

Physical and Morphological Properties of Periwinkle Shell-Filled Recycled Polypropylene Composites.

C. Onuoha¹, O.O. Onyemaobi², C.N. Anyakwo³, G.C. Onuegbu⁴.

^{1,2,3}Department of Materials and Metallurgical Engineering, Federal University of Technology, Owerri.

⁴Department of Polymer and Textile Engineering, Federal University of Technology, Owerri.

¹Correspondence Author: chukwudikeonuoha@gmail.com

ABSTRACT

Physical and morphological properties of periwinkle shell-filled recycled polypropylene composites were studied. Periwinkle shells used in this study were processed and sieved to three particle sizes of 150, 300 and 425 μm respectively. Filler loadings of 0 to 25 wt% were used in compounding the composites in an injection moulding machine and the resulting composites were extruded as sheets. Some physical and morphological properties were determined. Results showed that the incorporation of periwinkle shell powder into the recycled polypropylene matrix increased the specific gravity of the composites. Increase in filler loading resulted to increase in specific gravity probably due to enhanced dispersion of fillers. However, increase in filler particle size led to decreased specific gravity due to poor filler dispersion and consequent filler agglomeration. Water sorption was found to increase with increase in both filler loading and filler particle size due to the hydrophilic nature of the filler and enhanced porosity created by large particles. Flame propagation was found to decrease with increase in both filler loading and filler particle size due to the evolution of CO_2 in the combustion process, which suppresses the burning rate. There was increase in solvent sorption with increase in both filler loading and filler particle size. It was also noticed that solvent sorption was most pronounced in benzene, followed by toluene and lastly xylene. This is in accordance with the order of closeness of their solubility parameters with that of polypropylene. Morphological analysis revealed enhanced spherulization and dispersion with smaller particle sizes but enlarged spherulization and consequent agglomeration at larger particles sizes. Based on these results, periwinkle shell can be considered suitable for the production of recycled polypropylene composites.

Key Words: Physical Properties, Recycled Polypropylene, Morphology, Periwinkle Shell, Specific Gravity, Flame Propagation, Solvent Sorption.

1.0 Introduction

Materials are probably more deep-seated in our culture than most of us realize. Transportation, housing, clothing, communication, recreation, and food production - virtually every segment of our everyday lives is influenced to one degree or another by materials. Historically, the development and advancement of societies have been intimately tied to the members' ability to produce and manipulate materials to fill their needs. Advancement in the understanding of a material type is often the forerunner to the stepwise progression of a technology. For example, automobiles would not have been possible without the availability of inexpensive steel or some other comparable substitutes. In our contemporary era, sophisticated electronic devices rely on components that are made from what are called semiconducting materials (Calister & Rethwisch, 2010).

There is rapid increase in the use of polymeric materials such as plastics in various applications like engineering, medicine, automobile, sports, domestics, packaging, etc, as a result of effective modification of the properties of plastics using additives. This enables

polymeric materials to overcome its specific deficiencies during service and new environmental regulations which demand the search for materials that are eco-friendly (Nwanonenyi et al., 2013).

Plastic industry uses inorganic fillers such as talc, calcium carbonate, mica and glass or carbon fibres to modify the performance of thermoplastics. Inorganic fillers provide rigidity and temperature resistance; however, these fillers are costly and abrasive to the processing equipment (Cletus, 2002; La Mantia et al., 2005).

Organic fillers produced from agricultural wastes have gained tremendous attention from plastic industry, with primary advantages of low densities, low cost, non-abrasiveness, high filling levels, low energy consumption, biodegradability, availability of a wide variety of fibres throughout the world and generation of a rural/agricultural-based economy (Onuegbu & Madufor, 2012).

Several research works have been reported on organic fillers reinforced thermoplastic composites, which have proved their applicability in various fields. Such fillers include groundnut shell, cocoa nut shell, palm kernel shell (Ishidi, 2014), bean pod ash (Atuanya et al., 2014), snail shell powder (Onuegbu & Igwe, 2011), cocoa pod (Onuegbu et al., 2014), oyster shell powder (Nwanonenyi et al., 2013), saw dust (Saeed et al., 2005) and maize tassel (Onuegbu & Madufor, 2012).

Periwinkle (*Littorina littorea*) is a species of small edible sea animal, a marine gastropod mollusk. The shell makes up over 70% of the weight of the animal. The shells have no identified use and are found littered around markets and homes (Reid & Gofas, 2011).

Much research efforts are geared towards possible ways of recycling wastes for reuse to keep environment clean and safe (Atuanya et al., 2014). Hence, the use of periwinkle shell powder in producing recycled polypropylene composites is therefore hoped to convert wastes to wealth, tackle the problem of environmental pollution, reduce the material cost and produce biodegradable composites.

2.0 Materials and Method

2.1 Materials

Polypropylene (PP) used in this research was a product of SK Global Chemicals Limited, Korea obtained from CeePlast Limited Aba, Abia State. It has a melt flow index of 0.4g/10 min at 150 °C and density of 0.922g/cm³.

Recycled polypropylene was sourced from Ihiagwa village, Owerri West L.G.A., Imo State and was thoroughly washed and prepared.

The compatibilizer; maleic anhydride-grafted-polyethylene (MAPE) used was bought from CEEPlast Industry, Aba, a product of Sigma Aldarich Company, U.S.A. It has the following properties: maleic anhydride = 0.5 wt%, viscosity = 500 cP (140 °C) and saponification value = 60 KOH/g.

Periwinkle shell was obtained from Ihiagwa Market after the edible portion had been harvested. The shells were soaked in water for one week to thoroughly remove impurities. They were dried, ground and sieved to three particle sizes of 150, 300 and 425 µm. The chemical composition of the periwinkle shell is as shown in Table 1.

Table 1: Elemental composition of periwinkle shell

Elemental oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Mn ₂ O ₃	TiO ₂	LOI
%	33.84	10.2	6.02	40.84	0.48	0.26	0.14	0.24	0.01	0.03	7.6

2.2. Preparation of Polypropylene Composites

The polypropylene composites of periwinkle shell powder were prepared by thoroughly mixing 100g of virgin polypropylene and 100g of recycled polypropylene with appropriate filler contents (5, 10, 15, 20 and 25 wt%) as shown in Table 2, and 7 g of maleic anhydride was added to enhance compatibility between the hydrophilic filler and the hydrophobic polymer matrix.

Table 2: Composition of Evaluated Formulations.

Code	Virgin PP (g)	Recycled PP (g)	PS (wt%)
V (Control)	200	0	0
P ₁	100	100	5
P ₂	100	100	10
P ₃	100	100	15
P ₄	100	100	20
P ₅	100	100	25

Each mixture was melted and homogenized with the filler in an injection moulding machine. The operation was carried out at an injection pressure of 9.81 MPa and temperatures of 250 °C. The mixture was then extruded as sheets with dimensions of 150 x 150 x 4mm. Test samples were prepared from the sheets for the physical and morphological properties testing.

2.3 Testing

Determination of Specific Gravity (Relative Density) Test

The hydrostatic weighing method was used in this test. Since the samples float and do not sink in water unaided, a less dense liquid such as gasoline was used for this test instead of water. A massless thread was used in suspending the specimens in air and gasoline during measurement by means of a sensitive spring balance. The test specimen was first weighed in air to obtain the **weight in air** ($W_{s,air}$) and later immersed in gasoline to obtain the **weight in gasoline** ($W_{s,gas}$). The specific gravity of the specimen with respect to gasoline was calculated as follows:

Specific gravity wrt gasoline,

$$SG_{wrtgas.} = \frac{W_{s,air}}{W_{s,air} - W_{s,gas.}} \tag{1}$$

The actual specific gravity of the sample (i.e. relative to water) was calculated by multiplying equation (1) with the specific gravity of gasoline

Specific gravity of sample,

$$SG = \left(\frac{W_{s,air}}{W_{s,air} - W_{s,gas.}} \right) \times 0.74 \tag{2}$$

where the specific gravity of gasoline = 0.74.

Determination of Water Absorption

This was determined according to ASTM procedure (ASTM D96-06). Rectangular specimens were cut from each sample and weighed to the nearest 0.001g. The samples were immersed in water for 24 hours at room temperature. Excess water on sample surface was removed before reweighing. The percentage increase in mass during immersion was calculated to the nearest 0.01% using the following equation:

$$A_w (\%) = \frac{\text{Weight after 24 hrs} - \text{initial weight}}{\text{initial weight}} \times \frac{100}{1} \quad (3)$$

Determination of Flame Retardant Property

This was determined using a modification of ASTM D 4804. A 10 mm mark was measured and marked out on each of the cut samples. The specimen was then clamped horizontally on a retort stand with the marked 10 mm distance protruding out of the clamp. The free end of each sample was ignited and the time taken for the sample to ignite recorded as the ignition time (I_t). The sample was allowed to burn to the 10 mm mark (D_p) and the propagation time (P_t) was recorded. The rate of burning was calculated using the equation:

$$\text{Rate of burning (mm/s)} = \frac{D_p}{P_t - I_t} \quad (4)$$

Where D_p = Propagation distance (mm)

P_t = Flame propagation time (s)

I_t = Ignition time (s)

Determination of Solvent Sorption (Swelling Behaviour)

Samples were cut from the composites, weighed, labeled and put into 3 sample bottles labeled B, T and X. Thirty millilitres of benzene, toluene and xylene were respectively poured into the sample bottles. The set-up was left at room temperature for 24 hours. At expiration, each sample was removed from the bottle. The solvents adhering to the surface of the samples were carefully wiped out using filter papers. The net sample was weighed and recorded as follows:

M_1 = Mass of dry sample (g)

M_2 = Mass of wet sample (g)

ΔM = Change in mass ($M_2 - M_1$) (g)

The molar percentage uptake of each solvent per gram of the composite (Q_t) was calculated using the formula:

$$Q_t = \frac{\left(\frac{\text{Mass of solvent}}{\text{Molar mass of solvent}} \right)}{\text{Initial Mass of solute}} \times \frac{100}{1}$$

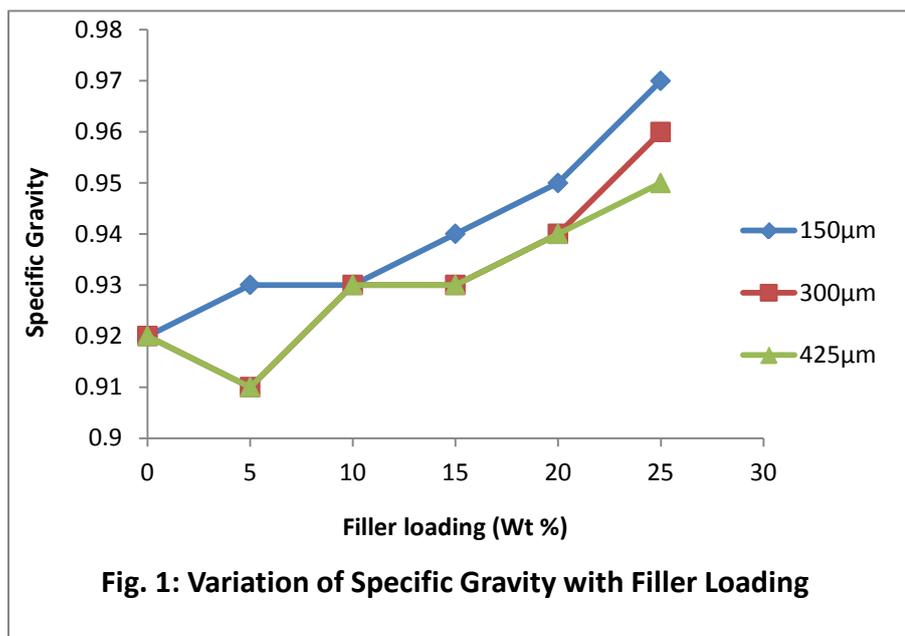
i.e. $Q_t = \frac{\Delta M}{M_1} \times \frac{100}{1} \quad (5)$

Morphological analysis was also carried out using Scanning Electron Microscope (Phenom: product of Phenom World, Eindhoven, Netherlands; Model: ProX). The specimen was made conductive by introducing a minimum of a 5nm gold onto it and then cut into 2 x 2 mm using a sputter cutting machine. The sample was then placed on the column of the Scanning Electron Microscope (SEM) where the image was focused on navigation camera and then transferred to electron mode in accordance to the desired magnification e.g. 50, 80, 100 or 200µm. The samples were thus analyzed to determine the microstructure of the composites, from which the distribution, orientation and interaction of the fillers in the composite and the interfacial adhesion of the filler and polymer matrix were examined.

3.0 Results and Discussion

Result of the specific gravity of the composites is presented graphically in Figure 1. The results revealed that composites of 150 µm particle size have specific gravities higher than the unmodified at all the filler loadings studied. Those of 300 and 425 µm particle sizes have higher specific gravities than the control only from 10 wt% filler loading. This is attributed to the fact that periwinkle shell is denser than polypropylene and as such, its incorporation into the polypropylene matrix enhances the density of the composites. However, specific gravity increased gradually with increase in filler loading and decreased with increase in filler particle size. Also, the same specific gravity was recorded for the three particle sizes studied at 10 wt% filler loading (see point of intersection in Fig. 1).

The increase in specific gravity with increase in filler loading is probably due to the enhanced dispersion of the filler in the polymer matrix leading to reduction of pores in the composite. Larger filler particles on the other hand led to poor dispersion of filler resulting in agglomeration and consequent reduction in specific gravity, evident in the decrease of specific gravity at larger particle sizes. This work is in agreement with earlier works carried out by Atuanya et al., (2014) and Machiadikwe, (2007).



Result of water sorption of the composites is shown graphically in Figure 2. All the values obtained for the filled composites were higher than the unmodified sample. It can be observed that water sorption increased with increase in both filler loading and particle size, with the least values obtained at 5wt% loading and 150 μm particle size. The filler used in this research is hydrophilic in nature and its incorporation into the polymer matrix enhanced the water sorption capacity of the composites. Hence, increasing the content of the hydrophilic filler led to increase in water sorption of the composites. Also, at higher filler loadings and larger particle sizes, there is the difficulty of achieving a homogeneous dispersion of fillers resulting in agglomeration of filler with consequent creation of voids (increased porosity) in the system. As a result, water molecules could more easily penetrate the interior of the polymer composite, leading to higher water sorption. Similar behaviour was reported by Tufan and Ayrimis (2016), Atuanya et al., (2014), Onuegbu and Madufor (2012) and Nwanonyi et al., (2013). One of the major obstacles to wider use of agro-based composites is their sensitivity to environmental effects, especially heat and moisture, which can cause components to deteriorate prematurely.

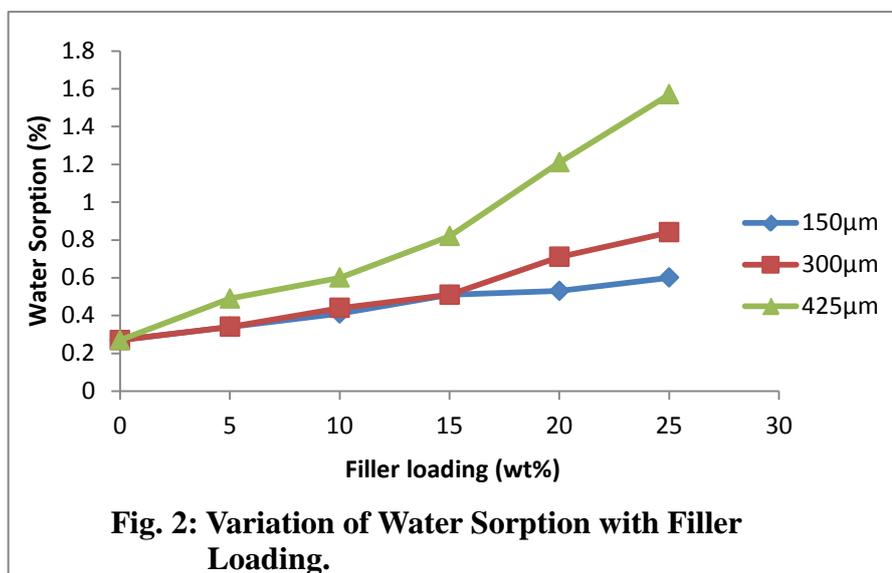
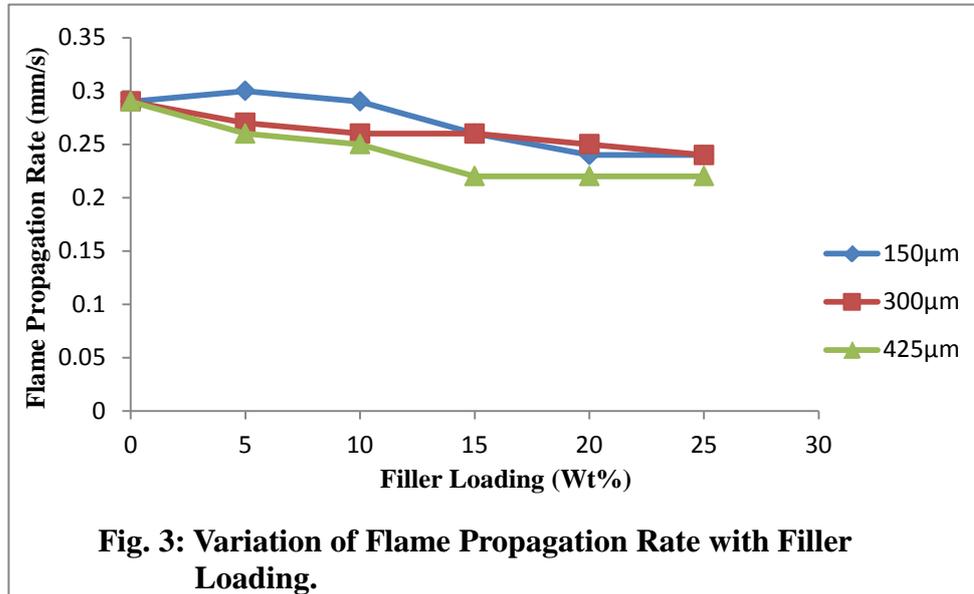


Fig. 2: Variation of Water Sorption with Filler Loading.

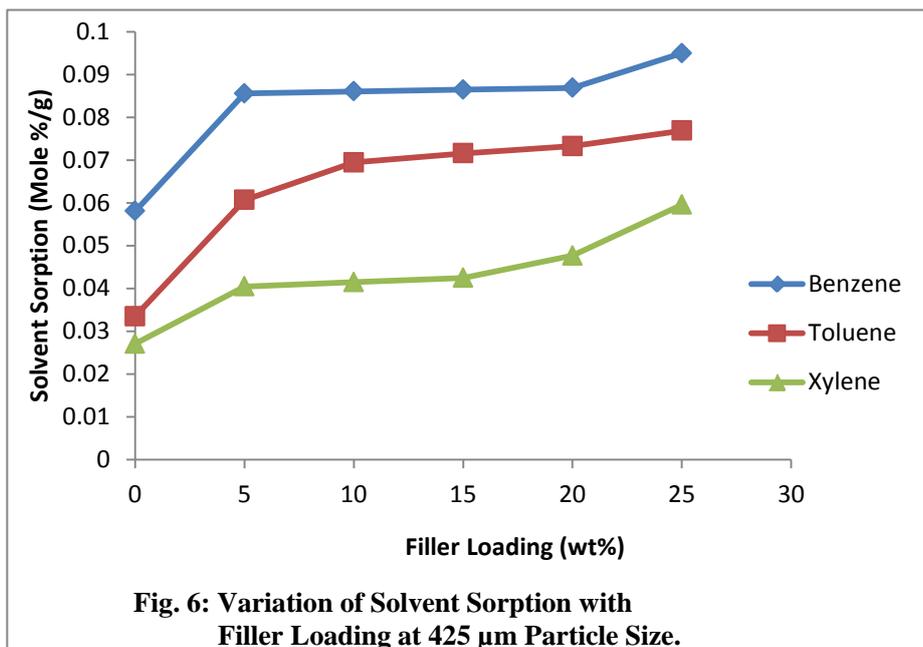
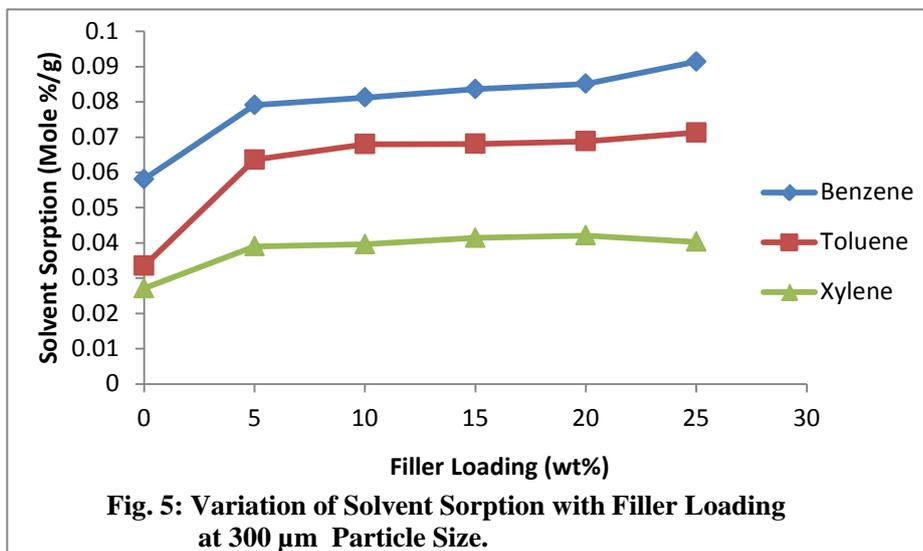
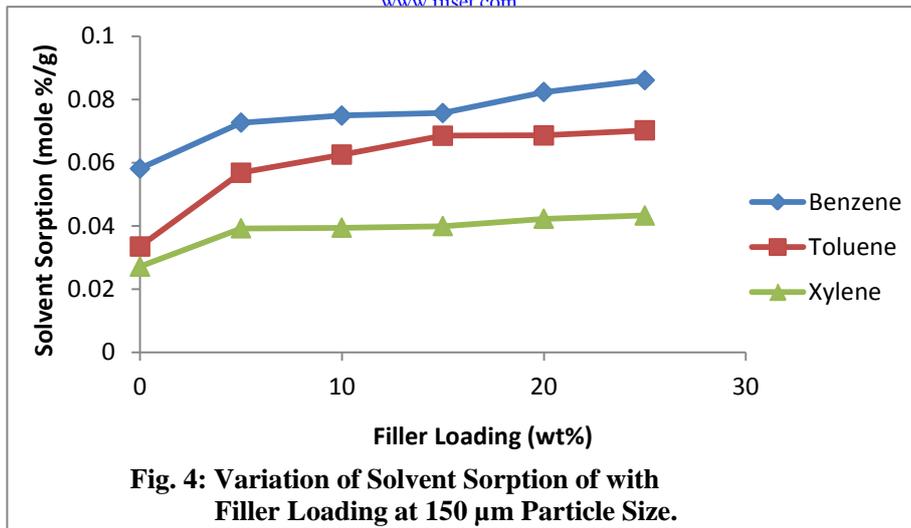
The flammability of polymeric materials is a major concern, especially in the manufacture of textiles, children’s toys and construction materials. Choice of suitable fillers may enhance flame retardant property of polymeric materials. Figures 3 shows the result of flame propagation rate of the composites. Values recorded were all lower than for the unmodified sample. It can be seen that the flame propagation decreased with increase in filler content. It also decreased with increase in particle size upto 15 wt%, above which 300 μm particle size gave higher flame propagation rate than the 150 μm particle size. The decreased flame propagation rate means that the flame retardant property of recycled polypropylene was enhanced by periwinkle shell powder. This behaviour is attributed to the fact that periwinkle shell contains high quantity of calcium carbonate (as shown in Table 1), which on burning releases carbon (iv) oxide, a known fire extinguisher. Shells are basically composed of calcium carbonate. On heating, calcium carbonate decomposes, according to the equation:



The carbon (iv) oxide evolved, which does not support combustion aids in retarding the flame. As more periwinkle shell powder is incorporated into the matrix, more CaCO_3 is decomposed, leading to more evolution of CO_2 , which in turn suppresses the burning rate of the substance. This agreed with the findings of Onuegbu and Igwe (2011) and Nwanonyi et al., (2013).



Results of solvent sorption (expressed in mole % of solvent per gram of polymer) of the composites in benzene, toluene and xylene are presented graphically in Figures 4 to 6. Solvent sorption was found to be higher for the filled samples than the unfilled in all particle sizes studied. It can be observed that solvent sorption increased with increase in filler loading at any particular particle size studied. Solvent sorption also increased with increase in particle size in all the samples produced and tested. This increase of solvent sorption with increase in particle size could be attributed to the fact that larger particles create more voids in the system as a result of poor dispersion in the matrix. The voids created provided better absorption sites in the system leading to more solvent sorption. It is also observed that highest solvent sorption occurred in benzene, followed by toluene and lastly xylene. This behavior can be attributed to solubility parameter of the three solvents. Miscibility and solubility can be expected or believed to be favoured if solubility parameters are close, but is not favoured if the parameters are much wider. Polypropylene has a solubility parameter of $9.4 \text{ (cal/cm}^3)^{1/2}$ (Michaels et al., 1968), benzene $9.2 \text{ (cal/cm}^3)^{1/2}$, toluene $8.82 \text{ (cal/cm}^3)^{1/2}$ and xylene $8.64 \text{ (cal/cm}^3)^{1/2}$ (Coenhen & Smolders, 1975). It can be observed that the solubility parameter of polypropylene is closest to benzene, followed by toluene and finally xylene, which is probably the same order observed in the sorption behaviour at all the particle sizes investigated.



The morphological analysis of the some selected composites was done using Scanning Electron Microscope and the micrographs are showed in Figures 7 to 10. It can be seen that the incorporation of filler into the polypropylene matrix resulted to increase in the number of spherulites in the structure as a result of increase in nucleation sites. More spherulites can be observed in the filled samples than in the control. Also, increase in filler particle size resulted in increase in the size of the spherulites.

Spherulites are spherical semicrystalline regions inside non-branched linear polymers. Their formation is associated with crystallization of polymers from the melt and is controlled by several parameters such as the number of nucleation sites (induced by impurities, plasticizers, fillers, dyes and other substances added to improve other properties of the polymer), structure of the polymer molecules, cooling rate, etc. Spherulites are composed of highly ordered lamellae, which result in higher density, hardness, but also brittleness of the spherulites as compared to disordered polymer.

This increase is due to the lamellae fraction within the spherulites, where the molecules are more densely packed than in the amorphous phase. Stronger intermolecular interaction within the lamellae accounts for increased hardness, but also for higher brittleness. On the other hand, the amorphous regions between the lamellae within the spherulites give the material certain elasticity and impact resistance (Spherulite, 2016).

The micrographs of the filled samples when compared to the control revealed that there is enhanced spherulization owing to presence of nucleation sites provided by the incorporation of fillers. However, at larger filler particles and at the same filler loading, there is poor dispersion of the fillers leading to cluster of the spherulites and subsequent increase in the size of the spherulites due to interaction with each other. This resulted to creation of pores in the system as can be observed in the micrographs (Fig. 10).

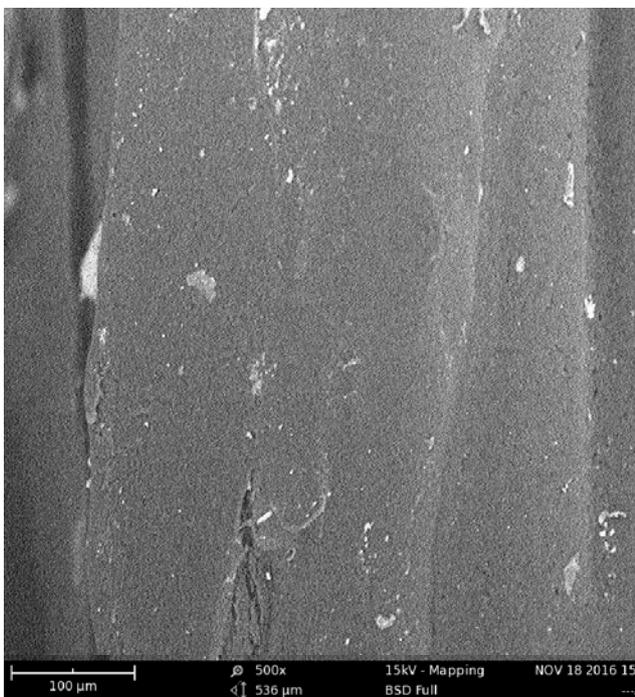


Fig. 7: SEM Micrograph of the control experiment.

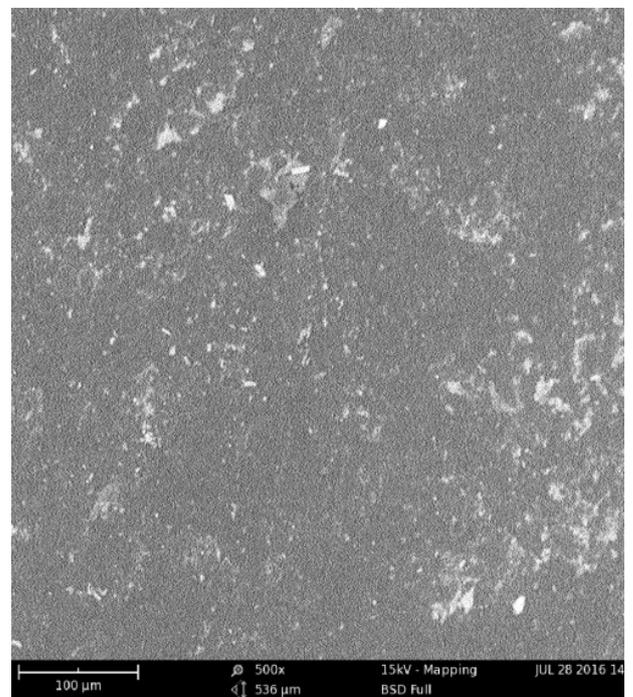


Fig. 8: SEM Micrograph at 15 wt% filler loading and 150 μm

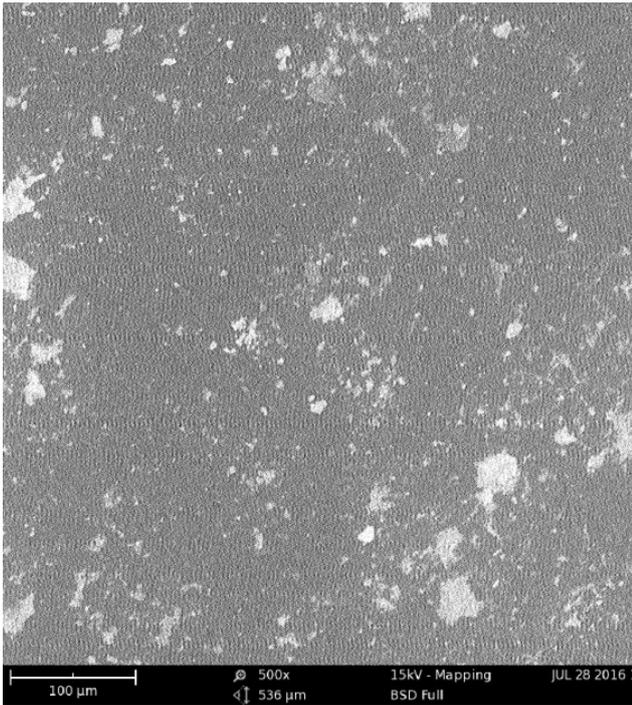


Fig. 9: SEM Micrograph at 15 wt% filler loading and 300 μm

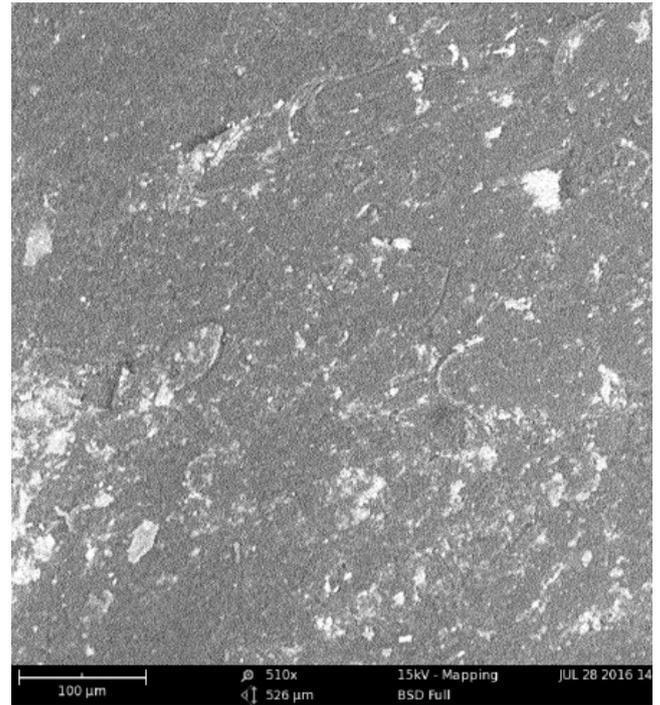


Fig. 10: SEM Micrograph at 15 wt% filler loading and 425 μm

REFERENCES

- Atuanya, C. U., Edokpia, R. O., & Aigbodion, V. S. (2014). The Physio-mechanical properties of recycled low density polyethylene/bean pod ash particulate composites. *Results in Physics* 4, 88-95 <http://dx.doi.org/10.1016/j.rinp.2014.05.003>
- Calister, W. D., & Rethwisch, D. C. (2010). *Material Science and Engineering – An Introduction*. Eight Edition. John Wiley and Sons Inc. Pp. 2-14, 610-614, 626-634. <https://doi.org/10.1017/s0001924000005947>
- Cletus, C. (2002). Wood-Plastic composites in the United States, the interfacing of two industries. *Journal of Forest Production*. 52, 10-14. <https://doi.org/10.1002/9780470165935.ch1>
- Coenhen, D.M. and Smolders, C.A. (1975). The determination of solubility parameters of solvents and polymers by means of correlations with other physical quantities. *Journal of Applied Polymer Science*. 19: 1166. <https://doi.org/10.1002/app.1975.070190423>
- Ishidi, Y. E. (2014). Physical properties of some agro-waste polymer composites. *World Journal of Engineering and Physical Services*. 2(2), 017-024. Available online at <http://wsrjournals.org/journal/wjeps>.
- La Mantia, F., Morreale, M., & Isak, Z. (2005). Processing and mechanical properties of organic filled-polypropylene composites. *Journal of Applied Polymer Science*, 96, 1906-1913.

- Machiadikwe, G. C. (2007). Mechanical and end-use properties of polypropylene filled with domestic wastes. Unpublished M.Sc. Thesis in the Department of Polymer and Textile Engineering, Federal University of Technology, Owerri. Pp. 15 - 20.
- Michaels, A.S., Vieth, W.R. & Alcalay, H.H. (1968). The solubility parameter of polypropylene. *Journal of Applied Polymer Science* 12(7) 1621-1624. <https://doi.org/10.1002/app.1968.070120711>
- Nwanonenyi, S. C., Obidiegwu, M. U., & Onuchukwu, T. S. (2013). Studies on the properties of linear low density polyethylene filled oyster shell powder. *International Journal of Engineering and Science (IJES)*. 2(7), 42-48.
- Onuegbu, G. C., & Igwe, I. O. (2011). The effects of filler contents and particle sizes on the mechanical and end-use properties of snail shell powder filled polypropylene. *Journal of Material Sciences and Application*. 2, 811-812. <http://dx.doi.org/104236/msa.2011.27110>
- Onuegbu, G. C., & Madufor, I. C. (2012). Effect of filler loadings on the end-use properties of maize tassel filled high density polyethylene. *International Research Journal in Engineering, Science and Technology (IREJEST)*. 9(1), 2.
- Reid, D. G., & Gofas, S. (2011). *Littorina littorea*. Accessed through: <http://www.marinespecies.org/aphia.php?p=taxdetails&id=140262> Retrieved 21-11-15.
- Saeed, K. N., Elham, H., & Mehdi, T. (2005). Mechanical properties of composites from saw dust and recycled plastics. *Journal of Applied Polymer Science*, 100, 3641. <https://doi.org/10.1002/app.23159>
- Spherulite. (n.d). In *Wikipedia*. Retrieved December 24, 2016 from [https://en.wikipedia.org/wiki/Spherulite_\(polymer_physics\)](https://en.wikipedia.org/wiki/Spherulite_(polymer_physics)).
- Tufan, M & Ayrilmis, N. (2016). Potential use of hazelnut husk in recycled high-density polyethylene composites. Bioresources.com. <https://doi.org/10.15376/biores.11.3.7476-7489>.