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Mechanical properties of calcium carbonate/eggshell particle filled polypropylene Composites

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ABSTRACT

Calcium carbonate is widely used as a filler material in the production of polymer matrix composites and studies have shown that eggshell contains about 94% calcium carbonate. The effect of calcium carbonate from eggshell particles in polypropylene was studied in this work and the result compared with unreinforced polypropylene. Industrially synthesized calcium carbonate/eggshell particles were used as filler in polypropylene matrix with varying mass fractions from 5 to 20 wt. % at 5 wt. % increment. The produced samples were mechanically characterized for indentation hardness and uniaxial tensile properties using a Rockwell hardness tester and universal mechanical testing machine respectively. These properties were measured at different compositions to determine its compositional dependence. Microstructural analysis of the composites top and fracture surface was also carried out using scanning electron microscope to examine possible failure mode. The results were compared to measure the effect of reinforcement and the replacement criteria for the conventional calcium carbonate. The results obtained showed that calcium carbonate reinforced polypropylene has its highest tensile strength, elastic modulus and modulus of rupture at 5 wt. %, ductility and modulus of resilience at 10 wt. %, and hardness at 15 wt. %. The results also showed that granulated eggshell can provided appreciable improvement in the mechanical properties of polypropylene as obtainable in mineral calcium carbonate reinforced polypropylene.

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1.0 INTRODUCTION

Recent research has shown increased focus on the use of natural or lignocellulose fillers to reinforce polymers. This is largely due to several positive contributions of these type of fillers to the composites [1]. Several natural fibers and fillers have been studied as thermoplastic reinforcement, including jute, sawdust, sisal, coconut fiber and coconut shell [2]. Many of the natural fillers reinforced polymer composites have found domestic and industrial structural applications [3]. For years, fillers have been used extensively to improve the mechanical properties of polymeric materials. The main benefits of incorporating fillers in plastics is for increased stiffness and lowered cost of the resulting composites [4]. Besides, polymer/filler composites also provide higher density as compared to unfilled thermoplastics. Previous studies have shown that calcium carbonate can act as a reinforcing agent in polymer matrix composites [5]. The use of calcium carbonate as filler in Polypropylene composites have grown since the 1980s [6] and the vast resources of calcium carbonate have driven plastic manufacturers to switch to it as a cheaper alternative to fill Polypropylene composites.

Eggshells have been identified to contain up to 94 % calcium carbonate [7], relatively economical and readily available [8]. The use of eggshell as a filler in reinforced polypropylene can provide means of cleansing the environment of pollution problem which the eggshells constitute and provide economic value for the eggshells. Its usage will also, provide an alternative to the predominantly used synthesized calcium carbonate for reinforcement of polymer matrices.

Previous studies by Isaac and Onuegbu, on the mechanical and end-use properties of eggshell and fish bone filled polypropylene determined at filler content of 0-40 wt. % resulted in the improvement in the tensile strength, tensile modulus, flexural and impact strength of the composite. The properties improved with increase in filler content and decrease in filler particle sizes. [9]. In a related study involving rice-husk flour filled polypropylene, four levels of filler loading (10, 20, 30 and 40 wt. %) was designed. The results showed tensile modulus improvement with increasing filler loading [10].

A study by Ahmed et. al. [11] utilized compounded eggshell with polypropylene polymer molded by using the extrusion compression molding (ECM) process. They study the effect of filler loading of 30 wt. % of eggshell and 30 wt. % eggshell with 5 wt. % of Maleic Anhydride grafted polypropylene (MAPP) on the mechanical and thermal properties. The addition of small amount of MAPP during melt extrusion improved the dispersion and bonding of $CaCo_3$ particles in polypropylene. The results showed 7.49 % decrease in tensile strength, 35.51 % enhancement in flexural modulus and 66.51 % increase in notched Izod impact energy. Adding 30 wt. % of eggshell filler and 5 wt. % MAPP to polypropylene delayed the flame propagation time by 99 seconds. In their conclusion, the thermal stabilities of the bio-composites was noted to be enhanced as compared to plain polypropylene [11].

In this study, mineral calcium carbonate and eggshell were used as reinforcing agent in polypropylene matrix to enhance the composite mechanical properties. It focusses on the mechanical and microstructural characterization of filler (mineral calcium/eggshell) reinforced polypropylene in relation to its application in engineering among others and also intends to justify the use of egg shell (particulate) as a possible replacement for synthesized calcium carbonate in particle reinforced polypropylene.

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2.0 MATERIALS AND METHODS

2.1 Preparation of fillers

The eggshells (filler material) used in this study was collected from waste bins of household food industries. Eggshell of 2.50 kg was soaked in about 8 liters of water and mixed thoroughly before being allowed to settle for 24 hours. It was remixed and the liquid was decanted from the mixture to remove impurities attached to the shells. The same procedure was repeated for another five days before the eggshell was air dried in an open container. The dried eggshells in lumps was crushed in a mortar with pestle and milled to obtain powdered eggshell. The powdered shell was sieved with a mesh size of 0.3µm (Fig. 1). Mineral calcium carbonate (Product number: CAZ-2380) with percentage purity of 98% was obtained from a retail store in Lagos, Nigeria.

(a) (b)



Figure 1: (a) dried eggshell and (b) sieved eggshell

2.2 composite preparation

Polypropylene obtained from a retail store in Lagos, Nigeria was weighed and poured in two containers labelled A and B. Mineral calcium carbonate and powdered eggshell was added respectively at 5 wt. %, 10 wt. %, 15 wt. % and 20 wt. % for each measured polypropylene. A third container C contain plain polypropylene, which served as the control. These constituent materials were mixed thoroughly in each of the container and transfer to an injection molding machine for compressive hot molding. The composite material was weighed, mixed, and poured into the hopper of the machine for compressive molding to produce a scoop. The composites were cooled in air and cut into samples with dimension 100 mm x 25 mm x 3 mm for micro-structural and mechanical characterization (Fig.2). Six samples were produced for each test to be carried out.

(a) (b)



Figure 2: (a) Scoop produced and (b) cutting of scoop to required sizes

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2.3 Microstructural analysis of Composite

The microstructural analysis of the particle filled polypropylene composites was carried out using a Carl Zeiss MA-10 Scanning Electron Microscope (SEM). The top and fracture surfaces were analysed to check the differences in the microstructure of plain polypropylene and the filler (mineral calcium carbonate/eggshell) reinforced polypropylene.

2.4 Micro-mechanical Characterization

An Instron 3360 series (Norwood, MA, USA) with a 50kN load cell was used for the determination of the uniaxial tensile properties of particle reinforced polypropylene composites. The samples were tested at room temperature with average relative humidity of 65%. Standard test method based on ASTM standard test method D 882 for tensile properties of thin plastic sheet was used [12]. The tensile specimens were deformed at a loading rate of 0.2 mm/s until fracture occurred by separation of specimens into two pieces. The tensile strength was then estimated using the following equation [13]:

$$\sigma = F_A/A_o \tag{1}$$

Where F_A is the peak load at the onset of fracture and A_0 is the initial cross-sectional area. A total of six tensile tests were conducted for each condition. The resulting stress-strain curve obtained from tensile test was used to estimate the elastic modulus given by:

$$E = \sigma/\varepsilon \tag{2}$$

This value corresponds to the slope of the elastic section of the stress-strain cure where σ is the stress and ε is the corresponding strain.

A three-point bend loading configuration was used to estimate the modulus of rupture (flexural/bend strengths). A loading span of 80 mm was used for the entire three-point bend test. The specimens were loaded monotonically at a loading rate of 3.3 N/s. For each composite formulation. The flexural/bend strength, σ_f, was obtained from [14]:

$$\sigma_f = 3FL/2BH^2 \tag{3}$$

F is the maximum load, L is the loading span, B and H are the specimen breadth and height, respectively.

Ductility in terms of the degree of the plastic deformation that has been sustained at fracture was calculated and expressed in percentage elongation (% EL) as:

$$\%EL = \frac{L_f - L_o}{L_o} \times 100 \tag{4}$$

Where L_f and L_0 are the final and original length of the tensile specimen [14].

The modulus of resilience, U_r was obtained using equation 5. Under a uniaxial tension test, it is mathematically expressed as [14]:

$$U_r = \frac{1}{2}\sigma_y\varepsilon_y \tag{5}$$

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Lastly, the composite hardness was measured using a Rockwell hardness apparatus (model HR – 150A Rockwell Apparatus, manufactured by Zhejiang Tugong instrument Co. Ltd). The hardness number was determined by the difference in depth of penetration resulting from the application of an initial minor load follow by a larger major load [15]. A steel ball indenter was used for the penetration using parameters in Table 1. The hardness of the composites was gotten from the average of five readings from different point on the composite's top surface.

Table 1: Penetrator and test force table [16]

Penetrator testing materials	**Used part hardness range**	**Penetrator needed**	**Test force (kgf)**	**Measuring tolerance**
Soft, middle, hardness or unquenched steel parts	HRB 20-100	Ø 1/16" steel ball penetrator	100	±1.5

3.0 RESULTS AND DISCUSSION

3.1 microstructural characterization

The surface morphology of samples observed using a scanning electron microscope at 500 x magnification are presented in Fig. 3. These show the difference in the microstructure of the plain polypropylene and composites. The micrographs show a very good blend between the reinforcement particles and the polypropylene matrix. Hence, delamination at the interface is expected to be very limited.

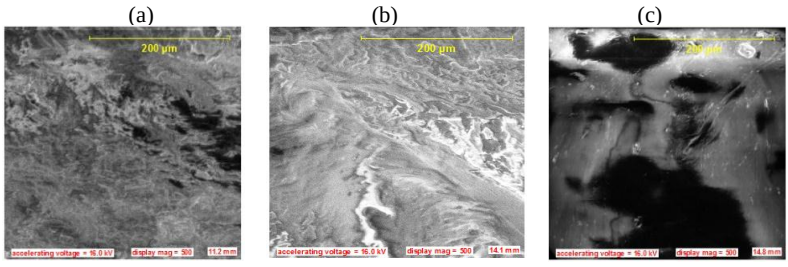


Figure 3: Micrograph showing the surface of (a) plain polypropylene, (b) 5 wt. % mineral calcium carbonate reinforced polypropylene (c) 5 wt. % eggshell particles reinforced polypropylene

The microstructural analysis of the fracture surfaces of the composites were also obtained at x500 magnification and the results presented in Fig. 4 and 5. The results also show the reduction in dimples as reinforcement is increased signaling a reduction in ductility of the composite and subsequently increasing strength and hardness.

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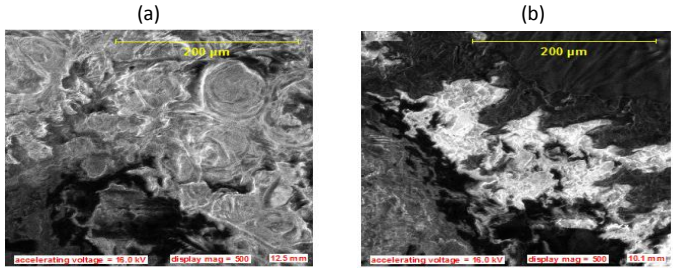


Figure 4: Micrograph of fracture surface for reinforced polypropylene composite at (a) 15 wt. % and (b) 20 wt. % mineral calcium carbonate particles.

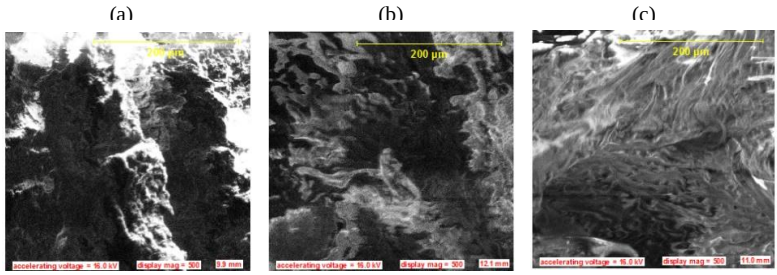


Figure 5: Micrograph of fracture surface for reinforced polypropylene composite at (a) 10 wt. % (b) 15 wt. % and (b) 20 wt. % eggshell particles.

3.2 Micro-mechanical Characterization

3.2.1 Tensile Strength and Elastic Modulus

The tensile strengths of the composites are presented in Fig. 6a. The results obtained shows that the strength is enhanced by introduction of filler ($CaCO_3$/Eggshell). Optimum tensile strength was obtained at a filler content of 15 wt. %. for both $CaCO_3$ and eggshell with values of 22.03 MPa and 19.55 MPa respectively. The results also show that the tensile strengths of the polypropylene composites reinforced with $CaCO_3$ and eggshell are comparable.

The modulus of elasticity of the samples were obtained Equation 2. The calculated elastic modulus is presented in Fig. 6b. The results showed that modulus of elasticity of $CaCO_3$ reinforced polypropylene with 5 wt. % filler is at maximum (with elastic modulus of 546.1 MPa) while the eggshell reinforced polypropylene has the highest modulus of elasticity at 10 wt. % (552.51 MPa). Both cases showed improved modulus of elasticity with the introduction of filler. They are also comparable for use as reinforcement in polypropylene matrix although, at different mass fraction for optimum property.

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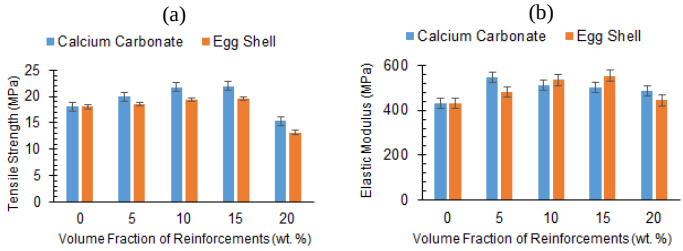


Figure 6: (a) Tensile strengths and (b) Modulus of Elasticity obtained for different volume fraction of filler materials in polypropylene composites.

3.2.2 Modulus of Rupture and Ductility

The modulus of rupture of the composites was estimated using the Equation 3. The results are presented in Fig. 7a and it shows that the $CaCO_3$ and eggshell particle reinforced polypropylene has highest modulus of rupture at 5 wt. % filler with a value of 1089 MPa and 985.85 MPa respectively. The modulus of rupture is enhanced by filler ($CaCO_3$ and eggshell particles) inclusion up to 5 wt. % but decreases afterword. Also observed is the similarity in the results obtained for both fillers.

From the elongation during the tensile test, the ductility obtained using Equation 4 and the calculated % elongation is presented in Fig. 7b. The composite proved to be most ductile when it was reinforced with $CaCO_3$ or eggshell particles at 10 wt. % filler, above which the ductility reduces. The unreinforced polypropylene matrix has the highest ductility. This implies that the introduction of the particles ($CaCO_3$/eggshell) increases the strength of the composites as shown in Fig. 6a.

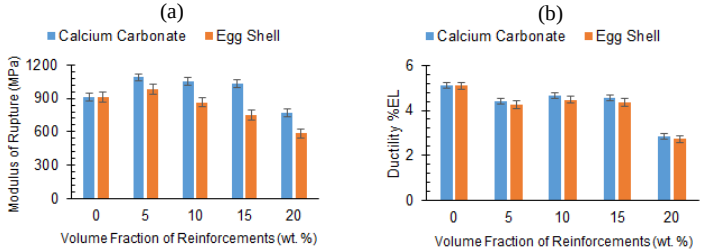


Figure 7: (a) Modulus of Rupture and (b) Ductility obtained for different volume fraction of filler materials in polypropylene composites.

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3.2.3 Modulus of Resilience and Hardness

The modulus of resilience was evaluated from the tensile test results using Equation 5. The unreinforced samples have the highest modulus of resilience while the composites reinforced with calcium carbonate/eggshell particles exhibited highest modulus of resilience between 10 wt. % to 15 wt. % filler as shown in Fig. 8a. These results also affirm that the inclusion of either $CaCO_3$ or eggshell particle into polypropylene matrix strengthens the materials. The slightly low values recorded for eggshell filled polypropylene can be with resolved with a reduced particle size [9], [17].

The measured hardness of the composites is presented in Fig. 8b. The results show that the measured hardness is lowest at 0 wt. % filler ($CaCO_3$ and eggshell particles). This implies that the composites lose ductility due to the particulate reinforcement resulting in the strengthening of the materials. The results also show that optimum composite hardness is obtained at 15 wt. %. This also validate earlier results presented in Fig. 6a where the composites tensile strength is enhanced by particle reinforcement.

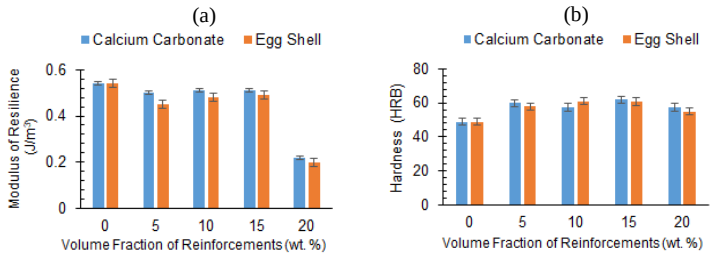


Figure 8: (a) Modulus of Resilience and (b) Hardness obtained for different volume fraction of filler materials in polypropylene composites.

4.0 IMPLICATIONS

The implications of this work are significant for the design of $CaCO_3$ and eggshell particle filled polypropylene composites with optimum properties. The results show improvement in mechanical properties of polypropylene when it is reinforced with either particles. This is obvious from the improvement in composite mechanical properties measured as the fraction of the fillers are increased considerably. This work also presents the possibility of replacing mineral $CaCO_3$ with eggshell particles for reinforcement of polypropylene thus providing economic benefit to the eggshell.

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5.0 SUMMARY AND CONCLUDING REMARKS

1. Composites consisting of polypropylene matrix reinforced with $CaCO_3$ and eggshell particles at different mass fractions were produced.
2. The uniaxial tensile properties and hardness of the composites were measured, and the results compared to determine the effects of the reinforcement and the optimum compositions.
3. The results show enhancement in composites strength with optimum properties 10 to 15 wt. % filler for the properties measured.
4. The strengthening resulting from the particle reinforcement was elucidated by the reduction in composite ductility and increase in hardness.
5. The results also show that eggshell particles can served as reinforcement materials to produce a particle filled polypropylene.

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REFERENCES

[1] H. S. S. Shekar and M. Ramachandra, "Green Composites: A Review," *Mater. Today Proc.*, vol. 5, no. 1, pp. 2518–2526, 2018.

[2] N. Saba, P. M. Tahir, and M. Jawaid, "A review on potentiality of nano filler/natural fiber filled polymer hybrid composites," *Polymers (Basel).*, vol. 6, no. 8, pp. 2247–2273, 2014.

[3] T. Huber, M. Misra, and A. K. Mohanty, "The effect of particle size on the rheological properties of polyamide 6/biochar composites," in *AIP Conference Proceedings*, 2015, vol. 1664, p. 150004.

[4] L. M. Matuana and N. M. Stark, "The use of wood fibers as reinforcements in composites," in *Biofiber Reinforcements in Composite Materials*, Elsevier, 2014, pp. 648–688.

[5] Y. Jing *et al.*, "Reinforcing polypropylene with calcium carbonate of different morphologies and polymorphs," *Sci. Eng. Compos. Mater.*, vol. 25, no. 4, pp. 745–751, Jul. 2018.

[6] Y. W. Leong, M. B. Abu Bakar, Z. A. M. Ishak, A. Ariffin, and B. Pukanszky, "Comparison of the mechanical properties and interfacial interactions between talc, kaolin, and calcium carbonate filled polypropylene composites," *J. Appl. Polym. Sci.*, vol. 91, no. 5, pp. 3315–3326, Mar. 2004.

[7] J. Neunzehn, T. Szuwart, and H. P. Wiesmann, "Eggshells as natural calcium carbonate source in combination with hyaluronan as beneficial additives for bone graft materials, an in vitro study," *Head Face Med.*, vol. 11, no. 1, p. 12, Dec. 2015.

[8] F. E. Robinson, G. M. Fasenko, and R. A. Renema, "Optimizing chick production in broiler breeders," *Spotted Cow Press*, pp. 1–24, 2003.

[9] G. C. Onuegbu and I. O. Igwe, "The Effects of Filler Contents and Particle Sizes on the Mechanical and End-Use Properties of Snail Shell Powder Filled Polypropylene," *Mater. Sci. Appl.*, vol. 02, no. 07, pp. 810–816, 2011.

[10] H. S. Yang, H. J. Kim, J. Son, H. J. Park, B. J. Lee, and T. S. Hwang, "Rice-husk flour filled polypropylene composites; mechanical and morphological study," *Compos. Struct.*, vol. 63, no. 3–4, pp. 305–312, Feb. 2004.

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[11] A. A. Hassen, M. Dizbay-Onat, D. Bansal, T. Bayush, and U. Vaidya, "Utilization of chicken Eggshell Waste as a Bio-Filler for thermoplastic Polymers: Thermal and Mechanical characterization of Polypropylene Filled With naturally derived caco3," *Polym. Polym. Compos.*, vol. 23, no. 9, pp. 653–662, Nov. 2015.
[12] ASTM International, *ASTM E459 - 05: Standard test method for measuring heat transfer rate using a thin-skin calorimeter*. 2011.
[13] M. M. Ashby and D. R. H. Jones, *Engineering Materials 1*. 2012.
[14] W. D. . J. Callister and D. G. Rethwisch, "Materials Science and Engineering: An Introduction Seventh Edition," in *Wiley*, 2007, pp. 131–173.
[15] Polzin T, "Hardness Measurment of Metals- Static Methods," in *In: Herrmann K (ed) Hardness Test. Princ. Appl., 1st ed. ASM International*, 2011, pp. 25–66.
[16] W. S. Liggett, S. R. Low, D. J. Pitchure, and J. Song, "Capability in Rockwell C Scale Hardness," *J. Res. Natl. Inst. Stand. Technol.*, vol. 105, no. 4, pp. 511–532, 2000.
[17] A. Nourbakhsh, A. Karegarfard, A. Ashori, and A. Nourbakhsh, "Effects of particle size and coupling agent concentration on mechanical properties of particulate-filled polymer composites," *J. Thermoplast. Compos. Mater.*, vol. 23, no. 2, pp. 169–174, Mar. 2010.

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