

Tribological Behaviour of Periwinkle Shell Powder-Filled Recycled Polypropylene Composites

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Abstract. Polymer composites are increasingly replacing metals in structures such as gears, wheels, clutches, housings, bushings and other areas where tribology is of great importance. Various ways are used to improve the tribological behaviour of neat polymers, and the most familiar method is the incorporation of fibres/fillers in the polymer to produce composites. In this present research, the tribological behaviour of periwinkle shell powder-filled recycled polypropylene composite was studied. Injection moulding was used for the preparation of the composites and the impact strength, wear resistance and fatigue strength were examined. SEM was utilized to support the discussion of the results. The results showed that the incorporation of periwinkle shell powder into polypropylene improved the wear resistance and fatigue strength but showed no improvement in impact strength.

Introduction

The applications of polymers, which are replacing traditional materials, are increasing [1]. In the recent years, consequent upon the specific properties of polymers, they have become materials of interest for various applications. These properties include light weight, ease of processing and cost-effectiveness. Hence, there have been series of attempts significantly made to make polymers suitable for use in different industrial applications. Such attempts include the incorporation of various kinds of fibres/fillers into polymers to improve their physical and mechanical properties. Thus, fibre reinforced polymer matrix composites are extensively attractive due to their lightweight, biodegradability, high strength, high stiffness, good corrosion resistivity, and low friction coefficient which are important mechanical and tribological properties encountered in most applications [2]. Today, due to these induced properties, polymer composites have found use in almost every area of human Endeavour such as engineering, medicine, aerospace, automobile, sports, domestics, packaging, etc as a result of effective modification of the properties of polymer using additives [3].

In the past, plastic industry relied entirely on inorganic fillers such as talc, calcium carbonate, mica, etc. to modify the performance of thermoplastics. Inorganic fillers provide rigidity and temperature resistance; however, these fillers are costly and abrasive to the processing equipment [4,5].

Recently, organic fillers produced from agricultural wastes have gained tremendous attention from plastic industry. These fillers have the advantages of low densities, cheapness, 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 [6].

Many research works have been reported on organic fillers reinforced thermoplastic composites, which have been shown to be of great use in various fields. Such fillers include snail shell powder [7], cocoa pod [8], oyster shell powder [3], groundnut shell, cocoa nut shell, palm kernel shell [9], bean pod ash [10], saw dust [11], periwinkle shell [12] and maize tassel [6].

Periwinkle shell (PS) is a by-product of agriculture. 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 uses and are found littered around markets and homes [13]. Globally, research efforts have been shifted towards possible ways of recycling waste materials so as to make them usable again, together with ensuring a clean and safe environment [10]. Hence, the use of periwinkle shell powder as filler in the polymer industrial will not only improve its mechanical properties, it will also convert wastes to wealth, tackle the problem of environmental pollution, reduce material cost and produce biodegradable composites.

Tribology is the science and engineering of interacting surfaces in relative motion. It includes the study and application of the principles of friction, lubrication and wear. In the past, researchers focused more on studying metal/metal and metal/ceramic contact tribology [14]. However, the use of metals and ceramics in structures involving tribology such as gears, wheels, clutches, housings, flexures, bush bearings, and artificial prosthetic, is fast diminishing. Such components are now being replaced with polymers [15]. They are readily formed by injection molding, casting or machining with minimal waste, to yield components that are lighter, cheaper, resistant to corrosion, noiseless, with little or no maintenance. Therefore, it becomes necessary to give more attention to the study of metal/polymer and polymer/polymer tribo-contacts. The tribology of polymer is more complex than that of metal. The well-established 'Laws of Friction' for the tribology of metal and ceramic contacts in relative motion, do not apply to polymer/metal contacts. The reasons for this hinge on the relative softness of polymers compared to metals, their much lower thermal conductivities associated with heat generation in contacts and also significantly lower melting points. Until the tribological properties of polymers are understood, then their applications in rolling, sliding or bearing components will remain a problem [14].

In general, there are various ways to improve the tribological behavior of neat polymers. The main approach is the incorporation of fibres/fillers in polymers to produce composites. Well-known fillers are glass fibres, aramid and carbon fibres which dominate the market in the composites industry. Several researches have been carried out on the possibility of replacement of conventional fillers with organic fillers [2]. For example, the tribological properties of polyester composites reinforced with woven glass reinforced polyester have been compared with seed oil palm reinforced polyester. The results revealed that the glass fibre reinforced polymer composites have better coefficient of friction and wear rate than seed oil palm reinforced polyester composites. However, the seed oil palm reinforced polyester composite reinforced by 35 vol. % of seed oil palm exhibited a promising wear result. Accordingly, the woven glass fibres can be replaced by the seed oil palm fibres in polymeric composites reinforcements [16].

The tribological properties of kenaf fibre reinforced epoxy composite was investigated [17] and it was observed that embedding kenaf as reinforcement can reduce the wear rate of polymer composites regardless of fibre orientation.

Majhi et al., [18] investigated the tribological properties of rice husk reinforced epoxy composite. Results revealed that embedding rice husk can improve the tribological properties by reducing the wear rate for all weight percentage of rice husk. In addition, the optimum weight percentage for rice husk content where the wear rate is minimum is 10%. Consequently, increasing the amount of fibres more than 10% has a reverse effect on wear rate and tends to increase in wear rate.

The tribological properties of brake pads from rice straw (RS) and rice husk dust have been investigated. These properties were found to be significantly enhanced as rice straw and rice husk dust were utilized in the composites and it was concluded that these composites can be effectively used in brake pad production [19].

The effects of date palm leaf as reinforcement on polyvinylpyrrolidone polymer matrix composite were evaluated. The wear rate was found to decrease by increasing the content of date palm leaves fibre up to 26 wt%, after which the wear rate increases with increasing the date palm leaves' content [20].

A study on the effect of oil palm fibre on the tribological properties of polyester composite and neat polyester showed that the presence of oil palm fibre in the polyester improved the wear property by about three to four times compared to neat polyester [21].

Tribological properties of polymer composites of different bio-wastes have been investigated. Agricultural wastes, such as coconut and wood apple shell were used, due to their good mechanical strength and thermal stability when compared to other agricultural wastes, to manufacture biodegradable polymer composites. It was observed that the bio-wastes decreased the wear rate of polymer composites rather than neat epoxy [22].

The availability of organic fillers and the ease of manufacturing have attracted the interest of researchers towards the study of the feasibility of their application as reinforcement and the extent to

which they satisfy the desired requirements in tribological applications. However, little information on the tribological behaviour of animal-based fillers like periwinkle shell powder reinforced composite material is available in the literature. This research is therefore aimed at investigating the tribological properties of periwinkle shell powder reinforced recycled polypropylene composites and to ascertain their applicability in various areas of engineering involving friction and wear.

Materials and Methods

Materials

Polypropylene (PP) utilized in this research was a product of SK Global Chemicals Limited, Korea gotten from CeePlast Limited Aba, Abia State. It has a melt flow index of 0.4g/10 min at 230 °C and density of 0.922g/cm³.

Recycled polypropylene was obtained from Ihiagwa village, Owerri West L.G.A., Imo State and was thoroughly washed, dried and sliced to tiny pieces.

The compatibilizer; maleic anhydride-grafted-polyethylene (MAPE) used was bought from CEEPlast Industry, Aba, a product of Sigma Aldarich Company, U.S.A.

Periwinkle shell (PS) 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.

Preparation of Polypropylene Composites

In the preparation of the polypropylene composites of periwinkle shell powder, 100g of virgin polypropylene and 100g of recycled polypropylene were mixed properly with appropriate amounts of filler (5, 10, 15, 20 and 25 wt%). This was done for the three particles sizes. Two control samples were prepared; (1) by using 200 g of virgin PP only and (2) by mixing 100 g of virgin PP and 100 g of recycled PP without the addition of any filler, as shown in Table 1. 7 g of maleic anhydride was added to enhance compatibility.

Table 1: Composition of the composites.

| Virgin PP (g) | Recycled PP (g) | PS (wt%) |
|---------------|-----------------|----------|
| 200 | 0 | 0 |
| 100 | 100 | 0 |
| 100 | 100 | 5 |
| 100 | 100 | 10 |
| 100 | 100 | 15 |
| 100 | 100 | 20 |
| 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 temperature of 250 °C. The mixture was then produced as sheets with dimensions of 150 x 150 x 4mm. Test samples were prepared from the sheets for testing.

Testing

Impact Strength

Notched Izod Impact method was employed here. It is a single point test that measures material's resistance to impact from a swinging pendulum. It is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. It was conducted according to standard (ASTM D256) using CEAST Resil Impactor (Model: 16650; Planezza Co. Ltd. Torino,

Italy). Test specimens of 80 x 10 x 3.5 mm were notched at the middle to a depth of 2 mm to create an area of stress concentration for crack initiation. The specimens were successively fixed on the CEAST Resil Impactor to receive a blow from the fast moving hammer released from a height on the machine to cause breakage of the sample. The impact energy absorbed by the specimen was read on the dial gauge on the machine and the impact strength calculated by dividing impact energy by the thickness (J/mm or J/m).

Wear Rate/ Abrasion Resistance

This was carried out in accordance with standard specification (ASTM D 4060) using Taber Oscillating Abrasion Tester (Model: 6160-F735). A 4-inch diameter disc sample with ¼ inch hole was placed on the abrasion tester. A 500 g load was placed on top of the abrader wheel and allowed to spin for 100 cycles. Weight of the sample was taken before and after the test and the weight loss per cycle computed in mm³/rev. to represent the wear rate which indicates the abrasion resistance.

Fatigue Crack

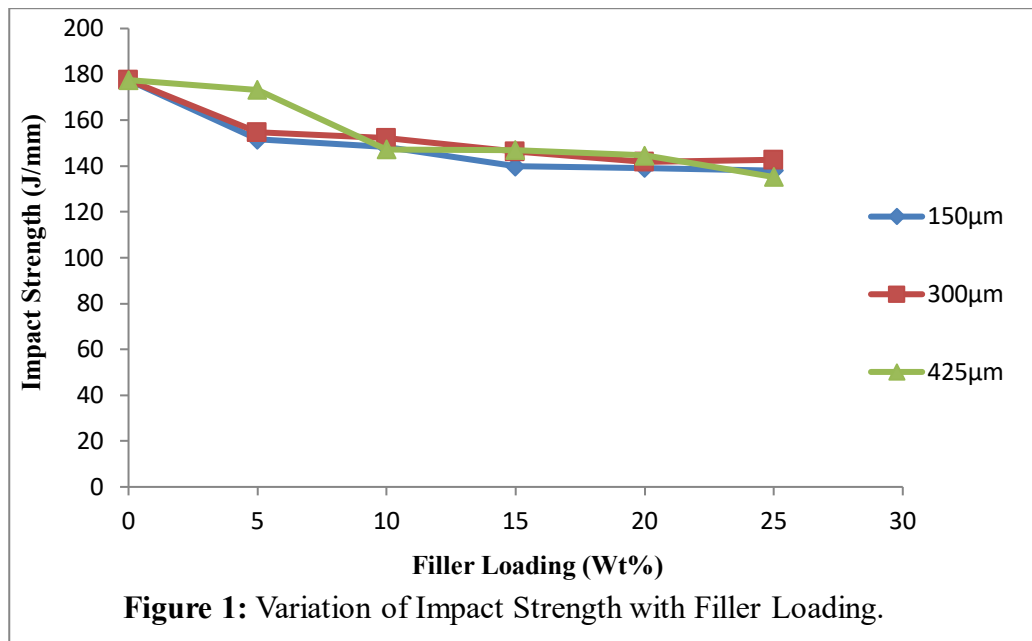
This was conducted in accordance with ASTM D 671 using DuPont Flex (Model: LCH-150; Vecomtech Co. Ltd., Viet Nam). A sample of 120 x 40 mm was subjected to repeated loading and unloading to produce failure. Fatigue crack was recorded and expressed in mm/cycle x 10³.

Morphological Analysis

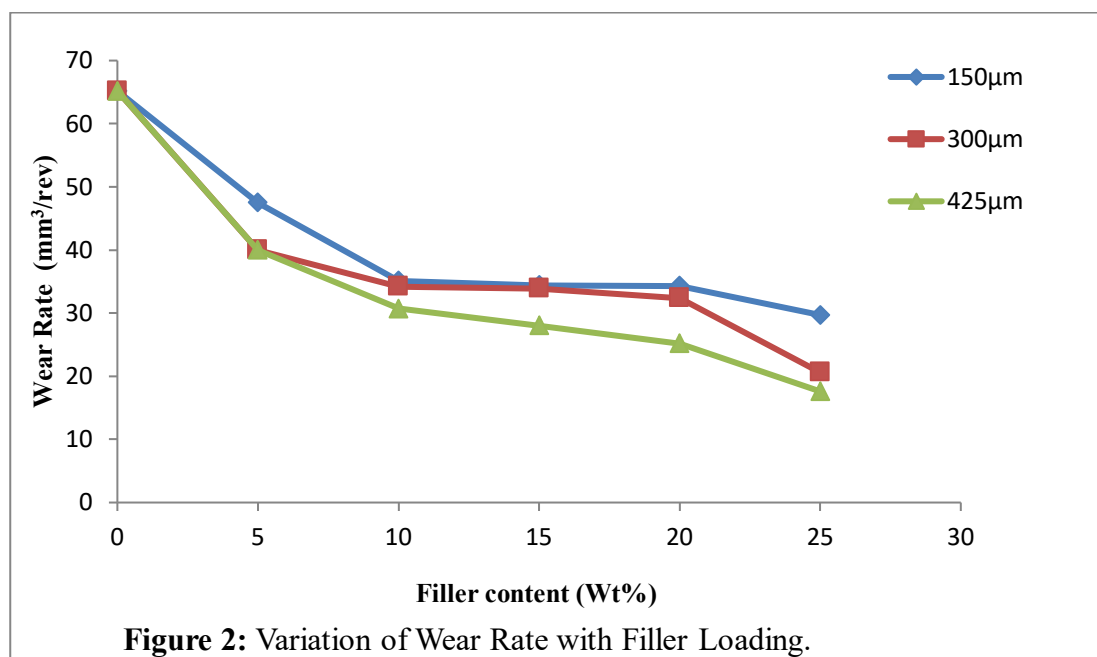
Morphological analysis was carried out using Scanning Electron Microscope (Phenom: product of Phenom World, Eindhoven, Netherlands; Model: ProX). A minimum of a 5nm gold was introduced onto the specimen to make it conductive. The specimen was cut into 2 x 2 mm using a sputter cutting machine. The sample was then properly positioned in the Scanning Electron Microscope (SEM) so that the image was focused on navigation camera and then transferred to electron mode in accordance to the desired magnification (500x). 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.

Results and Discussion

The results of impact strength are illustrated in Figure 1. The results showed that there is no improvement in impact strength by the incorporation of periwinkle shell powder, as the results obtained for the modified samples were smaller than for the unfilled. It can be noticed that impact strength decreased with increase in filler loading at all the filler particle sizes studied. A critical look at Figure 1 reveals that the impact strength decreased from 180 J/mm for neat polypropylene to about 150 J/mm for 25 % addition of periwinkle shell powder. Increase in filler loading resulted in the stiffening and hardening of the composites leading to reduction in its ductility, resilience and toughness. Since impact strength is the combined effect of tensile strength and ductility, it becomes obvious that ductile materials have the possibilities of possessing higher impact strength than brittle materials. Thus, the incorporation of the periwinkle shell powder resulted to harder composites with consequent reduction in impact strength. Similar behaviour was reported by [10,23,24] while [25,26] reported increase in impact strength with filler content. With respect to particle size, impact strength increased with increase in particle size, with the 150 µm particle size recording the least impact strength. This result is in line with the work of [26,27] who also reported an increase in impact strength with increase in particle size.



Results obtained for wear rate (abrasion resistance) are presented in Figure 2. From the results, the wear rate consistently decreased with increase in filler loading and particle size. This shows that the abrasion resistance of the composites increased consistently with increase in filler loading and particle size. Abrasion resistance is a direct measurement of hardness, which has been shown to improve by the incorporation of periwinkle shell powder [12]. This increase in abrasion resistance with increase in filler loading is attributed to the fact that the filler acts as reinforcing filler. Incorporation of the filler into the polymer matrix enhanced the stiffness of the material. The higher the percentage of the filler incorporated, the harder the material, and the more rigid it becomes. The harder a material is, the lower its rate of wear and tear. This is responsible for the difficulty encountered in machining very hard materials. The abrasion resistance obtained in this research attests to the fact that incorporation of fillers (periwinkle shell powder), into the polymer matrix assists in strengthening the surface which will result in enhancing the tribological behaviour of polymers [14].



Results of fatigue crack are illustrated graphically in Fig. 3. It can be seen that fatigue crack decreased with increases in both filler loading and particle size, hence the filler enhanced the fatigue strength of the composites.

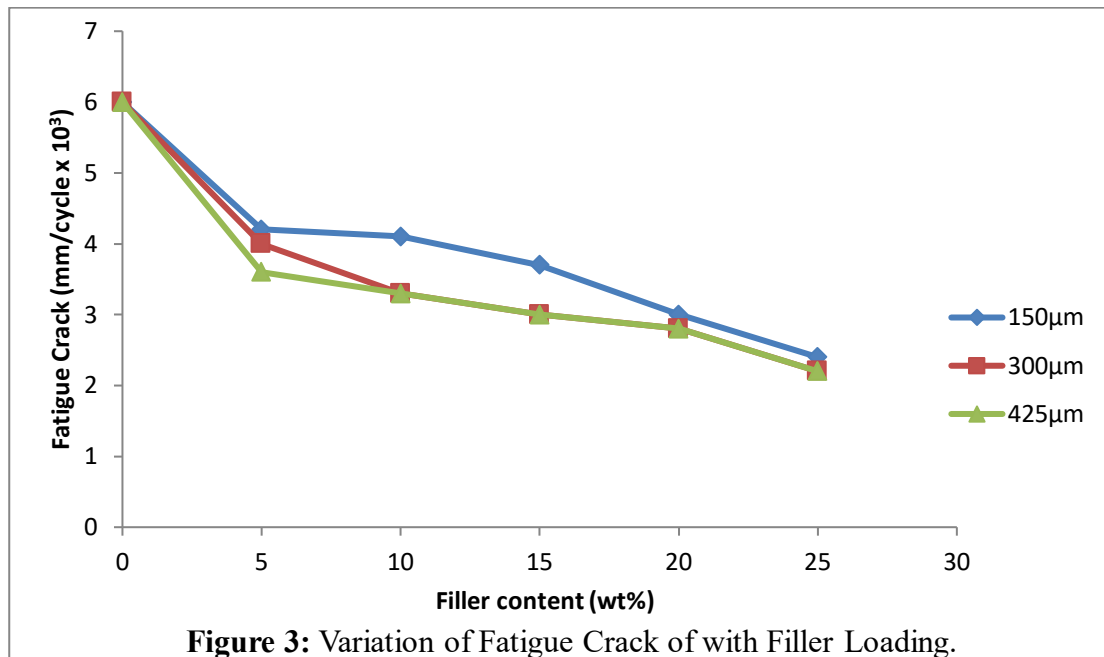


Figure 3: Variation of Fatigue Crack of with Filler Loading.

Fatigue and hardness have strong relationship because both are surface properties. For example, surface-hardening treatments for steels, such as carburizing and nitriding, which harden the surface, increase fatigue life while decarburizing, on the other hand, which softens a heat-treated steel surface, lowers fatigue life [28]. It was found that filler incorporation enhanced the abrasion resistance of these composites resulting to enhancement of the fatigue strength. The enhancement of fatigue strength found in the filled samples may be attributed to the presence of the dispersed fillers which serve as barriers to crack propagation. As filler loading increases, more barriers are introduced into the system resulting in higher fatigue strength.

The morphological analysis of the composite specimens was done using Scanning Electron Microscope and the micrographs are shown in Figs. 4 to 7. It can be observed that the use of periwinkle shell powder as filler in polypropylene matrix resulted to increase in the number of spherulites as a result of increase in nucleation sites. More spherulites can be observed in the filled samples than in the control. The formation of spherulites is associated with crystallization of polymers 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, etc. Spherulites are composed of highly ordered lamellae, which result in higher density and hardness as a result of the strong intermolecular interaction within the lamellae [29]. According to Friedrich, [14], two major factors are responsible for enhancement of polymer tribological properties and they are (1) strong adhesive bonding between the filler and matrix and (2) good dispersion of filler particles within the matrix. The microscopic observation of the specimen of the neat PP (Fig. 4) revealed a smooth surface with scanty spherulites. However, the filled specimens show increased number of spherulites as higher quantities of filler were incorporated. It can also be observed from Figs. 5-7 that the filler particles were well dispersed in the matrix resulting in a stronger adhesive bond, thereby resisting wear, tear and fracture of the specimen. This is probably the reason for the enhanced tribological performance of periwinkle shell powder in polypropylene.

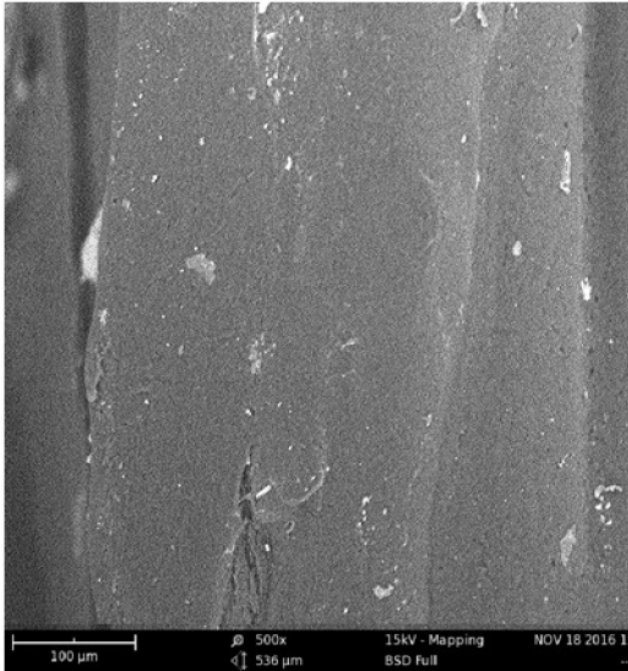


Figure 4: SEM Micrograph of the neat PP (control experiment).

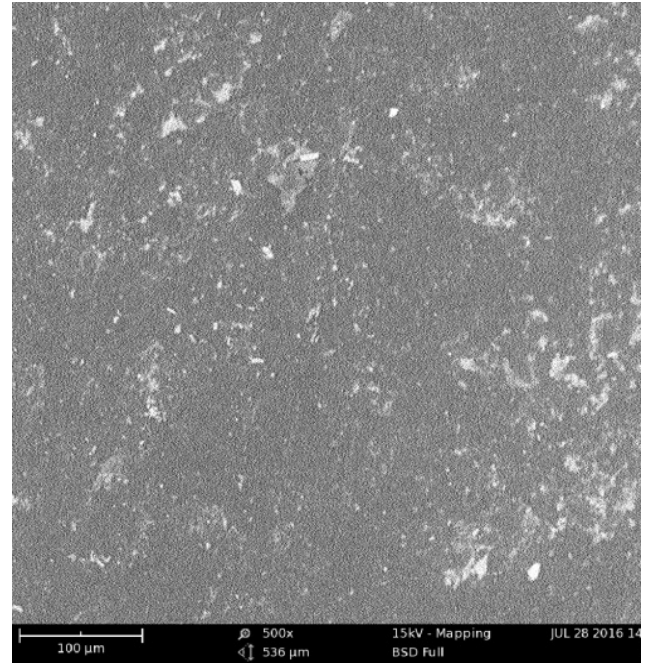


Figure 5: SEM Micrograph of PP-PS composite at 15 wt% filler loading and 150 μm.

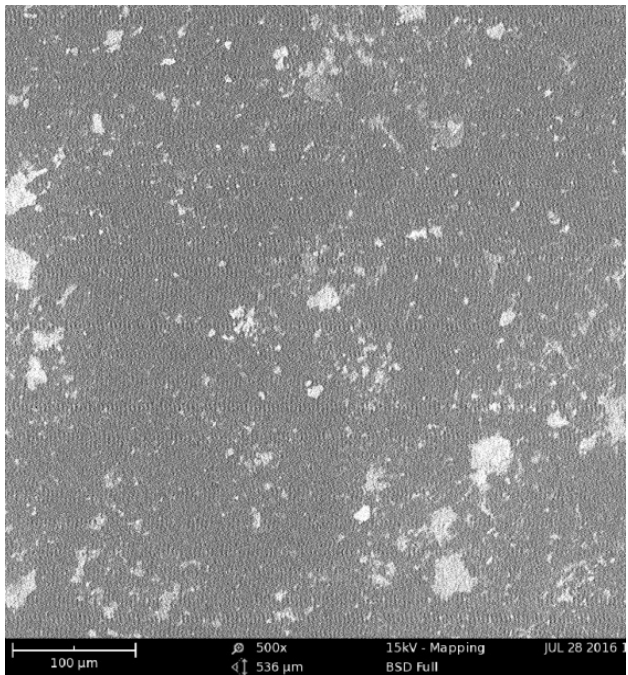


Figure 6: SEM Micrograph of PP-PS composite at 15 wt% filler loading and 300 μm.

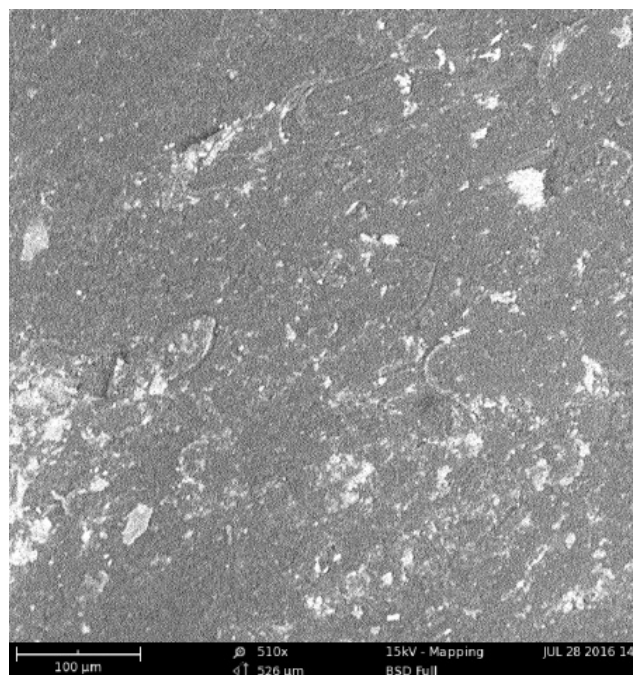


Figure 7: SEM Micrograph of PP-PS composite at 15 wt% filler loading and 425 μm.

Conclusions

The Tribological behaviour of periwinkle shell powder-filled recycled polypropylene composites was investigated in this research. Results showed that the wear resistance and fatigue strength of the composites improved consistently with increase in the percentage of periwinkle shell powder incorporated while there was decrease in impact strength. Therefore, it can be concluded that in general, the tribological behaviour of the composites was improved and hence, periwinkle shell can be utilized in the development of composites for tribological applications.

Conflict of Interest

The author declares that there is no conflict of interest regarding the publication of this paper.

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