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Structure Property Relationships of Waste Low-Density Polyethylene/Polystyrene Cow-Horn/Date-Seed Powder Nano Composite.

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Abstract

To enhance the interfacial interactions between the ground date seed/cow-horn and the waste low density polyethylene/waste polystyrene, the fillers were treated with 5 % sodium hydroxide. The effects of the fillers to the structure of crystalline/amorphous regions of the polymer were characterized using the XRD Diffractometer. The nano range of the filler was determined with the aid of the Zetasizer nano analyzer. The mechanical properties were achieved with the Instron machine. 100 g of the polymer matrix was used as the control sample and each of the polymer matrix was substituted with 50 g, 45 g, 40 g, 35 g, 30 g, 25 g, 20 g, 15 g, 10 g and 5g of date seed powder/Cow horn powder to respectively make up 100 g each. The XRD results on the WLDPE/CH 85/15g recorded the highest crystallinity of92.30 % with crystallinity index of0.916while that for WPS/DS 85/15 was 47.31% crystallinity and 0.113 crystallinity index. The crystallinity percent/crystallinity index for the WPS/DS 85/15 are 47.31% and 0.113. The 85/15% composition for WPS/CH and WPS/DS recorded the highest elastic modulus of 71.04 Mpa and 70.25Mpawhile the 90/10% composition for WLDPE/CH gave an elastic modulus of 27.08 Mpa.Abetter tensile strength results of 46.21 Mpa and 24.84Mpa were observed in the 95/5% composition for WLDPE/CH and WPS/DS and the elongation at break decreased with increasing filler loading in both WPS/CH, WPS/DS and WLDPE/CH. The 90/10% composition gave the highest elongation of 1019%.

Keywords: Nanofiller, Nanocomposites, Crystallinity, Waste-Polyethylene, Waste-polystyrene, Tensile-strength.

Introduction

Polymer Nano Composites

Nano fillers are materials that have particle size less than 100 nanometres. The fillers have high aspect ratio and they can be used for resistant fillers [13]. Polymer nano composites are materials where a small

amount of nano fillers is added to a polymer [8]. Owing to the high surface area of the nano fillers, the expectation is that this addition would cause a dramatic improvement in the bulk properties of the composites prepared. However, this improvement is highly dependent on the level of dispersion of the nano fillers/matrix adhesion [7**]**. The polymer nano composites consists of a polymer or copolymer having nano particles or nano fillers typically 10-100 nm in at least one dimension dispersed in the polymer matrix. These polymers may be of different shapes (example platelets, fibers, spheroids) and they belong to the category of multi-phase systems (Mps, viz, blends, composites and foams) that consume nearly 85 % of plastics production.These systems require controlled mixing/compounding, stabilization of the achieved dispersion [4]. Polymer nano composites over the years have shown substantial enhancement in material properties such as electrical conductivity, bulk modulus, yield strength and toughness. It has been proved that the addition of nano fillers like carbon black to rubbery polymers showed strong impact on the properties of the materials, such effects also were reported for polymer glasses and semi-crystalline polymers [9, 6]. The properties of polymer systems can be improved when the polymer is combined with a reinforcing material as filler and through this way a composite is produced. The properties of the composites are strongly depended on the filler characteristics among which the size of the filler plays dominant role [22].

Polymer composites with the size of the filler in the nanoscale regime generates the polymer nano composites and the related technology [12, 1]. The wide variety of natural, synthetic and semisynthetic polymers known today exhibit wide diversity of properties. Some are rigid, hard and dimensionally stable, while others are soft, flexible or largely deformable under stress. Some are soluble and fusible while others are more resistant to heat and solvents and may be even insoluble and infusible. All such properties vary from a polymer of one type to a polymer of another type [20].

The structure property relationships in polymers deals with the relationships in materials properties, especially mechanical properties, and materials structure which relates to factors like the arrangement of atoms or molecules in the solid state. The

structure property relationships in polymers of particular interest in this research are the crystallinity and the mechanical properties of the polymers. The tensile strength of a polymer quantifies how much stress the polymer will endure before failing. Tensile strength changes with change in polymer structure [11].

The fillers used for this research work are cattle horn (the white Bororo Fulani cow) and the date seed. A horn is a permanent pointed projection found on the head of various animals and consists of a covering of keratin and other proteins surrounding a core of the bone. True horns are found mainly among the ruminants like the cattle, goats, antelope etc. Horns usually have a curved or spiral shape, often with ridges or fluting. Horns starts to grow soon after birth and continue to grow throughout the life of the animal [14]. Cow-horns litter the environment and this constitutes a nuisance. Therefore, using them as filler will go a long way to eradicate this problem. Nigeria has surplus amount of cow-horn, with enormous potential that can be utilized as composites. Despite this fact, the contribution of cow-horn on the agro-economic sector of the country is very small [20]. The date seed is a hard coated, usually oblong, ventrally grooved, with a small embryo. Date pits weigh 0.5 g to 4 g and represent 6 to 20 % of the fruit weight depending on maturity, variety and grade [5]. Date seeds are traditionally used for animal feed. They can also be used as a source of oil (which has antioxidant properties valuable in cosmetics). It can be used as a coffee substitute, as a raw material for activated carbon or as an adsorbent for dye containing waters. In this research work, we used the powdered seed and that of cow-horn powder as a bio-filler by reducing the filler to nano-size particles for a better interfacial bonding between the filler and the matrix. Polyethylene of commerce are available in two major density ranges and the classified products are commonly known as: (a) low density polyethylene, LDPE (density range, 0.915-0.94 g/cm^3), and (b) high density polyethylene, HDPE (density range, 0.945-0.96 g/cm^3) [10].

Polystyrene is one of the largest volume thermoplastics. It is a versatile polymer whose principal characteristics include transparency, ease of coloring and processing, and low cost. It is usually available in general -purpose or crystal (GP-PS), high impact (HIPS), and expanded grades[19].

The commercial product or general-purpose polystyrene is atactic and as such amorphous and that was the grade that was used in this research work. However, GP-PS has a number of limitations, including brittleness, low heat-deflection temperature, poor UV resistance, and susceptibility to attack by a variety of solvents. (Density range 0.96-1.05 g/cm^3). Polystyrene is sensitive to foodstuffs with high fat or oil content. It crazes and turns yellow during outdoor exposure [2]. Reusing plastics waste could become an important driver of profitability for chemical companies. Incumbent players need to make the right moves now to tap this opportunity. Recycled materials are increasingly introduced into manufacturing processes, which were originally designed for new materials only. Therefore, efficient sorting, separation and cleaning processes become most important for high quality recycled plastics. When talking about plastics Waste Low density polyethylene/Polystyrene food packages when disposed indiscriminately block our drainage systems, and thus cause serious environmental problems. The processing of these waste polymers with the fillers will go a long way to solve this problem and also yield products that are of high industrial applications. Agricultural by- products such as date seed and cow horn have low economic values and they are readily available. Reda et al, [15] observed the effects of nanomaterials and particles on mechanical properties and fracture toughness of composites. They observed that the increment in the size of particles/distribution of the nanomaterials altered the enhancement of the mechanical

recycling industry, in this research work, we are concentrating mainly on recycling of low-density polyethylene and polystyrene which are meanwhile used for all kinds of liquid packaging like water, carbonated soft drinks, juice, beer, house hold chemicals and all kinds of electrical packaging/insulating materials. When recycled plastics are used to make new plastic products, more materials are conserved. Through the use of recycling, wealth is generated and job opportunities are created for young school graduates. It is estimated that 120,000 tons of polystyrene reaches the market each year. The polystyrene food wraps which are disposed into dumpsites are sorted out and recycled and mixed with just small amount of virgin polystyrene. Through this process more food packaging materials are being produced with less amount. Polystyrene is also found in buildings (as insulation) and home appliances and used as wedges.

properties of the bulk materials. Tagliafero et al, [16] studied the structure-property relationships in polyethylene-based composites filled with biochar derived from waste coffee grounds. Weak structural complexes were observed and this caused a retardation of the dynamics of the macromolecular chains of the composite. They observed that the crystallinity degree decreased as a result of biochar addition in the polymer causing a shift of melting temperature to a very low value. Bio-fillers have low thermal stability, and most times, this causes a problem since the degradation of bio-derived fillers occurs in the range typical of polymer processing and this behavior most times limits the choice of the polymer matrix. Natural fillers shows poor compatibility with most of the polymers. Chemical treatment of the bio-filler was carried out in this research work to enhance the polymer /filler interfacial contact.

MATERIALS AND METHODS

The materials that were used in this study are as follows: Cattle horn from white Fulani cows(white Bororo) slaughtered cows in the abatoir at Zango in Zaria. The seed of the sweet date seed was sourced from the local market in Samaru, Zaria. Waste low density polyethylene water satchets/polystyrene food packages were sourced from the refuse dumps in shops in Nigerian Institute of Leather and Science technology, Zaria and Ahmadu Bello University.

The cattle horn and the dateseed were thoroughly washed with clean water and allowed to dry completely under the sun for six hours. The materials were ground separately for two hours with the food premier grinding machine and the willey laboratory grinding machine. The powdered samples were thoroughly filtered with 75micronsieve size [21].

The particle size of the fillers were further reduced with the ball-milling machine for 18 hours and filtered again respectively with the 75 micron sieve size. Chemical treatment of the fillers were done using 5 % sodium hydroxide by dissolving 100g of sodium hydroxide in 2000cm^3 of distilled water. The fillers were soaked individually in each of the solutions for four hours to remove lignin, wax, hemi-cellulose which

may cause an inhibition in adhesion of the fillers and the matrices. The fillers were washed very well with water to remove excess sodium hydroxide and later dried in an oven for an hour at oven temperature of 70 ^{o}C. The inherent hydrophilicity of natural fibers decreases as a result of chemical treatment, and this improves the adhesion between the matrix and the fiber [17]. It has also been established from literature that chemical treatment of natural fibers roughens the surface of the natural filler, and removes surface impurities, thereby promotes better filler-polymer interfacial compatibility and bonding and through this, the overall performance of the bio-composites is enhanced [18]. 25 g of each of the fillers were taken to the centre for genetic engineering and biotechnology of the Federal University of technology Minna for nano measurements. The two-roll mill and the compression machines at the Nigerian Institute of Leather and Science Technology in Zaria were used for the compounding and hydraulic compression of the fillers and matrices to produce composite flat sheets that were later used for polymer characterization. The respective materials formulations of WLDPE/CH, WPS/DS, WPS/CH(100/0, 95/5, 90/10, 85/15, 75/25, 70/30/, 65/35, 60/40, 55/45, 50/50)g were used for the compounding/compression of the materials.

Plate I: Date Seeds

Plate 2: Cow Horn

Plate 3: Ground date seed powder

Plate 4: Ground cow horn powder

Plates 1, 2, 3 and 4 shows the diagram of the date seed and the horns of the white Fulani cows/the ground fillers.

The nano characterization of the date seed and the cow horn powder was done with the aid of the Zetasizer nano particle characterization system. The various measurements were done using the "Sop" (standard operating procedures) of the device manufactured by Malvern Instruments Ltd, Uk, version 7.01. 25 g of each of the fillers were measured separately in the same dispersant. The individual particle sizes of the fillers were measured in a dynamic light scattering (DLS) unit of the zetasizer system. The "DLS" measures the diameter of the sphere that diffuses at the speed as the particle being measured. The zetasizer device determines the size by first measuring the Brownian motion of the fillers [25]. The Brownian is defined as the random movement of particles in a liquid due to the bombardment of the molecules that surround them. Each of the particles in the liquid moved about randomly and their speed of movement was used to determine the size of the particles.

X -RAY DIFFRACTION METHODS

X-ray diffraction methods are the most effective methods for determining the crystallographic structure of a material [23]. The Benchtop X-ray diffractometer (miniflex600) of the materials engineering

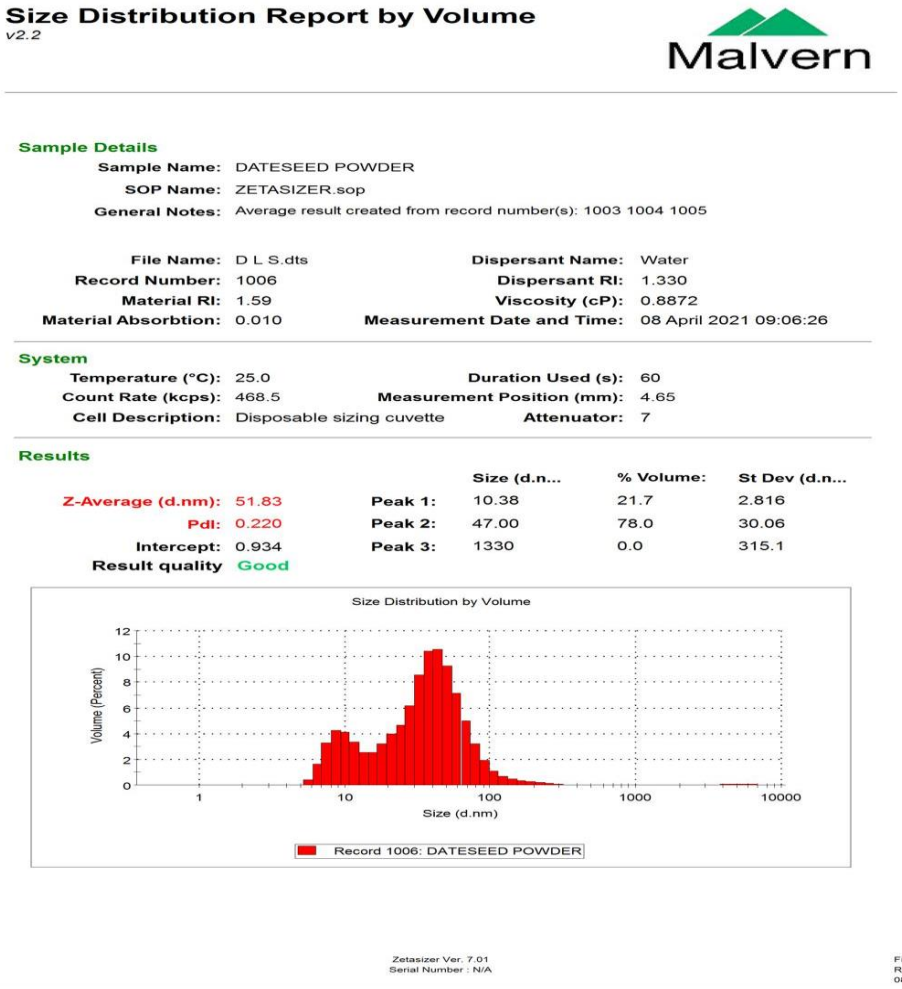
department of the Ahmadu Bello University was used for this research work. The composite samples were sliced to the size and dimensions of the X-ray diffractometer mounting plate which is 1.5 × 2×1.5 mm. The sample was fixed on the mounting plate and then later fixed on the goneometer of the system and then the machine door was closed. The samples were individually placed evenly and flat and the sample surface and the plate were set to be on the same plane to avoid angle error margin. Direct beam measurement of the machine is within the range of + 0.01. The machine was switched on after the door has been locked. In ideal conditions, an x-ray beam focuses on the specimen and the intensity of diffraction from the specimen was detected accurately at the 2 theta angle. However, the diffractometer is often used for examining samples of crystalline aggregates other than powder [24]. Polycrystalline solid samples and even liquids can be examined while the system generates x-rays, the x-ray warning lamps stays on. It took 7 mins for x-rays to be generated and absorbed on each of the samples. The detection of the crystalline and the amorphous phases on the samples was only for this period of time, and the system was switched off. The diffraction method used identified chemical compounds from their crystalline structure, not from their compositions of chemical elements. Therefore, different compounds (or phases) that have the same composition were identified.

THE MECHANICAL TEST OF THE POLYMERS USING THE INSTRON MACHINE

The mechanical properties of the composites were determined with the aid of the electronic universal testing machine (Instron model: WDW-1000 KN, Number 190536 of the Ahmadu Bello University, Zaria. The machine consists of the upper and lower jaw sections. The dumb-bell shaped samples were gripped on the jaws for the test process and it is a destructive process. The tests were done according to ASTM D 638. The instron machine is a full digital and standalone machine which is packaged as tower. A motor encoder/load cell is used to collect data while the machine is in tension. When a testing protocol was initiated, the center cross head of the machine travels vertically and this was propelled by large lead screws that was located inside the columns. The direction of travel of the gripped sample, the distance and the speed were determined by the testing of

protocol that has been programmed in the equipment. The Sample that was gripped at both jaws was pulled to elongate at a determined rate to the materials break point, but if the polymer is high ductile polymer, it may not reach it`s break point. The maximum load of the machine is 5 KN. During a tension test, the dumb-bell sample was held securely in the upper and lower wedge grips. The upper grip attached to the load cell and the lower grip to the fixed base plate of the crosshead. The crosshead travels downward during tension and the upper grid and load cell remains stationary. The machine plots stress/strain curves as the test goes on, and this was done automatically on the software provided by the manufacturer of the equipment.

RESULTS



Size Distribution Report by Volume
v2.2

Malvern

Sample Details

Sample Name:	DATESEED POWDER		
SOP Name:	ZETASIZER.sop		
General Notes:	Average result created from record number(s): 1003 1004 1005		
File Name:	D L S.dts	**Dispersant Name:**	Water
Record Number:	1006	**Dispersant RI:**	1.330
Material RI:	1.59	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date and Time:**	08 April 2021 09:06:26

System

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	468.5	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	7

Results

			Size (d.n...	**% Volume:**	**St Dev (d.n...**
Z-Average (d.nm):	51.83	**Peak 1:**	10.38	21.7	2.816
PdI:	0.220	**Peak 2:**	47.00	78.0	30.06
Intercept:	0.934	**Peak 3:**	1330	0.0	315.1
Result quality	Good				

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Zetasizer Ver. 7.01
Serial Number : N/A

File name: D L S
Record Number: 1006
08 Apr 2021 09:10:14

Figure 5 :Nano size measurement for date seed powder.

Size Distribution Report by Volume

v2.2

Malvern

Sample Details

Sample Name: COW HORN POWDER
SOP Name: ZETASIZER.sop
General Notes: Average result created from record number(s): 1011 1012 1013

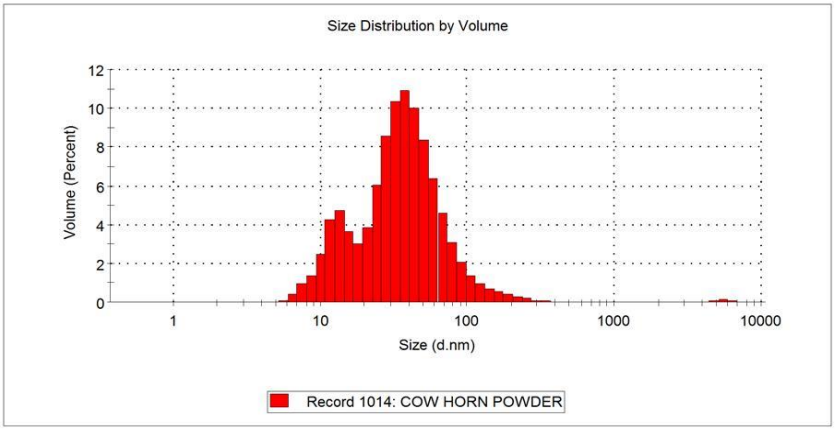
File Name:	D L S.dts	**Dispersant Name:**	Water
Record Number:	1014	**Dispersant RI:**	1.330
Material RI:	1.59	**Viscosity (cP):**	0.8872
Material Absorbtion:	0.010	**Measurement Date and Time:**	08 April 2021 09:09:46

System

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	468.5	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	7

Results

			Size (d.n...	% Volume:	St Dev (d.n...
Z-Average (d.nm):	79.21	**Peak 1:**	48.26	79.4	32.68
PdI:	0.329	**Peak 2:**	13.03	20.3	3.192
Intercept:	0.934	**Peak 3:**	5344	0.3	797.0
Result quality	Good				



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Zetasizer Ver. 7.01
Serial Number : N/A

File name: D L S
Record Number: 1014
08 Apr 2021 09:12:52

Figure 6

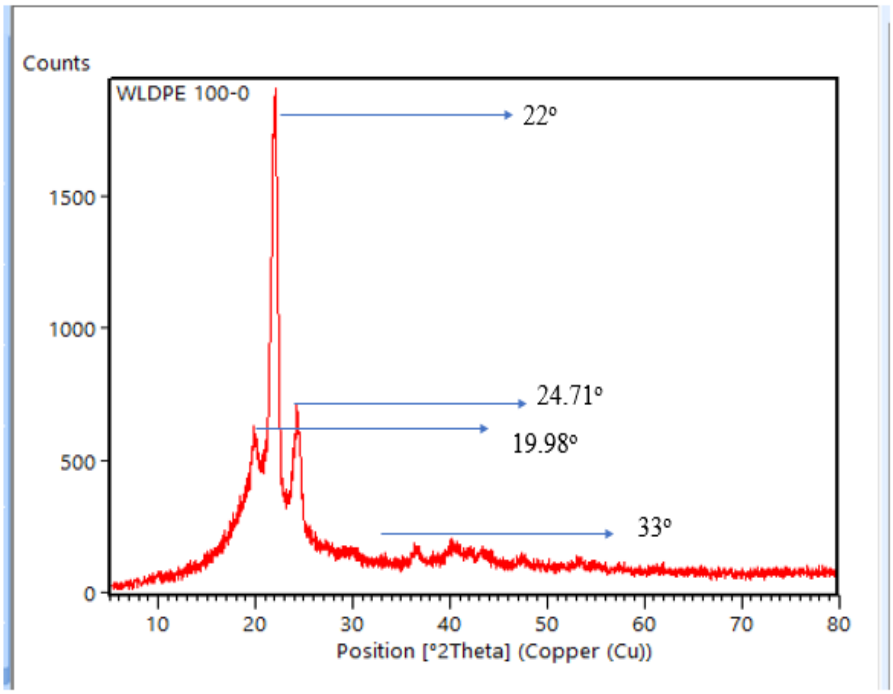


Figure 7: XRD micrograph for WLDPE 100 /0 (Control Sample)

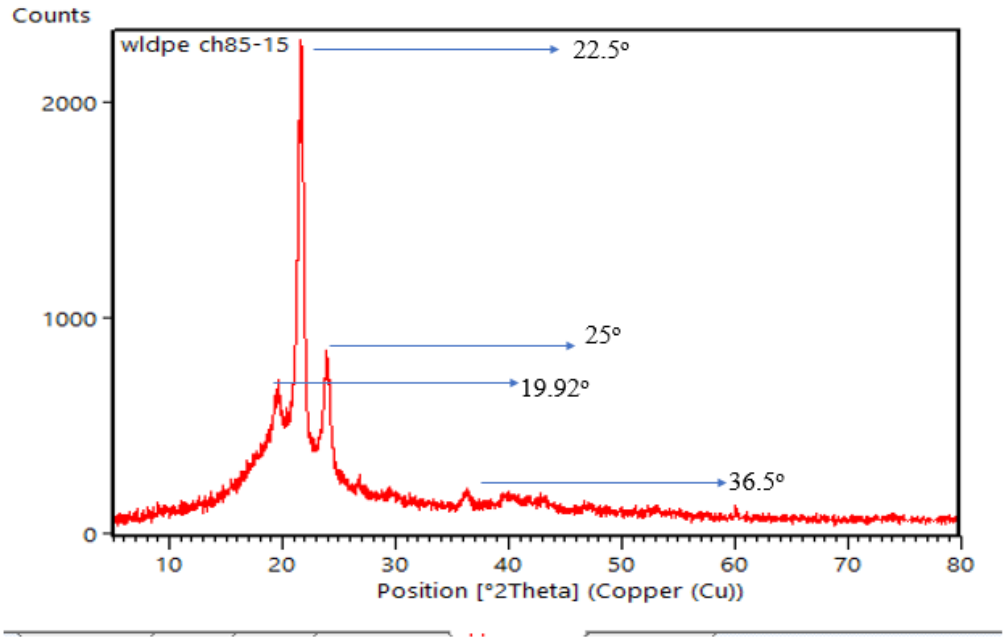


Figure 8: XRD micrograph for WLDPE/CH 85/15 (Composition)

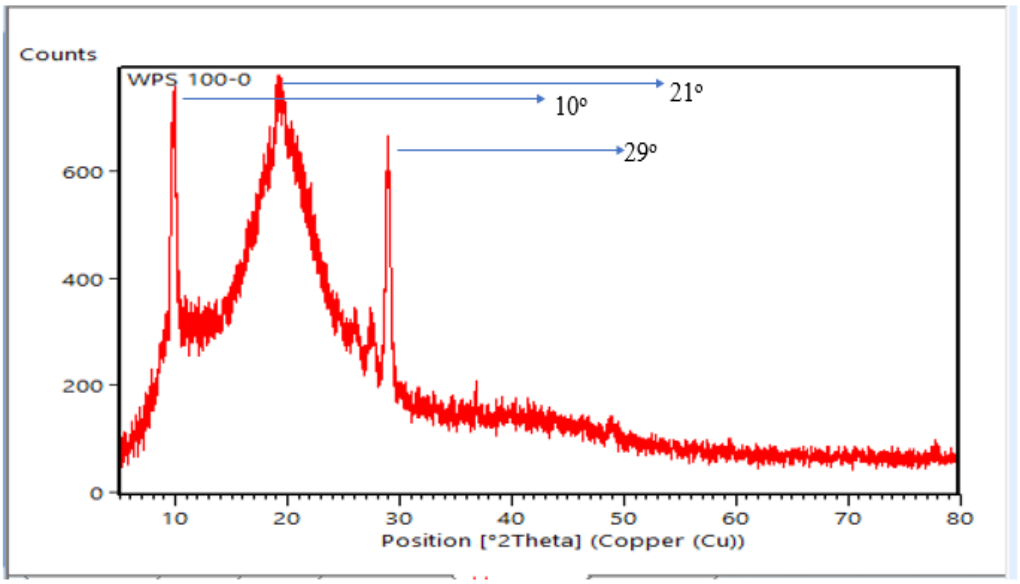


Figure 9: XRD micrograph for WPS 100 / 0 (Control Sample)

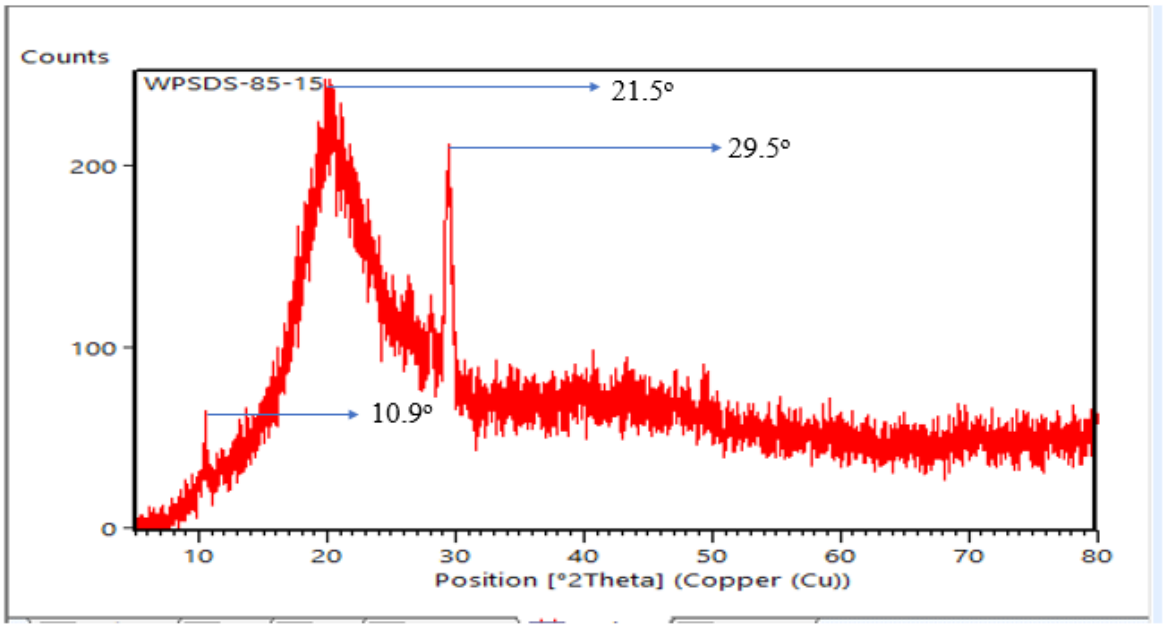


Figure 10: XRD micrograph for WPSDS 85 / 15 (Composition)

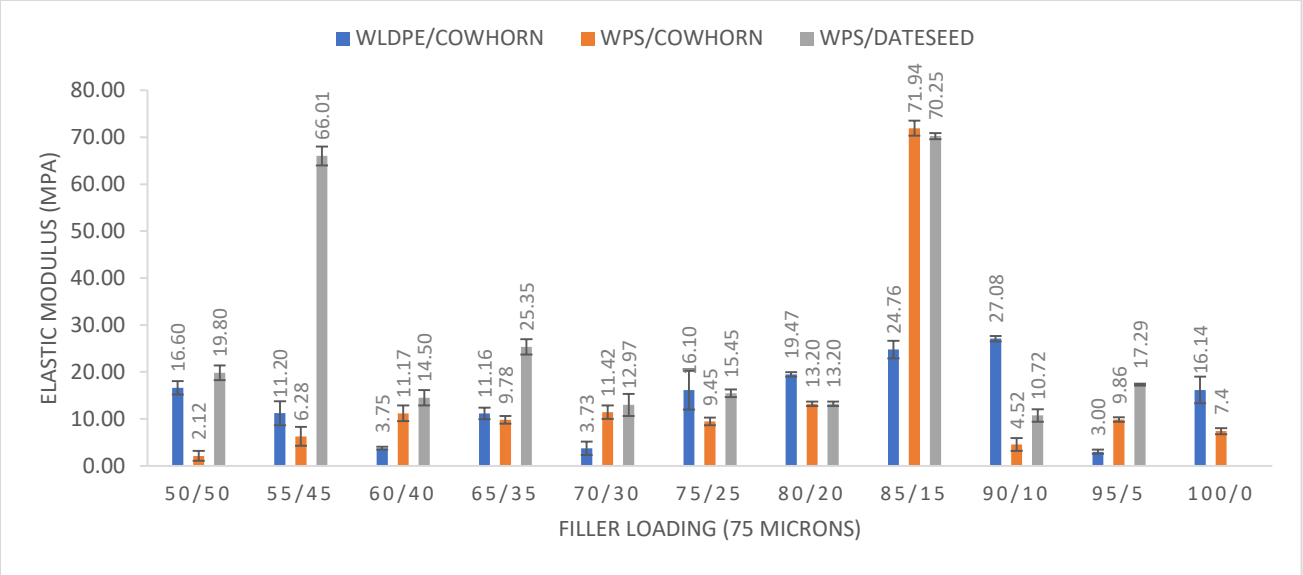


Figure 11: The elastic modulus of thewaste low density polyethylene/Cowhorn and waste polystyrene/Cowhorn and waste polystyrene/Dateseed and their various filler loading values.

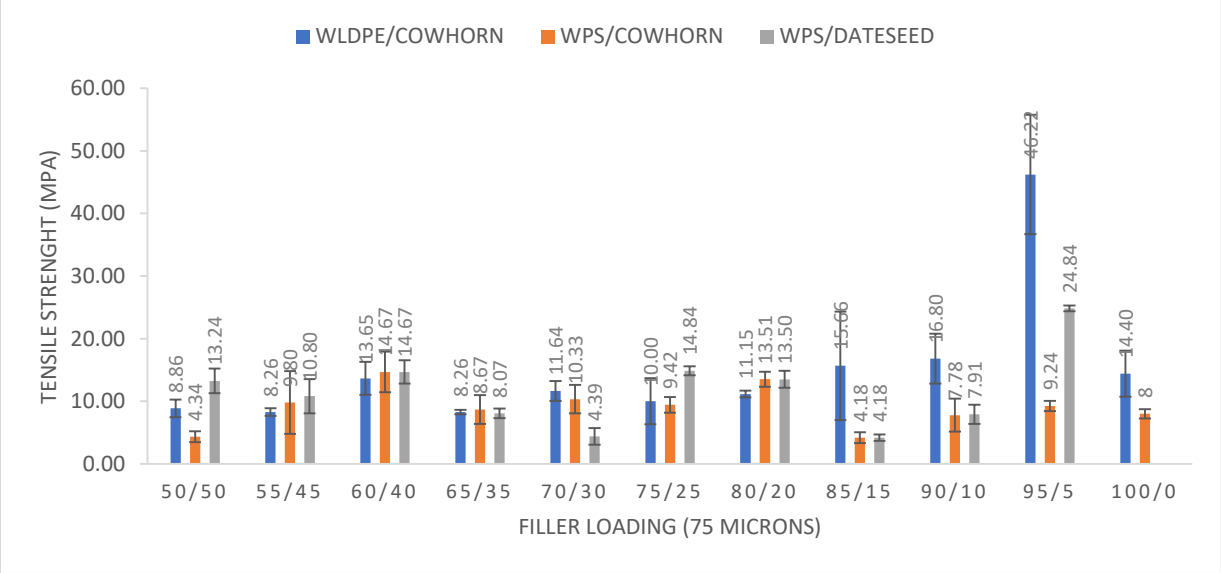
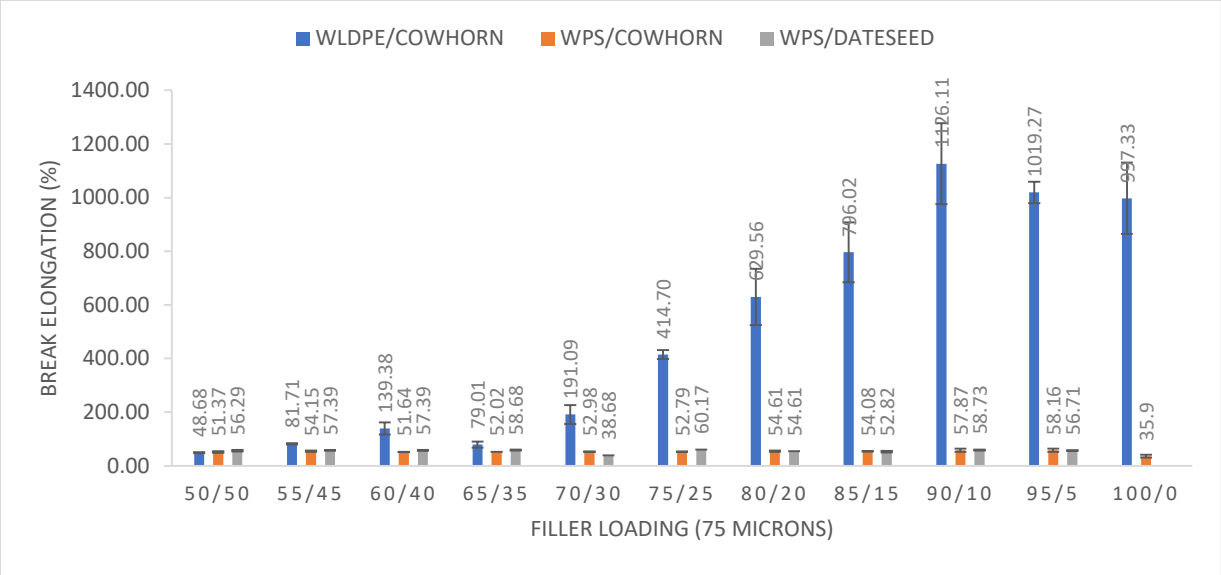


Figure 12; Tensile Strength of WLDPE/CH, WPS/CH and WPS/DS.



Figures; 13Elongation at break of the WLDPE and WPS on the fillers

DISCUSSION

The two experimental results in figures 5 and 6 illustrated the count rate for the two fillers. The count rate displays the number of photons detected in kilo-counts per second and this was used for monitoring the quality of the samples. The Z-average (d.nm) as shown in the results is known as the "cumulant mean" and this is the most important and stable result. The Z-average nano values for the date seed and the cow horn are 51.83 d.nm and 79.21 d.nm. The cumulant analysis apart from recording a mean value for the size, also recorded a width parameter results for the two samples known as the polydispersity index (pdi). The polydispersity index for the date seed and cow horn are 0.220 and 0.329 respectively. If the polydispersity index is over 0.5, according to the Zetsizer system standard, the Z-average mean for the size distribution cannot be relied upon. Therefore, from the experimental results, the two Z-average results can be relied upon since the respective pdi results are less than 0.5.

The figures 7, 8, 9 and 10 showed the crystalline and amorphous peaks for the WLDPE 100/0, WLDPE/CH 85/15, WPS100/0 and WPS/DS 85/15 Polymer nano composites compositions. High score plus software was used for the plotting of the crystalline and amorphous peaks in the composites. It was observed in the WLDPE 100/0 that the highest crystalline peak at 2 theta = 22 degrees with the count rate of 1904. The lowest peak at 2 thetha = 19.98 degrees at the intensity count rate of 635. The third crystalline peak at 2 theta = 24.71 degrees at 708 count rate. For the amorphous region, at 2 theta = 40.68 the count rate was 189.

$$\text{Percentage crystallinity} = \frac{I_{22}}{I_{22} + I_{am}} \times 100$$

Where I_{22} is the major diffraction crystallinity at 2 theta and the diffraction intensity at amorphous region at 2 theta. Therefore, the percentage crystallinity is 91.49 %.

The crystallinity index (C1)$=\frac{I_{22}-I_{am}}{I_{22}}=$ $\frac{1904-177}{1904}=0.907$

where I_{22} = major diffraction crystallinity at 2ɵ (angle)I_{am} = the diffraction intensity at 2 theta angle.

The 100/0 compositions are the two control samples for waste low density polyethylene

For the WLDPE/CH 85/15(waste low density polyethylene/cow horn 85/15) composition, the highest crystalline peak at 2 theta is 22.5 degrees at a count rate of 2400. The lowest peak at 2 theta is 19.92 degrees at a count of 800. The amorphous region at 2 theta is 36.5degrees at the count rate of 200. From the mathematical equation, the percentage crystallinity is 92.30 % while the crystallinity index is 0.916, The crystallinity percentage for the WPS 100/0 (waste polystyrene composite without filler) was 0.527 % and the crystallinity index was 0.102. The WPS/DS 85/15 (Waste polystyrene and date seed polymer nano composite) highest crystalline region at 2 theta is 29.5 degrees at a count rate of 220. The crystallinity percent is 47.31% and the crystalline index is 0.113. The more crystalline a polymer, the more regularly aligned its chain. Therefore, low density polyethylene is harder than polystyrene because it`s percentage crystallinity is higher than that of polystyrene which is more of an amorphous polymer. The two control samples had less crystallinity percent than the formulations with filler loading and waste polystyrene without any filler loading in figure 11. The modulus for the 100 % WLDPE and WPS are 16.4Mpa and

7.4Mpa. When 5 % filler was introduced into the matrix, the WPS/CH and WPS/DS elastic modulus increased from 9.86Mpa to 17.29 Mpa but that of WLDPE/CH decreased to 3 Mpa as a result of poor interfacial adhesion between the waste low density polyethylene and cow horn filler at that composition. The elastic modulus of the WLDPE/CH improved to 27.08Mpa when 10 % filler was loaded into the matrix while that of WPS/CH reduced to 4.52 Mpa and the WPS/DS also decreased to 10.72Mpa. A decrease in the elastic modulus could also be as a result of agglomerations which limits the transfer of load from the matrix to the nano fillers and this will cause cracks to initiate that may result to very low mechanical properties. A study that was conducted by Ervina *e*tal, [3] showed similar results. The WPS/CH 85/15 and the WPS/DS 85/15 yielded high elastic modulus of 71.94Mpa and 70.25Mpa more than the other compositions and this was an impression that there was a better interfacial interaction between the ground fillers and the waste polystyrene polymer. In all the compositions, the 50/50 % for WPS/CH showed the least elastic modulus of 2.12 Mpa. This confirmed that introducing higher percentage of nano filler into the matrix does not really give an optimum elastic modulus value.

Figures 12 and 13 showed the tensile strength and elongation at break of the WLDPE and WPS on the fillers. There was remarkable improvement of 46.21 Mpa and 24.84 Mpa on the tensile strength of WLDPE/CH and WPS/DS in the 95/5 % compositions. Therefore, for industrial applications, the tensile strength of these two polymers might be better utilized at the 95/5 % composition. In the break elongation charts, it was observed that an increase in the filler loading reduced drastically the break elongation in the WPS/CH and WPS/DS. This was as a result of the brittle nature of polystyrene polymer. The elongation at break increased with a reduction in the loading of the fillers. The waste polystyrene without filler (control sample) had the least elongation at break of 35.9 % while the waste low density polyethylene with cow horn recorded the highest elongation 0f 1126 % at the 90/10 %, and this was as a result of the ductile nature of the low-density polyethylene and cow-horn filler.

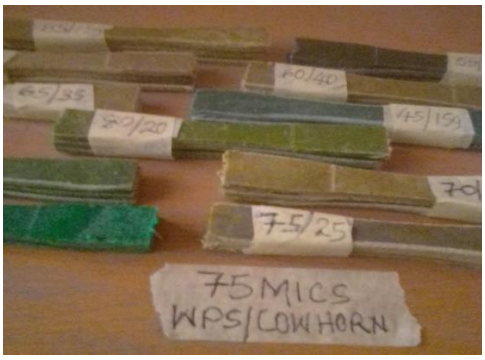


Plate 5: 75 Microns WPS/Cowhorn.

Plate 6: 75 Microns WLDPE/Cowhorn.

Plate7: 75 Microns WPS/Dateseed.

Plates 5, 6, 7: The dumb bell shapes of the compounded samples.

Acknowledgment

The authors express their appreciation to the department of Materials and Metallurgical Engineering laboratory of the Ahmadu Bello University, Zaria for their assistance in analyzing the composite samples.

Conclusion

Crystallinity degree in high performance polymers is very important because of its influence on mechanical and chemical properties of the polymer. The crystalline phase in the polymer increase stiffness and tensile strength of the polymer. The amorphous phase has more effectiveness in absorbing impact energy. The chemical treatment of the fillers improved their bonding properties. The brittle nature of polystyrene polymer affects its elongation at break by reducing the percentage elongation drastically. The low-density polyethylene is more ductile than polystyrene and this also showed in the elongation at break results. Low percentage of filler loading of 15 %, 10 % and 5 % enhanced the elastic modulus/Tensile strength results of the

WLDPE/CH, WPS/CH and WPS/DS. The use of bio-fillers and waste plastics in polymer processing will reduce environmental pollution, create employment and reduce the high costs of synthetic fibers.

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