Influence of Conductive Carbon Black from Waste Rubber Tire on Electrical and Mechanical Response of Polymer Composites

Chetan Sheth, B. R. Parekh, L. M. Manocha, Parul Sheth

Abstract*— The aim of this work has been to assess the influence of the conductive filler loading which is Carbon black from waste rubber tire into a polymer matrix such as epoxy resin on the electrical and mechanical properties of the composite. The attention was focused on a possible percolation effect due to the increasing conductive filler loading on DC electrical conductivity and the effect on bulk hardness and micro hardness with enhanced electrical and mechanical properties. Electrical and mechanical tests were performed on specimens showing an increased electrical conductivity along with bulk hardness and micro hardness of the composite with increasing filler loading. The electrical percolation threshold is found at low weight percentage of filler loading. The percentage weight loading of the carbon black ranged from 1% to 15%. The most notable feature of the present work is that we found a correlation of the percolation threshold concentration ($Ø_c$), which is detected from the DC electrical conductivity with micro hardness. This paper reports the DC electrical conductivity, bulk hardness and micro-hardness properties of composites with different amounts of filler content. Experimental measurements and microscopic observations of the epoxy composites are discussed in detail. The optical images also revealed that at critical filler concentration ($Ø_c$) carbon black particles form the conductive network. Thanks to a sensitive measurement technique using high resistance electrometer, we are able to measure the accurate DC electrical conductivity.

Index terms: Polymer* matrix*, composites, conductive fillers, DC conductivity, bulk hardness, micro hardness, epoxy resin, carbon black, percolation threshold, morphology.

I. INTRODUCTION

Polymer composites are intensively studied for the new properties which are given by the combination of the properties of the both polymer matrix and the filler respectively. Epoxy resins are electrically insulators. In order to dissipate electrostatic charges and to prepare materials with antistatic properties conductive particles such as carbon or carbon allotropes are dispersed in the polymer matrix [1].Conductive filler/insulating polymer composites become conductors when the filler content reaches a critical value ($Ø_c$) and their electrical conductivity show a sharp increase (percolation threshold) and at this value the continuous bulk network structure is formed.

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Among all the classes of micro additive–polymer materials, carbon black/polymer composites are of special interest because of relatively high conductivity values obtained at low carbon black concentrations [2, 3]. If electrically conductive filler **(**carbon black (CB)**)** is used, the composite properties can change from insulator to conductive ones. Electrical conductivity can change in the magnitude of the several orders [4]. It is applied for heating cables or screening desks and so on. Also, the network in the bulk increases the hardness of the composites [5]. The main problem of the CB network formation is Van Der Waals interaction between CB agglomerates. The interactions can be affected by many parameters. It can be pointed out that with increasing filler concentration packing density of the composites also increases. In particular, the influence of the filler concentration on the conductivity values and on the percolation threshold of the composites was highlighted [6]. A broad utilization of carbon-filled polymers as conductive polymeric materials often requires not only high electrical conductivity values but also an appropriate range of mechanical properties [7] .Micro indentation hardness has emerged in recent years as a new method for the evaluation of the mechanical properties of polymers and polymer composites. [8–11]. We have examined the influence of the additive on the mechanical properties of carbon black reinforced epoxy composites [12, 13]. Results reveal that the addition of carbon-based fillers greatly increases the micro hardness of polymeric matrices after critical concentration of filler (percolation threshold) but bulk hardness of the composites independently increases below and after percolation value. Earlier research using indentation tests to learn the mechanical properties of carbon black–polymer composites was mainly concerned with elastomeric matrices systems [14–19]. A few articles reported on the hardness of carbon black–semi crystalline composites[20-22] .The influences of carbon black content on the hardness of carbon-black-filled epoxy resin has been reported recently[20-22]. The present article aims to extend the above studies by reporting on an investigation of the micromechanical and bulk properties of carbon black-epoxy composites as revealed by micro indentation and bulk hardness. Balancing electrical conductivity with desirable mechanical behavior is one of the largest challenges for the use of filled polymer composites in various applications. In this work we focus on the effect of filler concentration to the electrical and mechanical behavior of the epoxy resin – carbon black composite system prepared from the hand mixing technique. In the analysis no reasonable differences were observed for the bulk hardness (Rockwell Hardness) at percolation value of the filler concentration. The more detailed study will be

presented in the next work.

II. EXPERIMENTAL TECHNIQUES

Materials:

The polymer used in this study is epoxy resin, LAPOX, L-12 supplied by M/s Atul Chemicals. The hardener used was LAPOX, K-6, supplied by M/s Atul Chemicals. The conductive filler carbon black (particle size 2-12 µm) from waste rubber tire was supplied from Gandhinagar, Gujarat. All the components of the system are commercial products and were used without purification.

Sample preparation and methods:

Sample preparation:

The Epoxy resin/Carbon black composites were prepared by the dispersion of the determined amount of CB in a glass beaker. Prior to that procedure, the epoxy resin (polymer matrix) was heated at 80^0C in order to decrease the viscosity. The stoichiometric amount of CB and solvent which is acetone was added to the epoxy resin and mixture is mixed by hand mixing technique to reduce the porosity. Again the mixture was heated at 70^0C in order to evaporate the solvent and reduced the viscosity. Then the mixture was magnetically stirred for seven hours at 260 rpm and degassed under vacuum for 20 minutes. Finally, the mixture was sonicated for 25 minutes in order to break up the CB agglomerates [23] and degassed again. Then the 10 % hardener of epoxy resin was mixed up drop by drop in to the solution till exothermic reaction starts. The homogeneous solution was poured in rectangular shaped open glass mold to developed three identical samples and cured at room temperature for 24 hours. Then samples were subjected to a post-curing procedure at 70^0C for seven hours in oven. At last samples were prepared for various characterization techniques. Series of three identical specimens were produced, each series with different filler content, starting from 0 weight % filler(neat epoxy), 1%, 35,5%,7%,9%,11%,13% and 15% w/w.

Density:

Densities of the CB/epoxy composites were calculated according to the ASTM C-838 t-91 which is given by the formula (1) [24]:

$$\text{Density (D)} = \frac{\text{Weight [W]}}{\text{Volume [V]}}, \text{ gm/cm}^3$$

Where W is the weight of the composite and V is the volume of the composite. Densities of the composites experimentally cross checked by the Archimedes technique in distilled water, where maximum deviation of the theoretically calculated density was 2.3 %. Each reading of the density is the average of five readings. Typical values of densities of the composites for different weight % of filler concentrations are presented in Table 1.

Table 1. Typical values of density for the different wt. % of Carbon Black (CB) used.

Wt. % of filler concentration	Theoretical Density (gm/cm^3)	Experimental Density (gm/cm^3)
0	1.25	1.247
1	1.25	1.254
3	1.26	1.258
5	1.27	1.273.
7	1.28	1.281
9	1.29	1.293
11	1.30	1.294
13	1.34	1.32
15	1.40	1.37

Vickers Micro hardness Analysis:

The Micro hardness of all CB composites was measured using Vickers micro-hardness tester by Omni Tech at the room temperature**. Fig. 1** shows the Vickers micro hardness tester.

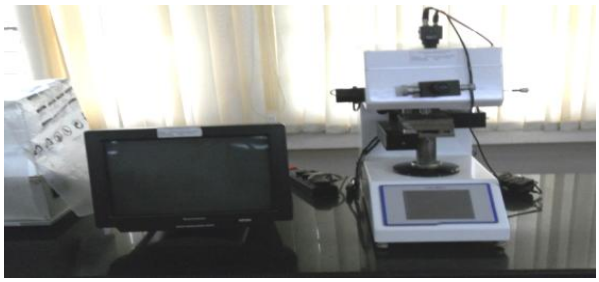
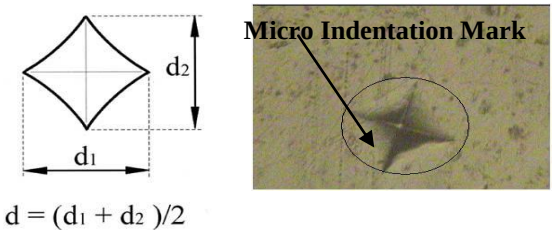


Fig 1. View of Vickers microhardness tester.

The Vickers indenter was used with load of 200 gm for 20 s of Dwell time at 100x magnification. Both surfaces of the CB composites were polished by fine sand papers in order to produce a flat surface for the indentation test. A total of six points on each of the CB composites were measured in order to get average readings. The unit and magnitude of the hardness are defined by Vickers hardness, H_v and determined by measuring the average diagonal length, d of the indentation (mm), i.e.

$$H_v = \frac{8F \sin(\text{ø}/2)}{(d_1+d_2)^2}$$

Where ø, d1, d2 and F denote the face angle of a pyramidal diamond indenter (136^0), two diagonal lengths and test load (N), respectively. In **Fig. 2**, the schematic illustration of Vickers hardness testing measurement and an indentation mark on a CB composite surface are shown.



$d = (d_1 + d_2)/2$

(a) **(b)**

Fig. 2(a), (b) shows the schematic illustration and micrograph of the indentation mark on the CB composite respectively.

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Rockwell (Bulk) hardness Test:

Rockwell tests are frequently used for polymers [25]. The determination of the Rockwell hardness (TRSDM) of a CB impregnated epoxy composite material involves the application of a minor load followed by a major load, and then noting the depth of penetration. Polymers are softer than metals and ceramics, and most hardness tests are conducted by penetration techniques, it is finally found that HRR scale is suitable with indenter size of ½" ball at load of 60 Kg/cm^2. **Fig. 3** shows the digital Rockwell hardness tester.

Fig 3. View of digital Rockwell hardness tester.

The main advantage of a digital Rockwell hardness tester is its ability to display digital hardness values directly, thus obviating tedious calculations involved in other hardness measurement techniques. It is typically used in engineering and metallurgy. Its commercial popularity arises from its speed, reliability, robustness, resolution and small area of indentation. In order to get a reliable reading the thickness of the test-piece should be at least 10 times the depth of the indentation. At different five places hardness readings were taken to obtain accurate average readings. Also, readings should be taken from a flat perpendicular surface, because convex surfaces give lower readings. A correction factor can be used if the hardness of a convex surface must be measured. Other indentation techniques employed are the Durometer and Barco [26].

Electrical conductivity measurements:

For the electrical measurements, specimens in the form of squares, 30x30 mm^2 were cut from the composite blocks with a thickness of about 1.5 to 2 mm. Three identical samples for each filler concentration utilized for measuring electrical resistivity/conductivity. Copper electrodes with silver coating on the surfaces of electrodes were used in order to ensure a good electrical contact with samples. The samples employed for electrical measurements were square blocks, which were sandwiched between circular copper electrodes. The DC volume (bulk) conductivity of samples measured with two point method as resistivity of specimens is enough high. The electrical leads from the meter were fixed to copper rods of designed assembly which is very close to ASTM D257 for measurement of high resistance [27].

The Alternating Polarity Resistance/Resistivity test is designed to improve high resistance/resistivity measurements [28, 29]. These measurements are prone to large errors due to background currents. By using an alternating stimulus voltage, it is possible to eliminate the effects of these background currents. When this test is run, the V-Source will alternate between two voltages (V-OFS + V-ALT) and (V-OFS - V-ALT) at timed intervals (measurement-time). Current measurements are taken at the end of each of these alternations and after calculation of I_{calc} resistance values are computed. I_{calc} is a weighted average of the latest four current measurements, each at the end of a separate alternation. The resistance value is then converted to a resistivity value if the meter has been configured for resistivity measurements. Resistivity of the specimen is given by the formula (2) [29]:

$$\rho_v = \left(\frac{K_v}{\tau}\right) R$$

ρ_v = volume resistivity

K_V = the effective area of the guarded electrode for the particular electrode arrangement employed.

τ = average thickness of the sample (mm)

R = measured resistance in ohms (V/I)

For circular electrodes:

$$K_v = \pi\left(\frac{D1}{2} + B\frac{g}{2}\right)^2$$

D1 = outside diameter of guarded electrode

g = distance between the guarded electrode and the ring electrode

B = effective area coefficient

Note: An effective area of coefficient (B) of 0 is typically used for volume resistivity.

The high voltage equals to 150 V having an alternating polarity, was applied through the specimen thickness for a 60 second period of a time for each alternating cycle. Total eight alternating cycles were used to remove unwanted effects due to high resistance. The DC conductivity measurements were made using a high resistance, Keithley 6517A programmable electrometer at 23^0 to 24^{0}C temperature in a controlled environment. **Fig. 4** shows the DC electrical conductivity measurement set-up.

Fig 4. Typical set-up for measurement of DC electrical conductivity of composites.

Morphology:

To study the microstructure of composites samples were cut in very small sizes for cross-sectional view. Then for optical microscopy samples were embedded in epoxy matrix and polished. Morphology of all composites was done by using Leitz optical polarized microscope.

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III. RESULTS AND DISCUSSION

The packing density:

Fig. 5 shows plots of theoretical and experimental densities of the CB composites. The pure epoxy has theoretical density of 1.25 gm/cm^3. The density of the composites increases as the % filler concentration increases. It is due to the packing density of the composites increases as some more percentage of carbon black particles having higher density **(**1.63 gm/cm^3**)** packed within definite volume of composite and due to the well dispersion of CB particles. Eventually there is a change of 13 to 14% in density compare to the density of pure epoxy. The experimental density of the composites containing up to 11 wt % CB is close to that of theoretical density. It indicates that the prepared composites are almost porosity free. However, the experimental density of the 13 wt% and 15 wt% composites is lower than that of the theoretical density by approximately 1.54 % and 2.3 %, respectively. This is due to the small formation of CB aggregates which hinder the infiltration of n polymer through the aggregates during processing [30].

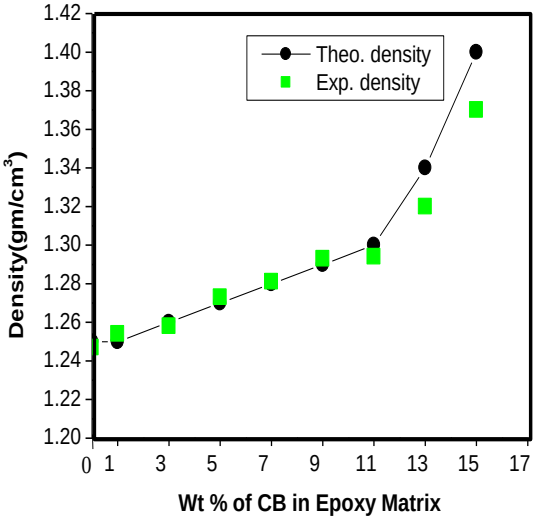

Fig 5. Theoretical and experimental density for the epoxy/CB composites.

The Vickers Micro hardness (H_v):

Fig. 6 illustrates the plot of the H_v values versus the carbon black % weight concentration, $\emptyset$, within the composite samples. The H_v values for the carbon black filled epoxy composites were determined using a Vickers micro hardness tester. Figure 4 shows that for low carbon black content values ($\emptyset \leq 7$ wt %), the micro hardness of carbon black–epoxy composites is little bit independent of $\emptyset$. However, at a critical $\emptyset$ value, $\emptyset c$, which depends on the type of carbon black and % filler concentration, the hardness values of the composites conspicuously increase with a further increase of filler content. **Fig. 6** also shows that the micro hardness of composites after critical filler concentration $\emptyset c$, is a function of CB content. The microhardness of the composites increased significantly with increasing content of CB in the matrix. The micro hardness increased from 55H_v for pure epoxy to 88.32 H_v for 15 wt% filler concentration in composite. It increased due to the resistance to the plastic deformation of the epoxy matrix from comparatively hard CB particles [31]. The significant improvement in micro hardness may be attributed to the better distribution of CB particles and good adhesion between the epoxy and CB particles. The better dispersion of the CB particles in the matrix is confirmed from optical microscopy.

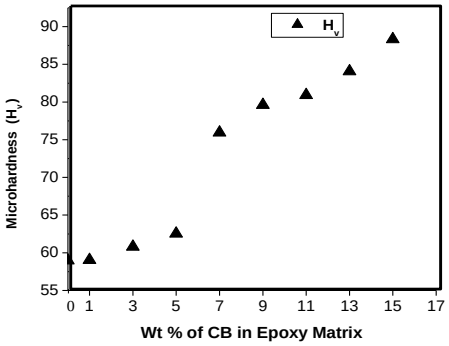

Fig 6. Microhardness of the epoxy/CB composites as a function of wt % of CB.

The Rockwell (Bulk) hardness (HRR):

Bulk hardness of composites was investigated as per ASTM D 785 on Rockwell hardness testing machine for 60 Kg load on HRR scale (for polymeric material). The results obtained from the mechanical testing are discussed below. The hardness values shown in **Fig. 7** indicated that increase in % filler concentration increases the bulk hardness. The addition of CB filler concentration increases the bulk hardness of composite material due to increase in the resistance strength of polymer to plastic deformation because CB particles are little hard in nature as compared to epoxy matrix. The composite with lower filler size yields higher hardness value than other filler sizes due to the better adhesion between the matrix and the filler. In this case, the polymeric matrix phase and the solid filler phase would be pressed together and touch each other more tightly. Thus the interface can transfer pressure more effectively in smaller size CB filler than larger one. This might have resulted in an enhancement of hardness [32].

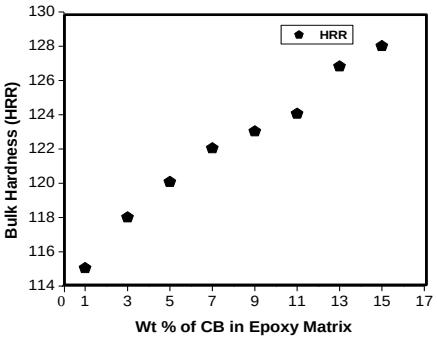

Fig 7. Variation of hardness as a function of CB proportion. Hardness scale: Rockwell HRR scale.

The DC Electrical Conductivity:

Fig. 8 shows the volume electrical conductivity of the composites prepared by hand mixing technique in open glass mold at ambient conditions as a function of CB content. The electrical conductivity of the pure epoxy is about 5.05 x 10^{-15} mho.cm^{-1}.

The electrical properties changing when CBs particles are added to the epoxy. The composites behavior evolves from insulating material characteristics to those of conductive materials. The effective utilization of carbon black in composite applications depends strongly on the ability to homogeneously disperse them throughout the matrix without destroying their integrity. The conductivity of the composites increased with increasing CB content. At very low concentrations of CBs the resistivity gradually decreases with increasing CBs content. The resistivity lower is caused by enrichment of higher conductive material components (According to percolation theory, electrical paths are made up of conductive inclusions in the direct-contact structure based on Ohmic behavior and the percolation threshold values strongly depend on the shape of particles) [33]. However, at 7 wt%, a sizeable reduction in resistivity is observed. This stepwise change in resistivity is a result of the formation of an interconnected structure of carbon black and can be regarded as an electrical percolation threshold. This simply means that at concentrations between 5 and 7 wt% CBs, a very high percentage of electrons are permitted to flow through the sample due to the creation of an interconnecting conductive pathway.(When the CBs are embedded into epoxy resin with up to 7 wt%, the electrical conductivity increases by six orders of magnitude)[18]. At concentrations above 7 wt% CBs, the resistivities are low and decrease marginally with increasing CBs content, and after 13% of CBs addition no change has been detected in the increase of electrical conductivity. These observations are in very good agreement with the [34, 35]. Interestingly, the measured values are in accordance with values given by Hagerstrom and Greene [36] who found a volume resistivity of 10^2 Ohm-cm for 5 wt% multi walled nanotubes (MWNT) in polymer composite (PC). So, here as per the percolation theory, the increase in conductivity does not exhibit a linear additive characteristic. A drastic increase in the electrical conductivity (i.e., percolation threshold) was observed between 5 wt% and 7 wt% CB content. It is due to the formation of the conductive network of CB particles through the polymer matrix and thus, composite becomes conductive [37]. These conductive networks have either physical contact between CB particles and/or they are separated by a very small distances across which electrons can tunnel. **Fig. 9** indicates the appearance of microstructure of CB filled epoxy composite before and after percolation.

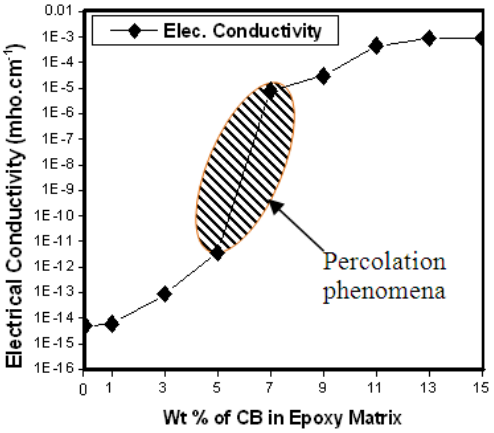

Fig 8. Electrical conductivity of the epoxy/CB composites as a function of wt% of CB. Hatched part shows the Percolation Threshold.

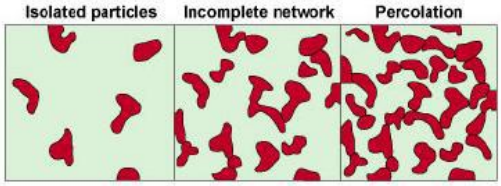

Fig 9. Appearance of microstructure of CB filled Composite before and after Percolation.

This effect may be attributed to the homogeneous distribution of CB particles and the formation of more number of conductive networks at higher filler concentration.

Microstructure of CB/epoxy composites:

The influence of magnetic stirring and sonication time on the dispersion of CB particles in the matrix is shown in **Fig. 10. Fig. 10(a, b)** shows the dispersion of CB particles in the prepared composites before and after percolation respectively. It can be seen that dispersion of CB particles is uniform due to magnetic stirring and sonication. Moreover, the CB particles are surrounded by the epoxy matrix making random structure. Optical microscopy clearly shows that at percolation interparticle distance reduced drastically and conductive networks formed. Due to this tunneling and hopping of electrons possible through composite and electrical resistivity reduced in a step like manner.

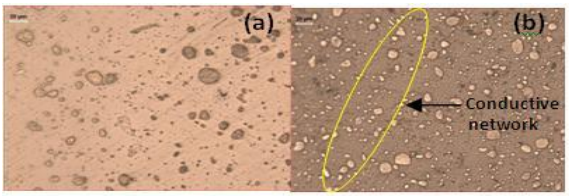

Fig 10. Optical micrograph images of composites containing 5 wt% CB (a) and 9 wt% CB (b) dispersion in epoxy matrix, indicating percolation network at 7 wt% of filler concentration in composite.

IV. CONCLUSIONS

A series of CB/epoxy composites were prepared using hand mixing technique followed by pouring of homogeneous mixture in open glass mold.

1) The percolation threshold of the composites was found at 7 wt % of CB. The electrical conductivity increased approximately six orders of magnitude at percolation.
2) Alternating polarity method is better technique to measure high resistance and gives stable results with high repeatability.
3) Below a critical filler content value, $\emptyset c$, the microhardness of carbon black–epoxy composites is independent of the volume concentration of carbon black $\emptyset$,while above $\emptyset c$, Hv conspicuously increases with increasing $\emptyset$.
4) Bulk hardness of the composites linearly and independently increasing with increasing filler concentration
5) Magnetic stirring and sonication results in a better distribution of CB particles.

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