

JOURNAL OF APPLIED SCIENCES RESEARCH

JOURNAL home page: <http://www.aensiweb.com/jasr.html>

2015 April; 11(5): pages 6-12.

Published Online: 27 January 2015.

Research Article

Effect of Surface Treatment on Carbon Black Filled Epoxy Composites.

Keat Yeoh, Cheow, Supri Abdul Ghani Leng Teh, Pei Luen Phua-Jin

School of Materials Engineering, Universiti Malaysia Perlis, 02600 Jejawi, Perlis, Malaysia

Received: 25 November 2014; Revised: 26 December 2014; Accepted: 1 January 2015

© 2015 AENSI PUBLISHER All rights reserved

ABSTRACT

Carbon black (CB) is often used to modify the properties of the medium in which it is dispersed and well known for its superior properties in mechanical, thermal and electrical properties. One major drawbacks of CB when introduced into polymer matrix, like epoxy, is its natural characteristic of being easily agglomerate and reagglomerate after mixed into the polymer matrix. In this paper, surface treatment through heat oxidation method was done to the CB powder, in order to improve the dispersion state of CB inside polymer matrix. The modified and unmodified CB filled epoxy composites were prepared and were compared in term of density, flexural, fracture toughness, electrical conductivity and thermal stability properties. The treated CB were furthered investigated using FTIR and XRD to verify the surface modification process. Heat oxidation of CB filled epoxy composites shows an improved properties in flexural, fracture toughness and electrical conductivity as compared to the unmodified CB filled epoxy composites.

Keywords: Epoxy; carbon black; composites, surface treatment.

INTRODUCTION

Carbon black (CB), often used to modify the mechanical [1-4], electrical [5-12] and optical [13-15] properties of the medium in which it is dispersed, usually polymer matrixes such as rubber and plastics. According to ASTM D3054-04, the standard defined CB as an engineered material, primarily composed of elemental carbon, obtained from partial combustion or thermal decomposition of hydrocarbon. The surface morphology of CB has a strong influence on its wettability in polymer matrix and properties on the final product [16, 17]. CB consists of aggregates, defined as the smallest dispersible units, which are composed of partially fused, reasonably spherical primary particles, and the surface area increase as the primary particle size is reduced [18].

Unmodified CB cannot be used directly for certain application, where the desired surface properties of CB cannot be obtained through traditional manufacturing process. Two approaches adopted for modification of CB are in-process modification, the addition of components for in situ modification of CB in reactor and post-process, the surface of carbon black is treated to improve its properties. According to Smith and Polley [19], when a standard carbon black is treated with air or oxygen at temperature from 300 - 650°C, a six fold increase in surface area will be noted, as measured by nitrogen adsorption, without appreciable reduction in particle diameter. Through heat treatment, oxidation

of CB occurs, thus increasing the amount of oxygen containing functional groups on the surface and even converting the CB to CO or CO₂, thereby roughening the surface, thus increasing the surface area [20].

The introduction of CB into epoxy matrix has been widely studied for the past decades. Under normal circumstances, untreated CB will have difficulties to form good interfacial interaction between the filler and matrix leading to weaken in mechanical properties of the composites. Epoxy, a thermoset polymeric material, well known for its superior properties and ease of process-ability and will undergo study in this paper with the addition of untreated and treated CB into it [21, 22]. In this paper, CB was undergone heat treatment using conventional furnace in air up to 500°C. The untreated and treated CB will be compare in term of FTIR, density, flexural, fracture toughness, electrical resistivity and conductivity, thermal stability, and fracture surface morphologies.

*Experimental:**Materials:*

Both epoxy resin DER 331, with density 1.16g/cm³, and clear epoxy hardener was provided by Euro Chemo-Pharma Sdn. Bhd. and was mixed according to the stoichiometric ratio. Carbon black, Conductex® K Ultra®, which was provided by Columbian Chemicals Korea, with average particle size 11µm, NSA 190m²/g, density 1.75g/cm³.

Surface treatment of CB:

The CB powder was heat treated and undergo oxidation in a furnace at 500°C for one and a half hour at the heating rate of 20°C/min. This is to remove the naturally oxidized group on surface of CB and to generate the carbon – oxygen (C=O) group on the CB's surface. After cooling process, the agglomerate CB powder were crushed into fine powder using lab mortar before proceed mix into epoxy resin.

Sample preparation:

Based on previous research [23], 15 vol.% of untreated CB was added into epoxy resin and mixed for 10 minutes and it was followed by the addition of clear epoxy hardener, according to the stoichiometric ratio. The mixtures was then cast into a mold and degassed for 10 minutes under vacuum. The samples were cured for 100°C for 1 hour and followed with post-cured for another 1 hour using a conventional air oven. The samples were cooled to room temperature before they demolded. The treated CB was also undergo the same procedures as mentioned earlier.

Characterization:

The functional groups of surface treated CB powder were analysed using Perkin Elmer Spectrum RX Fourier Transform Infrared Spectroscopy (FTIR) – Attenuated Total Reflectance (ATR). The FTIR spectra were recorded within the range of 650 – 4000cm⁻¹ with scanning number of 4. Density was determined using gas pycnometer density analyser, Micromeritics AccuPycII 1340 V1.05. Each samples were tested for 10 cycles, under flowing of helium gas, at room temperature. Flexural strength and modulus was determined using Instron 5569 Universal Testing Machine (UTM). The test was done according to ASTM D790 with 3-point bending at room temperature with crosshead speed of 2.38mm/min. Fracture toughness was done according to ISO 13586, using Instron 5569 Universal Testing Machine (UTM). The single edge notched samples were cut and subjected to static tensile loading (SEN-

T), with loading speed of 1mm/min at room temperature. The samples notching was done by sawing and sharpening with razor blade. Scanning electron microscopy (SEM) used was model JEOL JSM – 6460 LA and the samples surface were sputter coated with a thin layer of palladiums which using the auto fine coater, model JEOL JFC 1600. Electrical resistivity and conductivity were measured using Fluke 8845A/8846A 6.5 digit precision multimeter. Resistance was measured during the testing and bulk resistivity of each samples were calculated according to Equation 1 and 2.

$$\text{Bulk resistivity} = (R \cdot A) / h$$

$$\text{Bulk conductivity} = 1 / (\text{Bulk resistivity})$$

where,

R = resistance, Ω

A = cross-sectional area, cm²

h = samples thickness, cm

Result and Discussion

FTIR:

The FTIR spectra were recorded for the untreated and treated CB powders in Figure 1. From the analysis, the spectrum of treated CB powder display bands at wave number 1750 – 1500 cm⁻¹, which indicating the presence of carbonyl or carboxyl groups as compared to the untreated CB powder spectrum, which did not shows any bands at that particular wavelength. In addition, the treated CB powder spectrum also shows strong band at wave number 2500, indicating hydroxyl group.

Density:

The density of pure epoxy, untreated and treated CB filled epoxy composites was shown in Figure 2. The density of unfilled epoxy was recorded at 1.153g/cm³, while the CB filler loading for the untreated and treated CB filled epoxy composites were fixed at 15 vol.%. The density of CB filled epoxy composites after heat treatment did not show significant difference as compare to the untreated CB filled epoxy composites, at which the density of both composites recorded at 1.261g/cm³.



Fig. 1: FTIR spectra for untreated and treated CB.

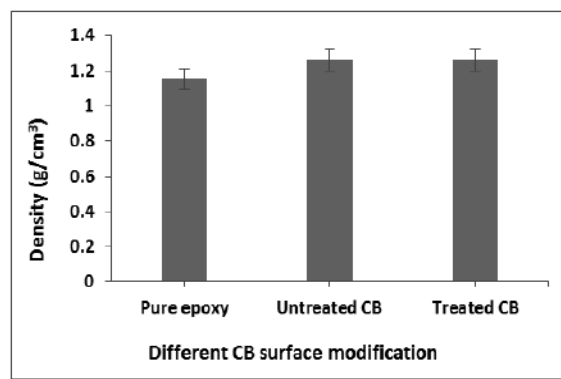


Fig. 2: Density of epoxy/CB composites with different surface treatment on CB.

Flexural strength and modulus:

The flexural strength and modulus of pure epoxy, with untreated and treated CB filled epoxy composites was shown in Figure 3. The flexural strength of untreated CB filled epoxy composites was weakened as compared to the flexural strength of pure epoxy, where the flexural strength of pure epoxy was recorded at 58.2 MPa. As expected, the flexural strength of treated CB filled epoxy composites were improved as compared to both pure epoxy and untreated CB filled epoxy composites.

For flexural modulus in Figure 3, the same behaviour as flexural strength was observed, where the flexural modulus of epoxy decreased with the addition of untreated CB into epoxy resin, but improved with the addition of treated CB. Modulus of elasticity from flexural test often referred as the rigidity of the material, where a relatively high modulus material is expected to withstand a higher force applied.

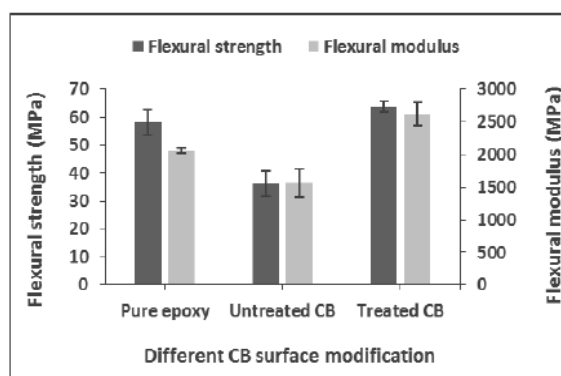


Fig. 3: Flexural strength and modulus of epoxy/CB composites with different surface treatment on CB.

As observed from Figure 4(a), the SEM micrograph of the flexural fracture surface of pure epoxy exhibit a glassy and smooth surface, which representing the typical characteristic of a brittle thermoset materials. With the addition of 15 vol.%, untreated CB into the epoxy resin, the flexural surface in Figure 4(b), become rough and uneven, where the crack lines become corrugated. This phenomena explained the poor flexural strength and modulus of untreated CB filled epoxy composites. In Figure 4(c), the SEM micrograph of treated CB filled epoxy composites exhibit a glassy-like surface. Upon higher magnification, the crack lines of treated CB filled epoxy composites is visible and uniform as compared to the SEM micrograph of untreated CB filled epoxy composites. This further explained the improvement of the flexural strength and modulus of the composites.

Fracture toughness:

Fracture toughness is a generic term for the measurement of material resistance to extension of a crack and is one of the important properties of materials for many design applications. Figure 5 shows the fracture toughness of pure epoxy, untreated and treated CB filled epoxy composites. The fracture toughness of untreated CB filled epoxy composites shows poor fracture toughness properties as compared to the unfilled epoxy. The natural characteristic of CB, which tend to agglomerate before and re-agglomerate after mixing into polymer matrix (Roy, Sengupta *et al.*) explained the poor fracture toughness performance of untreated CB filled epoxy composites. The treated CB filled epoxy composites show an improved fracture toughness as compared to unfilled epoxy and untreated CB filled

epoxy composites. The aim of heat treatment of CB powder under high temperature is to remove the

impurities on the surface of CB, hence increased the surface area and wettability of CB into epoxy resin.

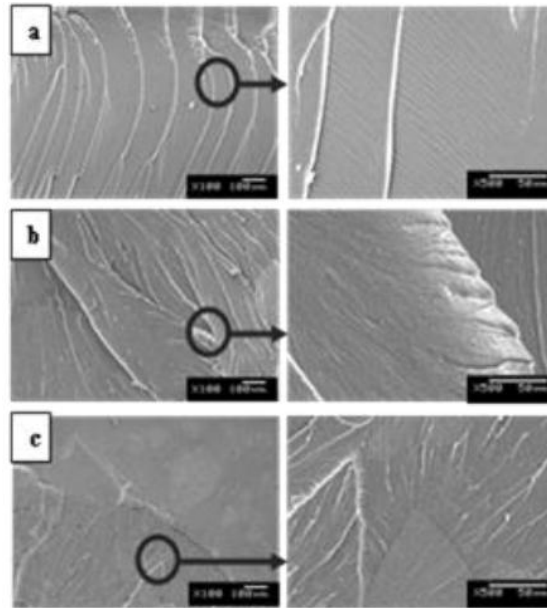


Fig. 4: SEM micrographs of the morphologies generated from (a) pure epoxy, (b) untreated CB and (c) treated CB filled epoxy composite.

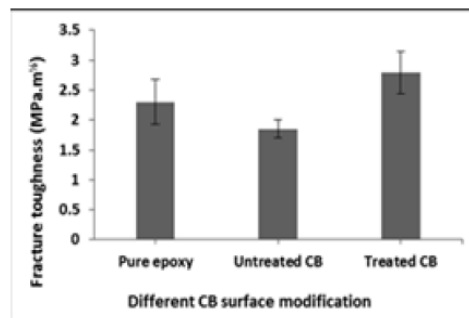


Fig. 5: Fracture toughness of epoxy/CB composites with different surface treatment on CB.

Electrical bulk resistivity & conductivity:

In Figure 6 shows the electrical bulk resistivity and conductivity of untreated and treated CB filled epoxy composites. Under normal circumstances, an unfilled epoxy, exhibit a high electrical bulk resistivity, around 1.0×10^{11} , which represent the properties of an insulator. Upon the addition of CB powder at 15 vol.% filler loading, as from previous study, the electrical bulk resistivity of untreated CB filled epoxy composites drop to 1.0×10^5 and further reduced to 1.0×10^3 , with the same filler loading of treated CB filled epoxy composites. The removal of the impurities on the CB surface is to believe in reducing the resistance of the CB, hence reduced the resistivity of the overall composites.

In definition, the electrical bulk conductivity is the reciprocal of the electrical bulk resistivity, giving

that the lower the resistivity of the composites dropped, the better the electrical conductivity of the composites. From the Figure 6, is observed that the treated CB filled epoxy composites increased 2 order of magnitude as compared to the untreated CB filled epoxy composites.

TGA:

The thermal stability (TGA) of pure epoxy, untreated and treated CB filled epoxy was shown in Figure 7. The pure epoxy shows a typical one step degradation, between temperature $350^\circ\text{C} - 450^\circ\text{C}$, as while as the untreated and treated CB filled epoxy composites. Table 1 shows the thermal stability of pure epoxy, untreated and treated CB filled epoxy composites at 5 and 50% onset degradation temperature.

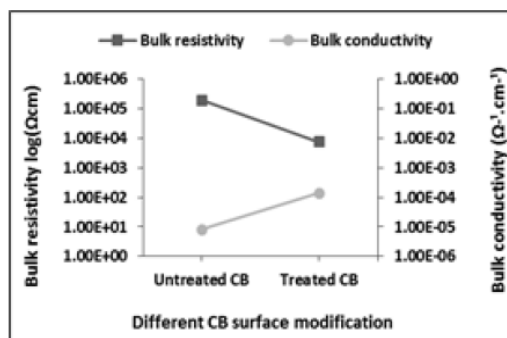


Fig. 6: Bulk resistivity and conductivity of epoxy/CB composites with different surface treatment on CB.

Based on observation, the 5% onset degradation temperature for pure epoxy shows a higher temperature as compared to untreated and treated CB filled epoxy composites. At 50% onset degradation temperature, untreated CB filled epoxy composites exhibit a higher degradation temperature as compared to pure epoxy and treated CB. With the addition of CB powder into epoxy resin, the distribution of CB and the interaction between CB powders with epoxy play an important role in affecting the thermal stability of the end product.

This can be explained by the effect of temperature on the interaction between matrix and

filler. At lower temperature, the cross-linked epoxy chains are fixed and cannot be moved freely, which locked down the interaction between the polymer matrix and filler. Upon reaching high temperature, the cross-linked chains of epoxy are scissored, hence the filler can move freely thus reduced the interaction at a greater rate. This can be further explained by the high thermal conductivity of carbon black as compared to epoxy, hence better heat transfer between the filler to matrix or matrix to filler was happened.

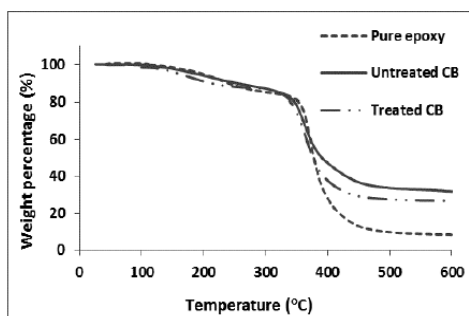


Fig. 7: Thermogravimetric analysis (TGA) curves.

Table 1: Thermal stability of epoxy/CB composites with different CB surface modification.

Different CB surface modification	Temperature (°C)	
	5% weight loss	50% weight loss
Pure epoxy	195.09	377.625
Untreated CB	187.17	391.27
Treated CB	162.43	376.54

4. Conclusion:

At the same filler loading of CB powder into epoxy resin, the untreated and treated CB exhibit a significance effect into the performance of the final composites. There is no obvious difference between the density of untreated and treated CB filled epoxy composites, while an improvement in flexural strength and modulus, fracture toughness, electrical bulk conductivity were observed as compared to untreated CB filled epoxy composites. In the aspect of thermal stability, untreated CB filled epoxy composites has a higher thermal stability as

compared to the treated CB filled epoxy composites. As conclusion, heat treated CB powder have a better wettability into the epoxy resin, hence, improved the overall performance of epoxy resin.

Acknowledgement

The financial support of Research Acculturation Grant Scheme (RAGS) grant no: 9018-00064 is gratefully acknowledged.

References

- Gong, J., *et al.*, 2014. *Combination of fumed silica with carbon black for simultaneously improving the thermal stability, flame retardancy and mechanical properties of polyethylene*. *Polymer*, 55(13): 2998-3007.
- Kasgoz, A., *et al.*, 2014. *Effect of different types of carbon fillers on mechanical and rheological properties of cyclic olefin copolymer (COC) composites*. *Composites Part B: Engineering*, 66(0): 126-135.
- Galimberti, M., *et al.*, 2015. *Delamination of organically modified montmorillonite for reducing the filler networking with carbon black in poly(1,4-cis-isoprene) based nanocomposites*. *Applied Clay Science*, 104(0): 8-17.
- Povacz, M., G.M. Wallner and R.W. Lang, 2014. *Black-pigmented polypropylene materials for solar thermal absorbers – Effect of carbon black concentration on morphology and performance properties*. *Solar Energy*, 110(0): 420-426.
- Wang, F., *et al.*, 2014. *Electrical and mechanical properties of ABS/EPDM composites filled with carbon black*. *Materials Letters*, 125(0): 48-50.
- Mandhakini, M., *et al.*, 2014. *Carbon black reinforced C8 ether linked bismaleimide toughened electrically conducting epoxy nanocomposites*. *Materials & Design*, 64(0): 706-713.
- Zhao, S., *et al.*, 2014. *Synergistic effect of carbon fibers on the conductive properties of a segregated carbon black/polypropylene composite*. *Materials Letters*, 129(0): 72-75.
- Kassim, S.A.E., *et al.*, 2014. *Modelling the DC electrical conductivity of polymer/carbon black composites*. *Journal of Electrostatics*, 72(3): 187-191.
- Cong, P., P. Xu and S. Chen, 2014. *Effects of carbon black on the anti aging, rheological and conductive properties of SBS/asphalt/carbon black composites*. *Construction and Building Materials*, 52(0): 306-313.
- Chen, J., *et al.*, 2013. *Synergistic effect of carbon nanotubes and carbon black on electrical conductivity of PA6/ABS blend*. *Composites Science and Technology*, 81(0): 1-8.
- Carmona, F. and J. Ravier, 2002. *Electrical properties and mesostructure of carbon black-filled polymers*. *Carbon*, 40(2): 151-156.
- Czech, Z., *et al.*, 2012. *Using of carbon nanotubes and nano carbon black for electrical conductivity adjustment of pressure-sensitive adhesives*. *International Journal of Adhesion and Adhesives*, 36(0): 20-24.
- Ibrahim, S., S.M.M. Yasin and M.R. Johan, 2013. *Influence of carbon nanotubes on the optical properties of plasticized solid polymer electrolytes*. *Applied Surface Science*, 276(0): 323-327.
- De Falco, G., *et al.*, 2014. *Optical and electrical characterization of carbon nanoparticles produced in laminar premixed flames*. *Combustion and Flame*, 161(12): 3201-3210.
- Bui, T.S., *et al.*, 2013. *High optical density and low dielectric constant black matrix containing graphene oxide and carbon black on color filters*. *Displays*, 34(3): 192-199.
- Bao, Y., *et al.*, 2011. *Tailoring the morphology of raspberry-like carbon black/polystyrene composite microspheres for fabricating superhydrophobic surface*. *Materials Research Bulletin*, 46(5): 779-785.
- Martínez, L., *et al.*, 2011. *Influence of friction on the surface characteristics of EPDM elastomers with different carbon black contents*. *Tribology International*, 44(9): 996-1003.
- Rwei, S.P., F.H. Ku and K.C. Cheng, 2002. *Dispersion of carbon black in a continuous phase: Electrical, rheological, and morphological studies*. *Colloid and Polymer Science*. 280(12): 1110-1115.
- Smith, W.R. and M.H. Polley, 1956. *The Oxidation of Graphitized Carbon Black*. *The Journal of Physical Chemistry*, 60(5): 689-691.
- Frysz, C.A. and D.D.L. Chung, 1997. *Improving the electrochemical behavior of carbon black and carbon filaments by oxidation*. *Carbon*, 35(8): 1111-1127.
- Biron, M., 5 - *Thermoset Processing*, in *Thermosets and Composites (Second Edition)*, M. Biron, Editor. 2014, William Andrew Publishing: Oxford, pp: 269-297.
- Brostow, W., S.H. Goodman and J. Wahrmund, 2014. 8 - *Epoxies*, in *Handbook of Thermoset Plastics (Third Edition)*, H. Dodiuk and S.H. Goodman, Editors. William Andrew Publishing: Boston, pp: 191-252.
- Phua, J., *et al.*, 2014. *Preparation and characterization of epoxy with carbon black : Effect of carbon black filler loading on electrical, flexural and thermal stability properties*. in *Proceeding of International Postgraduate Conference and Management 2014 (IPCEM 2014)*. Universiti Malaysia Perlis (UniMAP), Perlis.
- Rodrigues Junior, S.A., *et al.*, 2007. *Flexural strength and modulus of elasticity of different types of resin-based composites*. *Braz. Oral. Res.*, 21(1): 16-21.
- Zhu, X.K. and J.A. Joyce, 2012. *Review of fracture toughness (G, K, J, CTOD, CTOA) testing and standardization*. *Engineering Fracture Mechanics*, 85(0): 1-46.
- Roy, N., R. Sengupta and A.K. Bhowmick, *Modifications of carbon for polymer composites and nanocomposites*. *Progress in Polymer Science*, 37(6): 781-819.

27. Zhou, Y., *et al.*, 2006. *Fabrication and evaluation of carbon nano fiber filled carbon/epoxy composite*. Materials Science and Engineering, A., 426(1-2): 221-228.