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Electrically Conductive Poly(butadiene-*co*-acrylonitrile) [NBR]-Based Blends: Optimisation of Formulation

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The demand on conductive polymer has been increasing due to its diverse applications such as for electromagnetic shielding, sensors and antistatic material. The aim of this study was to determine the electrical and physical properties of peroxide-vulcanised poly(butadiene-*co*-acrylonitrile) [NBR] loaded with either polyaniline-dodecylbenzenesulfonate [PAni.DBSA] or carbon black. Different compositions of NBR wt%:filler wt% blends (97.5 : 2.5, 95 : 5, 92.5 : 7.5, 90 : 10, 80 : 20, 70 : 30, 60 : 40, 50 : 50) were prepared using a two roll-mill and vulcanised using peroxide system. Tensile tests, hardness, electrical conductivity, dispersion of fillers and morphological study (via transmission electron microscope) were conducted to evaluate the performance of the fillers. The results showed that the hardness, tensile strength and electrical conductivity increased with increasing concentration of fillers. Carbon black-filled blends exhibited better but comparable tensile strength and hardness compared to PAni.DBSA-filled blends. Nonetheless, PAni.DBSA demonstrated outstanding electrical conductivity with low percolation threshold (2.5 wt%) up to 0.1 $S.cm^{-1}$ compared to carbon black(1 x 10^{-4} $S.cm^{-1}$). The dispersion of fillers exceeded 90 % which indicates homogenised blends. As observed from the morphological study, conductive network paths built up by those phase separated regions of PAni.DBSA were increased with the PAni.DBSA content. Based on these results, peroxide-vulcanised NBR-PAni.DBSA blends (10.0 - 50.0 wt% of PAni.DBSA contents) could emerge as a potential raw material for all above mentioned applications.

1. Introduction

Conductive polymer are gaining attention in numerous applications such as for electromagnetic shielding, sensors and antistatic material with increasing processability and low cost materials with enhanced electrical and physical properties. For instance, conductive polymer such as poly[2,7-bis(carbazole)-N-hexylacridone] has shown encouraging performance in the development of optical biosensors (Cabaj et al., 2016). In the case where the consideration of weight and space is important, a host matrix such as rubber is used to make conductive composite. Since rubber is typically an insulator, a carrier network needs to be established in the rubber matrix by incorporating conductive fillers (Sau et al., 1999). Carbon black is a conventional and widely used filler due to its low cost, easy processability and high reinforcing effect on rubber. Nonetheless, carbon black is a poor electrical conductor (Yong et al., 2006) possibly due to poor dispersion and is prone to particle agglomeration (Hai et al., 2015). It was reported that the percolation threshold for conductivity of carbon black-filled compounds is high and the maximum conductivity value is only 1 x 10^{-8} $S.cm^{-1}$ (Vallim et al., 2000). In addition, the application of carbon black as conductive filler is limited to black coloured products which restricts the design of the final product. Polyaniline (PAni) is an intrinsically conducting polymer that has good environmental stability, redox reversibility and electrical conductivity (Jia et al., 2003). It is also easy to synthesise and relatively inexpensive (Jia et al., 2003). PAni can be doped with organic acids containing large alkyl group such as dodecylbenzenesulfonic acid (DBSA) to enhance its electrical conductivity and solubility in organic solvent (Poussin et al., 2003). The physical properties of PAni can be improved by blending with a host matrix such as rubber.

In present study, the performance of PAni.DBSA and carbon black as fillers for producing a good conductive composite were evaluated. Poly(butadiene-*co*-acrylonitrile) [NBR] was chosen as the host matrix due to its

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high resistance to chemicals (Vallim et al., 2000). The filler dispersion, electrical conductivity and physical properties of the blends were evaluated to obtain the best conductive rubber blend.

2. Experimental

2.1 Preparation of NBR blends

Polyaniline-dodecylbenzenesulfonic acid (PAni.DBSA) and carbon black N330 were used as conductive fillers and a commercial grade of NBR (Nipol DN3350) was used as the rubber host matrix. Dicumyl peroxide and benzothiole disulphide (Perkacit MBTS) were used as the vulcanising agent. Rubber blends were prepared by mixing the rubber and fillers using a two roll-mill according to the formulations displayed in Table 1. The samples were vulcanised at 150 °C using a hot press. The cured samples were tested for its tensile properties, hardness, electrical conductivity, filler dispersion and morphology.

Table 1: Composition of rubber blends

Composition (wt%)	i	ii	iii	iv	v	vi	vii	viii
NBR Nipol DN3350	97.5	95.0	92.5	90.0	80.0	70.0	60.0	50.0
Doped Polyaniline or Carbon Black	2.5	5.0	7.5	10.0	20.0	30.0	40.0	50.0
Dicumyl peroxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
MBTS	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

2.2 Physical testing

Five replicates of each NBR blend were used to determine the tensile properties. The tensile tests were conducted according to British Standard International Organisation of Standardisation [BS ISO] 37 using an Instron universal testing machine. Replicates of each blend were also used to measure the International Rubber Hardness Degrees [IRHD] according to British Standard [BS] 903-A26.

2.3 Electrical conductivity

A Keithley picometer Model 485 and resistivity adaptor Model 6105 were used. For each blend, three replicates of sample were tested for its volume resistivity by applying potentials between 100 V to 500 V at 100 V steps. The conductivity of rubber blends were calculated using the Eq(1) (Yong, 2014).

$$\sigma = \frac{L}{R \cdot A} \quad (1)$$

Where σ is the electrical conductivity, R is the mean of resistance, L is the electrode spacing distance and A is the cross-sectional area of electrode.

2.4 Filler dispersion and morphology

The cross sections of rubber blends were studied with an Alpha Tech DisperGrader to determine the dispersion of filler in the rubber. To illustrate the dispersion of the filler, an ultra-thin sample (ca. 150 nm) of each blend was cut using a microtome and viewed under FEI Tecnai G2 transmission electron microscope (TEM).

3. Results and discussion

3.1 Physical Properties

Hardness of a material measures the resistance of a material to change its shape. As depicted in Figure 1, the hardness of NBR blends decreased slightly but then increased with increasing concentration of PAni.DBSA. According to Poussin et al. (2003), this could be attributed to the glassy nature of PAni.DBSA and the reduced in stickiness and rubbery texture of the rubber blend. At equal amounts of filler, the addition of carbon black exhibited a higher degree of hardness compared to PAni.DBSA blends which suggests that the compounds have better abrasion and extrusion resistance. This was due to the hard and rigid nature of carbon black which increases the stiffness of rubber blends (Yong, 2011).

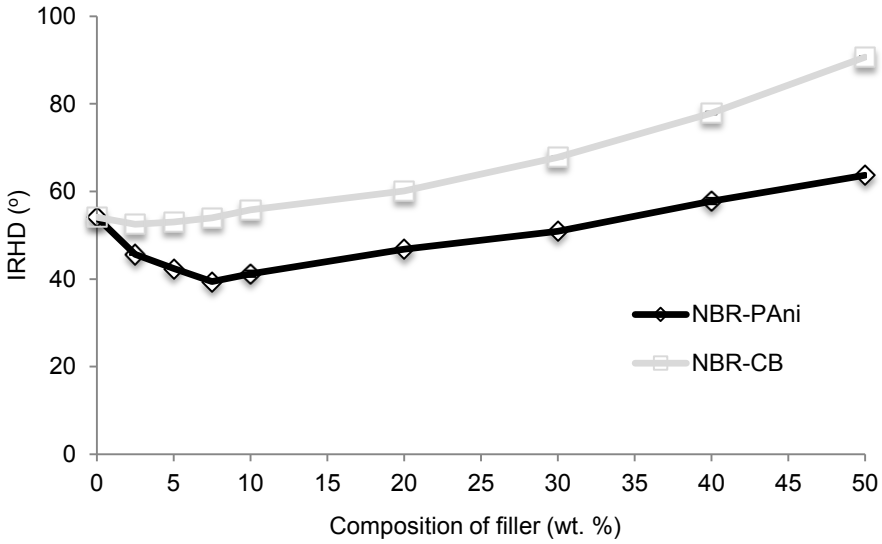

Figure 1: Hardness values of NBR blends with different types of filler

Tensile strength measures the capacity of material to withstand loads. It is clear from Figure 2 that the tensile strength of NBR compounds were greatly increased with the addition PAni.DBSA and carbon black fillers. Both PAni.DBSA-filled and carbon black-filled compounds showed similar tensile strength up 20.0 wt% filler loading. As the concentration of fillers was increased above 20.0 wt%, a visible discrepancies can be seen. The tensile strength of NBR-PAni.DBSA had increased up to 28 % whereas the tensile strength of NBR-carbon black had increased up to 56 % which is twice the increment of NBR-Pani.DBSA compounds. Contradictory, the elongation at break of NBR-PAni.DBSA compounds were higher than carbon-filled compound which implies that the addition of carbon black induces stiffness to the compound as shown in Figure 3. Schuur and Gaymans (2005) stated that the increased in stiffness is due to increasing crosslinking density and decreasing mobility of rubber chain as carbon black loading increases.

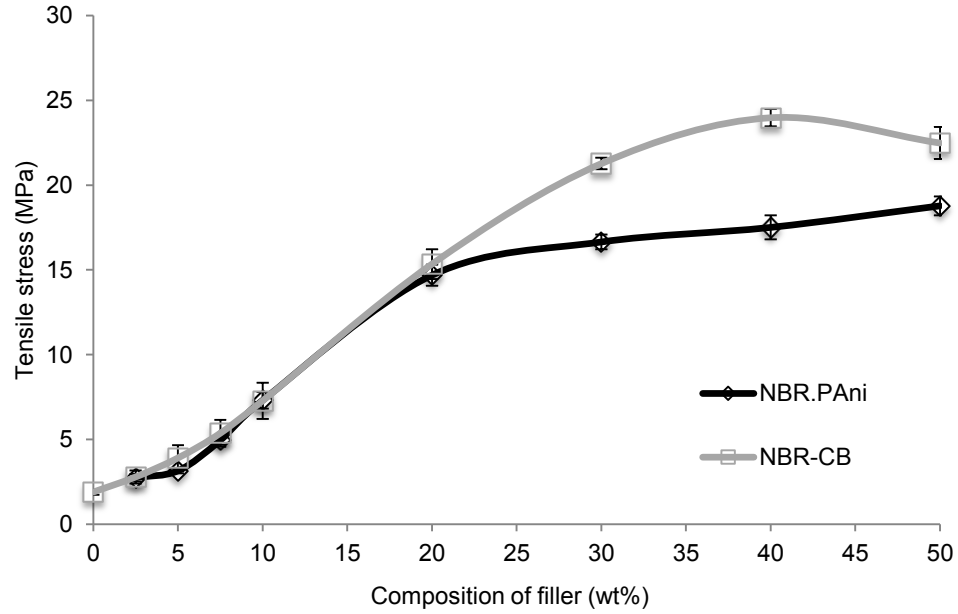

Figure 2: Tensile strengths of NBR blends with different types of filler

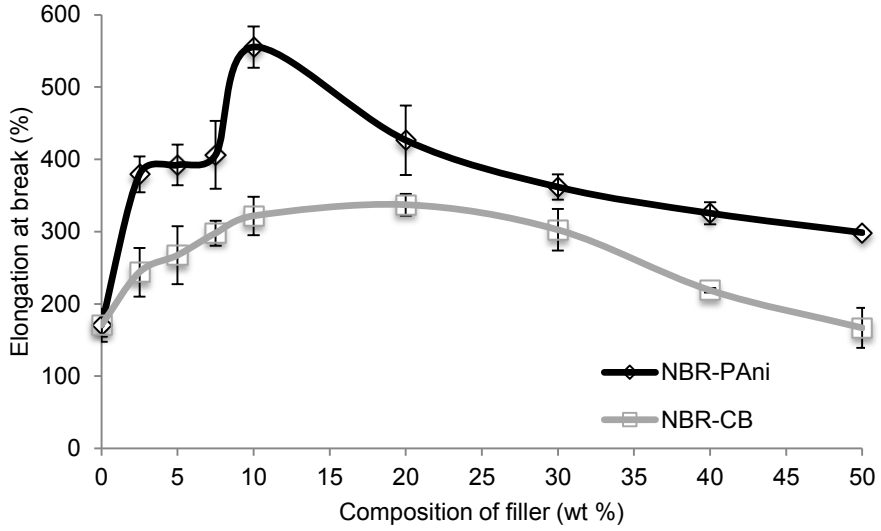

Figure 3: Elongation at break % of NBR blends with different types of filler

3.2 Electrical conductivity

Figure 4 shows the calculated electrical conductivity of NBR blends with different composition of fillers. No filled-NBR compound has a conductivity of 1 x 10^{-8} S.cm^{-1} which indicates a good insulation property. In general, the electrical conductivity of NBR blends improved by several orders of magnitude with the addition of either carbon black or PAni.DBSA. The conductivity of NBR-PAni.DBSA markedly increased as the proportion of PAni.DBSA increases. At the highest PAni.DBSA loading, the electrical conductivity calculated was 1 x 10^{-1} S.cm^{-1}. The electrical conductivity of carbon black-filled blends remained similar at 1 x 10^{-8} S.cm^{-1} before significantly increased after 30.0 wt% carbon black loading. At the highest carbon black loading (50.0 wt%), the electrical conductivity of NBR-carbon black blend was 1 x 10^{-4} S.cm^{-1}. It is clear that the electrical conductivity of PAni.DBSA blends were greater than carbon black blends.

Percolation threshold is the filler fraction in which a continuous path is formed, resulting in conductivity much higher than the value below percolation threshold (Chung, 2010). The estimated electrical conductivity percolation thresholds were obtained by fitting the data to a simple percolation model as shown in the Eq(2) (Yong, 2014).

$$\sigma = cf - f_p{}^t \tag{2}$$

Where c is a constant, t is the critical exponent, f is the filler fraction and f_p is the filler fraction at percolation threshold. As depicted in Table 2, the estimated percolation threshold for NBR-PAni.DBSA and NBR-carbon black blends were 2.5 wt% and 30.0 wt%. The critical exponent, t values for both types of blends were in the range of 3 - 4 which can be explained by a single-percolation model (Yong and Mt Saad, 2010).

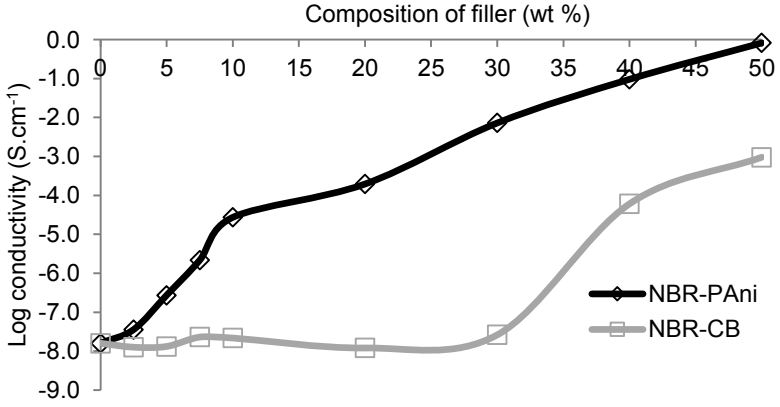

Figure 4: Electrical conductivities of NBR blends with different types of filler

Table 2: Electrical conductivity percolation threshold of NBR blends with different types of loaded filler

Filler	Estimated percolation threshold, wt%	Critical exponent, t	Correlation coefficient, R^2
PAni.DBSA	2.5	4.2	0.96
Carbon black	30.0	3.9	0.99

4. Filler dispersion and morphology

The dispersion of PAni.DBSA and carbon black fillers in NBR obtained from the DisperGrader were displayed in Figure 5. It is apparent that the dispersion of PAni.DBSA and carbon black fillers was comparable to each other. The dispersion of the fillers in NBR host matrix ranged between 89.9 - 99.8 % which indicates well distributed filler and homogenised compounds.

Examples of TEM images of 5.0 wt% and 50.0 wt% PAni.DBSA in NBR host matrix are displayed in Figure 6. It can be seen that PAni.DBSA particles were scattered and isolated at low concentration, but connected to each other as the concentration of PAni.DBSA increases, providing a conducting path. Shehzad et al. (2013) stated that as the proportion of PAni.DBSA increases towards the percolation threshold, the scattered PAni.DBSA fillers becomes closer to each other resulting in a continuous electrical conductivity network. Since there is a thin layer of insulating polymer i.e. rubber between the fillers, the electric current is transported by tunnelling (Li et al., 2007). It was reported that the ideal inter-particle distance for tunnelling is less than 1.8 nm (Li et al., 2007).

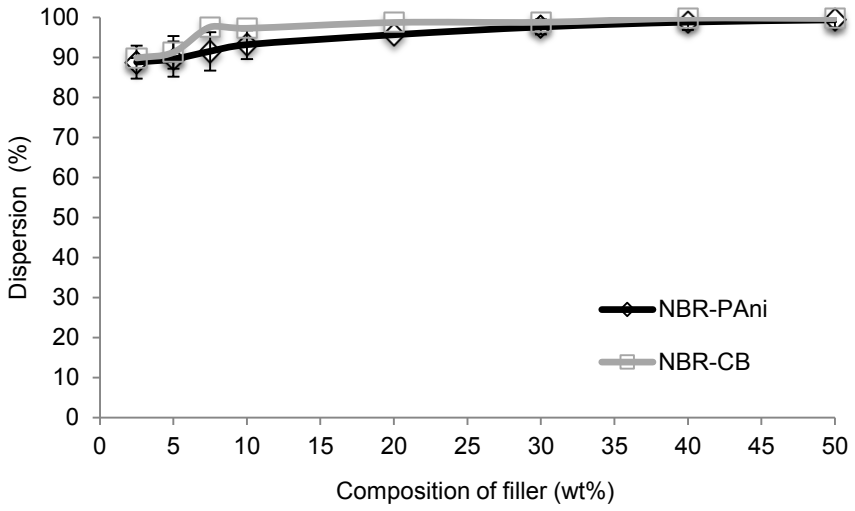

Figure 5: Filler dispersion (%) of PAni.DBSA and carbon black in NBR matrix

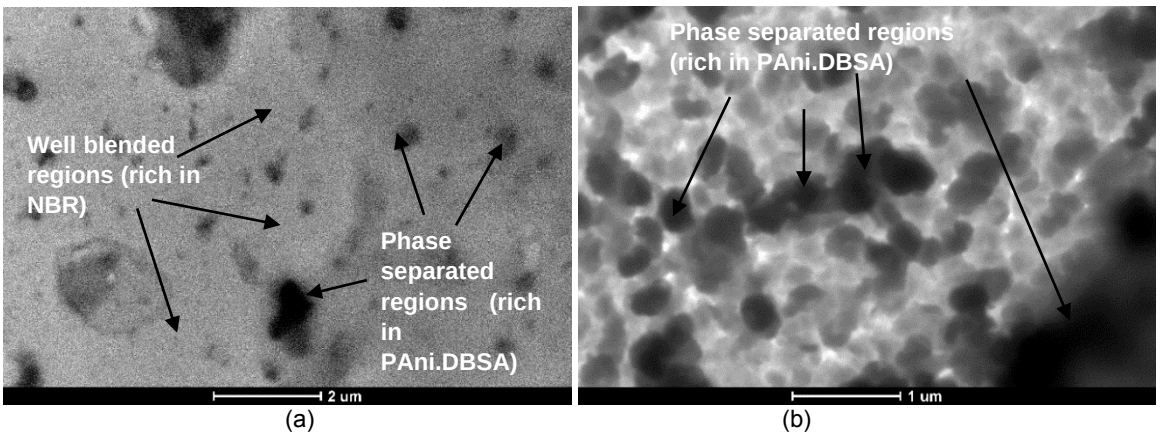

Figure 6: Transmission electron micrographs of NBR based blends; (a) at 5.0 wt% PAni.DBSA content (b) at 50.0 wt% PAni.DBSA content

5. Conclusions

Formulation of electrically conductive NBR based blends was successfully optimised via the evaluation of performance of PAni.DBSA and carbon black as selected conductive fillers. Both fillers were well distributed in the NBR matrix and all blends' physical properties improved with increasing filler loadings. PAni.DBSA offered similar physical strength reinforcement effect if compared to carbon black. PAni.DBSA-filled blends resulted in a more superior electrical conductivity with very low percolation threshold value at only 2.5 wt% (12 times lower than carbon black filled one). Transmission electron micrographs showed that more conductive networks formed as concentration of PAni.DBSA filler enhanced. The electrical conductivity of NBR-PAni.DBSA blends increased up to 1 x 10^{-1} S.cm^{-1} which is four magnitude orders higher than carbon black-filled blends. Due to excellent electrical and good physical properties, NBR-PAni.DBSA blends (10.0 - 50.0 wt% of PAni.DBSA contents) show potential as an emerging conductive material especially for electromagnetic shielding, sensors and antistatic material application.

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