PROPERTIES OF GRAPHENE NANO-FILLER REINFORCED EPOXIDIZED NATURAL RUBBER COMPOSITES

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ABSTRACT

Reinforcement of filled rubber is governed by the rubber-to-filler interactions at nano-scale. One of the potential nano-reinforcing fillers is graphene. Dispersing nano-filler into rubber matrix still remains a challenge despite many methods reported. This paper presents an investigation on the graphene nano-fillers reinforcement in natural rubber and epoxidized natural rubber. The effect of graphene dispersion on the filler-to-rubber and filler-to-filler interactions in carbon black- and silica-filled composite system is evaluated. The rheological, Payne effect and dynamic properties of graphene nano-filler natural rubber composite are presented. The presence of graphene reduces the Payne effect of epoxidized natural rubber-silica composite resulting from better dispersion of silica fillers. In addition, the physically bound rubber of epoxidized natural rubber-silica is increased with the addition of graphene indicating better rubber-to-filler interactions. The effect of graphene is more pronounced in modified natural rubber and silica system due to higher interaction of graphene with silica and epoxidized natural rubber.
Keywords: graphene; nan-filler; silica; natural rubber

INTRODUCTION

The field of nanotechnology has blossomed over the recent years, and the importance for nanomaterials has increased as miniaturization becomes more important in areas such as computing, sensors and biomedical. Rubber products are usually filled with reinforcing fillers to achieve useful properties for a wide range of applications [1]. Nano-fillers such as carbon nanotube and graphene have attracted a lot of attention because of its unique electrical properties, high strength and light weight [2-3]. Graphene is a two-dimensional monolayer of carbon atoms, which is the basic building block for graphitic materials such as nanotube, graphite and fullerene [3-4]. Morphology of graphene from SEM image is shown in Fig. 1. Combination of two types of nano-fillers or of nano-fillers with conventional fillers, such as carbon black and silica [5-6] is defined as hybrid reinforcement in rubber. More interestingly, the 'hybrid' fillers have a synergistic reinforcing effect on the rubber properties and at the same time retaining the benefits of the individual fillers [7].

Modification of Natural Rubber (NR) is used to alter the properties of NR so it can compete outside its conventional areas of applications [8]. The chemical modification of NR via epoxidation of natural rubber latex yields a specialty rubber called 'Epoxidized Natural Rubber' (ENR) [8-10]. Epoxidation increases the polarity of natural rubber [10]. The presence of polar epoxide groups in ENR results in the rubber compatible with highly polar fillers like silica. The strong interaction between ENR and silica results in unique properties [10-12]. Silica-filled ENR-25 composite provides low

rolling resistance together with high wet grip and offers the best balance required in green tyre application [13-14].
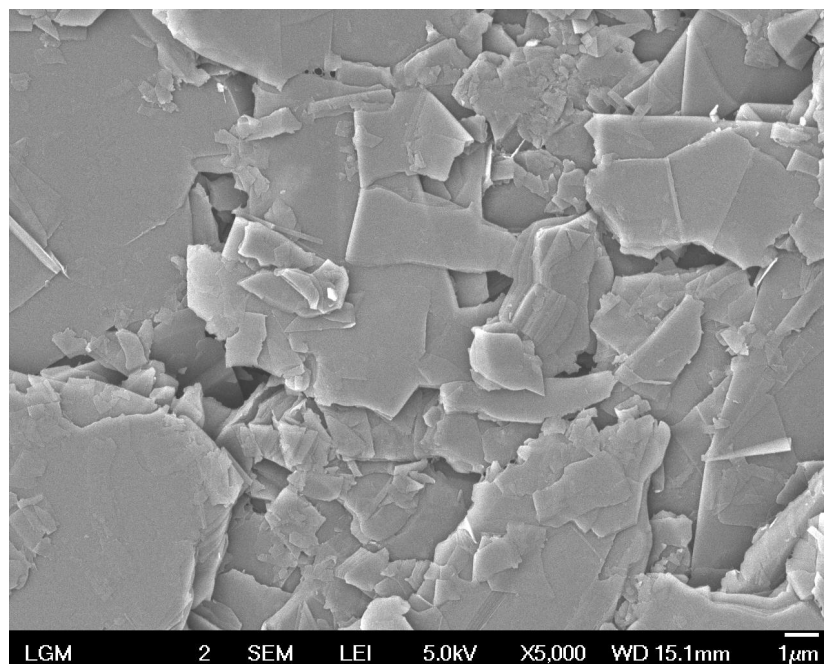

Fig. 1 Morphology of graphene evaluated in this study from SEM image

The properties of graphene composites largely reliant on the preparation process where graphene dispersion is needed [4,15] as well as the compatibility and properties of the polymer matrix used [16]. Several methods have been reported such as solution blending, latex mixing and melt mixing with the aim to increase the dispersion of graphene in rubber, however, there are still advantages and disadvantages [16]. In this study, graphene oxide is used in combination of carbon black and nano-silica. The effect of graphene as hybrid filler in unmodified and modified natural rubber composites is evaluated. The hydrophilic functionality on graphene oxide is expected to improve its dispersion in modified natural rubber and in the presence of silica fillers. The bound rubber content, Payne effect and dynamic properties as well as filler dispersion in natural rubber composites with silica and carbon black are compared with and without graphene.

EXPERIMENTAL

Materials

The natural rubber composites were prepared using formulation shown in Table 1 expressed as parts per hundred of rubber (phr). The rubbers used for this study are Natural Rubber (SMR 20) and Epoxidized Natural Rubber (Ekoprena-25) with 25% epoxidation produced by Felda Rubber Industries Sdn Bhd. The nano-fillers are graphene UG Pro608, carbon black N234 obtained from Cabot and highly dispersible silica, Zeosil 1165MP with CTAB surface area of 164 m^2/g obtained from Rhodia Solvay. Silane coupling agent, bis(triethoxysilylpropyl) tetrasulphide (TESPT) from Evonik was used for silica composites. All ingredients were used as received.

Methods

The composites were prepared in an internal mixer Farrel K1. The first step of mixing was done with fill factor of 0.7 using the mixing procedure as shown in Table 2. After dumping, the batches were sheeted out on a two-roll mill. The re-milling stage of mixing was done on silica composites only in the internal mixer. The curatives were mixed in the finalizing stage of mixing on two-roll mill.

Table 1 Formulation of the composites* (in phr**)

Ingredient	1 NR-CB	2 NR-CB-Grap	3 NR-Sil	4 NR-Sil-Grap	5 ENR-CB	6 ENR-CB-Grap	7 ENR-Sil	8 ENR-Sil-Grap
NR	100	100	100	100	-	-	-	-
ENR-25	-	-	-	-	100	100	100	100
Carbon Black	60	60	-	-	60	60	-	-
Silica	-	-	55	55	-	-	55	55
TESPT	-	-	5	5	-	-	2.5	2.5
Graphene	-	3	-	3	-	3	-	3

*Mixes also contain zinc oxide 3, stearic acid 3, calcium stearate 2, Antioxidant 2 , TDAE oil 8, wax 1, sulphur 1.5, TBBS 1.5 and DPG 2.

**phr = part per hundred rubber

Table 2 Mixing procedure

Time (minute)	Step
0	Add rubber
1	Add ½ filler, ½ silane[#]
2	Add ½ filler, ½ silane[#], oil
3	sweep
4	Add powder
5	dump

[#]Only for silica composites

Testing

The cure characteristics at 150ºC were measured using a MDR2000 from Alpha Technologies, under the conditions of 0.5° arc over 30 minutes at temperature of 150°C. Mooney viscosity and scorch were tested using Alpha Technologies MV2000 viscometer at 100 and 120°C respectively.

The Payne effect was measured in a Rubber Process Analyzer (RPA 2000, Alpha Technologies) by strain sweep at 100ºC and 0.5 Hz. The Payne effect was calculated as the difference between the storage modulus, G' at 0.56% and G' at 100.04% strain. Before the Payne effect measurement, the sample was vulcanized in the RPA 2000 at 150ºC for 10 minutes and subsequently cooled to 100ºC.

The bound rubber content (BRC) measurements were performed on uncured samples by extracting the unbound rubber with toluene at room temperature for seven days in both normal and ammonia environment. The ammonia treatment of BRC was done to obtain the chemically bound rubber as ammonia cleaves the physical linkages between rubber and silica [17]. The amount of BRC (%) was calculated by:

$$BRC(\%) = \frac{w_{dry} - w_{insol}}{w_o \times \dfrac{w_{filler,phr}}{w_{total,phr}}} x100\% \qquad (1)$$

where w_o is the initial weight of the sample, w_{dry} is the dry weight of the extracted sample, w_{insol} is the weight of insoluble (mainly filler) in the sample, $w_{filler,phr}$ is the total filler weight in phr and $w_{total, phr}$ is the total composite weight in phr. The total BRC is referred to BRC obtained from normal atmosphere while chemically BRC is the data obtained from ammonia treated BRC measurement.

Composites were prepared by curing the composites for their respective t_{95} (time to reach 95% of torque difference in the curemeter) at 150ºC using an electrical press at 100 bar. Tensile properties of the composites were measured according to ISO-37. The hardness of the cured samples was determined according to DIN-53505. The dynamic properties of composites: storage modulus, loss modulus and glass transition temperature were measured using a Mettler Toledo Dynamic Mechanical Analyzer (DMA1 Start system). The samples were cut from the vulcanized sheets of 2mm thickness. A temperature sweep measurement from -100 to +100°C was performed in tension mode at a frequency of 10Hz and dynamic strain of 0.1%.

RESULTS AND DISCUSSION

Filler-filler interaction is commonly measured by the so-called Payne effect: the drop in storage modulus in a dynamic mechanical test when the strain (deformation) is increased from low (0.56%) to a high value (100%) at constant frequency and temperature [18]. The storage modulus of filled rubber drastically decreases as strain increases as the result of breakage of physical bonds between filler particles, for example van der Waals, hydrogen bonds and London forces [19-20].

Filler-filler interactions as observed from Payne effect for the carbon black and silica composites are illustrated in Fig. 2. Silica nanocomposites show lower Payne effect than carbon black nanocomposites due to the reduced filler-filler interaction in the silica-silane system. The Payne effect for carbon black composite shows no changes with or without addition of graphene. The dispersion of graphene in carbon black nanocomposites also poor as observed in Fig. 3 where the presence of graphene can be easily detected. However, for silica composite the addition of graphene shows reduction in the Payne effect for ENR-silica system but not in the NR-silica. From the dispersion images for silica composites in Fig. 3, no sign of graphene is observed. This is due to better compatibility of graphene in ENR matrix because of its hydrophilic nature [15]. In addition, the fillers are better dispersed for ENR-silica-graphene composite compared to ENR-silica. It indicates the feasibility of graphene to improve the dispersion of fillers in ENR-silica-graphene composite by reducing the silica-silica interactions as reported previously [21].
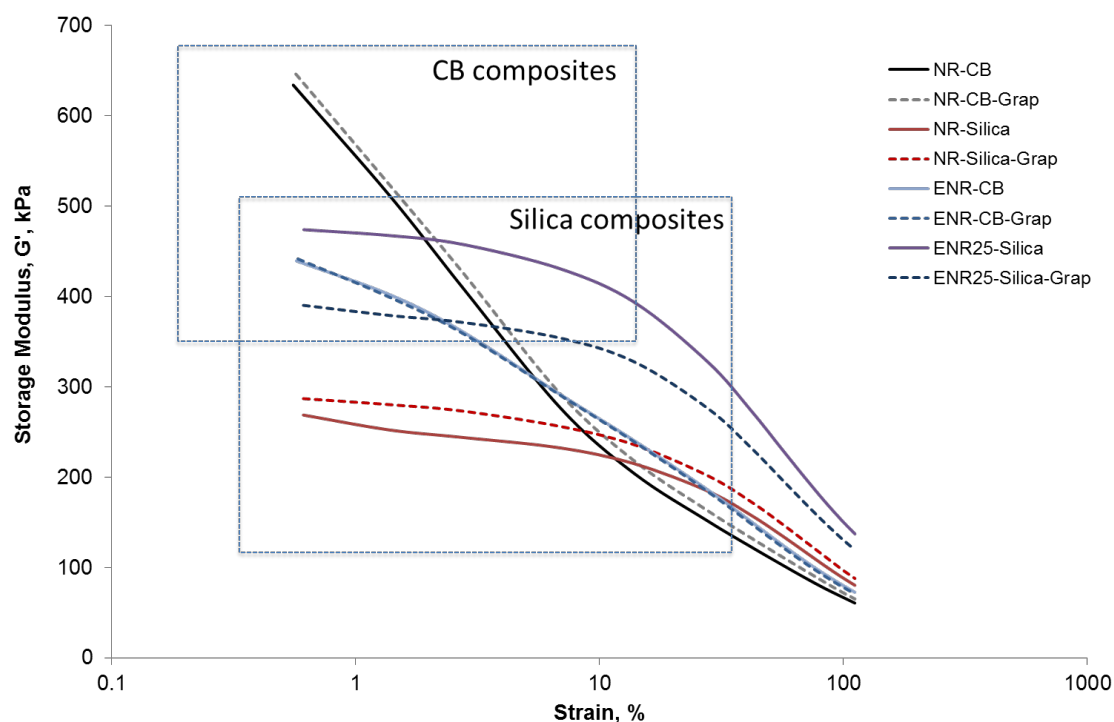
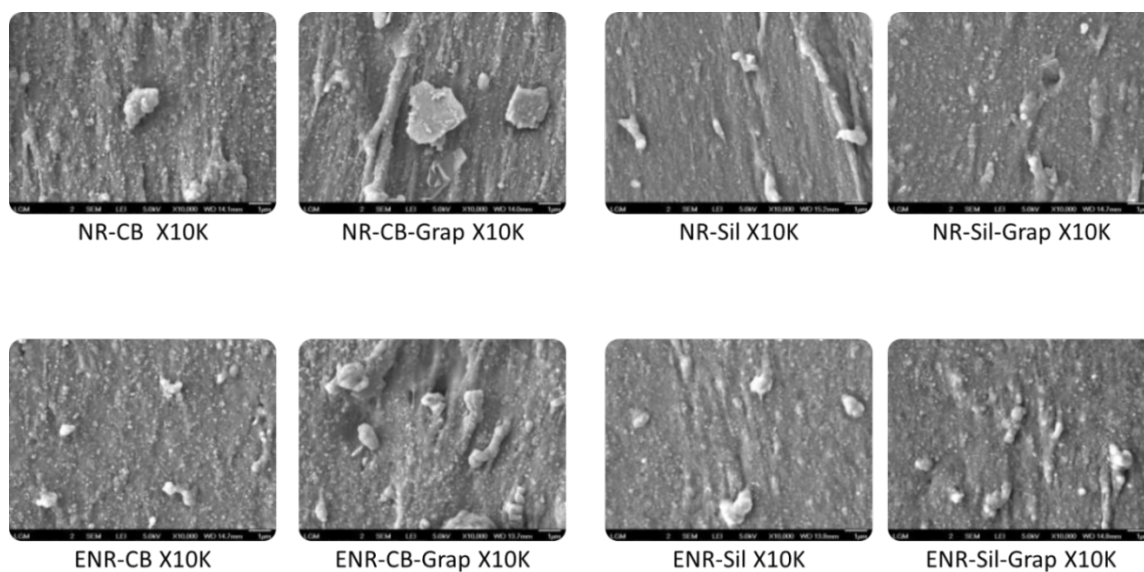**Fig. 2** Payne effect of nanocomposites with and without graphene

Fig. 3 Dispersion of nanocomposites with and without graphene from FESEM images

Rubber-to-filler interactions can be evaluated from the bound rubber content. Fig. 4 shows the bound rubber content of the nanocomposites with and without graphene. Ammonia treatment on the bound rubber of the composite separates the physically or loosely bound rubber and only chemically or tightly bound rubber was obtained [17]. It is observed that chemically bound rubber is higher than physically bound rubber for all composites. This is in agreement with previous work [22] as the silica composites system is using silane as coupling agent. As for carbon black composites, no difference is observed for normal and ammonia treatment of bound rubber [17] due to lack of hydrogen bonding and the value obtained is comparable with

previous work [22]. It is expected that bound rubber content for silica nanocomposite is higher than carbon black nanocomposite as reported earlier [22]. The results show that no effect of graphene to the carbon black composites. This can be related to similar Payne effect observed for black composites. However, for silica composites, there is an increase in the physical bound rubber for both NR and ENR composite with graphene. The higher physical bound rubber in the silica composites derived from interaction of graphene with ENR matrix and graphene with silica. This can be related to lower Payne effect for ENR-silica-graphene which reduces the filler-to-filer interactions and results in improvement in filler-to-rubber interactions. However, in the case of ENR-silica-graphene, the chemically bound rubber is reduced, but for NR-silica-graphene, the chemically bound rubber increases as compared to those without graphene. This can be explained by the competing interaction between graphene and silica as well as silane and silica in addition to the bonding created between silica-silane and NR or ENR matrix [23]. Many interactions and bonding occur simultaneously in silica-filled NR and silica-filled ENR [24]. Strong bonding between silica and ENR has been verified by Kaewsakul et al. using unmodified squalene and epoxidized squalene as a model for NR and ENR respectively in the presence and absence of TESPT silane coupling agent [25].
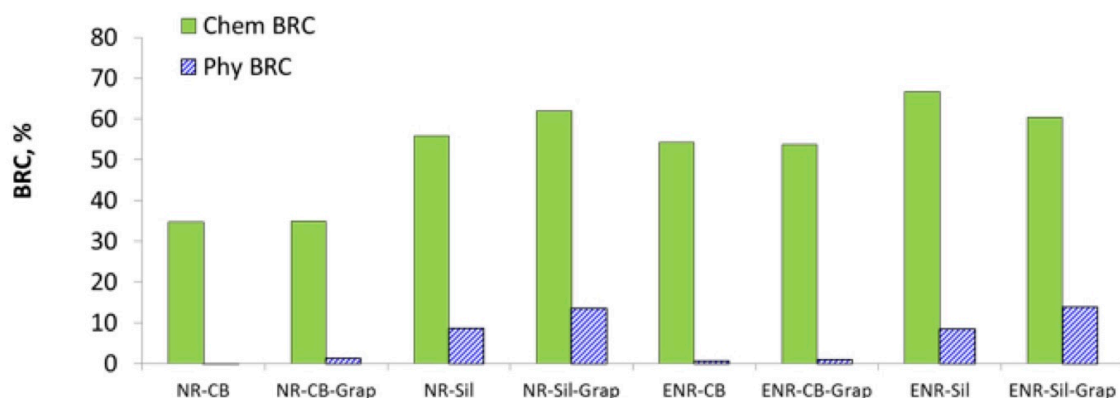

Fig. 4 Bound Rubber Content (BRC) of nanocomposites with and without graphene

The addition of graphene increases the hybrid reinforcement of nano-fillers in ENR-silica composites. The interactions in the ENR-silica-graphene consist of combination of ENR-silica bonding, ENR-silane-silica bonding, hydrogen bonding between the silanol group of silica with epoxide group in ENR; as well as interaction of graphene with silica and ENR [23-25]. The schematic interactions in the ENR-silica-graphene nanocomposites are illustrated in Fig. 5 where the silica-silica interactions are reduced. In this case, the rubber-to-filler interaction is improved where the graphene oxide interacts with epoxide group of ENR and provides a linkage to silica [21].
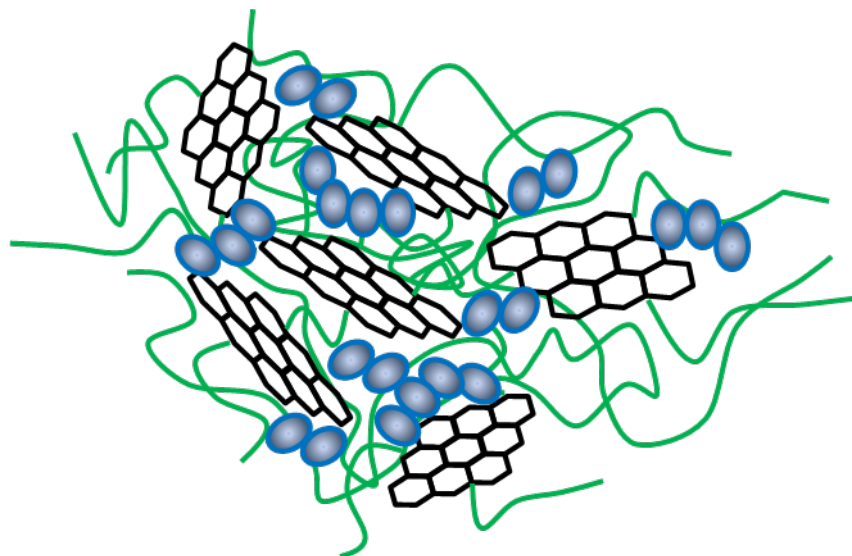
Fig. 5 Schematic representation on the interactions of graphene with ENR and silica

The dynamic properties of the nanocomposites measured at 10Hz are shown in Fig. 6. Commonly, the loss tan delta at 0°C and at 60°C of a cured compound is taken as indication for the wet grip and rolling resistance respectively of tires made thereof [26]. The higher the tan delta at 0°C, the higher the wet grip of the tyre is expected. However, for tan delta at 60°C, the lower the value the lower the rolling resistance of the tyre [24]. It is observed that the silica composites have higher tan delta peak than carbon black composites. This indicates higher degree of rubber-filler interaction in silica composites. The tan delta peak value also corresponds to the glass transition temperature (T_g) of the composites. The T_g of ENR-nano composites is about 25 degree higher than NR-nano composites due to the 25% epoxidation level in ENR. The results show that ENR-silica and ENR-carbon black composites exhibit higher tan delta at 0°C as compared to NR composites. This gives an indication of higher wet grip of the final products. Another indication is the tan delta at 60°C similar to all composites which show that the rolling resistance are maintained.
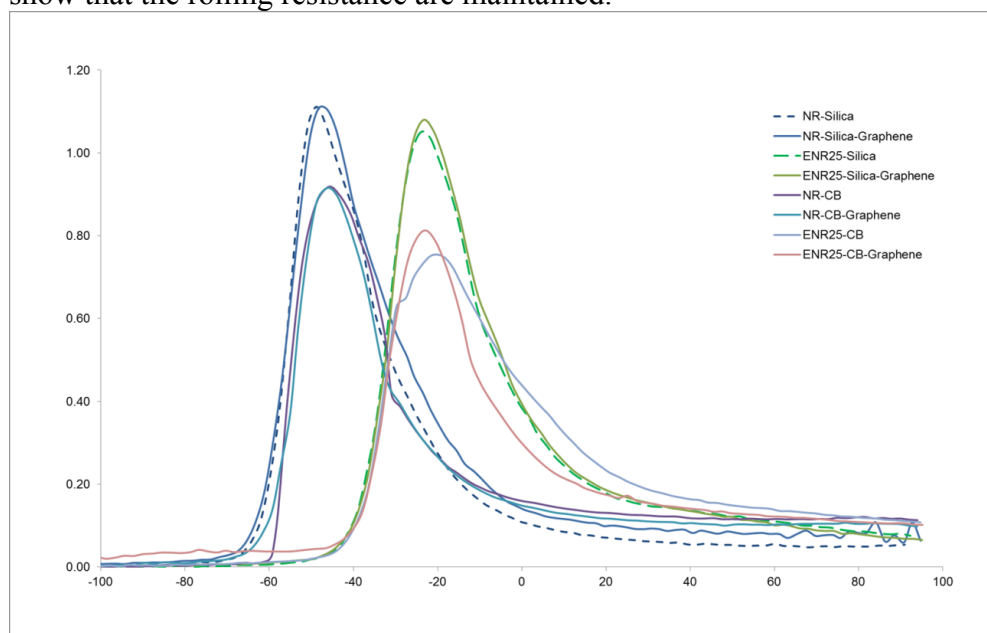

Fig. 6 Dynamic properties of nanocomposites with and without graphene

CONCLUSION

Graphene is used as hybrid nanofiller in silica and carbon black natural rubber composites at low graphene filler loading. The effect of graphene is more predominant in silica nanocomposite. The addition of graphene reduces the filler-filler interaction and increases the bound rubber content of ENR-silica composites. The hybrid reinforcement of epoxidized natural rubber with nano-silica and graphene is achieved. This resulted in improvement in the dynamic properties especially tan delta at 0°C for high wet grip for ENR-silica-graphene composite.

REFERENCES

1. John G. S, Engineered Rubber Products, Hanser Publications, Munich, (2009) 123 – 164.
2. M. Bhattacharya, Polymer Nanocomposites — A Comparison between, Carbon Nanotubes, Graphene, and Clay as Nanofillers, *Materials*, (2016) 262(9): 1-35.
3. V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker and S. Seal, Graphene based materials: Past, present and future, *Progress Mat. Sci,* (2011) 56:1178-1271.
4. T. Kuilla, S. Bhadra, D. Yao, N. H.. Kim, S. Bose and J. Hee Lee, Recent Advances in Graphene Based Polymer Composites, *Prog. Polym. Sci.*, (2010) 35:1350-1375.
5. Y. B. Liu, L. Li, and Q. Wang, Reinforcement of Natural Rubber with Carbon Black/Nanoclay Hybrid Filler, *Plast. Rubb. Comp.*, (2010) 39 (8):370–376.
6. N. Rattanasom, T. Saowapark, and C. Deeprasertkul, Reinforcement of natural rubber with silica/carbon black hybrid filler, *Polym. Testing.*, (2007) 26: 369–377.
7. N. I. Nik Ismail, A. Ansarifar, and M. Song, Effect of hybrid reinforcement based on precipitated silica and montmorillonite nanofillers on the mechanical properties of a silicone rubber, *Polym. Eng. Sci.*, (2013) 54 (8):1909-1921.
8. I.R Gelling and M. Porter, Chemical Modification of Natural Rubber, in: A.D. Roberts (Ed.) *Natural Rubber Science and Technology*, Oxford University Press, New York, (1988): 359-456.
9. C.S.L. Baker, I.R. Gelling, and A.B. Samsuri, Epoxidised Natural Rubber, *J. Nat. Rubb. Res.,* (1986) 1(2): 135-144.
10. I.R. Gelling, Epoxidised Natural Rubber, J. Nat. Rubb. Res., (1991) 6(3):184-205.
11. S.S. Sarkawi and C.S. Mt Saad, Reinforcement of Epoxidised Natural Rubber by Precipitated Silica Nanofiller: Studies on Cure Characteristics and Rubber-filler Interaction. *J. Ind. Tech.*, (2011) 20(1): 103-121.
12. W. Kaewsakul, K. Sahakaro, W.K. Dierkes and J.W.M. Noordermeer, Cooperative effects of epoxide functional groups on natural rubber and silane coupling agents on reinforcing efficiency of silica, *Rubber Chem. Technol*, (2014) 87(2) : 291-310.
13. P.J. Martin, P. Brown, A.V. Chapman and S. Cook, Silica-Reinforced Epoxidized Natural Rubber Tire Treads – Performance and Durability, *Rubber Chem. Technol*, (2015) 88(3):390-411.
14. S.S. Sarkawi, A.K. Che Aziz, T. Z. Zaeimoedin, M. Mustafa Kamal, (2014), Ekoprena in Green Retread, *MRB Rubber Technology Developments (MRTD)*, (2014) 14(2): 53-58.
15. M. Galimberti, V. Cipolleti, S. Musto, S. Cioppa, G. Peli, M. Mauro, G. Gaetano, S.Agnelli, R. Theonis and V. Kumar, Recent Advancements in Rubber Nanocomposites, *Rubber Chem. Technol.*, (2014) 87: 417-442.
16. Z. Yang, B. Guo and L. Zhang, Challenge of Rubber/Graphene Composites Aiming at Real Applications, *Rubber Chem. Technol.*, (2017) 87: 417-442

17. S. Wolff, M.-J. Wang, and E-H. Tan, Filler-Elastomer Interactions. Part VII. Study on Bound Rubber, *Rubber Chem. Technol*, (1993) 66:163-177.
18. A. R. Payne and R. E. Whittaker, Low Strain Dynamic Properties of Filled Rubbers, *Rubber Chem. Technol.*, (1971) 44: 440-478.
19. H-D. Luginsland, J. Fröhlich and A. Wehmeier, Influence of Different Silanes on the Reinforcement of Silica-Filled Rubber Compounds, *Rubber Chem Technol,* (2002) 75:563-580.
20. S.S. Sarkawi, W.K. Dierkes and J.W.M. Noordermeer, The influence of non-rubber constituents on performance of silica reinforced natural rubber compounds, *Eur. Polym. J.*, (2013) 49: 3199-3209.
21. S.S. Sarkawi, A. Abd Aziz, N.I. Nik Ismail, R. Abdul Rahim and A.K. Che Aziz, Novel Dual Filler: A Study of Dual-nanofiller Reinforcement of Epoxidized Natural Rubber, *Tire Technology International 2016*, (2016) 98-100.
22. S.S. Sarkawi, W.K. Dierkes and J.W.M. Noordermeer, Elucidation of Filler-to-Filler and Filler-to-Rubber Interactions in Silica Reinforced Natural Rubber by TEM Network Visualization, *Eur. Polym. J.*, (2014) 54: 118-127.
23. S.S.Sarkawi, A.K.Che Aziz, R.Abdul Rahim, R.Abdul Ghani and A.N.Kamaruddin, Properties of Epoxidized Natural Rubber Tread Compound: The Hybrid Reinforcing Effect of Silica and Silane System, *Polym. Polym. Comp.*, (2016) 24(9): 775-782.
24. S.S.Sarkawi, W. Kaewsakul, K. Sahakaro, W.K. Dierkes and J.W.M. Noordermeer, A Review on Reinforcement of Natural Rubber by Silica Fillers for Use in Low-Rolling Resistance Tyres, *J. Rubb. Res.* (2015), 18(4): 203-233.
25. W. Kaewsakul, K. Sahakaro, W.K. Dierkes and J.W.M. Noordermeer, Verification of Interactions between Silica and Epoxidised Squalene as a Model for Epoxidised Natural Rubber, *J. Rubb. Res.* (2014), 17(3): 129-142.
26. K.H. Nordsiek, Integral Elastomer, Paper 48, *125th Meeting of the Rubber Division, ACS*, Indianapolis, May8-10(1984).