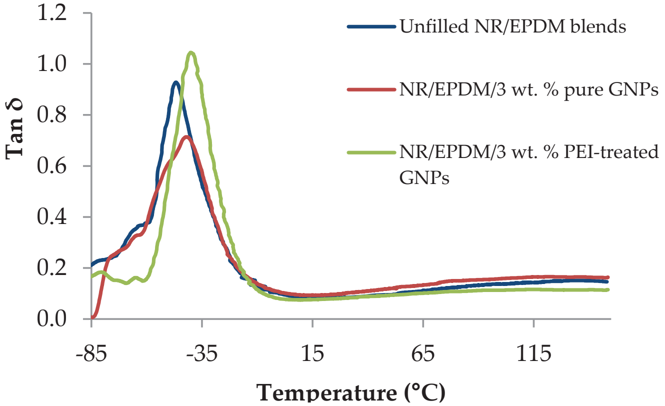

Figure 4: Tan δ of unfilled NR/EPDM blends and NR/EPDM filled GNPs nanocomposites

The *Tan δ* is the ability of materials to convert the mechanical energy to heat energy when subjected to an external load. The *tan δ* plot clearly showed the change of the nanocomposites, Tg. The glass transition temperature, *tan δ* plot of NR/EPDM filled with 3.00 wt. % PEI treated GNPs as shown in Figure 4 indicates a shift of Tg to higher values by as much as 10° (-35°C) in comparison with unfilled NR/EPDM blends (-45°C) and NR/EPDM filled with 3.00 wt. % of pure GNPs (-40°C). The Tg represents a major transition for many polymers, as physical properties change drastically when the material goes from a hard glassy to a rubbery state. It defines one end of the temperature range over which the polymer can be used, often called the operating range of the polymer. Since the Tg values are an indication of segmental mobility of polymer in presence of fillers, the addition of GNPs as well as treated GNPs were found to restrict the segmental mobility effectively. The segmental mobility of the polymer matrix was influenced by the interactions of the intercalated/exfoliated polymer chains with the nanofillers thereby enhanced Tg of the polymer. In addition, a single Tg obtained for all samples of NR/EPDM filled GNPs nanocomposites indicated a good compatibility between NR, EPDM and GNPs.

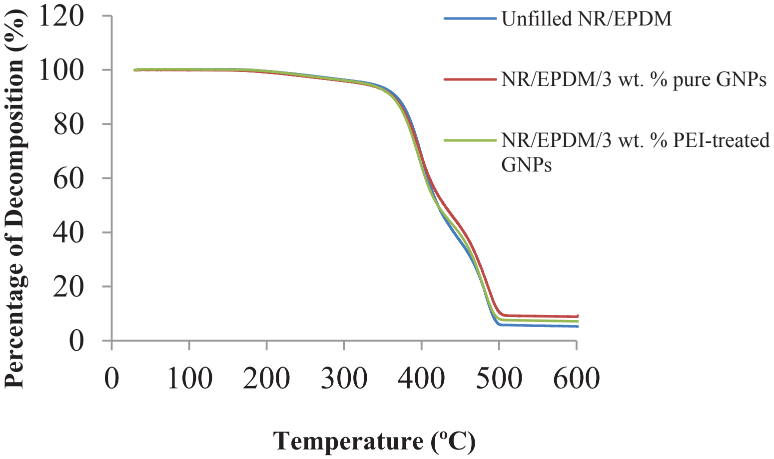

Figure 5: TGA curves for unfilled NR/EPDM blends and NR/EPDM filled GNPs nanocomposites

Figures 5 and 6 represent the TGA and DTG plot of unfilled NR/EPDM blends, NR/EPDM filled pure GNPs, and NR/EPDM filled PEI treated GNPs nanocomposites. Blends with the optimum GNPs loading (3.00 wt. %) were analysed in order to evaluate the contribution of GNPs surface treatment towards the degradation behavior and thermal stability of prepared nanocomposites. From the TGA and Differential Thermal Gravimetric, DTG thermal degradation, it was found that the blend system with 3.00 wt. % of pure GNPs was more thermally stable compared with the blends filled with 3.00 wt. % PEI treated GNPs and the unfilled NR/EPDM blend system, with the percent residue left based on the weight loss curves at 500°C were about 10.65, 8.07, and 6.05 % for each respective blend (Figure 5). The observed weight loss was attributed by a random scission of the main chain of rubber phases with probably the evolution of carbon and oxygen groups during the thermal heating [20].

The DTG curve represented a similar manner for all those blend systems with a distinct shift of decomposition percentage and DTG peaks, indicating the significant contribution of GNPs. Nanocomposites which shifted the peak temperature, *Tpeak* to higher temperature indicated that the polymer matrix near the nanofillers might degrade more slowly [20]. Increased thermal stability of nanocomposites with pure GNPs loading showed the ability of nanofillers in restricting the chain mobility of rubber matrix near the GNPs surface. During heating process, the nanoparticles had formed a jammed network of GNPs layers which retarded transport of decomposition products. The finding is in agreement with the previous experimental study by Kim et al. [3]. The unfilled NR/EPDM blends represented earlier onset decomposition temperature (*Tonset*) compared with filled NR/EPDM blends. This proved the theory of superior thermal properties of GNPs which undoubtedly provided thermal stability benefit to the blends containing them. Meanwhile, the blends filled with PEI treated GNPs experienced lower temperature of degradation onset and lower temperature of maximum weight loss (lower *Tonset* and lower *Tpeak*) which indicated poorer thermal stability, compared with blends with pure GNPs.

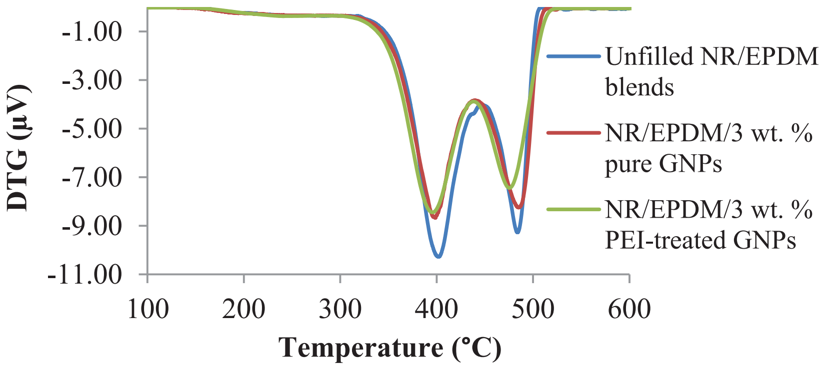

Figure 6: DTG curves for unfilled NR/EPDM blends and NR/EPDM filled GNPs nanocomposite

The presence of adsorbed polymeric layers on GNPs surfaces was responsible in providing a further degradation profile for PEI treated GNPs. This involved the removal of water molecules due to increased hydrophilicity of the nanofiller, the decomposition of oxygen-containing groups due to excess OH and O from the adsorbed PEI, removal of ethylene and amino groups, and lastly the degradation of GNPs [9]. All of these situations caused lesser thermal stability for the blend with 3.00 wt. % PEI treated GNPs compared with blend filled with pure GNPs at similar loading. Herein, pure GNPs retained the excellent thermal properties of graphene and increased the resistance of NR/EPDM nanocomposites to heat degradation.

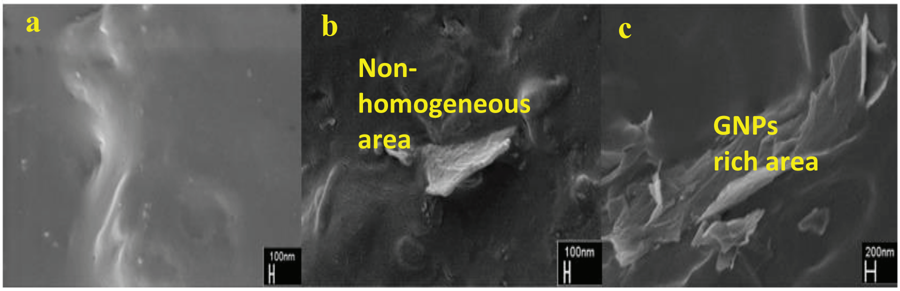

Figure 7: Fractured surface morphology of (a) unfilled NR/EPDM blends, (b) NR/EPDM blends filled with 3.00 wt. % PEI treated GNPs, and (c) NR/EPDM blends filled with 5.00 wt. % PEI treated GNPs

Tensile fractured morphologies of NR/EPDM filled with PEI treated GNPs nanocomposites were observed to support the observations in physical and tensile properties, as compared with unfilled NR/EPDM blends and NR/EPDM filled with pure GNPs nanocomposites. There were strong relationships between the resulting properties of the produced nanocomposites with the morphological characteristics of the fractured sample's surfaces. The unfilled blend (Figure 7a) showed a homogeneous distribution of the EPDM dispersed phase embedded within the NR continuous phase. This unfilled blend exhibited smooth surface without apparent yielding mechanism from reinforcing effects during matrix deformation. NR/EPDM Blends filled with 3.0 wt. % PEI treated GNPs represented rougher fractured surface resulted in the presence of GNPs within the rubber matrix (Figure 7b). Single layer of PEI treated GNPs was thickly coated with adsorbed elastomeric blends, indicating good dispersion of the GNPs nanosheet fillers and strong interactions between the treated GNPs with rubber blends. The strong interactions were responsible for improving the tensile performance of the resultant NR/EPDM nanocomposites. After all, surface treatment of GNPs had consistently dispersed the nanoplatelets within the rubber matrices with improved interface conditions induced by PEI's hydrogen bonding [21], giving sufficient mechanical strength to resist the applied forces during fracture stress. Meanwhile, NR/EPDM blends filled with 5 wt. % of PEI-treated GNPs showed stacked structure of GNPs (Figure 7c). This can be explained by the agglomeration of nanofillers in the matrix when the loading was too high, and therefore, initiating premature cracks in the composites under stress.

4.0 CONCLUSION

From the observation, it was found that the incorporation of PEI-treated GNPs in NR/EPDM blends has significantly reduced the T_{s2} and T_{90} of NR/EPDM blends filled GNPs nanocomposites compared with unfilled blend system and blend system with pure GNPs. The FESEM observations have confirmed the enhancement in the tensile properties which are highly attributed to the highly homogenous dispersion of PEI treated GNPs. The enhancement in the observed properties clearly shows that the properties of resultant blend nanocomposites are controlled by the GNPs filler loading and the applied noncovalent treatment, which has improved the overall interactions between the incompatible NR and EPDM phases. Besides, *Tpeak* from TGA analysis is found to decrease in blends system with 3.00 wt. % PEI treated GNPs compared with unfilled

NR/EPDM blends and blends system with 3 wt. % of pure GNPs. Presence of adsorbed PEI layers on GNPs surfaces has provided a further degradation profile which results in poor thermal stability of the nanocomposites. Moreover, DMA shows that the addition of 3 wt. % PEI-treated GNPs and presence of interfacial interaction have improved the compatibility of the blends due to single *Tg* peak and shifted *Tg* value to higher temperature. A highly homogeneous dispersion of GNPs and the presence of interfacial interaction between the matrix and reinforcement materials result in excellent thermomechanical properties of NR/EPDM filled GNPs nanocomposites.

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