Vol. 34, No. 4 (2012) 217-225

Tribology in Industry

www.tribology.fink.rs

RESEARCH

Development of Polyester/Eggshell Particulate Composites

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Keywords:

Eggshell
Polymer matrix composite
Mechanical properties
Uncarbonized
Carbonized
Particulate

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A B S T R A C T

The development of Polyester/Eggshell particulate composites has been carried out. Uncarbonized and carbonized eggshell particles were used as reinforcement in polyester matrix. 10 to 50 wt% eggshell particles at intervals of 10 wt% were added to polyester as reinforcement. The microstructural analyses of the polyester/eggshell particulate composites were carried out using SEM and EDS. The mechanical properties and density were carried out by standard methods. The results showed that the density and hardness values of the polyester/eggshell particulate composite increased steadily with increasing eggshell addition. The tensile strength increased from 15.182 N/mm^2 at 0 wt% eggshell addition to a maximum of 23.4 N/mm^2 at 40 wt% eggshell addition for uncarbonized eggshell; while it increased to a maximum of 28.378 N/mm^2 at 20 wt% eggshell addition for carbonized eggshell. Compressive strength increased steadily from 90.3 N/mm^2 at 0 wt% eggshell additions to a maximum of 103.6 at 50 wt% eggshell addition for uncarbonized eggshell and 116.5 N/mm^2 at 50 % eggshell addition for carbonized eggshell. Hardness value increased from 91 HR_F at 0 % eggshell addition to a maximum of 120.05 HR_F at 50 wt% eggshell addition for uncarbonized eggshell and 149.45 HR_F at 50 wt% eggshell for the carbonized eggshell. Flexural strength increased from 76.06 N/mm^2 at 0 wt% eggshell addition to a maximum of 97.06 N/mm^2 at 40 wt% eggshell addition for uncarbonized eggshell; however, it increased to a maximum of 106.66 N/mm^2 at 20 wt% eggshell addition for the carbonized eggshell. The impact energy also increased from 0.1 Joules at 0 wt% eggshell addition to a maximum of 0.35 Joules at 30 wt% eggshell addition for uncarbonized eggshell; it however increased to a maximum of 0.45 Joules at 20 wt% eggshell addition for the carbonized eggshell. Hence the development of polyester/eggshell particulate composites material with good mechanical properties and light weight which is relevant to the electronics, auto and building industries has been achieved.

1. INTRODUCTION

Polymer composite materials are being used in a wide range of structural applications in the aerospace, construction and automotive industries due to their lightweight and high specific stiffness and strength [1]. A variety of materials are being used ranging from lower performance glass fibre/polyester, used in small sail boats and domestic products, to high performance carbon fibre epoxy systems used in military aircraft and spacecraft. One sector where the use of composite materials is still evolving is the automotive industry. Composite materials offer great potential in reducing vehicle weight, thus increasing fuel efficiency and reducing CO2 emissions. In addition to weight reduction, the number of individual parts can be significantly reduced making the high-volume composite car concept cost effective [2-3].

In its most basic form a composite material is one which is composed of at least two elements working together to produce material properties that are different to the properties of those elements on their own. In practice, most composites consist of a bulk material (the 'matrix'), and a reinforcement of some kind, added primarily to increase the strength and stiffness of the matrix [4].

In recent years there is a perceived shortage of wood fibre for composite products due to competition for fibre by pulp mills, reduced harvesting and manufacturing and diminished log quality. Also, there is pressure from environmentalists to reduce forest use and regulatory legislation pending on disposal of agri-fibres [4-5]. For example, any potential to reduce field burning is an environmental benefit and helps address the issue of restricted open burning. There are tremendous quantities of agricultural biomass available for non-agricultural uses such as paper and composite products.

Previous studies have proved that Chicken eggshell (ES) is an agriculture byproduct that has been listed worldwide as one of the worst environmental problems, especially in those countries where the egg product industry is well developed. In the U.S. alone, about 150,000 tons of this material is disposed in landfills [6]. ES contains about 95 % calcium carbonate in the form of calcite and 5 % organic materials such as type X collagen, sulfated polysaccharides, and other proteins [6-8]. Although there have been several attempts to use eggshell components for different applications, its chemical composition and availability makes eggshell a potential source of filler in polymer composites [6-8]. Report we have shown, among other characteristics that ES has a relatively lower density compared to mineral calcium carbonate. Egg shell is a biomaterial containing 95 % by weight of calcium carbonate in the form of calcite and 5 % by weight of organic materials, such as (Al_2O_3 , SiO_2 , S, Cl, P, Cr_2O_3 , MnO) [8].

The generalized egg shell structure, which varies widely among species, is a protein lined with mineral crystals, usually of a calcium compound such as calcium carbonate These characteristics qualify ES as a good candidate for bulk quantity, inexpensive, lightweight and low load-bearing composite applications, such as the automotive industry, trucks, homes, offices, and factories. Eggshell has been used as a reinforcer in polymer composites. Some of the work carryout's on the use of eggshell in polymer composites are: Patricio Toro et al. [7], studied eggshell, a new bio-filler for polypropylene composites. The work proved that ES composites showed lower modulus of elasticity values than talc composites, talc filler could be replaced by up to 75 % with ES while maintaining a similar stiffness and modulus of elasticity compared to the talc composites.

Abdullah et al. [8] studied the Water absorption and mechanical properties of high – density polyethylene/egg shell composite, It found that the addition of egg shell powder to the polymer leads to decrease in the tensile strength, modulus of elasticity, shore-D hardness on other hand it increases the % elongation at break and impact strength. Water absorption of the composites behavior's as function of days was also investigated, and it increases by increasing exposure time for the same filler content, while the absorbed amount of water increases, by increasing the wt.% of egg shell constant exposure time. The potential of using eggshell particles as a reinforcer has not been explored. It is in the light of the foregoing researches that investigation into the possibility of using eggshell in polymer matrix particulate composite for engineering applications was motivated. The present investigation has been focused on the utilization of abundantly available eggshell in useful manner by dispersing it into polymer matrix to produce composites by stir casting method.

2. FRICTIONAL HEAT GENERATED BETWEEN CONTACT SURFACES

2.1 Materials/Equipment

The polyester resin used in this research is the thermosetting type in paste form and was cured using curing agents and catalyst. The eggshell used in this work was brown eggshell from tea sellers in Samaru, Zaria Nigeria and was used in two forms, uncarbonized and carbonized. The eggshell was washed with water and sun dried to remove the membranes, ground to small particle sizes using the grinding machine and carbonized. Figure 1 below shows the eggshell in the two forms.

(a) (b)

(c) (d)

Fig. 1. Eggshell samples: (a) Uncarbonized; (b) Uncarbonized (ground); (c) Carbonized; (d) Carbonized (ground).

Petroleum jelly was used as a releasing agent to prevent the polyester from sticking to the mold during removal. 2 % each of solution of cobalt nephthalate and Methyl-ethy-ketone (MEK) peroxide were used as accelerator and catalyst respectively.

Sieves, measuring cylinder of 100 ml capacity, a digital weighing balance, crucible furnace, molding (casting) boxes, hacksaw, file, scriber, Hounsfield Tensometer, universal compressive testing machine, a digital Rockwell Hardness machine and Charpy Impact machine are equipment used in this research work.

2.2 Method

The polyester resin was first mixed thoroughly with the accelerator and catalyst (for every 10 ml of polyester used 0.2 ml of catalyst and 0.1 ml of accelerator were used) without any reinforcement for casting of the control sample. Petroleum jelly was used as a releasing agent inside the mold cavity. The mix was then poured immediately into the wooden box and was allowed for some minutes to cure. The polyester resin was then mixed with a varying amount of ground eggshell from 10 wt% to 50 wt% at interval of 10 wt% to produce the polyester/eggshell particulate composites.

The densities of the samples were obtained by cutting the samples and weighing each on the digital weighing balance. The volume of each specimen was then determined and density was determined as the ratio of mass over the volume.

The microstructure and the chemical compositions of the phases present in the eggshell particles and polyester reinforced with eggshell particles composite test samples were studied using a JEOL JSM 5900LV Scanning Electron Microscope equipped with an Oxford INCA™ Energy Dispersive Spectroscopy (EDS) system.

The hardness test of the samples was done on the Rockwell hardness machine using the F scale. A sample of thickness 7 mm was cut and placed on the machine. A minor load of 3 kg was first applied followed by a major load of 60 kg [9].

The impact energy test of the polyester/eggshell particulate composite samples was carried out on the samples on Charpy impact machine to determine the impact energy. Samples were cut to 10 mm × 5 mm × 55 mm dimensions using hack saw. A V-notch of 2 mm deep was then cut on the narrow face which provides stress concentration during the impact test. The sample was then placed on the machine and the pendulum was raised and allowed to swing-fall under the gravity hitting the specimen [10]. Tensile test of the samples was carried out on the Hounsfield tensometer tensile test machine.

The samples were cut to dimension 60×20×5 mm and a gauge length of 30 mm was marked using the scriber. Each sample was then tested and the maximum stress (ultimate tensile strength) and maximum strain were recorded and used for tensile strength calculation [10].

Flexural strength was also carried out on the Hounsfield tensometer tensile test machine. Samples of dimension 60×20×5 mm were cut and bended using an improvised support and a center point load to breaking point [10-12].

Compressive Samples were cut to dimensions 36×18x18 mm and tested on the universal compressive testing machine. A compressive load was applied and the maximum load was read directly from a digital meter [10].

3. RESULTS AND DISCUSSION

From Fig. 2, it can be seen that the density of the polyester reinforced with eggshell particles composites increases with the wt% eggshell addition. This is due to the fact that the eggshell (reinforcing component) is denser than the polyester (matrix) used. The density of the polyester reinforced with uncrabonized (fresh) eggshell particles is, however, higher than that of the polyester reinforced with carbonized eggshell particles composites. This is because volatile components and some organic matters in the eggshell were burnt off to form a mixture of carbonaceous material and ash which are of lower density.

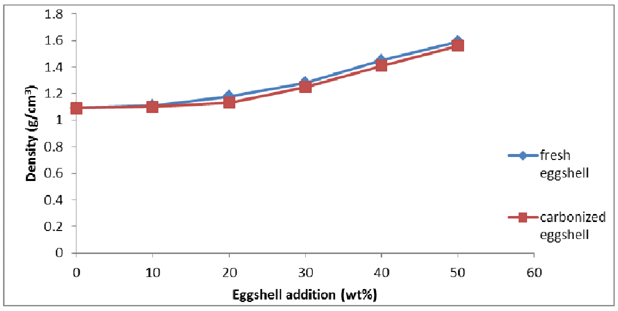
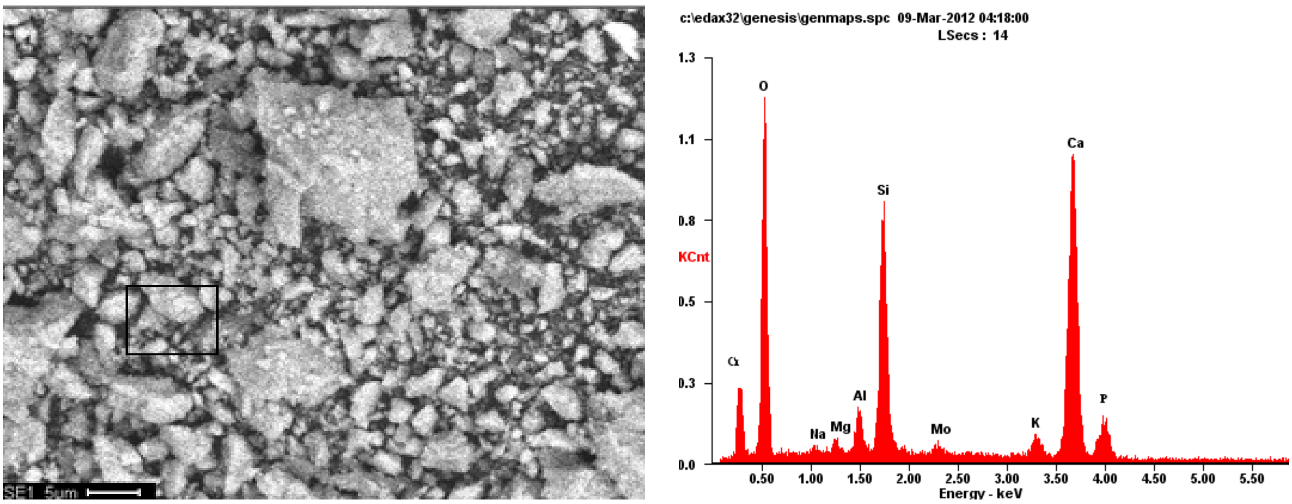


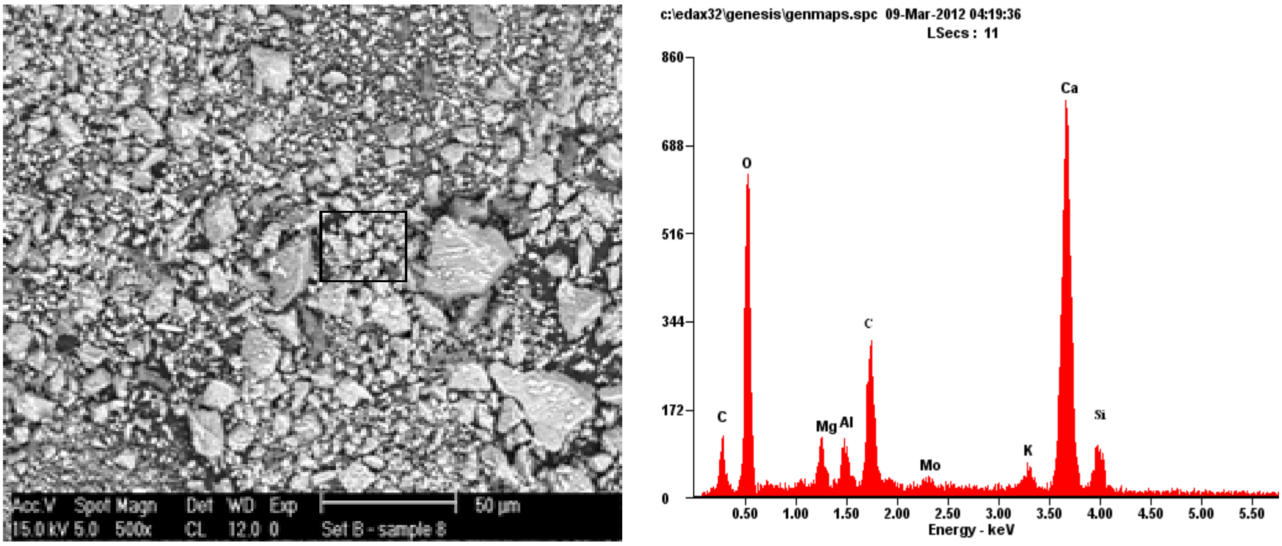
Fig. 2. Variation of density of polyester reinforced with wt% eggshell addition.

The microstructure of the eggshell particle (Uncarbonized and Carbonized) reveals that the size and shape of the particles vary; however, they consist of porous irregular shape particles. The EDS of the eggshell particles reveals that the particles contain Ca, Si, O, C, Mg, p with the presence of C in the carbonized eggshell particles. The carbon presence is due to the carbonization process (Micrographs 1-2). These elements confirm that, the eggshell particles consists of calcium carbonate in the form of calcite ($CaCO_3$), the carbonized eggshell have carbon in graphite form etc. These analyses are in par with others analysis of reinforcement used by other authors [6-8].

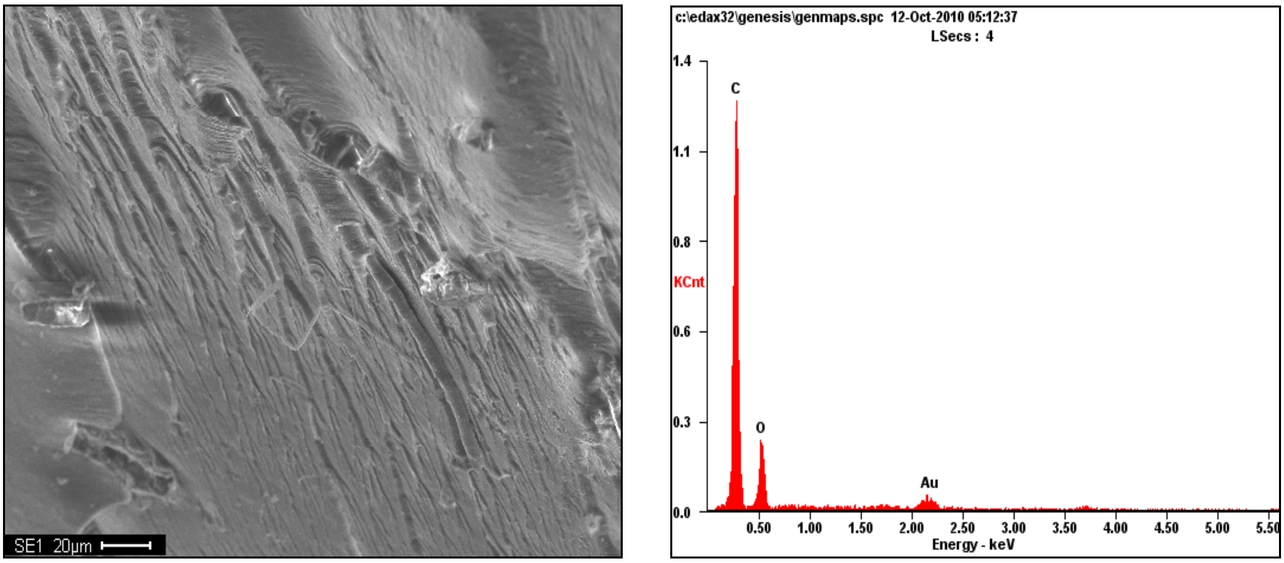
The SEM/EDS microstructures of the composites are shown in Micrographs 3-7.



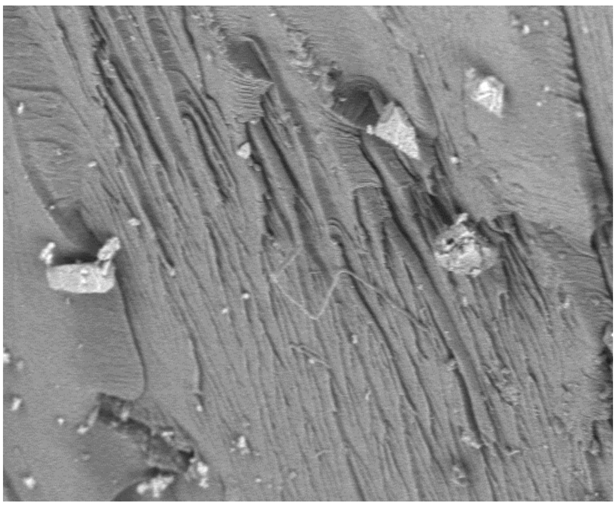
Micrograph 1. SEM/EDS Microstructure of the uncarbonized eggshell particles.



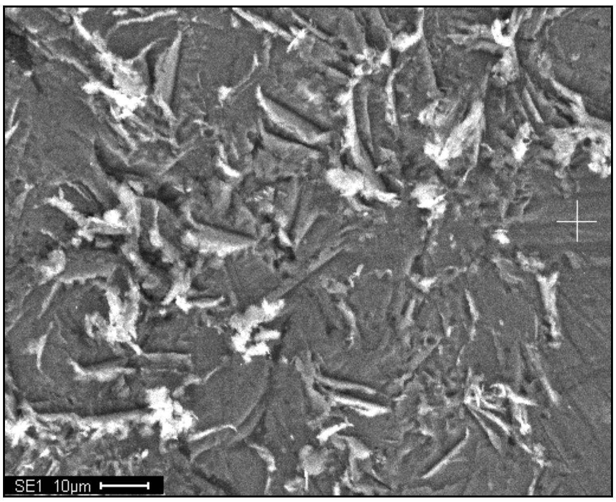
Micrograph 2. SEM/EDS Microstructure of the carbonized eggshell particles.



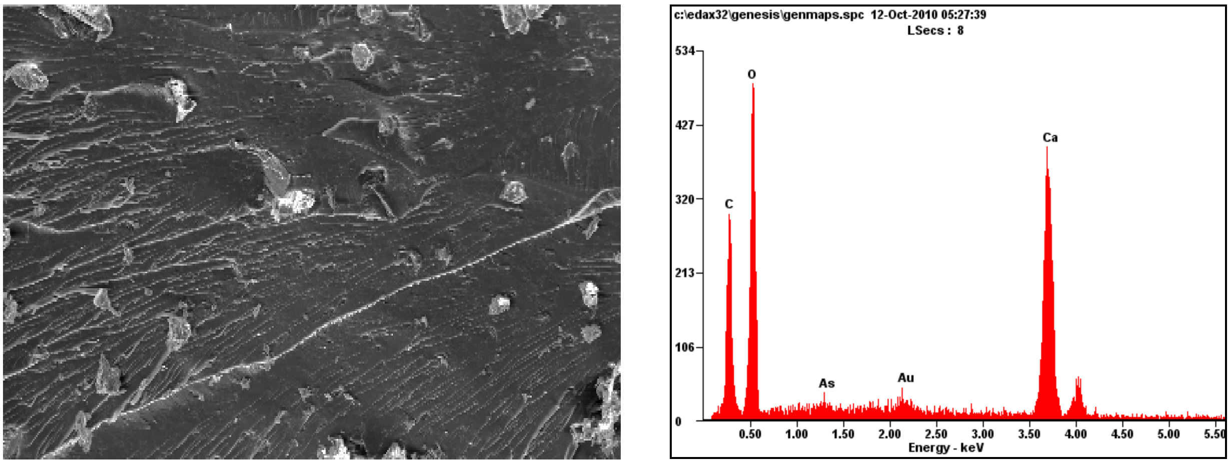
Micrograph 3. SEM/EDS Microstructure of polyester matrix (500×).



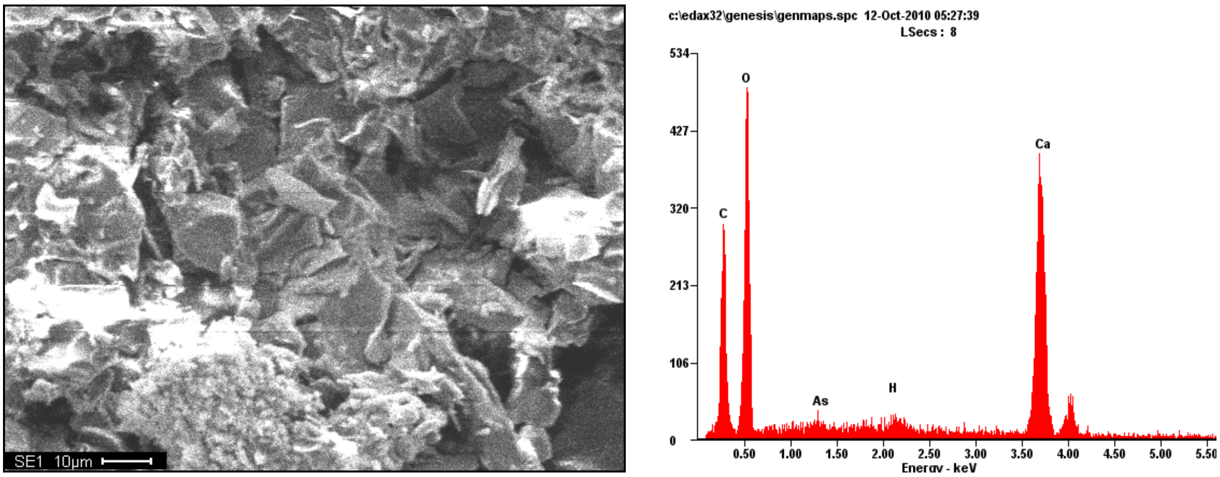
Micrograph 4. SEM Microstructure of 20 wt% uncarbonized eggshell addition polyester composites.



Micrograph 5. SEM Microstructure of 20 wt% carbonized eggshell addition polyester composites.



Micrograph 6. SEM/EDS Microstructure of the 40 % uncarbonized eggshell addition composites.



Micrograph 7. SEM/EDS Microstructure of the 40% carbonized eggshell addition composites.

SEM is used to study the morphology of polyester/eggshell particulates composites produced. Micrograph 3 shows the SEM/EDS micrograph of the polyester, while Micrographs 4-7 shows the SEM/EDS micrographs of the composites. Morphological analysis using SEM clearly show difference in the morphology of the polyester and its composites (see Micrographs 3-7). The microstructure clearly shows that when the eggshell particle was added to the polyester, morphological changes in the structure took place. The microstructure of the polyester matrix reveals chain of lamellae and interlammeller amorphous structure with linear boundaries between adjacent spherulites boundaries (Micrograph 3). From the EDS spectrum, it can be clearly seen that the functional group of the polyester was revealed [12-16].

Morphological study showed that the eggshell as a reinforcement having smooth spherical surface have more surface area for interaction. There is a good dispersion of eggshell particles in the polymer matrix. Micrographs 4-7, clearly show that there is proper intimate mixing of eggshell particles with the polyester resin. Particles-matrix interface plays an important role in composite properties. A strong particles-matrix interface bond is critical for high mechanical properties of composites [13-15]. The result of the tensile strength is shown in Fig. 3.

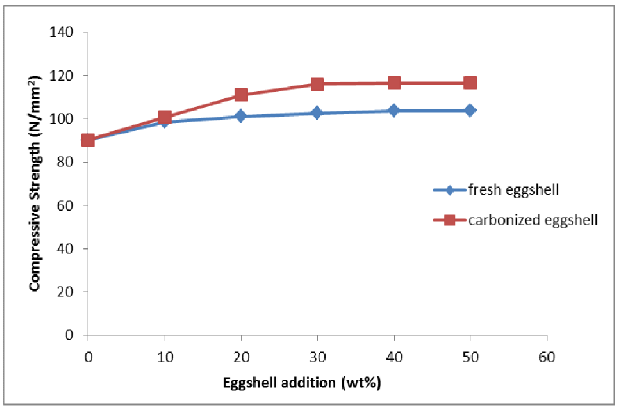


Fig. 3. Variation of UTS of polyester/eggshell composites with wt% eggshell addition.

From Fig. 3, the UTS of the uncarbonized eggshell reinforced polyester matrix composite increases as the wt% eggshell additions increase from 15.182 N/mm² at 0 % eggshell to a maximum of 23.4 N/mm² at 40 % eggshell addition. That of the carbonized eggshell reinforced polyester matrix composite increased to a maximum of 28.378 N/mm² at 20 % eggshell and then decreased steadily to 19.013 N/mm² at 50 % eggshell. The strengthening effect of the carbonized eggshell particles, however, is generally greater than that of the uncarbonized eggshell particles as the UTS of the corresponding percentage of eggshell for the carbonized is greater than that of the uncarbonized (Micrographs 4). The strengthening effect of the carbonized eggshell is attributed to the better-increased surface area of particles in the matrix than uncarbonized eggshell particles (Micrographs 4-5). As the eggshell particles loading increased, thereby increasing the interfacial area, there was fairly good interfacial bonding between the hydrophilic particles and hydrophobic matrix polymer, which leads to increase in the tensile strength [4]. The result of the compressive strength is shown in Fig. 4.

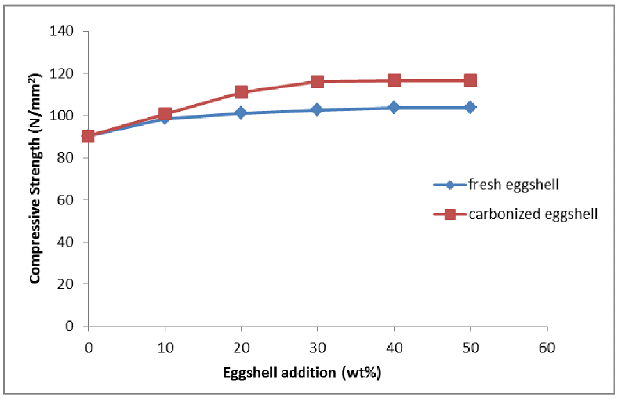


Fig. 4. Variation of Compressive strength of polyester/eggshell particulate composites with wt% eggshell addition.

From Figure 4, it can be observed that the compressive strength of the uncarbonized (fresh) eggshell reinforced polyester composite increased rather steadily from 98.5 N/mm² at 10 % eggshell to 103.6 N/mm² at 50 % eggshell as compared to that of the carbonized eggshell particles addition which increased at a higher rate from 90.3 N/mm² to 116 N/mm² at 30 % eggshell and remained virtually at this value up to 50 %. However, there was no decrease in the compressive strength due to the nature of the load which tends to compact the material the more, closing voids and reducing porosity (Micrographs 4-5). Also because of the high load bearing capacity of the eggshell particles, that helps in strain hardening the polymer matrix

From Fig. 5, the flexural strength of the uncarbonized eggshell reinforced polyester composite increased from 76.06 N/mm² at 0 % eggshell addition as the wt% of eggshell is increased to an optimum value of 97.06 N/mm² at 40 % eggshell addition it then decreased to 83 N/mm² at 50 % eggshell. The flexural strength of the carbonized eggshell reinforced polyester composite, on the other hand, increased to a maximum of 106.66 N/mm² at 20 % eggshell addition and then decreased steadily to 93.33 N/mm² at 50 % eggshell addition. The flexural strength of the carbonized eggshell reinforced polyester composite is generally greater than that of the uncarbonized eggshell reinforced polyester composite and the increase and decreased of flexural strength correspond to that of the UTS values. The decreased in the flexural strength after the optimum are attributed to weak interfacial bonding as the wt% eggshell shell particles increased to 50 wt% which resulted to weak the bending load carrying by the matrix [1-4].

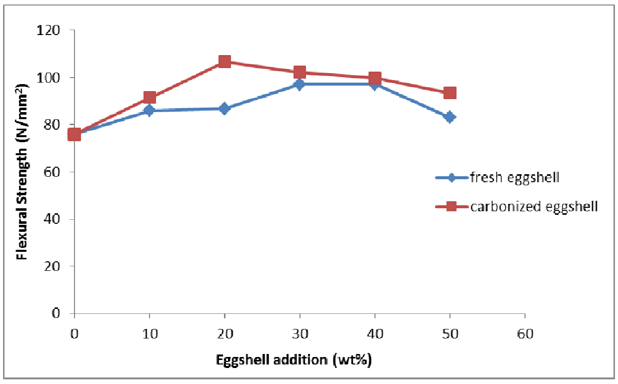


Fig. 5. Variation of Flexural strength of polyester/eggshell particulate composite with wt% eggshell addition.

Figure 6 shows that the hardness value of the polyester/eggshell particulate composites produced increased gradually as the wt% eggshell additions is increased. The hardness of the carbonized eggshell reinforced polyester composite is however greater than that of the uncarbonized eggshell reinforced polyester carbonized. This is because when organic matters are carbonized they tend to increase in hardness and stiffness. From the Fig. 6, it is seen that the hardness values of the polyester/eggshell particulate composite reinforced with carbonized eggshell is greater than that reinforced with uncarbonized eggshell particles. This may be attributed to the fact that carbonized eggshell particles may contains more carbon, has given off all combined moisture and therefore increase in the hardness of the composite.

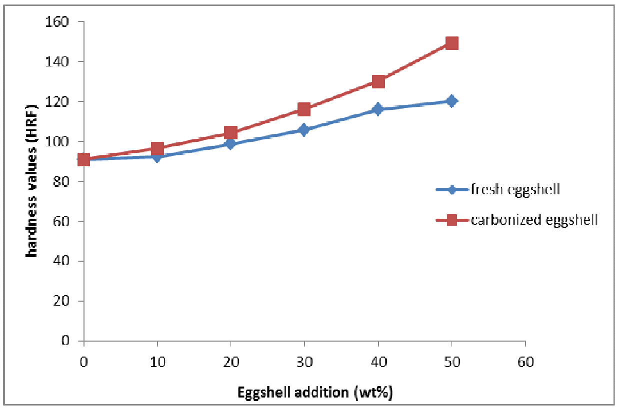


Fig. 6. Variation of hardness value of polyester/eggshell particulate composite with wt% eggshell addition.

The impact energy increased sharply from 0.1 J at 0 % eggshell to a maximum of 0.35 J at 30 % eggshell and 0.45 J at 20 % eggshell for the uncarbonized eggshell and carbonized eggshell reinforced polyester composites respectively (Fig. 7). The polyester/eggshell particulate composite developed can therefore be said to exhibit impact properties similar to that of the glass-reinforced polyester [6-7].

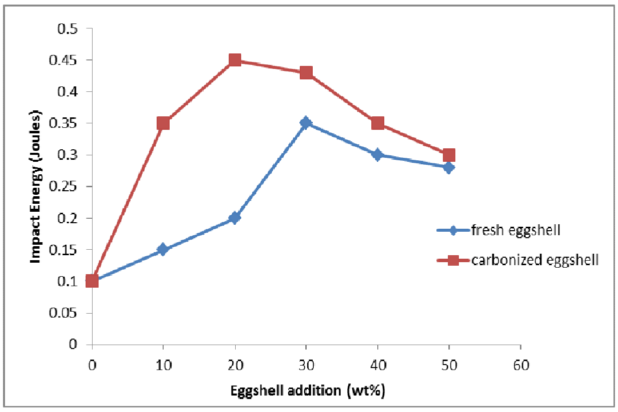


Fig. 7. Variation of impact energy of polyester/eggshell particulate composite with wt% eggshell addition.

4. CONCLUSIONS

The following conclusions can be drawn from the results of this research:

1. Polyester/eggshell particulate composites were successfully produced by casting method.
2. The tensile and bending strengths of the composite increase with increasing percentage of the eggshell particles.
3. Hardness values obtained when reinforcing polyester with eggshell as particles increases as the weight of the particles increased in the polyester matrix.
4. The better strengthening effect of the carbonized eggshell can be attributed to the better interfacial bond between carbonized particles and polyester matrix as revealed from the SEM studies.

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