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Mechanical Properties of Natural Carbon Black Reinforced Polymer Composites

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ABSTRACT: This article describes the development of new carbon black material from agricultural waste (wood apple shells) by using pyrolysis method at various carbonization temperatures (400, 600, and 800°C) and used as reinforcement in polymer composites. The wood apple shell carbon black (WAS-CB) particulates are characterized by proximate analysis, energy dispersive spectroscopy (EDS), and scanning electron microscope (SEM). Results showed that due to increases in carbonization temperature the percentage of carbon improved in the carbon black particles. Furthermore, various tests were performed to determine the effect of new carbon black material on the mechanical properties of composite at different filler loading. The results indicated that mechanical properties like tensile strength, tensile modulus, flexural strength, and flexural modulus are improved as the increase in the carbonization temperature and filler loading. The filler-matrix bonding was analyzed by SEM. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41211.

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INTRODUCTION

In the last two decades, researchers have extensively focused their attention on the selection of variety carbonaceous materials from different source because carbon itself one of the magnificent elements, which have revolutionized materials science. Carbon provides materials with excellent properties such, as well developed pore structures and high internal surface area and they have been employed in a wide number of industrial applications like purification of gases, used as an absorbent for the removal of organic pollutants from water, used as a catalyst and also one of the best electrically conducting materials (graphite electrode).[1,2] Over the last century carbon black were obtained from thermal cracking of natural gas. As the price of commercial carbon black has fallen continually so, increasing interest has now shifted to the use of other low-cost and abundantly available agricultural by-products.[3] Such agricultural by-products are usually inexpensive, for which the effective utilization has been desired. Many researchers have made efforts for preparing natural carbon black from agricultural by-products such as coconut shell,[4] oil palm shell,[5] and bamboo.[6]

The huge majority of carbon black finds uses as reinforcement in polymer industries for advanced application and to improve the performance of the matrix[7] over other established materials. The properties of carbon black used in the composites mainly depend on the origin, processing conditions, and chemical treatments. The addition of such type of fillers with different shapes, particle size, and different sources into the polymer matrix may result in different microstructures and have different effects on the properties of the polymer composites. These bio fillers are fully biodegradable, environmental friendly, renewable, abundantly available, high stiffness, cheap, low density, and high degree of flexibility during processing. These bio fillers can be converted into carbon black thereby reducing unwanted agricultural residues into useful, high-value materials. On the other hand, high content elemental carbon filler results in the material being of highly hydrophobic nature when dispersed in water.[8] As examples, carbon black filled polyethylene composites have been used as pipelines in extreme weather conditions, while polypropylene geotextiles carbon black composites are practical for soil reinforcement and for many construction purposes.[6]

Among the various agricultural wastes, wood apple shell is also a carbonaceous waste fiber. Wood apple shells have no economic value and their disposal is not only costly, but may also cause environmental problems. Wood apple shells are suitable for preparing carbon black due to its excellent natural structure, high carbon content, high potential, high porosity, and low ash content.[9] Some researchers like Anusha et al.[10] and Ahmad et al.[11] used wood apple shell particulates as an absorbent for the removal of iron or Congo red dye from waste water using

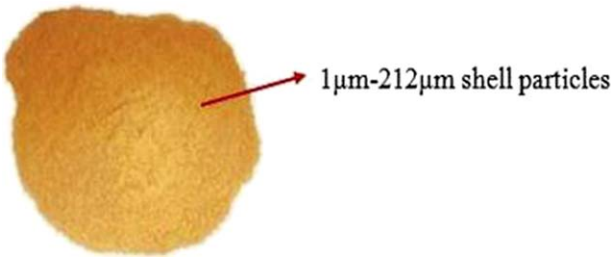

Figure 1. Raw wood apple shell particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wood apple shell carbon. The literature mentioned above gives a brief overview about the effects of the addition of carbon black filler on mechanical properties of epoxy composites. To the author's knowledge, no research has been done to determine the potential of carbon black wood apple shell particles used as filler in polymer composite.

The objective of this article is to fabricate a new set of natural carbon black particulate filled polymer composite prepared from agricultural waste wood apple shell. The effect of carbonization temperature on mechanical properties of the carbon black composite was investigated.

EXPERIMENTAL

Materials

Wood apple (Aegle marmelos) belongs to family Rutaceae is a highly reputed medicinal tree commonly known as the "Stone apple" or "Bael" shown in Figure 1. It is an indigenous fruit of India and found abundantly from sub-Himalayan forest, Bengal, central and south India. Among the different natural fibers, wood apple shell (Aegle marmelos) appears to be promising material because of the high hardness and toughness. The wood apple shells used in the present investigation are initially washed with water to remove the impurities and dried in an oven at 110°C for 24 h to remove the excess water content and moisture. The dried shells are converted to a fine powder using a ball milling process for 24 h and followed a sieve analysis to measure a particle size. The shell particles chosen for the experiments are in the range of 1–212 μm.

The Processing of the Carbon Black Wood Apple Shell (Carbonization) Particles

The main purpose of carbonization process is to remove the noncarbon elements and to create porosity in the carbon black. The carbonization process consists of loading, operation, cooling, and unloading. Subsequently, the raw wood apple shell particles were loaded on a ceramic boat, which was placed inside a muffle furnace. The shell particles were heated up to desired carbonization temperature, i.e., 400°C, 600°C, and 800°C, at a heating rate of 5°C/min and held for at least 2 h at the carbonization temperature under inert atmosphere. To avoid oxidation, which could subsequently cause ashing, an inert environment was created by the passage of Nitrogen gas at the time of carbonizing process. After completion of carbonization a soaking time of 1 h was given after the furnace was switched off. The produced carbon black is shown in Figure 2.

Figure 2. Carbon black wood apple shell particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of Shell Particles

Initial characterization of the filler was done to give an insight on the expected behavior of filler. The proximate analysis of wood apple shell particles has been done under the ASTM standards E-871, E-1755, E-872; for moisture, ash, and volatile matter, respectively. In addition to this, fixed carbon content was calculated by using the eq. (1)

$$\%FC = 100 - (\%ASH + \%VM + \%M) \quad (1)$$

where %FC, %Ash, and %VM, respectively indicates the weight percentage of fixed carbon, ash, and volatile matter of both raw and carbon black wood apple shell particles.

Elemental Analysis

The elemental composition of wood apple shell particles is determined by energy dispersive spectroscopy (EDS). The EDS was obtained in a "spot mode" in which beam is focused on a single area selected within the field of view.

Specimen Preparation

The composites were prepared by hand layup technique with raw and carbon black as filler in polymer composites using four different compositions (5, 10, 15, and 20 wt %). The methods of preparation of specimen are as follows:

- A wooden mold of (150 × 60 × 5) mm^3 is used for manufacturing the composite. For quick and easy removal of the composite a mold release sheet is placed on the top and bottom of the wooden mold.
- The mold release spray is also applied to the inner surface of the mold wall to facilitate easy removal of the composite specimen.
- Epoxy resin, LY 556 (Bisphenol-A-Diglycidyl-Ether) having density 1.2 g/cm^3 is used ad polymer for the fabrication of composites. Hardener HY-951 [NN0 (2-amineethylethane-1, 2-diamin)] with density 0.99 g/cm^3 is used as curing agent.
- A calculated amount of epoxy resin and hardener (ratio of 10:1 by weight) was thoroughly mixed in a container for 2–5 min at room temperature (25°C).
- After 5 min calculated amounts of filler materials were mixed with the mixture of epoxy-hardener and a mechanical stirring process is applied in the liquid to obtain a homogenous mixture.
- The mixture was poured uniformly into the mold and after 2–5 min a mold release sheet is placed on the top of the mold for the quick and easy removal of specimen.

- Before the reaction will be started between epoxy and filler materials, a wooden board placed on the top of the mold and put some load of about 30 kg in 24 h.
- Due to apply of load some polymer squeezes out from the mud. Care is taken to ensure that the expel polymer not to squeeze out from the mold.
- When the composite was hardened it was removed from the molds and cut for required test with a diamond cutter according to ASTM standard.
- For accuracy each five specimens were prepared for testing purpose.

The other composite samples with carbon black particulate fillers of various weight percentages are fabricated by the same technique. Carbon black particles were dried in the oven for 24 h prior to moisture elimination. But at the time of carbon black composite preparation, carbon black particulate was added carefully and gradually to avoid the loss of carbon black during the process and also ensure that the carbon black blended well with a matrix. For comparison purpose a neat epoxy (EP) was prepared by the same procedure. Test specimens of suitable dimensions are cut according to ASTM Standard with a diamond cutter for further analysis and studies.

Flexural Property Characterization

Flexural strength (FS) is the ability of the composite material to withstand bending forces applied perpendicular to its longitudinal axis. To evaluate the value of FS, the short beam shear tests (generally it is three-point bend test) are performed on the samples at room temperature. The three-point bend test is conducted on a universal testing machine INSTRON H10KS as per ASTM D790 standard. The five specimens per test condition should be carried out for accuracy of testing the polymer matrix composite materials. The span of 70 mm and a cross-head speed used for the flexural tests (three-point bending) was 5 mm/min. The machine is designed to elongate the specimen at a constant rate, and to continuously and simultaneously measure the instantaneous applied load and the resulting elongations using an extensometer. The FS in a three-point bending test is found out by using the eq. (2).

$$\sigma_{max} = \frac{(3P_{max}L)}{(bh^2)} \quad (2)$$

where P_{max} is the maximum load the span length (N), L is the span length (mm), b and h are the width and thickness of the specimen (mm), respectively.

The flexural modulus is calculated from the slope of the initial portion of the load-deflection curve, which is found out by using the eq. (3).

$$E = \frac{(mL^3)}{(4bh^3)} \quad (3)$$

where m is the initial slope of the load deflection curve. Five specimen average results are taken for consideration.

Tensile Property Characterization

The tension test is generally performed on flat specimens. The most commonly used specimen geometries are the dog-bone specimen and straight-sided specimen with end tabs. The standard test method as per ASTM D 3039-76 has been used; length of the test specimen used is 125 mm. The tensile test is performed in the universal testing machine (UTM) INSTRON H10KS. A rate of loading of 0.5 mm/min is used for testing. Five identical specimens were tested and the average result is taken for consideration.

Micro Hardness

The hardness property of the samples was determined using Vickers hardness tester. A diamond indenter in the form of a right pyramid with a square base and an angle 136° between opposite faces is forced into the material under a load of 5 N.

Morphological Analysis

Scanning electron microscopy (SEM) was used to monitor the fracture surface of the composites after mechanical test of each sample. SEM analysis was performed using Nova Nano SEM 450 at an accelerating voltage of 15 kV. The composites were splattered with a layer of gold/palladium before the measurements.

RESULTS AND DISCUSSION

The characterization of the composites reveals that the inclusion of any particulate filler has a strong influence on the mechanical properties of composite. A comparative study of the modified behavior of the composites against the unfilled composite is presented.

Proximate Analysis

From Figure 3 it is clearly observed that the raw wood apple shell particles having 19.11% carbon but after pyrolytic decomposition, the carbon percentage increases drastically up to 87.43%. This is only due to the removal of noncarbon elements from the raw particles at various stages of carbonization temperature. These parameters are essential to determine the level of fillers in the polymer which effectively affect the properties of the final product.

Elemental Analysis (EDS)

Figures 4 exhibits the inspection spectra of wood apple shell particulate surface elements acquired for wood apple shell. The particulates surface exhibit spectra containing mainly carbon, oxygen, silicon, aluminum, and small amount of zirconium and calcium. However, these elements are slowly removed from raw

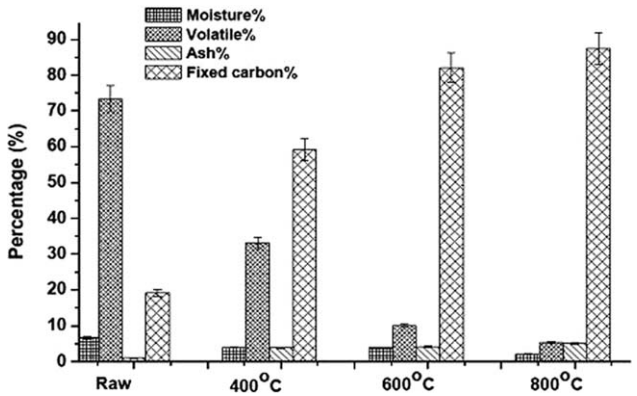

Figure 3. Proximate analysis of wood apple shell particles.

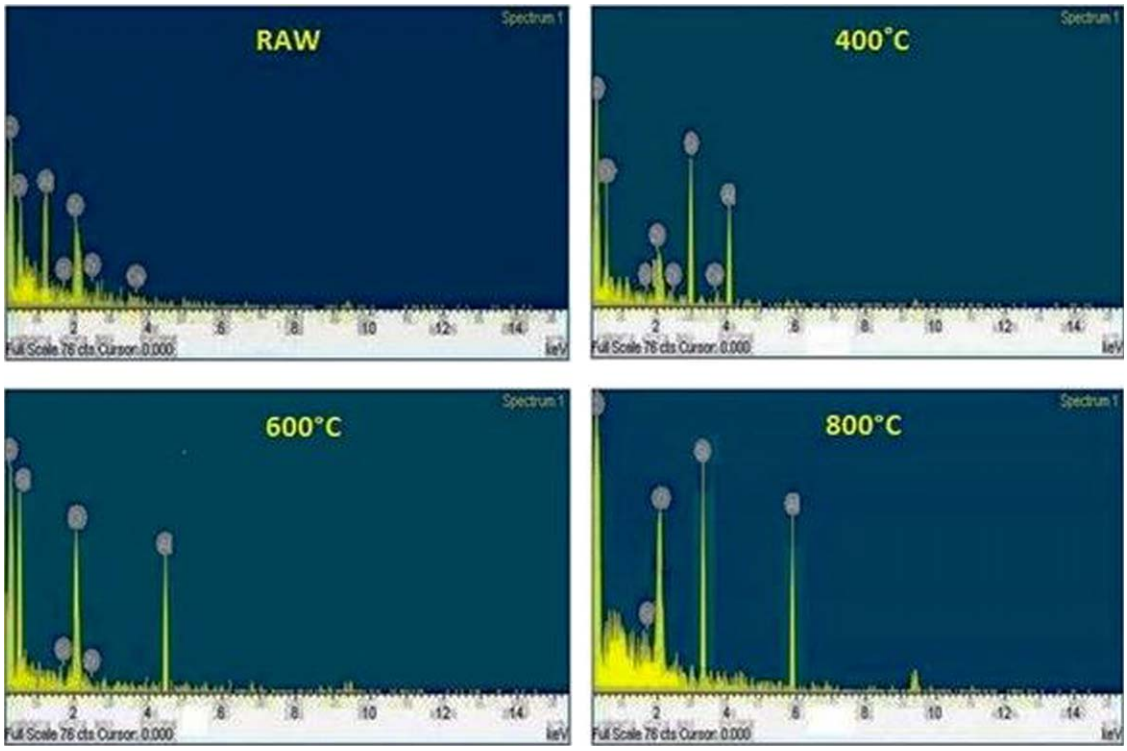

Figure 4. EDS of wood apple shell particulates at various carbonization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wood apple shell particulates by pyrolytic decomposition of shell particulates at various carbonization temperatures i.e., 400°C, 600°C, and 800°C. Also the figure indicates that the carbon percentage in wood apple shell particulates gradually increase at different stage of carbonization temperature. Because of the presence of hard elements like SiO_2 and Al_2O_3, the raw wood apple shell powder can be used as particulate reinforcement in various polymer matrixes. The microstructure of the wood apple shell particle reveals that the size and shape of the particles vary; however, they can be sorted into three main groups such as prismatic, spherical, and fibrous. The prismatic particles consist mainly of Si and O. The spherical ones contain Si and O as well as Ca, Al.[12]

Mechanical Properties

The flexural, tensile and hardness tests were analyzed to determine the mechanical properties of the composites. Mechanical properties of the bio fillers composites depend on several factors such as the fillers concentration, matrix phases, phase weight fractions, distribution and orientation of the fillers relative to one another.

Micro Hardness. From the result of micro-hardness test indicated in Table I, it is clearly observed that the filler addition affects the hardness values. This is an expected trend attributed to the fact that as more filler loadings are incorporated into the epoxy matrix within the condition of wet ability, the composite become more rigid. As expected the hardness values of carbon black polymer composites are found to be higher than that of unfilled composite and the hardness value improves with an increase in carbon black particles in the polymer composite. The test results obtained from samples with 10 wt % raw fillers show best harness value for raw filler composites. As the carbonization temperature increases the hardness value increases in all the composites when compared with the raw filler composites. The maximum hardness is observed in 20 wt % carbon black (CB) (800°C) filled composite as compared to other filler composite.

Tensile Properties. Figure 5 shows the ultimate tensile behavior of the composites based on raw and carbon black as filler. Results demonstrated that ultimate tensile strength increased due to filler loading of raw and carbon black from 5 to 20 wt

Table I. Hardness Value of Wood Apple Shell Particulates Polymer Composite

Filler (wt %)	Raw	400°C carbon black	600°C carbon black	800°C carbon black
5	23.58	23.92	24.26	24.85
10	25.3	25.9	26.1	26.5
15	24.55	26.5	26.7	26.9
20	23.6	25.3	27.3	27.5

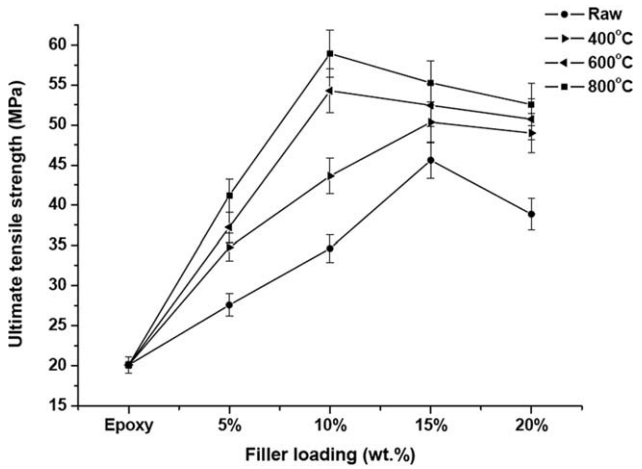

Figure 5. Effect of filler loading on ultimate tensile strength of wood apple shell particulate filled polymer composite.

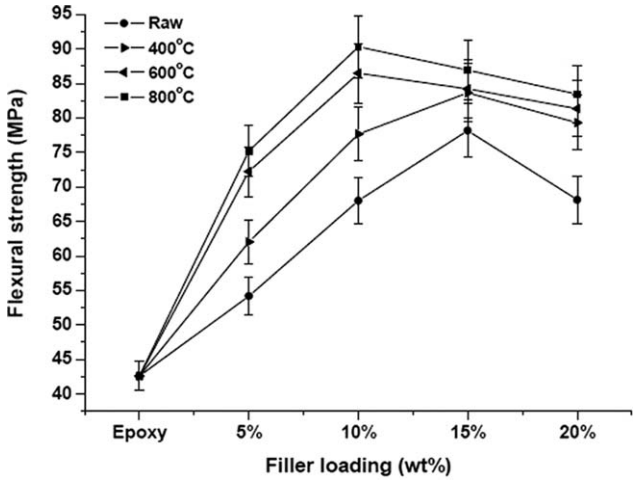

Figure 7. Effect of filler loading on the flexural strength of wood apple shell particulate filled polymer composite.

% in the neat epoxy composite when compared with the epoxy strength. In the current studies four different types of fillers with different percentages added to the neat epoxy. From the results it is observed that the ultimate tensile strength of the raw wood apple shell particulate composite shows higher strength in 15 wt %, whereas as the carbonization temperature increases the maximum strength obtained for 10 wt %, this may be due to the density variation in the fillers. The strength increases in all the portions of filler composites as the carbonization temperature increases. In general the carbon black particles (800°C) filled composite was recorded optimum ultimate tensile strength at 10 wt % filler with 58.917 MPa among other filler composites. As earlier pointed out, the effectiveness of filler may be measured by its carbon content. Hence, due to the increase of carbon content in the filler material shows the increase in strength of the composite. Okieimen and Imanah[13] used agricultural waste as fillers in rubber compounds. In their research it is observed that filler with higher carbon content provide greater reinforcement than those with lower carbon content because carbon it is very good reinforcing filler. However, further addition of filler at 20 wt %; the strength of the composite slightly decreases because of improper bonding between the filler and the polymer matrix. One possibility is that the chemical reaction at the interface between the filler particles and the matrix may be too weak to transfer the tensile stress.

Figure 6 shows the plot of young's modulus of both composite. The young's modulus of the entire carbon black filled epoxy composite steadily increased as compared to neat epoxy and raw filler composites. The highest modulus value 2.561 GPa represented by composites filled with 10 wt % carbon black at 800°C carbonization temperature.

Flexural Properties. The effect of filler loading on flexural properties of neat polymer and biomass based carbon black filled polymer composites used in this study are shown in the Figure 7. It can be observed that the carbon blacks resulted in reinforcing effect of the polymer matrix. Carbon black which is prepared at various carbonization temperatures (400, 600, and 800°C) significantly influenced the FS of the carbon black filled

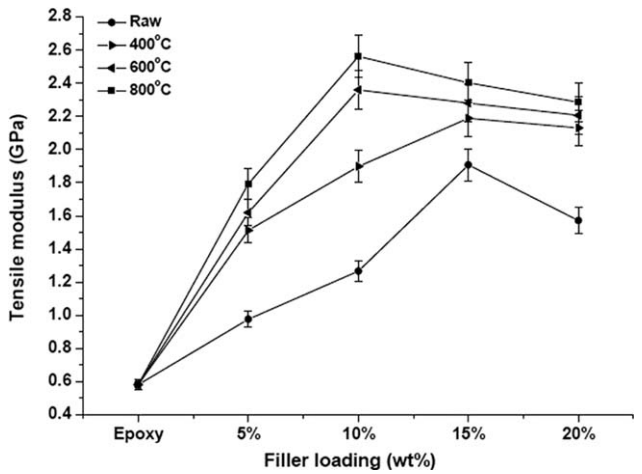

Figure 6. Effect of filler loading on young's modulus of wood apple shell particulate filled polymer composite.

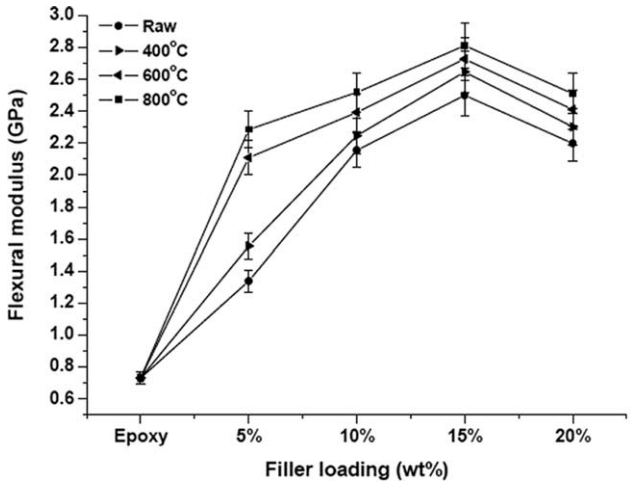

Figure 8. Effect of filler loading on flexural modulus of wood apple shell particulate filled polymer composite.

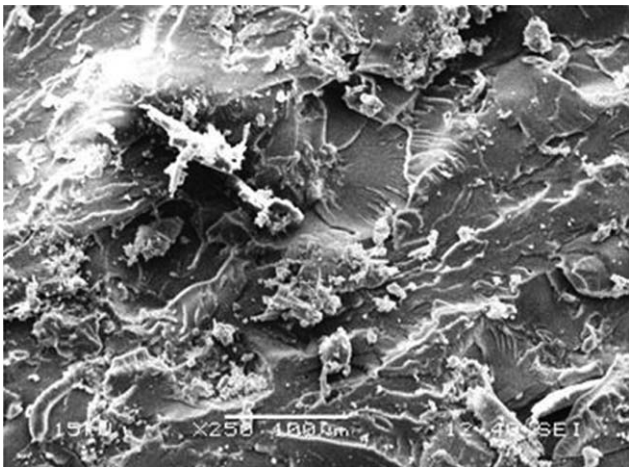

Figure 9. SEM of 10 wt % tensile specimen.

composite than neat polymer composite. Among the different carbon black filled epoxy composites studied, a wood apple shell particle, which is prepared at a 800°C carbonization temperature shows the highest FS as compared to other filler composites.

A similar trend was observed with a flexural modulus of the carbon black filled polymer composite in Figure 8. However, the highest flexural modulus of 2.751 GPa was recorded for wood apple shell carbon black composite at carbonization temperature 800°C. This value of the carbon black composite was higher than 0.731 GPa recorded for unfilled polymer composite. This similar observation is found by Etika et al.[14] that carbon black influenced on mechanical properties of epoxy composites using DMA analysis.

Surface Morphology. The SEM micrograph of the fractured surfaces of the 800°C carbon black wood apple shell composites with 10 wt % are shown in Figures 9 and 10. It is clearly observed that a good interfacial bonding between carbon black fillers and matrix materials are formed. Hence, no void and filler chip out found on the surface of the carbon black composite. From Figure 10, it is clearly observed that no cracks formed due to apply of maximum flexural load on carbon black

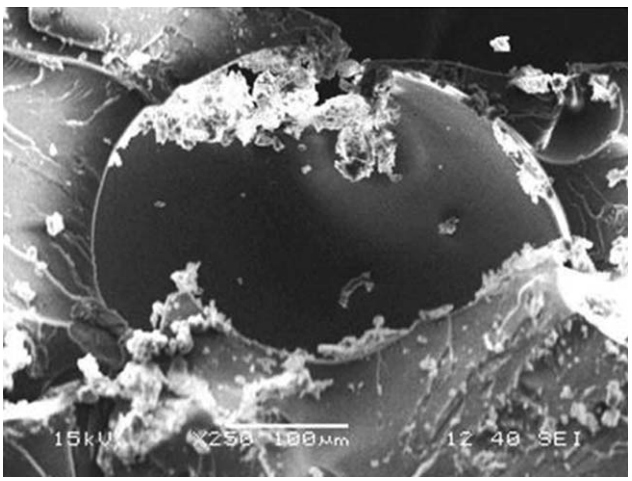

Figure 10. SEM of 10 wt % flexural specimen.

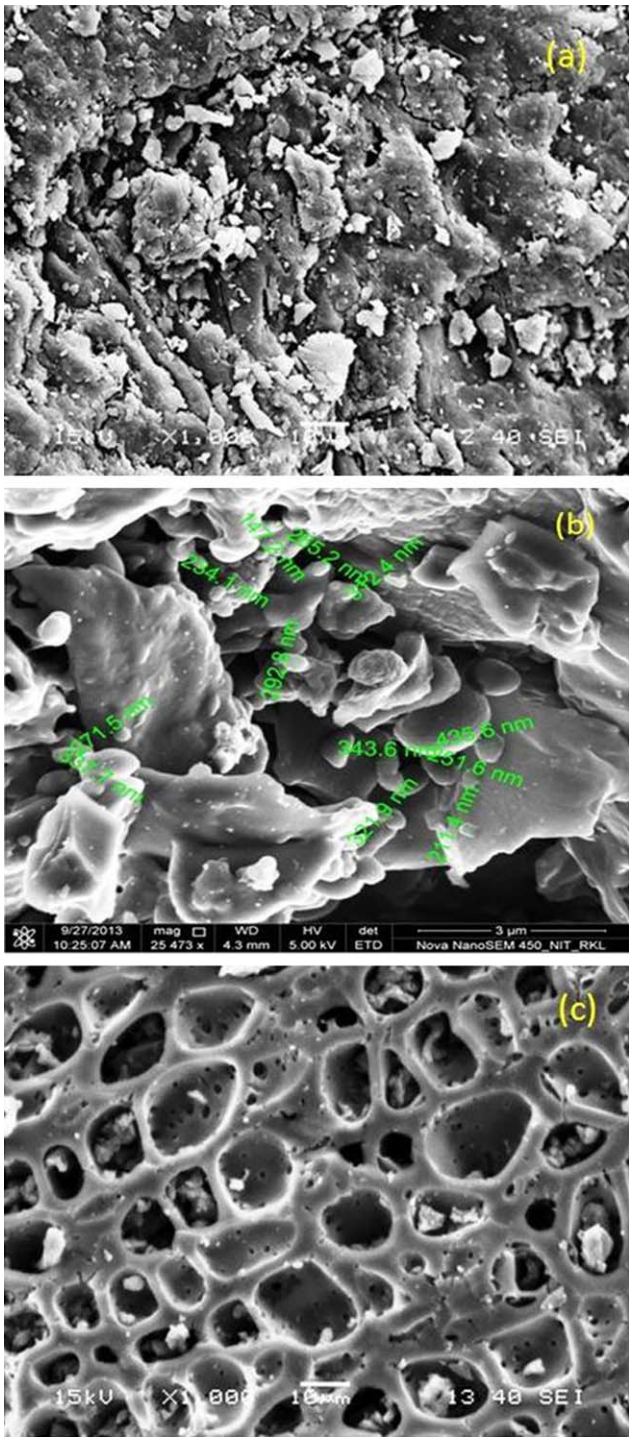

Figure 11. (a) Raw wood apple shell particles. (b) Carbon black wood apple shell particles (600°C). (c) Carbon black wood apple shell particles (800°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite. This suggests that the fillers have some interaction with the matrix, which led to better stress transfer between the matrix material and the fillers.

The SEM of raw wood apple shell particles compared with the derived carbon blacks gave information about changes induced by

the carbonization process as shown in Figure 11(a–c). Initially there were no visible pores in the raw wood apple shell particulates and also these particulates come under the range of 1–212 μm is shown in Figure 11(a). However, after pyrolytic decomposition, the shell particulate comes under nano range, which is shown in Figure 11(b) and due to carbonization process, it generates microporous on the surface of the wood apple shell particulates. WAS-CB particulates possessed numerous micropores with regular size. After every stage of carbonization the porous structure of the particles is wider than the size of the existing pores is shown in Figure 11(c).

CONCLUSION

On the basis of the research presented in this article the following conclusions are drawn.

1. New wood apple carbon black epoxy composites are prepared with different weight fractions of carbon black fillers.
2. Carbon black prepared at 800°C temperature contains the highest percentage of carbon due to the effect of carbonization temperature.
3. The tensile strength and tensile modulus of the carbon black composites are much higher than the raw wood apple shell particulate composites.
4. The FS and flexural modulus of the carbon black composites range between 60–95 MPa and 1.2–3.0 GPa, respectively. These values are higher than the value obtained for neat epoxy and raw powder polymer composite.
5. Carbon black wood apple shell particles improve the hardness of the polymer matrix composite when compared with the neat epoxy and raw shell particulate composite.
6. Scanning electron microscopy of the fracture surface of the composites revealed that addition of WAS-CB improved the interfacial adhesion between the cellulose filler and the polymer matrix. The porous structure of the wood apple shell particles, improves with an increasing in the carbonization temperature.

We predict that these studies will optimize the use of this bio-waste based carbon black for utilization in other advanced composites.

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