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Mechanical properties of linear low density polyethylene composites: Effects of eggshell and de-oiled cashew nutshell

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Abstract

The effects of de-oiled cashew nutshell powder (CNSP) and eggshell powder (ESP) on the mechanical properties of linear low density polyethylene (LLDPE) composites were studied. The LLDPE composites were prepared with 150 µm particle sizes of 30%wt. ESP and varying amount of CNSP (10, 20, 30 wt.%) using injection molding machine at a hopper and nozzle temperatures of 200°C and 220°C respectively and at rotor speed of 60 rpm. Results showed that the tensile, flexural and impact properties decreased with increasing CNSP filler. Whilst the mechanical properties of ESP-filled composites were lower than those of the non-ESP composites, there was a drastic drop in the composite with 20%wt. CNSP.

Keywords: mechanical, polyethylene, eggshell, de-oiled

Introduction

Compositing in the plastic industry has stemmed from one of three main reasons, *viz* strength improvement, enhancement of biodegradability and reduction in production cost (Carraher, 2014) [2]. In the area of strength improvement, these composites contain non-plastic materials which act as an interfacial adhesive; these non-plastic constituents are mostly organic fibers and tend to have an interfacial interaction with the plastic constituent. It is only in minimal case that there is breakage and formation of chemical bonds between the plastic and non-plastic constituents (Kutnar and Muthu, 2016) [6]. The interfacial adhesion helps to hold particles of the plastic together. One effective way of corroborating this principle is to characterize for the mechanical properties of these composites and compare it with that of the pure plastic. Many studies have been reported on the mechanical properties of composites which yielded either enhanced or reduced properties when compared to those of the parent material. In terms of reduction in production cost, it is observed that the filler materials are mostly wastes and as such are acquired at little or no cost, therefore, plastic materials is more costly than these supposedly worthless non-plastic materials. Thus, compositing reduces the amount of plastic material used, thereby driving down the cost of production (Carraher, 2014; Shama *et al.*, 2018) [2, 15]. Humans have been fabricating composites right from the Stone Age and an example of an ancient composite is mud brick, which is composed of mud and straw. Cake of mud is not easily squashed but breaks when bent, this is unlike straw which has significant tolerance for stretching but yields when squashed. Therefore, bricks made from mud and straw have significantly greater compressive strength and tensile strength than straw and mud respectively. Another household example is concrete which is made up of gravel bound together by cement. Cement has greater compressive strength, but gravel is lighter than cement, therefore a composite of both materials would have a reduced amount of cement, thereby making the composite lighter whilst still being as strong as pure cement. The tensile strength can be improved with the incorporation of rods which gives a composite popularly referred to as reinforced concrete (Elhajjar *et al.*, 2017; Lechtman and Hobbs, 1986) [4, 7].

The primary function of eggshell is to protect the albumen and yolk against contamination, whilst aiding embryogenesis through regulation of gases and water absorption (Nys *et al*, 2004) [11]. Once the albumen and yolk are removed, the eggshell becomes waste; these “wastes” have been discovered to contain a lot of nutritional benefits because its major constituent is calcium carbonate (Burley and Vadehra, 1989). Recently, protein has been observed to be a significant constituent of eggshell which has seemingly increased its demand (Nys *et al*, 2004) [11]. According to estimates, roughly 80,000 tonnes of eggshell are produced in Nigeria each year (Matson and Hecht, 1999), of which 26% are utilised to produce fertiliser, 20% are used to produce animal feed, and 5% are used for other purposes, leaving us with 49% (or 39,200 tonnes) that are discarded each year (Daengprok *et al*, 2002) [3]. These eggshells are excess in the environment and thus pose challenges with disposal. Recent innovations in the eggshell industry have devised ways to separate the calcium rich eggshell from the protein rich inner membrane, thus expanding the applications of eggshell. Some applications of eggshell include: its use as abrasive agents, stabilizing agents to improve soil properties, coating pigment for ink-jet printing paper additive, calcium source for both human and animal nutrition.

Cashew nutshell powder is the residue or waste obtained after the extraction of the cashew nutshell liquid. The cashew tree is grown in the tropical region of the world, notably the Ivory Coast, Vietnam, Indian, North and Southern America including the Caribbean Islands. The cashew is made up of the cashew seed (cashew nut) and the cashew shell (cashew nutshell). The cashew seed is either eaten or used in other food recipes while the shell is used in the production of lubricants, water proofing paint and arm production dating back to the Second World War. In the 21st century, cultivation of cashew in Africa geometrically increased due to the demand for cashew milk as an alternative to diary milk. In Brazil, cashew seed is pulped and fermented into alcoholic beverages, such as, cachaca, and they are also used as cheese or flour. Some of the suspected health benefits of cashew seed, includes promotion of healthy muscles and nerves, boosting the immune system, acting as a cancer chemo-preventive agent, decreases risk of stroke, prevention of anemia (Morton, 1987) [9]. The cashew nutshell contains oil compounds consisting of phenolic lipids, anacardio acid and cardanol which are collectively referred to as cashew nutshell liquid (Morton, 1987) [9].

Experimental

Materials

The Linear low density polyethylene (LLDPE) of density range 0.915-0.925 g/cm3 was supplied by Indorama Eleme Petrochemicals Limited, Port Harcourt, Rivers State, Nigeria. De-oiled Cashew nut shell (CNSP) was obtained after the extraction of its liquid with acetone and then carefully processed to obtain powdered cashew nut shell of mesh size 150 µm. The cashew nutshell was sourced from Auchi, in Edo State, Nigeria. Eggshells were also sourced from Okpunor pastries, Rivers State, Nigeria and then processed to obtain same mesh size as CNSP which was used for the study.

Method

Preparation of Cashew nut shell and eggshell filled composites

The moisture contents of the filler materials were measured after they had been originally oven-dried in powder form. The composites were produced and compounded at Ceeplast Industry, Ltd. in Aba, Nigeria. The final composites, which are shown in Table 1, were created by mixing the ESP (30 wt.%), CNSP (10, 20, and 30 wt.%), and LLDPE in various ratios. They were inserted via the hopper at 200°C into the injection moulding machine (4.6 KW, 10 H, Taiwan). The average thickness of the composites produced was between 3.5 and 4 mm, and the mixing was carried out at temperatures of 200 °C for the hopper and 220 °C for the nozzle, respectively, and 60 rpm for the rotor**.**

Table 1: Composition of CNSP and ESP filled polymer composites

Samples	Percentage weight Composition		
	LLDPE	**CNSP**	**ESP**
NEAT LLDPE	200	-	-
LLDPE/CNSP-10	190	10	-
LLDPE/CNSP-20	180	20	-
LLDPE/CNSP-30	170	30	-
LLDPE/CNSP-0/ESP-30	170	-	30
LLDPE/CNSP-10/ESP-30	160	10	30
LLDPE/CNSP-20/ESP-30	150	20	30
LLDPE/CNSP-30/ESP-30	140	30	30

LLDPE: Linear low density polyethylene; CNSP: Cashew nut shell powder; ESP: Eggshell powder

Mechanical Properties

Tensile Test

The tensile strength and its complementing properties were tested using the ASTM D638 procedure, which is the method used for testing materials of between 1-14mm thicknesses. The samples were cut into standard dumb-bell shaped specimens of length (57 mm) and width (13 mm) and were tested individually using the tensile/flexural testing machine. Vertically positioned in the machine's grips, the sample was tightened uniformly and firmly to the required degree to avoid slippage but not to the point where the specimen would be crushed. The extensometer was connected, and the test speed was set at 1 mm per minute. The test was conducted at room temperature, and each sample's mean value across three runs was recorded**.**

Flexural Tests

The flexural strength and its complementing properties were tested using the ASTM D790 procedure. The samples were cut into standard horizontal bars of length (100mm) and width (12.7 mm) and they were tested individually using the tensile/flexural testing machine. The sample was placed on two supports in such a way that the supports are at one-third the length of the sample from both ends of the sample. The load was aligned parallel to the supports and midway between the supports (which is the midpoint of the sample). The load is then delivered to the sample at a crosshead rate of 0.01 mm/min after the sample has been positioned such that it is perpendicular to the load. The test was conducted at room temperature, and each sample's mean value across three runs was recorded**.**

Impact Tests

The notched Izod impact strength was tested using the ASTM D236 procedure. Each of the samples was cut into a rectangular bar of length (100mm) and width (12.7 mm). The sample was clamped in position using the vice, in such a way that the long axis of the sample is vertical and at right angles to the top plane of the vice. The sample was clamped at the notched point, with the top plane of the vise bisecting the angles of the notch. The pendulum was then struck on the sample at a velocity of 3.46 m/s and the impact strength were then recorded. For each of the composites, different values resulting from the three runs were acquired, and the average value was calculated**.**

Results and Discussion

Tensile Strength

Tensile strength: Figure 1 depicts how filler loading affects the tensile strength of composites filled with CNSP and CNSP/ESP. This is the maximum stress that a material can endure before it breaks when it is stretched or pushed. As the quantity of CNSP filler in the composite grew, it was found that the tensile strength decreased. Both ESP-filled and non-ESP filled composites showed this tendency, and the findings were consistent with earlier research by Nwanonenyi and Chike-Onyegbula (2013) [10] and Lumlong *et al* (2018) [8]. This loss in tensile strength can be brought on by the filler particles clumping together and the filler matrix's poor adherence. Because CNSP filler and LLDPE interacted with each other more effectively than CNSP/ESP filler and LLDPE, the tensile strength of the CNSP composites was greater than that of the CNSP/ESP composites. The decrease in tensile strength of composites, according to Salmah *et al*. (2005) [14], Nwanonenyi and Chike-Onyegbula (2013) [10], and Shuhadah and Supri (2009) [16], is caused by poor interfacial adhesion of the filler-matrix to the polymer material as well as low compatibility between the filler and polymer material. The 30 g-ESP composites produced better results than the 30 g-CNSP composites, perhaps as a consequence of ESP's superior interfacial adhesion to LLDPE. Accordingly, a composite made using ESP as the sole filler would have more tensile strength than one made using CNSP alone. The tensile strength of the 20 g-CNSP composites significantly decreased when compared to that of other formulations**.** This may be attributed to poor mixing or uneven dispersion of the filler in the compound mix.

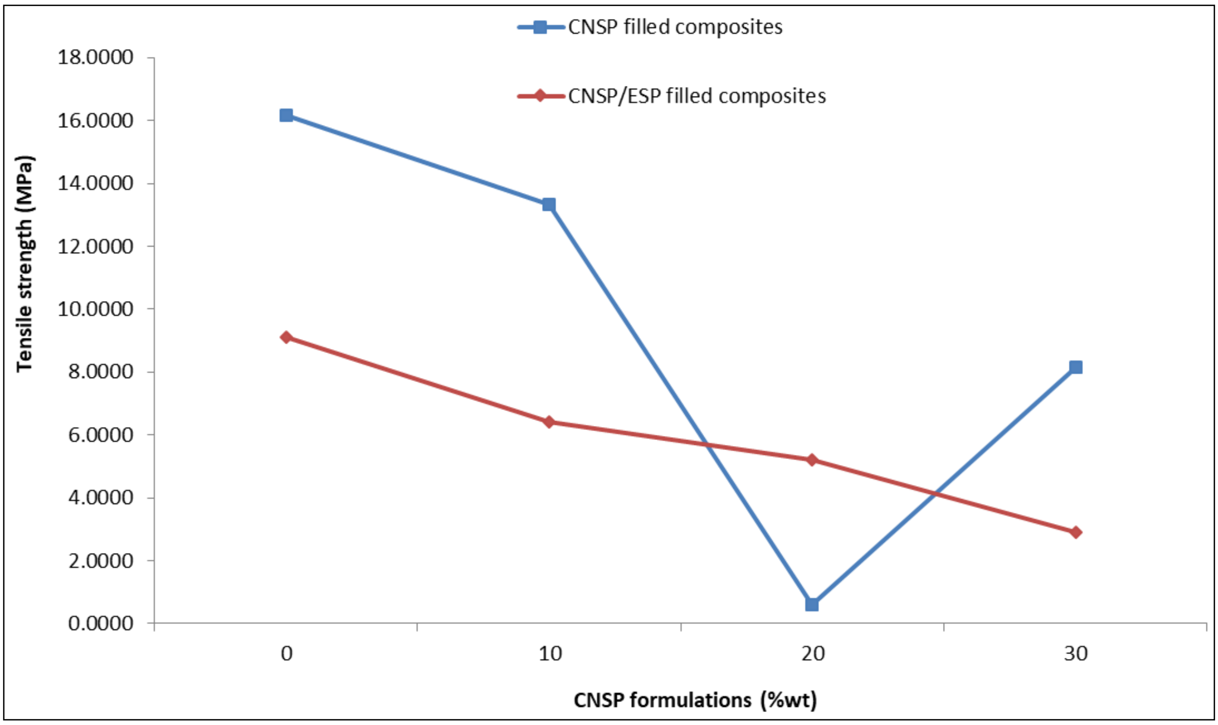

Fig 1: The tensile strength of CNSP and CNSP-ESP filled composites at different filler loadings (P-value for both the CNSP and ESP were less than 0.05)

Tensile Modulus

The effect of filler loading on the tensile modulus of the CNSP, and CNSP/ESP filled composites is shown in Figure 2. This is the mechanical property that predicts the deformation of sturdy materials under a precise force. For both the ESP and non-ESP composites, it was found that the tensile modulus decreased as the quantity of CNSP filler in the composite increased; this tendency is consistent with the findings of Ardhyananta *et al* (2007) [1]**.** The decreasing modulus with increasing filler, despite exhibiting high stiffness may be due to the incompatibility of the fillers with the LLDPE. This decreases its ability to withstand greater loads thus the composites break apart more easily under tension. Therefore, irrespective of the fact that the fillers filled the pores of the LLDPE, CNSP and CNSP/ESP filled composites are far weaker than the neat LLDPE. Another reason may be due to interfacial voids created when composites are subjected to tension. The voids acted as stress concentrators and thus propagated more rapidly, leading to deformation at a reduced tensile stress. The tensile modulus of the CNSP composites were higher than those of the CNSP/ESP composites which is possibly due to better compatibility between the CNSP filler and LLDPE compared to CNSP/ESP filler and LLDPE. According to Salmah *et al*. (2005) [14] and Ardhyananta *et al*. (2007) [1], the development of interfacial voids that serve as stress concentrators causes the tensile modulus to drop with an increase in filler. The 30 g-ESP composite produced better outcomes than the 30 g-CNSP composites, which is presumably because ESP and LLDPE work better together than CNSP and LLDPE do. The tensile modulus of the 20 g-CNSP composites significantly decreased as compared to other formulations, which may have been caused by insufficient mixing or uneven dispersion.

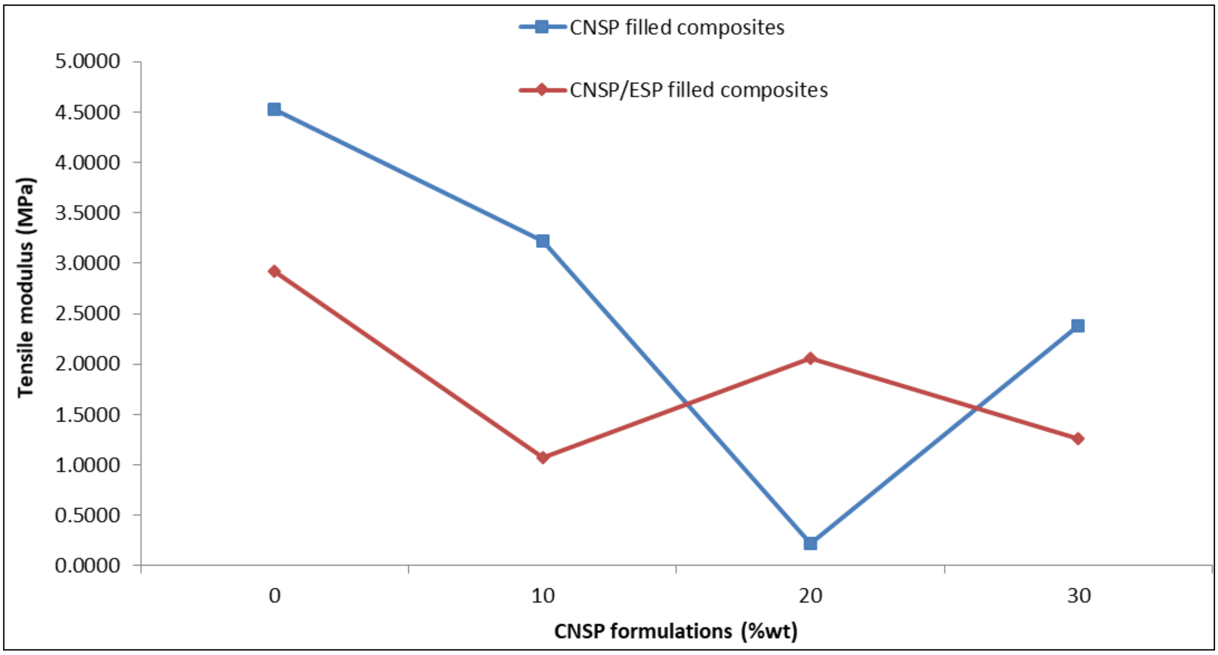

Fig 2: The tensile modulus of CNSP and CNSP-ESP filled composites at different filler loadings (P-value for both the CNSP and ESP were less than 0.05)

Elongation at break

The effect of filler loading on the elongation at break of the CNSP and CNSP-ESP filled composites is shown in Figure 3; it expresses the capability of a material to resist changes without crack formation and was calculated using the formula:

$$\textbf{\textit{Elongation at break}}\ (\%) = \frac{\triangle l}{l}\ x\ 100\ \%$$

For both ESP and non-ESP composites, it was shown that the elongation at break reduced as the quantity of CNSP filler in the composite increased. This behaviour is also consistent with the pattern noted by Lumlong *et al*. (2013) and Nwanonenyi and Chike-Onyegbula (2013) [10]. (2018). This is most likely because the composite stiffened and hardened as a consequence of increased filler loading in the LLDPE matrix. This decreased its hardness and resilience, which resulted in less elongation at the break. Therefore, the filler's decreased capacity to sustain the stress transfer from filler to polymer matrix is shown by the decreasing elongation at break. The elongation at break of the CNSP composites was greater than that of the CNSP/ESP composites, likely as a result of the CNSP filler's superior interfacial adhesion to LLDPE compared to the CNSP/ESP filler, as well as the fact that CNSP and ESP are incompatible with one another. This tendency is linked to the filler's inability to sustain the stress transfer from polymer filler to matrix, per (Jacob *et al*., 2004; Lumlong *et al*., 2018) [8]. The 30 g-ESP composite produced better results than the 30 g-CNSP composite, which is presumably attributable to the improved compatibility of ESP and LLDPE compared to CNSP and LLDPE. The 20 g-CNSP composites' elongation at break significantly decreased as compared to that of other formulations, which might be explained by an uneven distribution of filler inside the polymer matrix. Similar trends from earlier investigations have been ascribed to the filler's inability to sustain the stress transfer from the polymer filler to the matrix (Lumlong, *et al*, 2018; Jacob, Thomas & Varughese, 2004, 955-965) [8, 5].

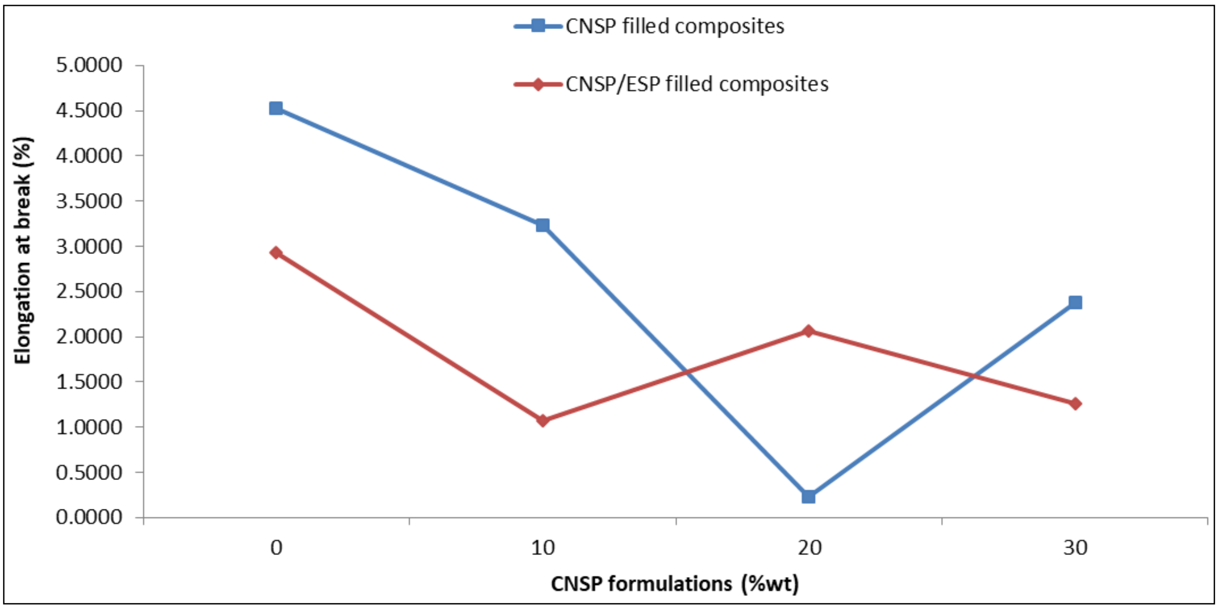

Fig 3: The elongation at break of CNSP and CNSP-ESP filled composites at different filler loadings (P-value for both the CNSP and ESP were less than 0.05)

Flexural Strength

The effect of filler loading on the flexural strength of the CNSP, and CNSP-ESP filled composites is represented in Figure 4. It is the maximum bending stress that can be applied to a material before it yields. It was observed that the flexural strength reduced as the amount of CNSP filler in the composite increased for both the ESP and non-ESP composites. These results were similar to the trend reported by Ardhyananta *et al*. (2007) [1] and it is probably due to the fact that as the amount of filler in the composite increases, the composite becomes highly non-homogenous which leads to defects. Therefore, when the composite material is subjected to bending force, these defective sites tend to localize the stress potentially creating localized weakness, the material therefore fractures (snaps) at these sites. The flexural strength of the CNSP composites were higher than those of the CNSP/ESP composites, this is probably because of the increased non-homogeneity of CNSP, and ESP used together as fillers in compositing. According to Salmah *et al*. (2005) [14], this is due to the non-homogeneity of the polymer/filler matrix. The 30 g-ESP composite produced better outcomes than the 30 g-CNSP composites, which is possibly because ESP and LLDPE adhere to one another more effectively than CNSP and LLDPE do**.** There was drastic drop in the flexural strength of the 20 g-CNSP composites compared to that of other formulations, and this could be attributed to random orientation or uneven dispersion of filler in polymer matrix.

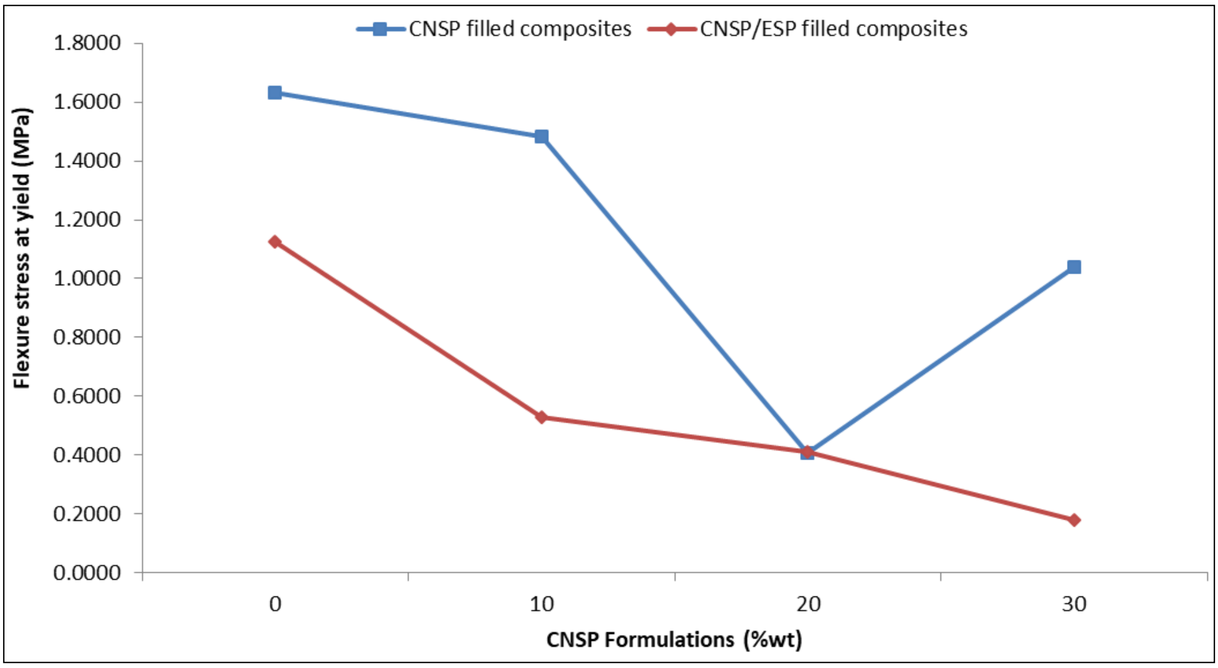

Fig 4: The flexural strength of CNSP and CNSP-ESP composites at different filler loadings (P-value for both the CNSP and ESP were less than 0.05)

Flexural Modulus

Figure 5 depicts the impact of filler loading on the flexural modulus of CNSP and CNSP-ESP filled composites. Flexural modulus is a measure of a material's propensity to withstand bending. For both ESP and non-ESP composites, it was shown that the flexural modulus decreased as the quantity of CNSP filler in the composite increased. This pattern coincided with the research done by Ardhyananta *et al* (2007) [1]. This demonstrates that the capacity of the composites to withstand bending decreases as the filler concentration in the composite rises. The enhanced non-homogeneity of CNSP and ESP when utilised as fillers in compositing is likely the reason why the flexural modulus of the CNSP composites was greater than that of the CNSP/ESP composites**.** According to Salmah *et al*. (2005) [14], this is probably because of the non-homogeneity of the polymer/filler matrix. The results of the 30 g- ESP composite was higher than that of the 30 g-CNSP composite, this it is probably due to better adhesion between the ESP and LLDPE when compared to CNSP and LLDPE. There was drastic drop in the flexural modulus of the 20 g-CNSP composites when compared to that of other formulations; this could be attributed to uneven dispersion of the filler in the polymer matrix.

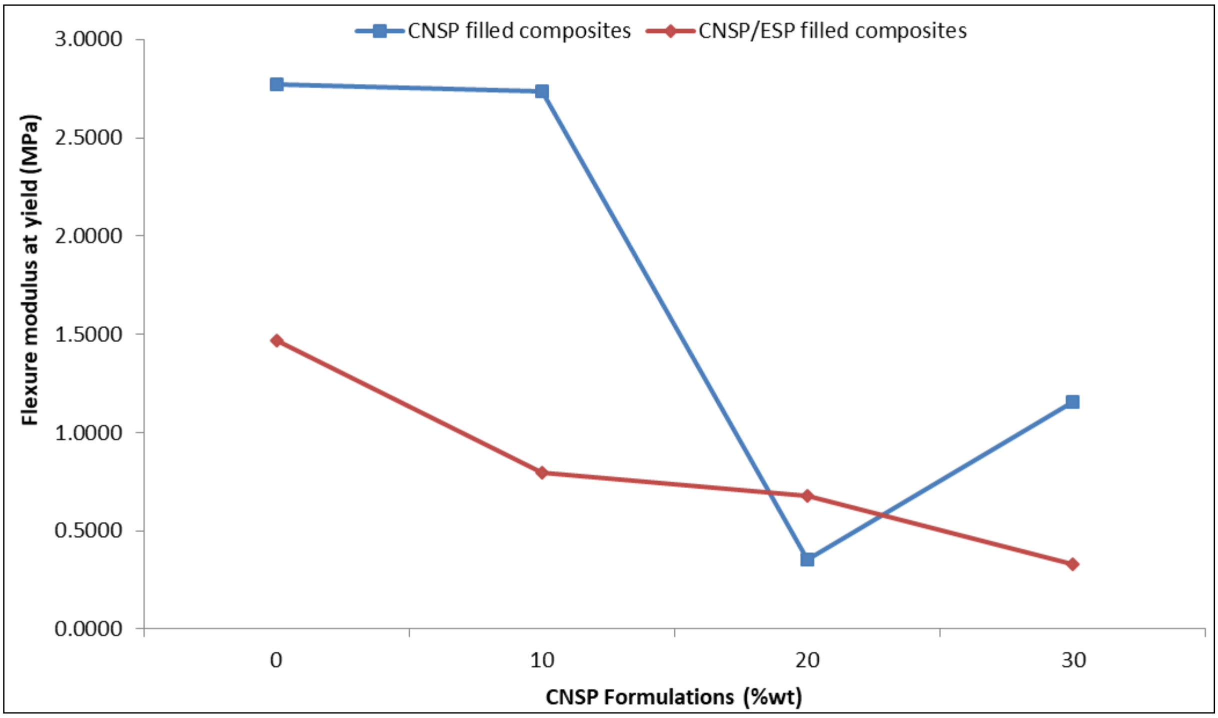

Fig 5: The flexural modulus of CNSP and CNSP-ESP composites at different filler loadings (P-value for both the CNSP and ESP were less than 0.05)

Impact Strength

Figure 6 illustrates how filler loading affects the impact strength of CNSP and CNSP-ESP filled composites. It is the maximum amount of energy a substance can hold before breaking. Results revealed that the impact strength decreased for both ESP and non-ESP composites as the quantity of CNSP filler in the composite increased; this tendency was consistent with the research of Lumlong *et al* (2018) [8]. This is explained by the fact that the polymer/filler matrix has weak interfacial adhesion, which lowers the composites' shock-absorbing capacity as filler concentration rises. Lumlong *et al*. (2018) [8] claim that it is because LLDPE and the filler have poor adherence**.** The result of the 30 g-ESP composites was higher than the 30 g-CNSP composites, and this may be because ESP has better interfacial adhesion to LLDPE when compared to CNSP. This means that a composite produced with ESP as the only filler would have better impact strength than that produced with only CNSP. There was drastic drop in the tensile strength of the 20 g-CNSP composites compared to that of other formulations. This may be attributed to poor mixing or uneven dispersion of the filler in the compound mix.

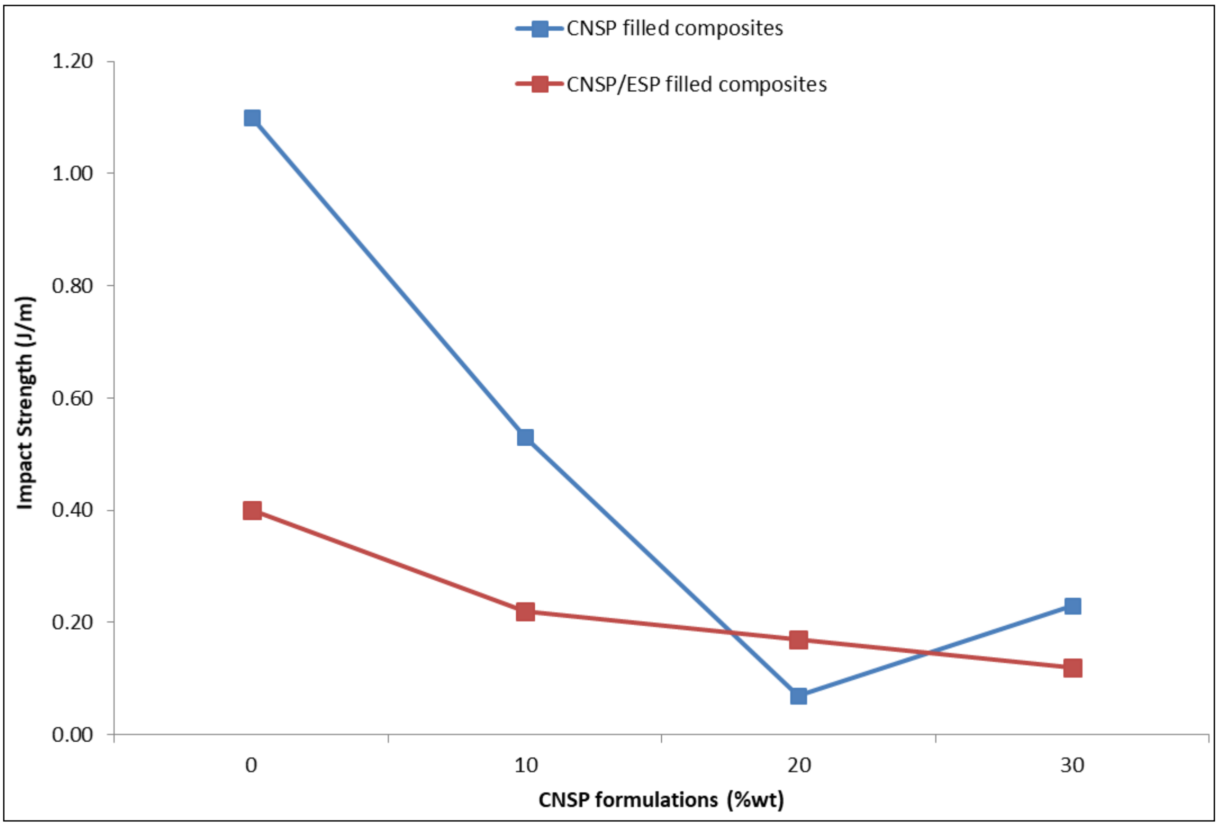

Fig 6: The impact strength of CNSP and CNSP-ESP composites at different filler loadings (P-value for both the CNSP and ESP were less than 0.05)

Conclusion

The mechanical properties of LLDPE/CNSP gave the highest values when compared to LLDPE/CNSP/ESP composites. Both the CNSP and CNSP-ESP filled composites had a reduction in the mechanical characteristics of tensile strength, tensile modulus, percent elongation, flexural strength, flexural modulus, and impact strength with increase. The ESP-filled composite (17:3) had better mechanical characteristics than the CNSP-filled composite (17:3)**.**

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