The effect of graphene loading on natural rubber latex/graphene stretchable conductive material

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Abstract. The demand for the soft and flexible stretchable electronic has been increased due to the flourish development of electronic field nowadays. This can be achieved by incorporating graphene nanoplatelet (GNP) into natural rubber latex (NRL). This paper was aimed to investigate the effect of the GNP content on the properties of the NRL/GNP composites. The incorporating of GNPs into NRL increased the density and modulus of the composite but reduced the tensile strength, elongation at break and crosslink density. On the other hand, the NRL/GNP has reached the percolation threshold at 7phr of GNP, at this content the composite became electrically conductive.

1. Introduction
The demand for the stretchable electronic has been increased due to the flourish development of electronic field. This became a big challenge for the material engineers since conductivity and stretchability were hard to coexist in a material due to stretching tend to lengthen the bonding and increased the resistivity of the material [1]. By the effort they paid, they successfully created few methods in order to made the stretchable electronic devices which able to withstand the repeat stretched, twisted and banded without compromising on the conductivity [2]. In this paper, graphene nanoplatelet (GNP) was incorporated into natural rubber latex (NRL). Latex which acted as the matrix endued elasticity for the composite while GNP improved the mechanical properties of the composite materials. As percolation threshold achieved, the GNP particles contacted with each other and the composite became conductive.

2. Materials and Method
Natural rubber latex (NRL) with TSC 60% was supplied by MG Color Sdn. Bhd. The 50% dispersive compounding additives such as zinc oxide (ZnO), sulfur, zinc diethylthiocarbamate (ZDEC) and zinc 2-mercaptobenzothiazole (ZMBT) were purchased from Furben Technique (M) Sdn. Bhd. Furthermore, stearic acid (SA) was supplied by Acidchem International Sdn. Bhd while the stabilizer, potassium hydroxide (KOH) was purchased from Johchem Scientific & Instruments Sdn. Bhd. Lastly, graphene nano-platelet (0540DX) was purchased from SkySpring Nanomaterials Inc, United State.

First, the KOH solution, ZnO, SA, GNP and accelerators were added by followed the sequence and stirred until homogeneous by using the magnetic bar. Then, sulfur was added into the mixture after sonification and stir until homogeneous. The mixture was then degassed by using the vacuum bump and desiccator before cast in mold. Lastly, the casted composite material was let for maturation under...
room temperature for 48 hours and post cure in the oven. The steps were repeated with different GNP loading (0phr, 1phr, 3phr, 5phr, 7phr and 9phr).

3. Characterization
To determine the crosslink density of the composites, weighed samples (~0.2g) were immersed into the toluene until the sample weight reach equilibrium. Then, crosslink density of the composites was calculated by using the Flory-Rehner equation:

\[ \nu = \frac{1}{M_{cr}} = -\left[ V_2 + x V_2 + \ln(1-x V_2) \right] \rho_2 V_1 \left( \frac{\xi}{2} - \frac{3}{2} \right) \]

Where \( \nu \) is the effective number of moles of crosslinked chains per gram of polymer in mol/g; \( M_{cr} \) is the molecular weight between crosslink in g/mol; \( V_2 \) is the volume fraction of polymer in the swollen mass; \( V_1 \) is the molar volume of the solvent in ml/mol; \( \chi \) is the polymer-solvent interaction parameter while \( \rho_2 \) is the density of the polymer in g/cm\(^3\). The density of the conductive materials was determined by using the pycnometer density analyzer with model Micromeritics AccuPycII 1340v under the flow of helium gas at room temperature. Furthermore, tensile properties were determined by using the Instron 5569 Universal Testing Machines (UTM) according to the ASTM D412. Then the electrical conductivity test, was tested according to the ASTM D257 by using the Fluke 8845A/8846A 6.5-digit precision multimeter in direct current mode with voltage supply of 5V at room temperature. Then, both the bulk resistivity and bulk conductivity were calculated by using the Equation 2.

\[ \text{Bulk Conductivity, } \sigma = \frac{d}{r \cdot A} \]

Where \( r \) is resistance of resistor, \( A \) is the area of the specimens in cm\(^2\) and \( d \) stand for the thickness of the specimens in cm.

4. Results and Discussion

[Figure 1: Crosslink density of composites with different GNP loading.]

[Figure 2: Density of composites with different GNP loading.]
Figure 1 shows crosslink density of the composite. The crosslink density decreased as the GNP loading increased from 0phr to 9phr. Localized of GNP between the interlayer of the NR macromolecular chains, restricted the formation of the C-S-C crosslinking between the sulphur and the rubber chains [3]. The crosslink density gave a significant effect on the physical properties such as solvent diffusion and tensile strength.

Then, the density of the conductive materials with different GNP contents was not significant as shown in Figure 2. The density was decreased as GNP loading increased from 0phr to 3phr and then increased from 3phr to 9phr. There were some remained additives and agglomerated GNP within sample as shown in Figure 3. The low interfacial adhesion between the matrix and the solid additive caused the formation of void around the interface resulting the reduction of the density. As more GNP added, the compounded mixture became denser. The increased of the overall mass caused the increased of the density as GNP loading increased from 3phr to 9phr.

Figure 3: SEM of composites with different GNP loading (a) 0phr; (b) 1phr; (c) 7phr and (d) 9phr

Figure 4 shows tensile strength of composites with different GNP loading.

Figure 5: Elongation at break of composites with different GNP loading.
Figure 6: Modulus at 100% (M100) strain of composites with different GNP loading.

Figure 7: Modulus at 500% (M500) strain of composites with different GNP loading.

Figure 4 and Figure 5 show the tensile strength and the elongation at break of the composites. Both increased from 0phr to 1phr GNP and then decreased as the subsequent increased of GNP loading. While for the modulus in Figure 6 and Figure 7, the M100 and M500 show a decreased trend from 0phr to 3phr GNP loading and then increased as the further increased of the GNP loading from 3phr to 9phr.

Better dispersion of GNP within the latex matrix allowed the GNP offer good stress transfer ability for the composite at 1phr GNP loading, resulting higher tensile strength [5]. As GNP loading increased, the strong cohesive forces between these carbonaceous particles tend to agglomerate with each other to form cluster form. The occurrence of filler agglomeration became serious as the GNP loading increased, since higher loading had a higher tendency to contact with each other during mixing and formed more GNP clusters. Then, The larger additive particles and the agglomerated GNP acted as the stress concentration point where the deformation initiated [4]. On the other hand, the high GNP content restrict the chain mobility the chains became unable to move freely, leading to the reduction of the elongation but increased in the modulus of the composites [6]

Figure 8: Bulk resistivity of composites with different GNP loading.

Figure 9: Bulk conductivity of composites with different GNP loading.

The GNP particles with high cohesive force tend to form agglomerate [7]. These GNP agglomerate structure help to improve the electrical conductivity of the composite [8]. When the GNP come contact with each other, the conductive pathway started to construct and allowed the electrons to move along the matrix and the composite started to conduct electricity once the percolation threshold achieved [7]. As the GNP added continuously, more conductive network formed, leading to a significant improvement of the conductivity. In this study, the percolation threshold was achieved at 7phr of GNP loading as shown in Figure 8 and Figure 9 where the bulk resistivity decreased significantly and there was a sudden increased of the conductivity.
5. Conclusion

The incorporation of the GNP particles into the NRL gave significant effect on the properties. The localization of the GNP particles between the NRL macromolecular chains restrict the formation of the C-S-C linkage, reduced the crosslink density which in turn reduced the tensile strength of the composites. Furthermore, the additives remained and the agglomerated GNP particles leading the reduction of density. As the GNP loading increased, the increased of the overall mass caused the increased of the density. Besides, the increased of the GNP loading restrict the mobility of the chains, resulting the reduced of the elongation at break of the composites but increased the modulus at 100%, and 500% strain. On the other hand, the GNP endowed electrical conductivity to the NRL matrix and achieved the percolation threshold at 7phr.

Acknowledgement

The financial support of Fundamental Research Grant Scheme (FRGS) grant no: FRGS/1/2018/TK05/UNIMAP/02/13 is gratefully acknowledged.

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