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Electrical and Mechanical Properties of Silicone Electrical Conductive Adhesives (ECAs) Filled Carbon Black Treated with 3-Aminotriethoxysilane at Elevated Temperature

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Abstract: In this study, different formulation of silicone filled carbon black electric conducting adhesive (ECAs) were successfully fabricated. Carbon black (CB) was treated with 3-aminotriethoxysilane to improve the surface adhesion by grafting of amide functional groups on the surface of the CB. Various loading of untreated and treated CB (0%,5%,10% and 15%) on silicone ECAs using film casting method were prepared and characterized. The characterization was performed on the conductive adhesive film by using Fourier Transform Infrared Spectroscopy (FTIR), hardness and tensile testing. While for the electrical property, electrochemical impedance spectroscopy (EIS) was investigated. The FTIR spectrums confirmed the surface modification of CB with 3-aminotriethoxysilane and amide functional groups was presence at 1549 cm-1, 1250.7 cm-1, 1126.6 $cm^{-1,}$ 976.16 cm^{-1} and 860.02 cm^{-1} corresponding to the N-H, SiO-H, Si-O-Si, C-N and C=C stretching vibrations of the amino groups ($-R-NH_3^+$) respectively. The conductivity of the ECAs was dependent on the CB loadings. As the CB loading increased, the conductivity of adhesive conductive film was increased up to 10% of CB loading and decreased when at 15% of CB loading. This is due to the gap distance of interparticle of silicone and CB is high. Whilst the tensile strength of the silicone filled CB increased with increasing of CB content both untreated and treated CB at 0.05954 MPa and 3.3027 MPa respectively. This is supported by hardness testing also showed the same trend with increment of CB loading, the hardness value also increased. The optimum value was found at 42 and 54 for untreated and treated CB respectively. The optimum formulation of electric conductivity was found at 10% loading of CB at 1.75E-08 □/cm. The conductivity of ECAs filled CB at elevated temperature exhibits increment trend of untreated/treated CB at temperature of 100 °C to 160 °C however decreased at 180 °C. It is believed that with increasing the temperature, the interparticle average distance increase due to the difference in the thermal expansion of silicone and carbon black. The utilization of treated CB in silicone ECAs improved the conductivity and mechanical properties giving way to a full potential of using CB as filler.

Keywords: Electrical conductive adhesive, silicone, conductivity, mechanical properties, electrochemical impedance spectroscopy (EIS)

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1. Introduction

An electrical conductive adhesive (ECAs) is a glue that is primarily used for electronics application. The ECAs offer numerous advantages compared to soldering technology such as more environmentally friendly, lower processing temperatures, less steps in processing that reduce the processing costs, and increase the capacity of fine performance due to small sized conductive fillers. ECAs are mainly composed from organic or polymeric matrices usually epoxy, silicone, polyurethane or polyamide and filled with conductive metal fillers such as carbon black, graphite flakes, and micron or nano-sized metal particles such as silver, nickel, copper or aluminum [1,2]. The electrical properties are provided by conductive fillers whilst polymer matrices give mechanical properties.

Among all the polymeric matrices, ECAs based silicone have seen tremendous growth recently in rapid development of flexible and stretchable electronic because of their unique elasticity combination, moisture resistance, thermal stability, bio-compatibility and flexibility. Apart from that, silicone are high value polymers that contain a Si-O-Si-O chain rather than of C-chain. The larger Si-O bond energy (~110 kcal/mol) compared with C bond (~80 kcal/mol) provides superior stability and durability against ultraviolet light and high temperatures [3]. Although they have excellent mechanical characteristics, the electrical efficiency of silicone-based ECAs is limited thus prevents their prevalent usage in electronic industry. This limitation of electrical conductivity deteriorates the performance of silicone-based ECAs in the electronics application. Therefore, the incorporation of conductive filler is compulsory in order to improve the electrical properties. Carbon black (CB) is introduced as an alternative. Although CB's conductivity is not superior to silver and copper, it can provide an effective alternative to electricity conductivity and the cost is cheaper than other conductive fillers [4]. CB is found in everyday nickel hydride, lead acid and rechargeable lithium-ion batteries.

The right amount of conductivity can be obtained from the incorporation of small amount of CB to the systems. However due to the incompatibility of CB and silicone, hence, the surface modification is proposed. Surface modifiers containing functional groups of amines can improve the electrical conductivity of CB in particular [5]. Increasing the surface properties increases the filler and polymer affinity for achieving a well-integrated structure 3-Aminopropyltriethoxysilane (APTES), which conventional silane coupling agent, is therefore used as surface modification devices. CB surface filling chemistry is altered by the addition of functional groups to improve electrical conductivity, wetting property and filler dispersion. In this study, silicone based ECAs filled with various amount of carbon black was study at elevated temperature. 3-Aminopropyltriethoxysilane are used as surface modifier to improve electrical conductivity by altering the surface chemistry of the CB. The solution was made of casted glass slide mold with different CB loading (0%, 5%, 10%, 15%) and the effect of conductivity and mechanical properties of ECAs was study at elevated temperature (100 °C, 120 °C, 140 °C, 160 °C, 180 °C).

2. Materials and Method

2.1 Materials

Polydimethylsiloxane (PDMS) was bought from Celtite Sdn Bhd and carbon black was bought from Sigma Aldrich. Both were used as received.

2.2 Method

Surface treatment of carbon black

APTES solutions were prepared by diluting APTES silane coupling agents with distilled water to achieve a composition of the surface modifier of 1 wt% then mixed with carbon black particles. The mixture was agitated using mechanical stirrer at 350 rpm at room temperature for 10 min in a beaker [6].

Preparation of carbon black filled silicone film

Table 1 depicts the formulation used in this study. The 6.24 g of silicone were mixed with different loading (0%, 5%, 10%, 15%) of treated carbon black in a beaker. The mixture was stirred using mechanical stirrer at 350 rpm at room temperature for 10 minutes. It is then were poured into a cleaned glass slide mold (75 mm x 26 mm) and cured in the oven at 100 °C for 1 hour.

Table 1 - Formulation of CB and silicone used

Sample	CB (%)	Silicone (g)
Si/CB_0	0	6.24
Si/CB_5	5	6.24
Si/CB_{10}	10	6.24
Si/CB_{15}	15	6.24

2.3 Characterization and Testing

The samples were tested using electrochemical impedance spectroscopy (EIS) at elevated temperature [7], Fourier Transform Infrared (FTIR) spectroscopy, hardness test (ASTM D2240-05 (2010) type A) and Instron Tensile Tester (DIN EN 53504).

3. Results and Discussion

3.1 FTIR

Figure 1 shows the presence of peak at 3771.7 cm-1 and 1805.25 cm-1 attributed to the presence of hydroxyl groups (-OH) and (C=O) respectively, on the surface of the untreated CB. According to [8], bulk structure of CB contains large amount of active carbon sites owing to its high surface area and these active sites are the potential centers for a chemical reaction such as oxidation. The FTIR spectra of treated CB reveal the same result as there is increase in the intensity of absorption peak at 3740 cm-1 was observed for the -OH functionality and peak at 1840.13 cm-1 is due to the C=O bending deformation in -COOH. All the observations indicated that the surface of CB has been functionalized by the oxidation of active carbon sites during surface treatments of 3-aminopropytriethoxysilane.

Although 3-aminopropyltriethoxysilane treated CB shows the larger amount of surface carbonyl groups (C=O) when compared to untreated CB, treated CB improves electrical conductivity much more than untreated CB does (Koysuren et al. 2007). This reason was supported by amide functional groups that appeared on the treated CB surfaces. Hence, the new bands appeared at 1549 cm-1, 1250.7 cm-1, 1126.6 cm-1, 976.16 cm-1 and 860.02 cm-1 corresponding to the N-H, SiO-H, Si-O-Si, C-N and C=C stretching vibrations of the amino groups (-R-NH3+), respectively. These spectrums indicate the reaction of 3-aminopropytriethoxysilane on the surface of CB.

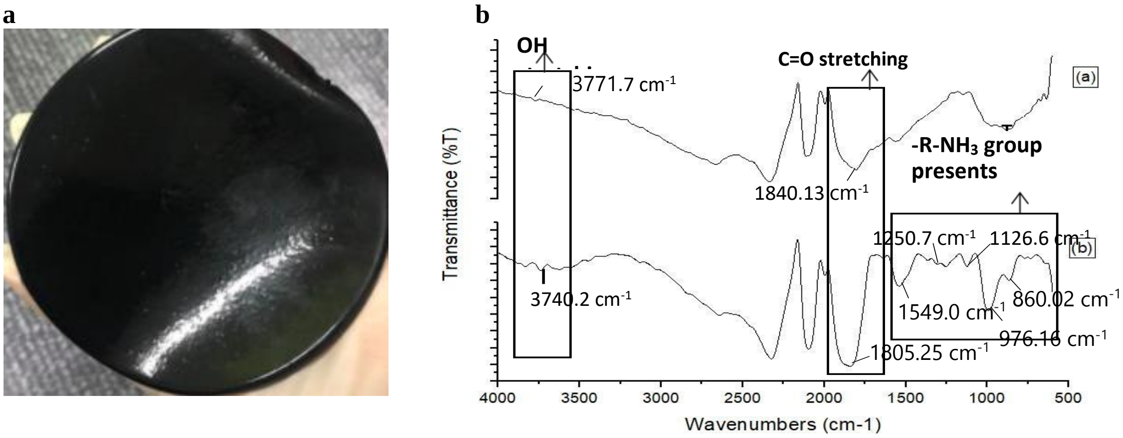

Fig. 1 – (a) Sample of silicone electrical conductive adhesives filled carbon black; (b) FTIR spectra of treated and untreated carbon black; (c)untreated CB; (d) treated CB

3.2 Tensile

Figure 2 shows the effect of CB loadings on the tensile properties of silicone ECAs filled untreated and treated carbon black conductive polymer film. It can be seen that untreated samples display increment in tensile strength with increasing in the CB content. The modification of CB with 3-aminopropytriethoxysilane had shown better improvement in tensile strength up to 80% as compared to untreated CB. This is due to the present of the amide functional groups to the CB surface making more interaction can be formed. It is apparent that the tensile strength was gradually increase with increasing CB content until 10% for both untreated and treated carbon black at 0.05954 MPa and 3.3027 MPa respectively. In addition, as similar reported by Siti *et al.* (2014) increasing of carbon black loading increased the surface interaction of carbon black, which was decreased the chain mobility of silicone filled treated carbon black.

However, at 15% CB loading for treated/untreated, it is found that its presence hindered the mobility of macromolecule chain segments in silicone blends at 0.04781 MPa and 2.9601 MPa for untreated and treated CB respectively. Similar finding is reported by [8], the strength of micro fiber composite-structured fibers reduced when the nominal carbon black level in the composite formulation is raised

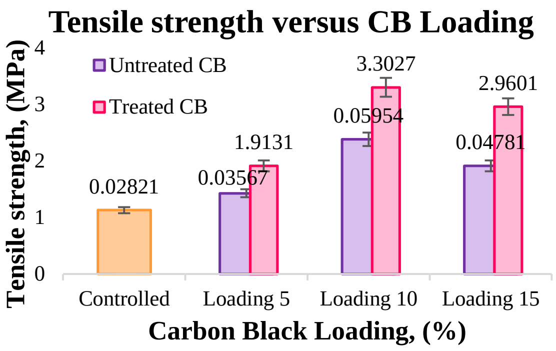

Fig. 2 - Tensile strength with various loading of CB

3.3 Hardness

There is an increment in hardness of silicone ECAs with increasing of CB loadings. Similar finding reported that as expected hardness increases continuously with increasing filler content [10]. The treated CB filled ECAs display greater in hardness in comparison with untreated CB at 52 and 42 respectively. However, at 15% of CB loading, the hardness value decreased because of poor surface interaction of CB, which decreased the chain mobility of silicone filled treated carbon black [11].

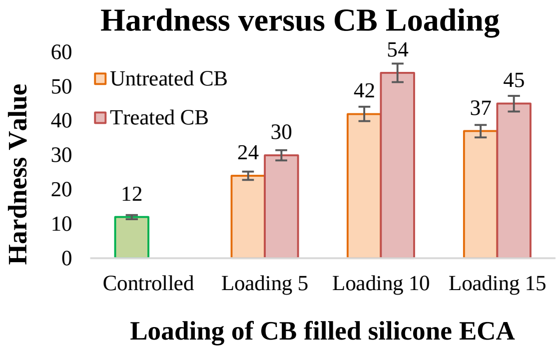

Fig. 3 - Hardness value with various loading of CB

3.4 Conductivity

Figure 4 and Figure 5 shows the change of volume resistivity and conductivity as a function of untreated/treated CB on the silicone ECAs. As the CB loading is increased, in a certain region the resistivity decreases rapidly by 8 to 10 orders of magnitude as stated by [12].

The higher the CB loading, the higher the conductivity of the silicone film and the optimum found at 10% carbon black loading where 1.75E-08 s/cm while the resistivity of the silicone film was decreased at 10% carbon black loading of 3.78E-04 s/cm. The conductivity of the treated CB at 1.75E-08 s/cm shows the greater values when compared to the untreated CB at 1.43E-08 s/cm due to presence of APTES as surface treatments. This was supported by Li et al., al that the higher structure of APTES having high surface area, easy formation of conductive networks at lower loading of CB and exhibit a lower resistivity [12]. However, after the optimum CB loading, the conductivity of the film decreased due to the interparticle distance are smaller hence increased the resistivity.

In addition, the temperature dependence of resistivity and conductivity at different CB loading was also observed as shown in Figure 6 and 7. The optimum temperature obtained at 160 °C regardless with or without the treatment. According to Li et al., it is believed that with increasing the temperature, the interparticle average distance increase due to the difference in the thermal expansion of silicone and CB [1,12,13]. It means that the interparticle of untreated CB which are van der walls bonding have the lower bonding when compared to interparticle of treated of carbon black. The higher the interparticle average distance, the higher the gap of silicone and carbon black therefore, the thermal expansion is larger which means that the silicone film can conduct the electrical at optimum value of 160 °C. However, after the optimum temperature, at 180 °C, the conductivity of the silicone film decreased due to the thermal expansion are smaller, hence reduce the conductivity.

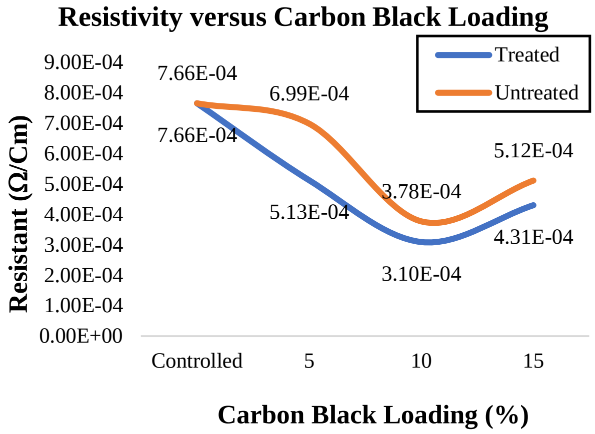

Fig. 4 - Resistivity of various carbon black loading filled silicone

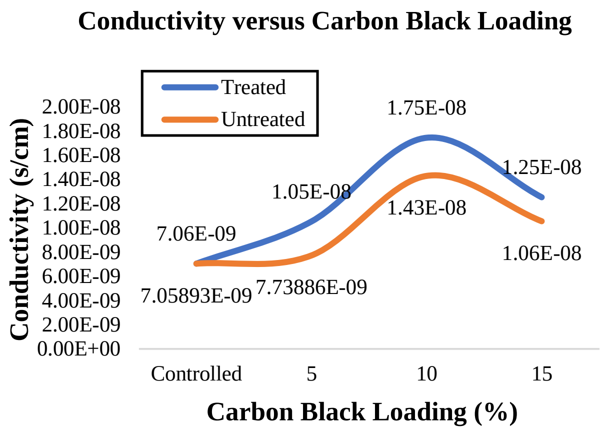

Fig. 5 - Conductivity of various loadings of untreated and treated carbon black filled silicone

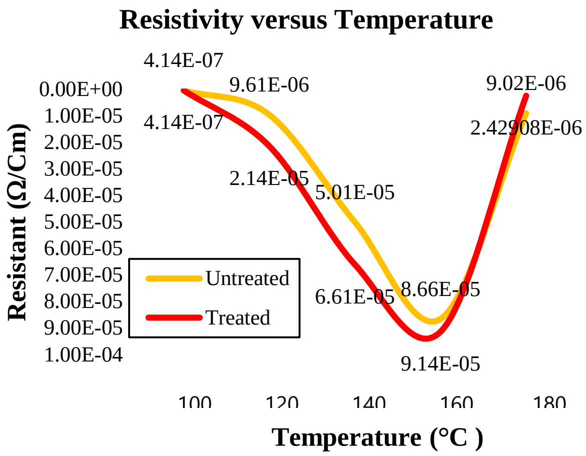

Fig. 6 - Resistivity of temperature for various loadings of carbon black filled silicone at elevated temperature

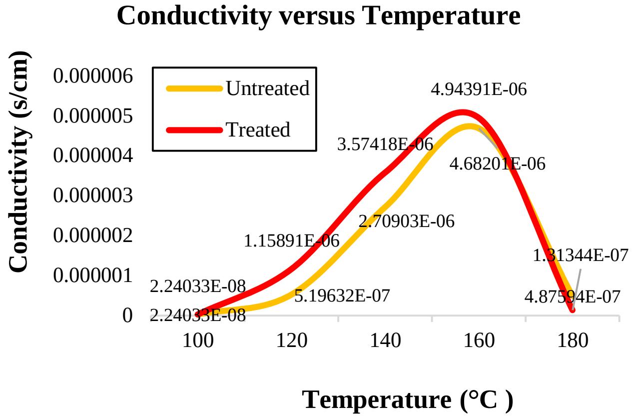

Fig. 7 - Conductivity versus temperature for untreated carbon black and treated carbon black filled silicone

4. Conclusion

As conclusion, the modification of CB with APTES has been successfully improved he mechanical and electrical properties of the silicone ECAs. The FTIR spectrums show the appearance of amino groups on the surface of the CB. The intensity of N-H, SiO-H, Si-O-Si, C-N and C=C peaks also shifted upwards as the loading of treated CB increased. This is because treated CB film absorb higher transmittance. Whilst the incorporation of CB treated and untreated up to 10% increase the electrical conductivity of the film but further increment produces low electrical conductivity. The highest conductivity was achieved when carbon black loading at 10% with 1.75E-08 s/cm but when carbon black loading at 15%, the conductivity decreased at 1.25E-08 s/cm. This is due to increasing of CB loading in silicone, it will increase the conductivity of the film. Furthermore, when the surface treatment of carbon black was done, the conductivity of the film increased then the untreated CB due to amide functional groups that presents on the surface of treated CB. The same trend is obtained in mechanical properties such as tensile and hardness at 10% CB loading regardless treated on untreated at. This is due to the larger surface interaction of carbon black, which decreased the chain mobility of silicone filled treated CB.

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