The effect of the GNP-SDS loadings on the properties of the NRL/GNP-SDS composites

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Abstract. Stretchable conductive polymer composites (CPCs) are fabricated by incorporating the conductive particles into the polymer matrix. In this paper, CPC was fabricated by incorporating the sodium dodecyl sulfate (SDS) modified graphene nanoplatelet (GNP) into natural rubber latex (NRL) by varying loading from 0phr to 9phr using a simple mechanical stirring method. The effect of the GNP-SDS loadings on the properties of the composites were study by investigated the crosslink density, tensile properties, morphology of the tensile fracture surface and electrical conductivity. The crosslink density of the composites shows a decreased trend. Then, due to the well dispersed GNP-SDS, the tensile strength increased but decreased at high filler loading caused by the agglomeration issue. The tensile modulus also increased with increasing filler loading due to the intrinsic high modulus of GNP and the reduction of chain mobility. However, the electrical properties of the composites improved as GNP-SDS loading increased and achieved a percolation threshold at 7phr.

1. Introduction

Stretchable conductive polymer composites (CPCs) made from insulating polymer can be fabricated by incorporating the conductive particles into the polymer matrix [1]. Besides for endowing an electrical conductivity to the CPCs, the conductive particles also acting as a reinforcing filler for the composites by playing the role as load bearing component. Nevertheless, the properties of the CPCs mainly depend on the filler dispersion within the matrix and the filler-matrix interfacial interaction [2]. Natural rubber latex is a good candidate to be chosen as the matrix for the stretchable CPCs due to its environmentally friendly, low cost, high elasticity, tailorable characteristic by compounding with design formulation and additives many other attractive properties [3].

On the other hand, graphene nanoplatelet (GNP) is the most common conductive nanoparticles to be used to fabricate the CPCs nowadays. This is due to its high electron mobility which contribute to its excellent electrical conductivity. These useful properties combined with high specific surface area, high tensile strength and modulus make it attractive filler to fabricate CPCs [4]. However, the interfacial interaction between the hydrophilic NRL and hydrophobic GNP is low, leads to the filler agglomeration issue and result in failure. Therefore, surfactant such as sodium dodecyl sulfate (SDS) is required to be added into the composite in order to improve the interaction and dispersion of the GNP within the matrix. SDS consist of a hydrophobic hydrocarbon tail and a hydrophilic sulfate head. So, it can be adsorbed on the GNP to intercalate and exfoliate the GNP sheets and at the same time improved the interfacial interaction between the GNP and NRL matrix [5]. Due to lack of functionality on the GNP, the properties of the composite mainly dependence on the dispersion degree of the GNP and GNP loading within the NRL matrix. Therefore, this paper was aimed to investigate the effect of the GNP-SDS loading on the physical, mechanical and electrical properties of the NRL/GNP-SDS composites.

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2. Material and Sample Preparation
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 (S), zinc diethyldithiocarbamate (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. Moreover, graphene nano-platelet (0540DX) was purchased from SkySpring Nanomaterials Inc, United State and sodium sulfate dodecyl (SDS) was purchased form Sigma-Aldrich Corporation.

First, the GNP-SDS was prepared by dispersing the GNP within a 2% SDS solution with concentration and stirred for 24 hours by using magnetic stirrer. After 24 hours, the GNP was filtered and washed several times to remove the excess SDS by using distilled water. In order to prepare the NRL/GNP-SDS composite, all the additives were mixed with NRL and stirred for overnight. After that, the compounded latex was filtered and casted on a glass mold. Later, the casted NR sheet was cured at room temperature for 72 hours and post cure in an oven. The steps were repeated with different GNP loadings (0phr, 1phr, 3phr, 5phr, 7phr and 9phr).

3. Testing and Characterization
The crosslink density was determined by immersed the weighed samples (~0.2g) into the toluene until the sample weight reached equilibrium. Then, the crosslink density of the composites was calculated by using the Flory-Rehner equation:

\[ \nu = \frac{1}{\rho_{cs}} = \left[ \frac{V_2 + \chi V_2 + \ln(1 - V_2)}{\rho V_2 \left( \frac{V_2}{2} - \frac{1}{2} \nu_2 \right)} \right]. \]  

Where \( \nu \) is the effective number of moles of crosslinked chains per gram of polymer in mol/g; \( M_c \) 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 \( \rho \) is the density of the polymer in g/cm\(^3\).

Furthermore, tensile properties were determined by using the Instron 5569 Universal Testing Machines (UTM) according to the ASTM D412. Then, the fracture surface was observed by using scanning electron microscopy (SEM) after coated with a thin layer of palladiums. Furthermore, 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. After that, the bulk conductivity was calculated by using the Equation 2.

\[ \sigma = \frac{d}{r \cdot A}. \]  

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. Result and Discussion
Figure 1 and Figure 2 show the crosslink density and swelling index of NRL/GNP-SDS composite with increasing loadings. The swelling index was inversely proportional to the crosslink density. As the GNP-SDS loading increased, the high surface area GNP sheets localized in between the NRL chains interfered the crosslink formation between the NRL chains and thus reduced the crosslink density. Then, as the crosslink density decreased, the toluene able to diffuse through the loosely crosslink structure, resulting the increment of swelling index.
Figure 1. Crosslink density of NRL/GNP-SDS with increasing of GNP-SDS loadings.

Figure 2. Swelling index of NRL/GNP-SDS with increasing of GNP-SDS loadings.

Figure 3 shows the tensile properties of the NRL/GNP-SDS composites. As the composites loaded with 1-5phr of GNP-SDS, the tensile strength increased and then dropped significantly as GNP-SDS loading increased to 7-9phr as compared to the pure NRL vulcanizates. At low filler loading, the GNP sheets were dispersed well and acts as the load bearing component, leading to an increase of tensile strength and only slightly reduced for the tensile strength as GNP-SDS loading increased to 5phr. As the filler loading increased continuously, agglomeration occurred. This reduced the routes for stress transferring from matrix to GNP-SDS, increasing the stress concentration points which act as the preferential sites for crack initiation and finally reducing the tensile properties [6]. For the elongation at break, low GNP-SDS loading facilitated the chain sliding to occur. Nevertheless, as filler loading increased, the GNP-SDS in between the NRL chains held the chains tightly and reduced the chain mobility. Additional to the intrinsic high modulus properties of the GNP-SDS, the modulus of the composites increased at increasing loadings but reduced the elongation at break [7].
Figure 3(a). Tensile strength of NRL/GNP-SDS with increasing GNP-SDS loadings.

Figure 3(b). Elongation at break of NRL/GNP-SDS with increasing GNP-SDS loadings.

Figure 3(c). Tensile modulus of NRL/GNP-SDS with increasing GNP-SDS loadings.

Figure 4 shows the fracture surface of the composites with different GNP-SDS loadings obtained by using SEM. The GNP-SDS sheets were dispersed well within the matrix at 3phr and 5phr and act as the load bearing component during stress applied. This support the increment of tensile strength as
compared to the pure NRL vulcanizate. On the other hand, as filler increased to 7phr and 9phr, agglomeration of GNP-SDS occurred. This reduced stress transfer efficiency of the composites and also act as the crack initiation points of the composites. This explained the decrement of the tensile strength as filler loading increased.

![Image of fracture surface of NRL/GNP-SDS composites with different filler loadings at 1000X magnification.](image)

**Figure 4.** Fracture surface of NRL/GNP-SDS composites with a) 3phr; b)5phr; c)7phr and d) 9phr at 1000X magnification.

Figure 5 shows the electrical properties of NRL/GNP-SDS composites with increasing GNP-SDS loadings. At low filler loading, the electrical conductivity of the composites behaved like the neat NRL which exists as an insulator. As the filler loading increased, the GNP-SDS sheets came closer and interacted with each other to construct the conductive pathway to allow electrons to travel along within the matrix [8]. Then, as the GNP loaded to 7phr, the percolation threshold achieved and the composites transformed into a conductor.

![Image showing electrical properties of NRL/GNP-SDS composites with increasing GNP-SDS loadings.](image)
Figure 5. Electrical properties of NRL/GNP-SDS composites with increasing GNP-SDS loadings.

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