



## DISPERSION OF CARBON BLACK IN EPOXY RESIN AND THE ELECTRICAL PROPERTY OF THE NANOCOMPOSITE

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### ABSTRACT

The enhanced property of nanocomposite depends largely on the physical property of the dispersed nanoparticle and the state of dispersion of the nanoparticle, a well-dispersed structure generally results in additional enviable nanocomposite properties. In this paper, the carbon black nanoparticles were characterised using XRD, SEM, FESEM, TEM and SAP/BET techniques to establish the morphology and other physical properties of the particle. The CB nanoparticles were dispersed in epoxy resin using a combination of different dispersion techniques to obtain an epoxy resin nanocomposite with a network of carbon black conducting particle. The electrical properties of the nanocomposite were measured with respect to the %wt loading of CB and the percolation threshold was found to be 20 – 25 %wt of CB. The electrical resistivity of the nanocomposite was found to be influenced by the size of the nanoparticles, morphology and the loading content of the CB nanoparticles.

**Keywords:** dispersion, epoxy resin, carbon black, resistivity, conductivity, nanocomposite.

### INTRODUCTION

Epoxies are thermoset and represent the most studied materials in this group of polymer, epoxies have exceedingly broad array of manufacturing applications, such as aerospace, sport gears, automobile, electrical circuit boards, exterior coatings, anti-scratch and anti-corrosive material which possess high bonding strength, hardness, excellent chemical and thermal resistance [1]. Such a wide scope of realistic application is obtained by the suitable choice of the resin-hardener system and with the use of the proper curing environment [2]. There are much up-and-coming application where it is required to disperse nanoparticles into a polymer such as epoxy resin, for instance, Fausan *et al.* [3] fabricated an electronic nose which is a device that can be used to imitate biological human nose by dispersing carbon black in a suitable polymer.

The dispersion of nanoparticles in material matrix are primarily used to increase or advance the properties of the composite material such as electrical properties, mechanical strength, wear resistance, toughness, thermal properties, Optical properties and others.

Dispersion of nanofiller is a key problem in nanotechnology and, therefore, forms an integral aspect of polymer nanotechnology [4]. To enhance physicochemical properties, particle sizes are reduced to the nanometre realm, in that way increasing the general active surface area [5]. Nanoparticles have a high surface to volume ratio which adds to the number of particle-matrix interactions thus increasing the effect of the material properties on the whole. A well dispersed structure generally results in additional enviable nanocomposite properties. Unfortunately this large surface area and reduced size make nanofiller have the tendency to aggregate or cluster owing to the overriding intermolecular Vander Waal interaction between them.

Nanoparticles are unique with size range between 1-100 nm and possess high surface area, they interact with one another in different ways due to quantum changes at

subatomic level and exhibit friction and surface tension in the presence of Vander Waal forces causing them to have the propensity to stick together. Particle agglomerate decrease material performance by the addition of void that acts as favoured site for material failure or dysfunction particularly in nanoscale range.

Another bough of science studies the condition in which some particles dispersed in liquids aggregate. This premise of colloids adequately defines the relations between dispersed particles in addition to the configuration and dynamics of the aggregate arrangement. Even though the correlation to filled polymers is evident, its relevance on filled polymers is not fully recognized.

Nanofiller can be organic or inorganic and can be classified according to their geometry as 3D fillers or particulate, nanofibres or nanowires, nanotubes and nanoplatelets [6]. The configuration of nanofillers describes the cluster morphology of main agglomerate which can be highly compacted (low structure) or highly loose (high structure).

It is broadly established that the conductivity of insulating polymers containing dispersed conductive particles is a consequence of the growth of an arrangement of contacting reinforcing particles. In theory, numerous percolation models have been proposed to describe the situation, particularly the critical reinforcing volume fraction, at which a set of connections is developed in the conductive polymer material [7]. The most well-known was developed by Kirkpatrick [8]

In this geometrical model, a normal assortment on which spherically formed particles are dispersed statistically is examined. In the representation, the essential least amount of reinforcing volume fraction is 16 vol%. This amount agrees with nearly every experimental establish readings, since for nearly every polymer and powdery reinforcement, the experimentally establish critical volume fraction for percolation is 5 to 20 vol%.

Polymer electrically conductive composite basically consist of an electrically conductive agglomerate



entrenched in a polymer matrix. polymer conductive composite are sometime use as sensors for measurement of variation in applied mechanical deformation [9]. Broad research endeavor has been put forward to understanding the percolation theory which is frequently used to define the correlation between conductive particle contents such as CB and the electrical conductivity [5].

Contescu and Burchell [10] suggested that both physical and chemical properties of CB affect its dispersibility also Supova *et al.*[6] stated that the shape and morphology of the dispersed nanoparticles dictate to a significant degree the properties of the produced nanocomposite and this was also confirmed by Minkyung *et al.* [11]. In their review, they stated that nanofibres such as multiwalled carbon nanotube (MWCNT) or carbon nanofibre (CNF) can induce a good conductivity properties on polymer but are however highly anisotropic, while spherical nanoparticles such as CB gives an isotropic electrical property to the polymer nanocomposite.

Despite numerous studies a better understanding of the relation between the physical property of the CB and the electrical behaviour of the produced nanocomposite has received little attention from researchers. This paper seeks to characterise the CB nanoparticles using different techniques and to establish a relation between these physical quantities and the electrical behaviour of epoxy resin CB nanocomposite.

## EXPERIMENT

In this experiment, the thermoset was fabricated based on two epoxy and hardener components manufactured by Smooth-On Inc, the resin is EpoxAmite® 100 and the hardener or the curing agent is 102 Medium. The resin to curing agent weight ratio is 100:29 as advised by the manufacturer. The CB used is commercially available Vulcan® X72 manufactured by Cabot Corporation

A mass of 2.4 g representing 10 %wt CB was dissolved in methanol and sonicated for 15 minutes using an 800 ml digital ultrasonic bath at 42 KHz. The obtained solution was stirred using a pensonic PM-112 hand mixer at 500 rpm for 5 minutes and then sonicated for 15 minutes to achieve a well-dispersed mixture. 20g of epoxy resin (part A) was then poured into the mixture and further sonicated for 30 minutes. For good dispersion, the sonicated mixture was subjected to magnetic stirring at 750 rpm and the mixture was heated to 76 °C to evaporate the methanol. 4.8 g of hardener was added and stirred using a magnetic stirrer at 750 rpm for 10 minutes to obtain a homogenous suspension.

The produced nanocomposite was poured into a mold with dimension 50 x 50 x 5 mm and cured at ambient temperature for 24 hours. This procedure was repeated for 15, 20, 25, 26, 27, 28, 30 %wt of CB. The nanocomposite was placed between two aluminum plate and using a DT9205A digital multimeter the resistance R was measured. The resistivity and conductivity are obtained using the formula in equation (1) and (2) below respectively

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

Where L is the length, A being cross-sectional area of sample and  $\rho$  is the resistivity, the conductivity is given by

$$C = \frac{1}{\rho} \quad (2)$$

The characterization of the CB and the nanocomposite was done using FESEM, TEM, SEM, XRD and SAP analyses.

## Field emission scanning electron microscope

The elemental constituent, particle size and surface morphology CB and the produced nanocomposite were investigated using a variable Pressure Field Scanning Electron Microscope model Zeiss Supra55 VP ready with energy dispersive x-ray (EDX) microanalysis system which recognize the x-rays emitted from the test piece because of the rich-energy electron ray piercing into the test piece. The x-ray spectra were retrieved and examined, to obtain a quantitative data of the basic constituent of the test piece. The procedure resulted to an accurateness of 1-2 % and sensitivities for a number of elements down to 0.1 weight percent.

## Transmission electron microscope

A Zeiss Libra 200 model TEM was used for the morphological studies of CB samples, the sample was dispersed in methanol solvent using sonication for 90 minutes, The sonication process yielded a homogeneous suspension, drops of the suspension were placed on lacey carbon grid for the electron microscopy examination. A Zeiss Libra 200/FEG TEM, operating at 200 kV with Koehler illumination was used. firstly, the area having CB sample was sited in TEM mode and using a condenser orifice of 15  $\mu\text{m}$  and a convergent ray of 5 nm in dimension, the wide direction dark-field STEM imaging benefit of the Libra was utilised to acquire a scanning image of the located area as shown in Figure 1. to acquire an unambiguous diffraction outline, the STEM fixed ray service of the Libra was then used to create a tiny, nearly parallel ray with a bore of about 300 nm.

## Surface area analyzer and porosimetry

The CB test piece was also examined for its surface area property by utilising a Micromeritics ASAP 2020 and porosity analyzer. The pore textural properties together with Langmuir and BET exact surface area, pore volume, and pore size were obtained by examining the nitrogen adsorption and desorption isotherms with the aid of Micromeritics ASAP 2020 integral software. Firstly the CB test piece was degassed in situ at 300°C for 4 h to eliminate every alien particle from the pores of the CB sample.

## XRD

The XRD information analysis was carried out using a Bruker AXS D8 Advance X-ray diffractometer at



mechanical engineering laboratory of the University Teknologi, PETRONAS. Powdered sample were scanned from  $10-80^{\circ}$  in 2 theta scope with  $0.03^{\circ}$  movement interval and 2s/step respond time. Origin lab- 8.0 software was used for deconvolution of the diffractogram in the 2 theta region of  $18-32^{\circ}$ .

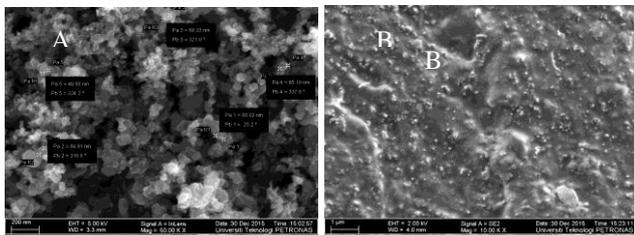
### SEM

The SEM micrographs was obtained with a scanning electron microscope of model Phenom Pro X at a working voltage of 15 kV after auto sputter coating of the Test piece exterior.

## RESULTS AND DISCUSSIONS

### Aggregation of CB

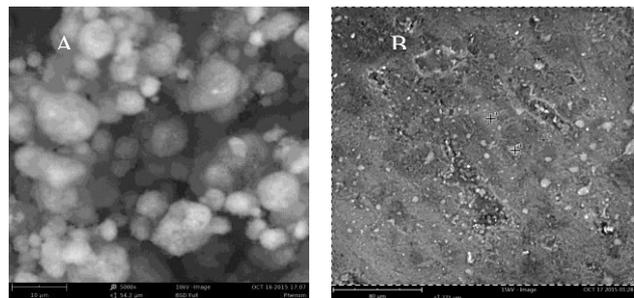
The FESEM image of Figure 1A shows a highly agglomerated CB particle of particle diameter of 50–70 nm and the Figure 1B shows a well dispersed CB particle within the epoxy matrix.



**Figure-1.** FESEM image of (A) CB nanoparticle and (B) the epoxy CB nanocomposite containing 10 %wt CB.

### Surface morphology of nanocomposite

The SEM micrograph of CB nanoparticle is shown in Figure-2A the surface morphology of the CB is observed to be un-consistent. The micrograph shows the formation of carbon nanosphere on the surface of the nanoparticles. SEM photographs of Figure-2B present the formation of uniformly dispersed carbon black nanoparticle in the polymer matrix after the dispersion process.

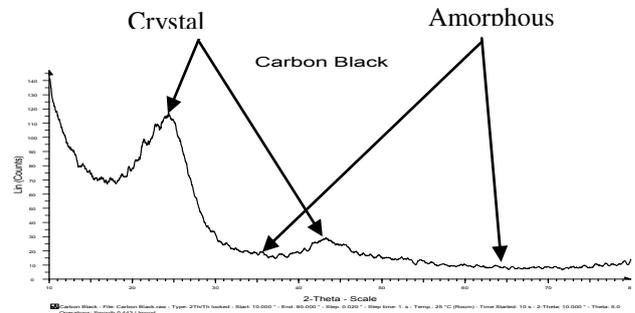


**Figure-2.** SEM image of (A) CB nanoparticle and (B) the epoxy CB nanocomposite containing 10 %wt CB.

### The morphology of the nanoparticle

The XRD profiles of the samples presented in Figure-3 present two unique peaks at  $25^{\circ}$  of high intensity and a somewhat broaden peak at  $43^{\circ}$ . The important (002)

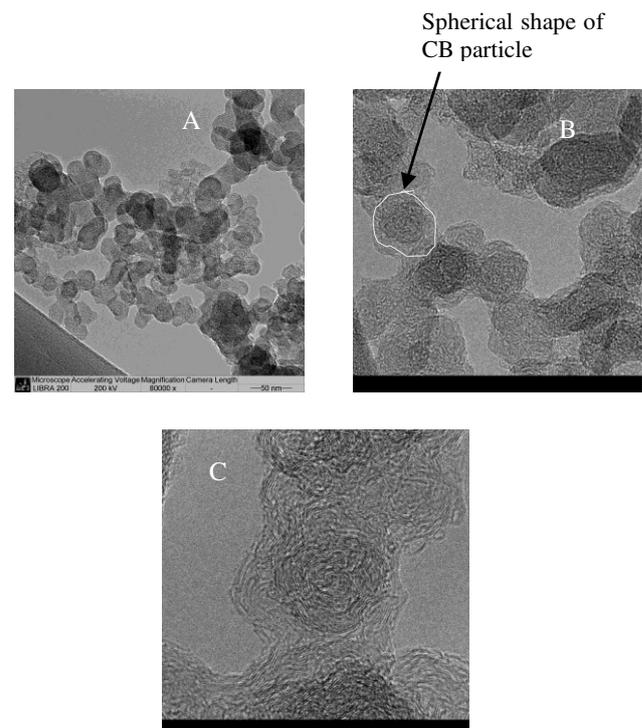
peak at  $25^{\circ}$  is assign to the graphitic carbon in the sample. This peak situated at  $2\theta$  angle of  $43^{\circ}$  can be easily assign to (100) diffraction of graphene. The image shows the existence of both amorphous and crystal structure in the morphology of CB, the high structure as shown in the TEM image of Figure-4B. Explains the existence of the amorphous phase.



**Figure-3.** The XRD pattern of CB nanoparticles.

### High structure of the CB

The TEM image of Figure-4 shows the presence of a big fraction of particles with key internal voids as well as hollow shells, the hollowness is clearly shown by the micrograph in Figure-4B and Figure-4C. The TEM image also shows trace presence of solid spherical elementary particles, this morphology is responsible for the high structure of the CB



**Figure-4.** TEM micrograph of (A) CB nanoparticle showing aggregation (B) CB nanoparticle showing the spherical shape (C) High structure of CB with porous feature.



### Surface area of CB

The SAP analysis shows a nanoparticles size of 65-70 nm and a BET surface area of 221 m<sup>2</sup>/g the CB black nanoparticles when dispersed in epoxy matrix creates a nanofiller - epoxy interface which make up a greater area within the bulk of the nanocomposite. This interfacial region is described of having properties

different from the bulk epoxy matrix because of its nearness to the CB nanofiller [12]. The interface helps to communicate between the epoxy matrix and the CB nanoparticles hence an increased interfacial region translate to a greater influence on the electrical properties of the nanocomposite even at a low filler loading.

**Table-1.** Surface area analysis of CB nanoparticle.

BET (m <sup>2</sup> /g)	Langmuir surface area (m <sup>2</sup> /g)	BJH adsorption cumulative volume of pores (cm <sup>3</sup> /g)
221.06	327.58	0.45

### Resistivity

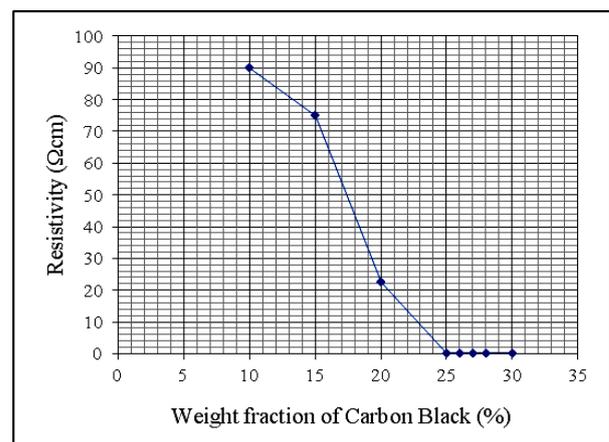
The structure of CB (Vulcan Xc-72R) as shown in Figure-3 shows characteristics amorphous and crystal structure having a porous sphere with extremely high structure and BET analysis indicate a large surface area of 221 m<sup>2</sup>/g. This structure has a profound effect on the resistivity of the nanocomposite when mixed with the epoxy resin matrix the hollow sphere fracture and interpenetrate the epoxy chain forming chains and aggregate (Figure 1B) having a dimension in the nanometre range separated by a narrow gap. At very low CB content the resistivity of the nanocomposite is in the insulator state and, therefore, has a high value. Further addition of CB lowers the resistivity of the nanocomposite until a critical CB concentration is reached at which a little change in CB loading result in large change in the resistivity. This critical concentration of CB at which a large change in resistivity is associated with a small addition of CB is known as percolation threshold and is influenced by the arrangement and dispersion of CB within the epoxy resin.

Figure-6 shows the percolation threshold at 20 - 25 wt% CB. The percolation threshold is largely affected by shapes and sizes of the carbon aggregate and these values are affected by the degree of dispersion and morphology of the CB nanoparticles.

The electrical behaviour of the nanocomposite with respect to the CB loading can be categorised into three distinct divisions: the dielectric, transition and the conducting state.

The concept of electron tunnelling in dispersed CB offers an acceptable explanation for the electrical conductivity of the nanocomposite [13]. According to this mechanism, electron may pass through thin insulating epoxy films existing between adjacent CB particles or aggregate. The existing current is an exponential function of the distance between the particles [14]. It can be inferred that the lesser the particle size, the more is the gap distance between them (the CB particle size is 50-70 nm in diameter). At high loadings, this gaps distance is exceedingly small probably in nanosize range and the resistance within the gaps reduces to a negligible value thereby achieving conductivity. Thus high structure as seen in Figure 4 consisting of porous structure containing cavities displays a smaller distance than solid particles,

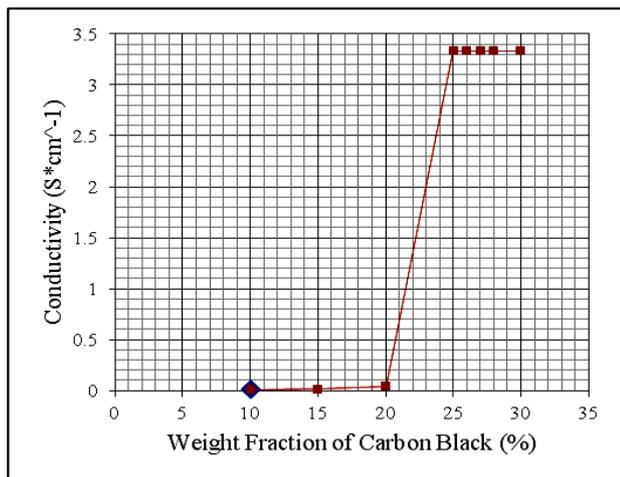
and this invariably lead to considerable improved electrical conductivity.



**Figure-5.** Relation between weight fraction of CB and the electrical conductivity

loading.

The result shows that electrical conductivity of the nanocomposite depends on the CB nanofiller loading, Figure 5 clearly shows the relation between weight fraction of CB and the electrical conductivity. At low filler loading, the CB nanoparticle are insulated from each other within the matrix resulting in low or no conductivity. There is a transition from the insulating property of pure epoxy which has a resistivity value of  $9.56 \times 10^{16}$  Ωcm [15] to a conductive nanocomposite at 10%wt with a low resistivity value of 90 Ωcm and conductivity of about 0.011 S/cm, further loading increases the conductivity until a percolation threshold is observed at 20-25%wt of CB with maximum conductivity observed at 33%wt of CB. Any further loading does not change the conductivity of the nanocomposite.



**Figure-6.** Conductivity of Nanocomposite with CB Filler loading.

## CONCLUSIONS

The conductivity of the epoxy resin carbon black nanocomposite is caused by the conductive property of CB nanoparticles and is influenced by the particle size (50-70 nm), high structure and the low density of the CB, however, this same factors are also responsible for the high propensity of the CB nanoparticles to agglomerate. The combined effect of shear mixing, sonication and magnetic stirring have resulted in the uniform dispersion of CB nanoparticles within epoxy matrix as seen in Figure 1B and Figure 2B. The resistivity of epoxy decreases with CB loading from 90 Ωcm at 10 %wt of CB to 0.3 Ωcm at 25 %wt of CB.

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