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Mechanical Properties of Graphene-Rubber Nanocomposites

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Abstract. This research focused on development of wearable sensor device by using Prevulcanized Natural Rubber (PV) and Epoxidized Natural Rubber (ENR 50) latex incorporated with graphene oxide (GO), graphene paste, graphene powder and reduced graphene oxide (rGO) powder. The compounding formulation and calculation were based on phr (parts per hundred rubber) and all the samples were then tested for mechanical properties using Instron 5565 machine. It was found that the sonication effects on tensile strength may have better quality of tensile strength compared to non-sonicated GO. For PV incorporate GO, the optimum loading was best determined at loading 1.5 phr with or without sonication and similar result was recorded for PV/G. For ENR 50 incorporate graphene paste and rGO powder nanocomposite shows the best optimum was at 3.0 phr with 24 hours' sonication.

1. Introduction

The development of wearable device technology has widely increased and are demanded especially in healthcare industry. Recently, researchers are moving towards carbon based material as filler such as graphene for wearable sensor by reinforce with flexible polymer materials such as natural rubber to produce high flexibility and good conductivity of the device. Graphene is an atomic-scale honeycomb lattice made of carbon atoms [1] which possess extraordinary properties such as high specific area with approximately 2630 m^2/g [2], high Young's modulus (approximately 1100 GPa) [2] and high thermal conductivity (5000 W/m-K) [2] which is a promising material for biocompatible sensing as reported by [3,4]. J. H. Lee et. al. [4] discovered that the properties of graphene such as excellent electrical conductivity and high surface area allowed it to act as an "electron wire" between the redox centers of an enzyme or protein and an electrode's surface. The unique properties also possess the properties of high carrier mobility that can allows high signal-to-ratio and hence is a promising material for conductivity for electronic device applications.

In order to determine the best material to use as substrate and to have flexible and wearable device, this research will reveal the best nanocomposite material which used prevulcanized natural rubber incorporated graphene oxide (PV/GO) and graphene powder (PV/G) with and without sonication, and epoxidized natural rubber incorporate graphene paste (ENR 50/G) and reduced graphene oxide ENR 50/rGO).

2. Materials and Methods

2.1. Materials and sample preparation

Prevulcanized Natural Rubber (PV) and Epoxidized Natural Rubber (ENR 50) were obtained from Rubber Research Institute of Malaysia (RRIM). Graphene paste with 50% solid, water based material, graphene oxide (GO) and graphene powder were supplied individually by RRIM. Reduced graphene oxide (rGO) powder was supplied with purity of more than 99 wt. %. The compounded latex materials were categorized into 4 types of samples, A (control), B with loading 1.0 phr, C with loading 1.5 phr and D with loading 3.0 phr, respectively.

There were 3 groups of experiments conducted for this research as for group 1; PV incorporated GO paste with no sonication done labelled with PV/GOpa-ns, for group 2; PV incorporated GO paste with 24 hours sonication labelled with PV/GOpa-s and PV incorporated graphene powder with 24 hours sonication labelled with PV/Gpo-s, and finally, for group 3, ENR 50 incorporated graphene paste with 24 hours sonication labelled with ENR 50/Gpa-s and ENR 50 incorporated rGO powder with 24 hours sonication labelled with ENR 50/rGOpo-s.

Group 1 and 2 were done by redispersed graphene to 10 % (0.2 % of sodium dedocyl sulfate, SDS surfactant and 98 g of water) in aqueous medium and sonicated by using tip sonication Fisher Scientific Model 705 Sonic Dismembrator with 80 % amplitude for 24 hours (separated by a rest every 15 min). For group 3, the same method was applied but without any addition of surfactant.

2.2. Mixing and compounding latex

The compounding formulation was calculated based on phr (parts per hundred rubber) and summarized in Table 1 for group 1 and 2 and Table 2 for group 3. Both PV and ENR 50 latex was stirred by using IKA RW 20 Digital at 110 rpm for 1 hour to generate uniform latex. Then, the latex was sieved, weighed, compounded and stirred overnight. After 24 hours, the compounded latex was diluted to 30 % total solid content (TSC) by adding distilled water and continued stirring for 1 hour. The compounding latex was then casted on 12 cm x 12 cm plates and left to dry at room temperature for 2 to 3 days. The cast films were then vulcanized in an oven with 70 ºC temperature for 2 hours directly on the plates. Figure 1 shows the physical state of mixing and compounding between PV and ENR 50 latex at different loading. It was observed that the higher the loading concentration, the darker the colour of the samples for PV and ENR 50 latex.

Table 1. Parts per hundred rubber formulation of PV latex and graphene for group 1 and 2.

Material	Samples			
	A (control)	B	C	D
phr[a]	-	1.0	1.5	3.0
PV latex (gm)	250.00	250.00	250.00	250.00
Graphene (gm)	0.00	15.13	22.69	45.38
Water to add (gm)	254.17	244.08	239.04	223.92

[a] Parts per hundred rubber.

Table 2. Parts per hundred rubber formulation of ENR 50 latex and graphene for group 3.

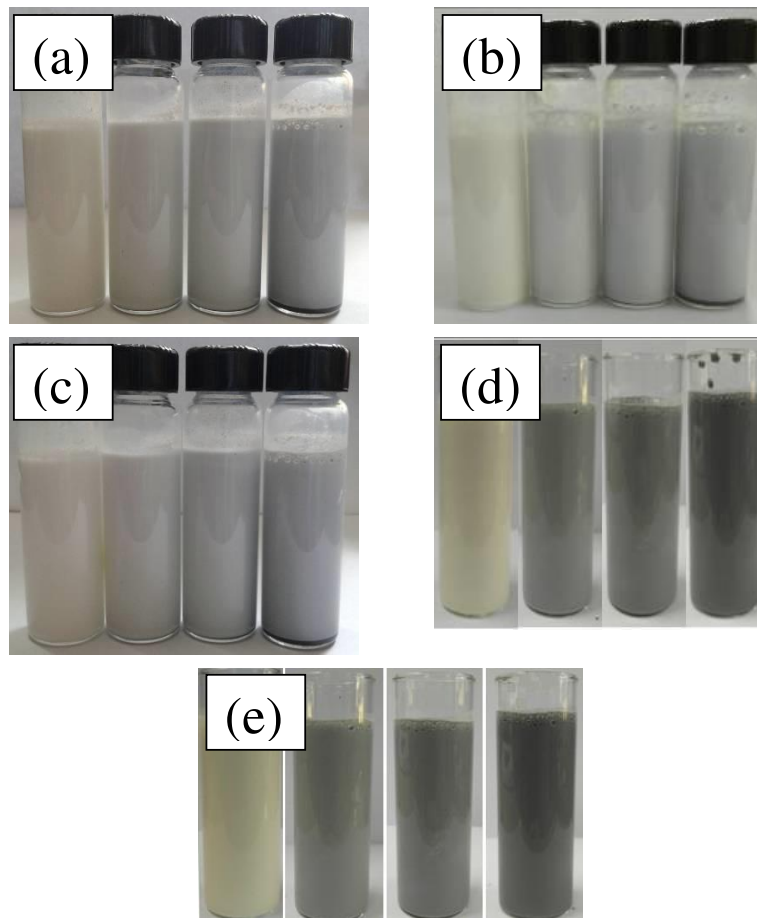| Material	Samples			
	A (control)	B	C	D
phr[a]	-	1.0	1.5	3.0
PV latex (gm)	250.00	250.00	250.00	250.00
Graphene (gm)	0.00	12.50	18.75	37.50
Water to add (gm)	166.67	158.33	154.16	141.67

[a] Parts per hundred rubber.

Figure 1. Samples of; (a) PV/GOpa-ns, (b) PV/GOpa-s, (c) PV/Gpo-s, (d) ENR 50/rGOpo-s, (e) ENR 50/Gpa-s, for loading from left; control, 1.0 phr, 1.5 phr, and 3.0 phr.

2.3. Measurement of tensile properties

Tensile properties for each sample were performed by using Instron machine (model 5565) equipped with a 10 N load cell at room temperature. The films were cut to dumbbell shape for 5 films every each samples and tested for every extension of 100 mm, 300 mm, 500 mm and 700 mm.

3. Results and discussions

3.1. Effects of GO paste sonication on tensile strength for PV latex

Figure 2 shows the effects of GO sonication on tensile strength of PV latex for group 1 (PV/GOpa-ns) and group 2 (PV/GOpa-s). For PV/GOpa-ns, it shows increasing of tensile strength from loading 1.0 to 1.5 phr with 16.6 MPa to 18.8 MPa. But, at loading 3.0 phr, the tensile strength decreased to 17.1 MPa. Compared to PV/GOpa-s, the tensile strength increased from 14 to 15 MPa for loading 1.0 to 1.5 phr. However, when loading further increased to 3.0 phr, the tensile

strength drops to 13 MPa. This phenomenon was believed to be percolation phenomenon where the increasing of loading filler will subsequently increase the tensile strength but eventually it will level off at certain level (maximum level) as reported by A. Celzard *et.al* [5]. It was clearly observed that PV/GOpa-ns has better tensile strength compared to PV/GOpa-s. It can be pre-concluded that the best loading for PV incorporate GO paste was at 1.5 phr with or without sonication done. The effect GO sonication is not following the pattern as reported [6, 7]. It was expected that the longer the GO sonication time, the better the tensile strength of PV latex. However, this incident is still unclear as no finding was reported supporting this problem.
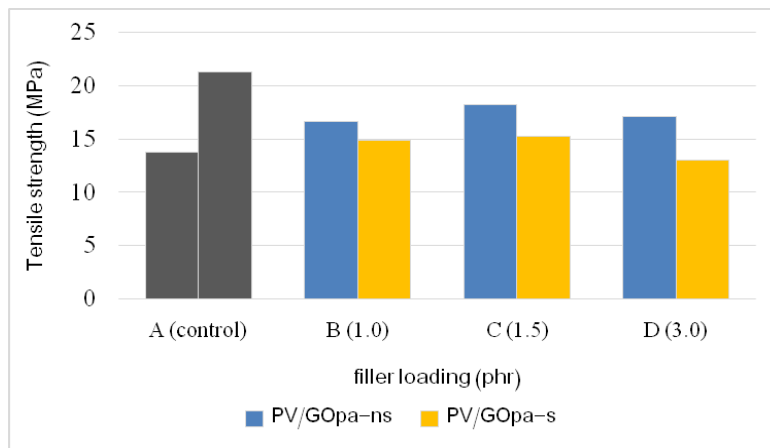

Figure 2. Effect of sonication of GO on tensile strength of PV/GOpa-ns and PV/GOpa-s at different loading.

3.2. Modulus at 100 % elongation (M_{100}) for PV/Gpa-ns and PV/Gpa-s

Figure 3 shows the modulus at 100 % elongation for PV/GOpa-ns and PV/GOpa-s. From this graph, it can be observed that the modulus at 100 % elongation (M_{100}) for PV/GOpa-s was directly proportional to tensile strength as M_{100} increased from 0.61 MPa to 0.69 MPa for loading 1.5 to 3.0 phr. It can be pre-concluded that the effect of sonication for GO paste may play its role on good dispersion in liquid media and strengthen the rubber network [8]. Subsequently, incorporation of GO has improved the mechanical properties of the PV latex. PV/GOpa-ns show a decreasing of tensile strength from 0.53 MPa to 0.42 from loading 1.0 to 3.0 phr. This incident mainly due to the inhomogeneous structures formed with the incompletely exfoliated graphene oxide flakes [9]. Even though the PV/GOpa-ns has higher tensile strength than PV/GOpa-s, it has very low fracture strength and toughness as reported by J.C. Feng et. al [9]. Hence, it can be concluded that the sonication of GO paste has improved the mechanical properties PV latex.
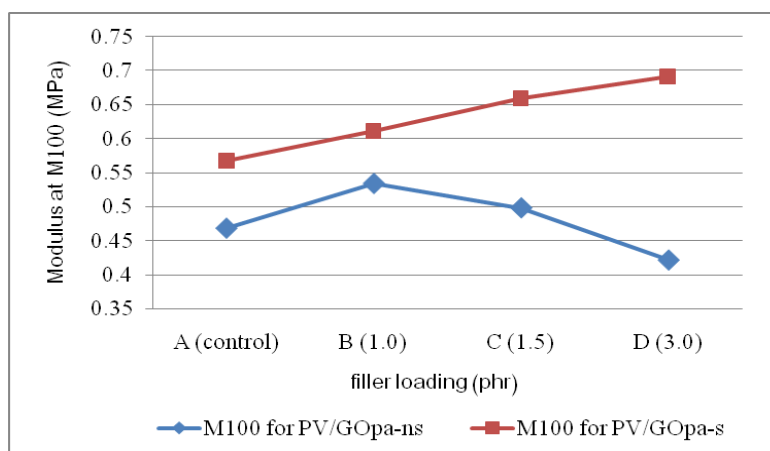

Figure 3. Effect of sonication of GO on modulus at 100 % elongation (M_{100}) for PV/GOpa-ns and PV/GOpa-s at different loading

3.3. Effect on tensile strength for PV/Gpo-s

Figure 4 shows the effect of PV latex tensile strength by the presence of graphene powder. It was observed that the increasing of tensile strength from 20.3 to 29.4 MPa for loading 1.0 to 1.5 phr. However, tensile strength decreased to 24.73 MPa at loading 3.0 phr. This finding is similar to group 2 (PV-GOpa-s) nanocomposite which shows the best loading was at 1.5 phr loading.
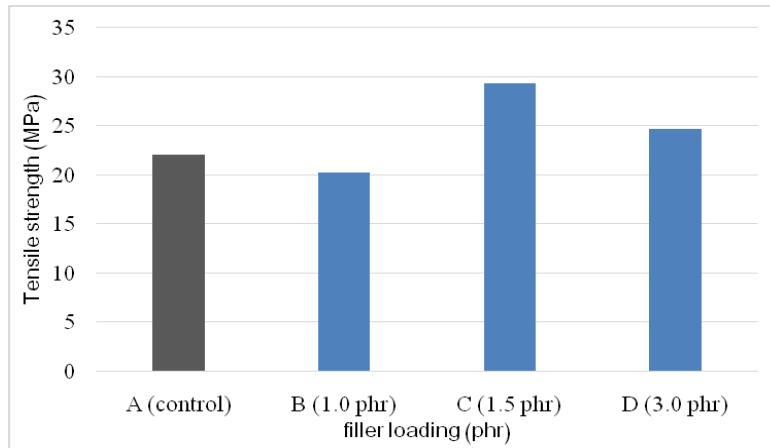

Figure 4. Effect of the presence of graphene powder on tensile strength of PV/Gpo-s at different loading

3.4. Modulus at 100 % elongation (M_{100}) for PV/Gpo-s

The modulus at 100 % elongation (M100) was investigated as shown in Figure 5. The presence of graphene in PV latex was observed to enhance the modulus at 100 % elongation for PV-graphene nanocomposite. The increasing of modulus was recorded from 0.67 to 0.81 MPa towards loading from 1.0 to 3.0 phr. It can be summarized that the good dispersion of graphene powder in PV latex solution has been achieved by sonicated the solution for 24 hours and subsequently increased the modulus at 100 % elongation.
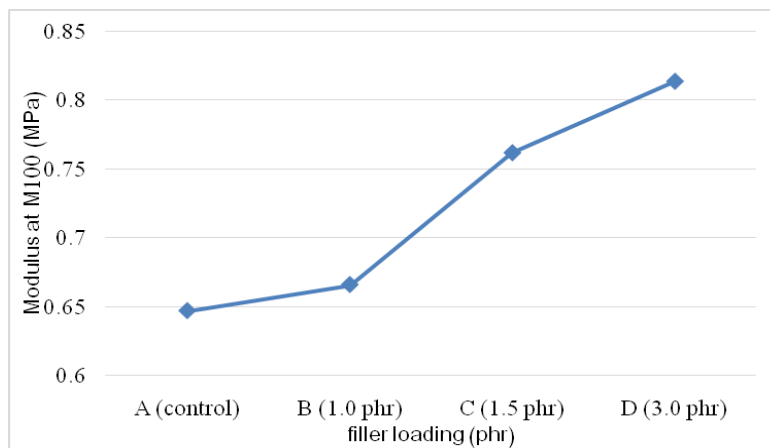

Figure 5. Effect of the presence of graphene powder on modulus at 100 % elongation (M_{100}) of PV/Gpo-s at different loading

3.5. Comparison of tensile strength at maximum load (MPa) between ENR 50/Gpa-s and ENR 50/rGOpo-s

The comparison of tensile strength at maximum load (MPa) between ENR 50/Gpa-s and ENR 50/rGOpo-s were carried out as shown in Figure 6. It was clearly observed that tensile strength of ENR 50/Gpa-s shows the dramatically drop from 1.3 MPa to 1.0 MPa by increasing the loading from 1.0 phr to 3.0 phr. It has been reported the percolation point of ENR latex incorporated graphene nanocomposites takes place at extremely low filler content which is less than 0.1 phr [10] and subsequently explain the reason on the decreasing of tensile strength of ENR 50/Gpa-s. For ENR 50/rGOpo-s shows the decreasing of tensile strength from 1.0 phr to 1.5 phr by 1.3 MPa to 1.2 MPa. But at loading of 3.0 phr, the tensile strength rises up to 1.3 MPa. This phenomenon led to the

presence of epoxide group with adjacent double bond at ENR 50 rubber matrix [8]. It provided a strong intermolecular interaction and high cohesion energy which increase the tensile strength and toughness of the rubber [8].
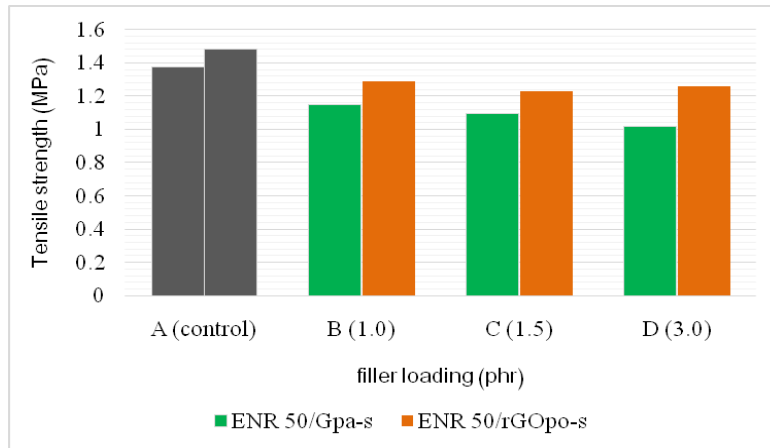

Figure 6. Comparison of tensile strength between ENR 50/Gpa-s and ENR 50/rGOpo at different loading

3.6. Modulus at 100 % elongation (M_{100}) between ENR 50/Gpa-s and ENR 50/rGOpo-s

Figure 7 shows the modulus at 100 % elongation (M_{100}) between ENR 50/Gpa-s and ENR 50/rGOpo-s. For ENR 50/Gpa-s, it shows that the tensile strength was increased by the increasing of loading which from 0.27 MPa to 0.4 MPa. This pattern was repeated for ENR 50/rGOpo-s from 1.0 to 3.0 phr by 0.35 MPa to 0.39 MPa. It was believed that the modulus at 100 % elongation (M_{100}) was directly proportional to tensile strength. Therefore, it can be concluded that the presence of graphene incorporated inside ENR 50 has greatly improved the tensile strength at 100 % modulus.
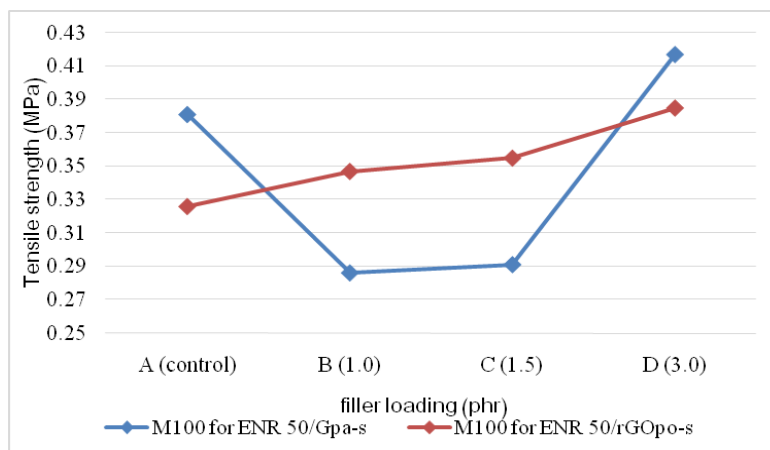

Figure 7. Comparison of modulus between ENR 50/Gpa-s and ENR 50/rGOpo-s at different loading

4. Conclusions

The effect of GO sonication into PV latex was successfully studied in term of its tensile strength. GO sonication gives the impact on increasing of modulus and fracture strength for PV latex. In general, the presence of sonicated GO in natural rubber has increased the tensile properties by 2 MPa. It was shown that the best loading for GO incorporate PV latex was at 1.5 phr with sonication done similar to PV/Gpo-s. The presence of graphene in PV latex enhanced the mechanical properties of the polymer. Hence, it has improved that graphene-PV latex nanocomposite is a promising material to enhance the mechanical properties of the stretchable polymer for future wearable device. For ENR 50 latex, percolation point had taken place at very low filler loading which less than 0.1 phr. Even though the tensile strength for this nanocomposite is not good as pure ENR latex, the presence of the carbon based material may slightly improve the modulus for the ENR nanocomposites. For ENR 50/Gpa-s and ENR 50/rGOpo-s, the best loading was recorded at 3.0 phr. The powder type rGO (ENR 50/rGOpo-s) can withstand higher stress for a longer time compared to the paste type of graphene (ENR 50/Gpa-s). The increasing of mechanical properties of ENR 50 such as modulus for graphene paste and rGO powder, is the result from the mobility of graphene that is grafted onto the surfaces of rubber [10]. Hence, it can be concluded that the presence of graphene may enhance the mechanical properties of the stretchable polymer such as natural rubber. Thus, this carbon based nanocomposite material is a promising material for the researchers to develop more wearable devices for future technology.

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