Characterization of a Polypropylene Filled Composite using Scanning Electron Microscopy and X-Ray Diffraction

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Abstract:
The objective of the present study is to understand the influence of cashew nutshell powder and calcium carbonate composition on the crystallinity and microstructure of polypropylene matrix.
The microstructural characterization and change in the crystallinity of the polypropylene composites prepared by thermal compression was carried. Morphological properties and the crystallinity of the pure polypropylene, polypropylene/calcium carbonate and polypropylene/cashew nutshell powder are reported. Scanning Electron Microscopy (SEM) and X-ray Diffraction methods were used for the sample analyses. Scanning Electron Microscopy (SEM) revealed that the composites of ratios, both 60 g PP: 40 g CaCO₃, 60 g PP: 40 g CNSPand 50 g PP: 50 g CaCO₃, 50 g PP: 50 g CNSP are completely compatible at which there are no phases that are grossly separated. The XRD analysis has shown that there was increase in d spacings of the Polypropylene composites of fillers content 40 g and 50 g (both Cashew Nutshell Powder and Calcium Carbonate) compared with the Polypropylene without filler shift of peak positions to lower positions was also observed in the polypropylene composites compared with the unmodified Polypropylene. The crystallinity index was calculated and the highest value was obtained as (87.50%) for the Filled polypropylene (50 g: 50 g) Cashew Nutshell Powder compared to the remaining composites of the same filler's compositions.

Keywords: Cashew Nutshell Powder, Calcium Carbonate, Polypropylene composite, Scanning electron microscopy and X-ray diffraction Analysis.

1. Introduction

Global demand for filler for the plastics industry has been estimated to be about 15 million tones, (Mahajan, 2003). Primary end-use markets are building or construction and transportation, followed by appliances and consumer products; furniture, industrial or machinery, electrical or electronics, and packaging comprise of small market segment. Impact strength, Flexural modulus and heat resistance are the three critical properties of plastics that are enhanced by the inclusion of performance minerals. Automotive exterior parts, construction materials, outdoor furniture, and appliances components are examples of applications benefitting from enhanced Impact resistance. Environmental acceptance and improved sustainability of automotive parts are attributes of composites containing natural fibres, (Joshi *et al.* 2004) reported that there are a significant number of technological advances that will undoubtedly contribute to the additional growth in the usage of certain functional fillers.

Di Lorenzo *et al.* (2002) successfully polymerized poly ethylene terephthalate (PET) with coated and uncoated $CaCO_3$ particles of 40 – 80 nm size. They found that stearic acid coated $CaCO_3$ resulted in a stronger polymer-filler interaction compared to the uncoated grade. The strong interfacial adhesion between the phases resulted in significant increase in the glass transition temperature (14^oC shift) and melting temperature (8^oC shift) of the nanocomposites.

Chan *et al.,* (2002) prepared PP/ $CaCO_3$ nanocomposites by melt mixing in a Haake mixer using various mixing time (15, 30 and 45 minutes) with filler loadings of 4.8, 9.2 and 13.2 volume percents. The dispersion of Calcium carbonate nanoparticles in PP was good for filler content below 9.2% volume. Their Differential Scanning Calorimetry results indicated that the nano $CaCO_3$ are very effective nucleating agent for Polypropylene.

Tensile tests showed that the modulus of the nanocomposites increased by approximately 85%, while the ultimate stress and strain as well as yield stress and strain were not much affected by the presence of $CaCO_3$ nanoparticles. The results of the tensile test can be explained by the presence of the two-counter balancing forces: the reinforcing effect of the $CaCO_3$ nanoparticles and the decrease in the spherullite size of the Polypropylene. Izod impact tests suggested that the incorporation of $CaCO_3$ nanoparticles in PP has significantly increased its impact strength by approximate 300%. J-integral tests showed a dramatic 500% increase in the notched

fracture toughness. Micrographs of scanning electron microscopy revealed the absence of spherullitic structure of PP matrix. In addition; DSC results indicated the presence of a small amount of β-phase PP after the addition of the $CaCO_3$ nanoparticles.

Ustarroz Taketa, Lomov and Verpoest(2005) reported that the Carbon/PP and carbon/self-reinforced PP hybrid composites have been produced byfilm-stacking. Tensile tests in carbon/PP composites show that the Elongation break -modulus is 15%lower than expected. Compared to carbon/PP materials, hybrid composites show an increase of 6-20% in ultimate strain and 10-15% in strength, while at the Elongation break-modulus iskept as predicted.

Sihama *et al.*(2013) revealed that the Comparative studies on the mechanical properties of High density polyethylene/polypropylene (HDPE: PP) and Low density polyethylene/ Polypropylene (LDPE: PP) binary blend. Morphological Analysis using Scanning Electron Microscope, Preparation of Samples by melt mixing in an extruder, Mechanical Tests, Hardness Test, Impact Test and Creep Test. Binary Blends (HDPE: PP) gave higher values of tensile strength, fracture strength, young modulus, hardness, creep rate and creep modulus than LDPE: PP with the blend of ratio 20% HDPE: 80%PP showing superior Mechanical properties.

Gul *et al.*,(2007) studied the comparison between two types of polypropylene (PP) with different molecular structure, namely, homogeneous polypropylene (HPP) and polypropylene block copolymer (PPC) blended with low density polyethylene and found that the mechanical properties of the LDPE/PPH blend were much higher than that of LDPE/PPC blend, which was attributable mainly to the fact that the mechanical properties of the neat PPH are stronger than that of the neat PPC. Mamza *et al.,* (2009) used density measurement and viscometric method and reported that the morphology of some reinforced blends of Polystyrene (PS) and Polyvinyl Acetate(PVAc) increase the densities of the blends with 30/70, 20/80 and 10/90, PS/PVAc having highest values than other compositions. Also, photomicrographs of the different blends show a two phasesystem appearing bright (PVAc phase) and the other appearing black (PS phase) in virtually all them icrographs, even though the heterogeneity due to phase inversions is relevant for some compositions. For some composition a domain distribution shows considerable miscibility within the range of compositions.

Also Dikabe and Luyt (2010), studied the morphologies as well as the mechanical properties of two types of blends, polypropylene/linear low density polyethylene and maleic anhydride grafted polypropylene MAPP: LLDPE, PP/LLDPE blends. They showed better properties and thermally stable than the (PP/LLDPE) as a result of stronger interaction between MAPP and LLDPE as compared with PP and LLDPE.

2. Experimental Procedure

2.1. Scanning Electron Microscopy
The morphologies of the cross-section of the composite of different filler loading, both virgin and the filled polypropylene matrix were examined by Scanning Electron Microscope N.J.F (SEM, Jeol, JSM-840 SEM)at magnification of 1000 X (at the Department of Chemical Engineering, Ahmadu Bello University, Zaria).

The prepared CNSP specimen was taken for scanning electron microstructure test in order to determine and characterize the microstructural contents of the CNSP at its molecular level. The processed sample was mounted in to the sample holder and result was shown on the display screen (Figures 1-3).

2.2. X-Ray diffraction
The composites sample of the CNSP and $CaCO_3$ were taken for XRD Analysis for the characterization of the compounded specimen, result obtained with respect to Bragg's Law. The samples were loaded on to the machine and run in the sample chamber of the of the Shimadzu X-ray diffraction machine and maximum voltage (30kv) and a maximum current (1mA) was applied to produce the X-rays to excite, the sample for a preset time (10minutes) in this case.

3. Results and Discussion
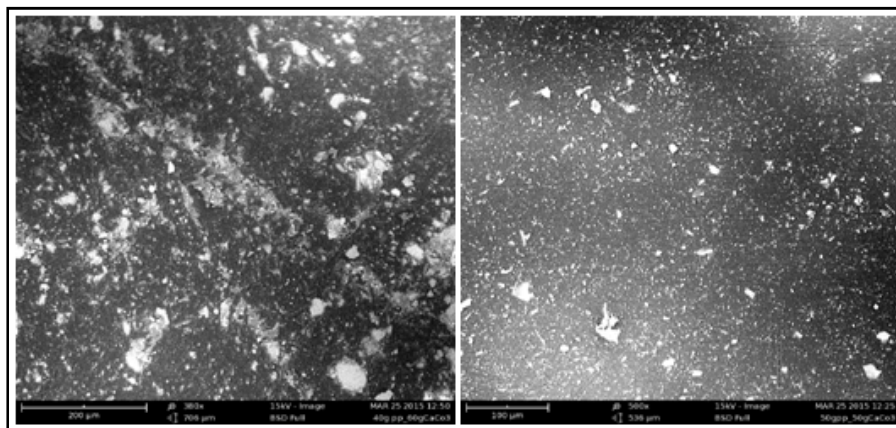
3.1. Morphology Results

Figure 1: SEM micrographs of (40g PP: 60 g $CaCO_3$ and 40g PP: 60g CNSP) polypropylene composite
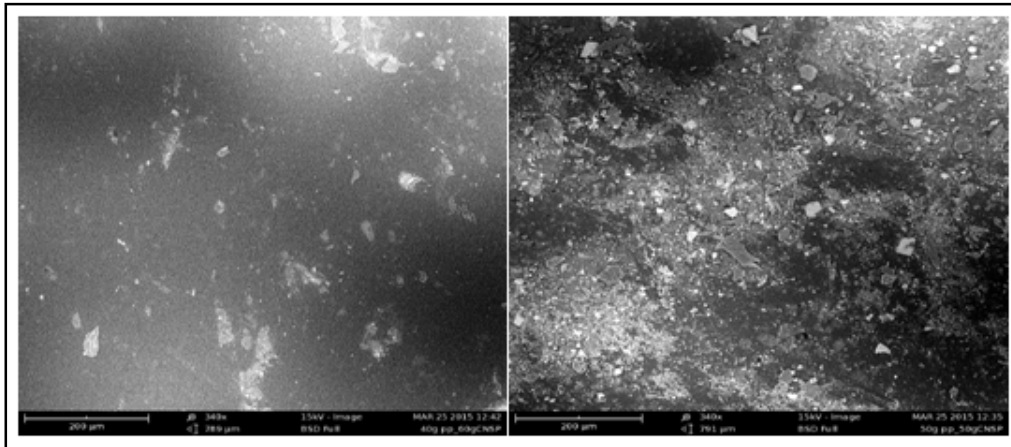
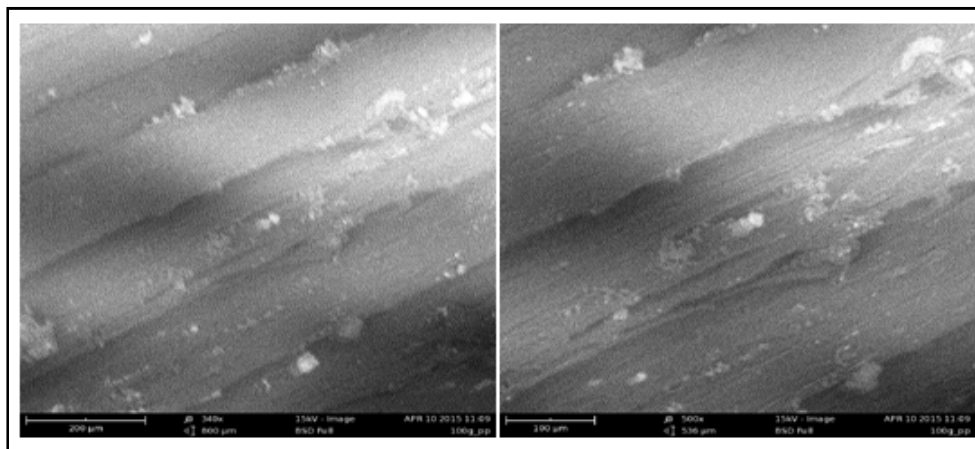*Figure2: SEM micrographs of (50gPP: 50 g CaCO₃ and 50g PP: 50g CNSP) polypropylene composite*

Figure 3: SEM micrographs of (100gPP) polypropylene

Morphological studies on the PP, PP: CaCO₃ and PP: CNSP Composites Figures 1 to 3 show the photomicrographs of the neat PP and the PP:CaCO₃ and PP:CNSP composites at the different filler's loading.

The Scanning Electron Microscopy micrographs polypropylene composites and the neat polypropylene matrix are shown in Figure 1, 2 and 3 respectively. The purpose of this analysis is the therefore to investigate the dispersion properties of Calcium Carbonate or Cashew Nutshell Powder in polypropylene, excellent dispersion of CNSP was found (see Figure1). Agglomerations in the polypropylene matrix were observed from the micrographs (see Figure1- 3) of infused polypropylene samples prepared through mechanical mixing and thermal pressing methods, respectively. These agglomerates area create stress concentration zones which might act as a hardness initiator. Strong attractive van der Waals forces cause Calcium Carbonate to agglomerate, which reduces the strength of the nanocomposite by stress concentration effect. Agglomerates of is called nanoropes, are difficult to separate and infiltrate with matrix. They entangle and form nest like structures due to their curvature and high filler ratios. Both disagglomeration and dispersion in resins depend on the relative van der Waals forces, curvature, and on the relative surface energy the two fillers (either CNSP or CaCO₃)versus that of the resin.

High magnification SEM micrograph in Figure 1 clearly exhibits that both fillers at these weight ratios are well uniformly embedded in the 60g polypropylene resin system. It can also be easily observed that the interfacial bonding between the CNSP or CaCO₃ and matrix was very compact which would allow filler to be anchored in the embedding matrix. In essence, these fillers are likely to interlock and entangle with the polymer chains in the matrix [Li et al., 2008].

The SEM micrographs clearly show the difference of the morphology of the polypropylene filled composites (50 gpp:50 gCaCO₃), (40gpp:60g CaCO₃), (50gpp:50gCNSP) and (40gpp:60gCNSP) composites are compatible there is high degree of miscibility. That is, the adhesion between the fillers and the polypropylene were clearly observed.

However, the compatibility decreased with filler loading (both CaCO₃ and CNSP) these owned to the less interaction between the pp and the both fillers of those compositions which may be as a result of the disorderliness of the structural molecular arrangement of the repeating units in the polypropylene chain that occur at higher filler dose.

3.2. Structural Characterization of the Polypropylene Composites Prepared
Figures 4-8 represent the XRD pattern from Bragg's angle of 2θ 5° − 55° showing intensity against 2θ angle.
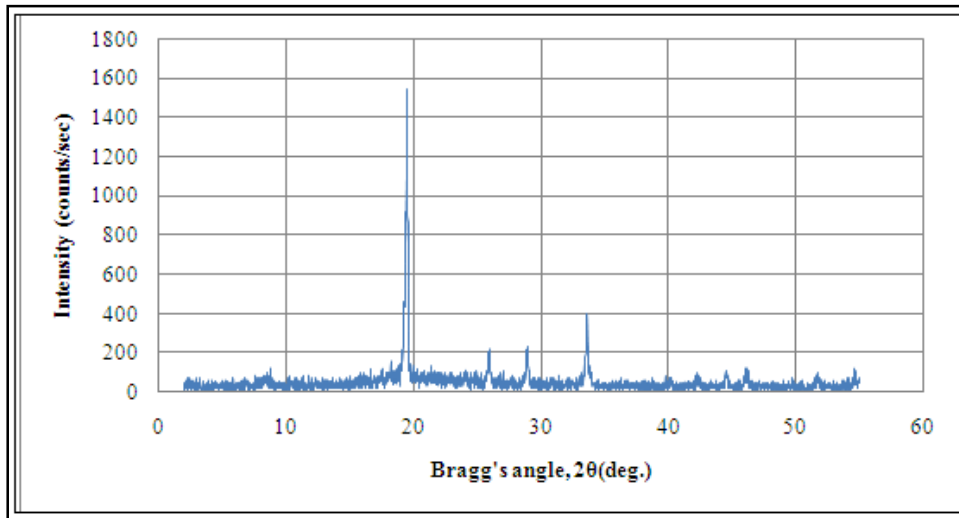
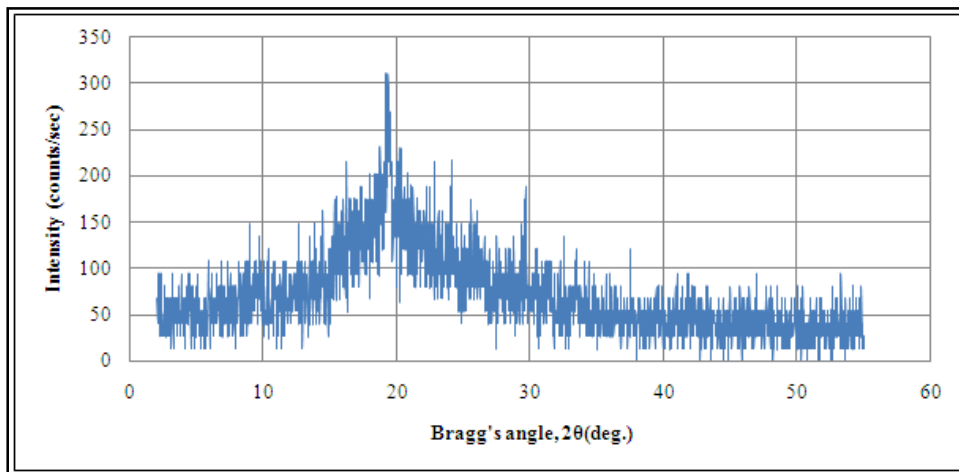*Figure 4: XRD pattern unfilled polypropylene*

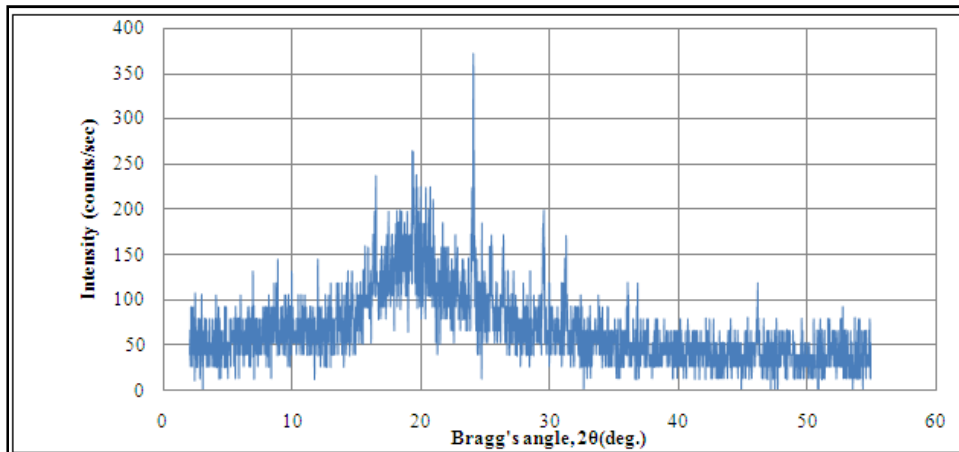*Figure 5: XRD pattern of 60gPP:40gCNSP*

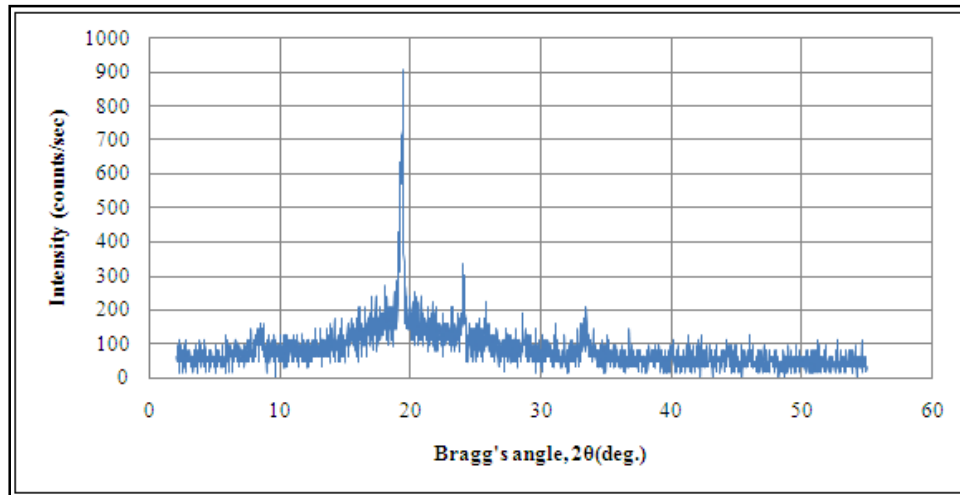*Figure 6: XRD pattern of50 g pp:50 g CNSP*
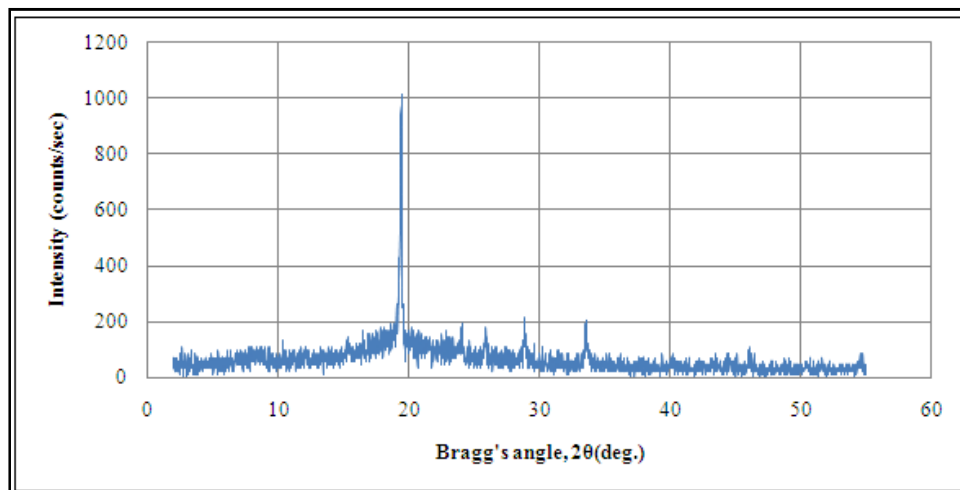
Figure 7: XRD pattern of 60gPP:40gCaCO₃

Figure 8: XRD pattern of 50gPP:50gCaCO₃

The X-ray diffractometer used for this research work was using Shimadzu 6000 X-ray diffractometer in the reflection mode which had a graphite monochromator and a Cu Ka radiation source (0.954Å) at a scan rate of 5.0000 (deg/min) and scan range 5.000 - 65.000^{o}. The X-ray analysis was performed at room temperature on the moulded specimens. Both for the neat Polypropylene, Polypropylene Calcium Carbonate and Polypropylene Cashew Nutshell Powder composites XRD was recorded using operation at 40Kv, 30mA and at wavelength, 1.5406m. The Bragg's spacing d and reflection of the samples was calculated from Bragg's equation by monitoring the diffraction angle 2θ from scan range 5.000 - 65.000^{o} at a scanning speed of 5.0000 (deg/min). The following changes in XRD patterns were observed (a) increase in d spacings of the Polypropylene composites of fillers content 40g and 50g (both Cashew Nutshell Powder and Calcium Carbonate) compared with the Polypropylene without filler, for instance the Polypropylene without filler has d-spacing value of 2.66410Å at 2θ=33.6130^{o} compared with 2.84384Å at 2θ=31.4316^{o} and 2.67443Å at 2θ = 33.4794^{o} for both 60g PP : 40g CaCO₃ and 60g PP : 40g CNSP respectively, (b) shift of peak positions to lower positions can be seen in the polypropylene composites dosed with fillers compared with the unfilled or the unmodified Polypropylene and (c) Physical changes can also be observed in the XRD parameters as the two fillers loading increase in the polypropylene composites. The crystallinity index was calculated and the highest value was obtained as (94.82%) for the Filled polypropylene (50g: 50g) Cashew Nutshell Powder compared to the remaining composites of the same filler's compositions. In the present research work, the crystallite size was calculated from the observed XRD pattern of different compositions of 60gPP:40gCaCO₃, 60gPP:40gCNSP and the pure Polypropylene respectively. XRD is a commonly used technique for the evaluation of crystal structure, because, it relies on coherent scattering from many unit cells in a spatially time averaged fashion. The crystallite size of the composites can be calculated from the full-width at half-maximum (FWHM) measurement for the prominent X-ray diffraction peaks using Scherrer formula Srivastava, 2011. The conditions for carrying out the analysis were: Radiation source: Cu K á; Voltage: 40Kv; Current:30mA; Scanning with step of 0.02°; Scanning, Time rate: 5°/min; Interval of scanning: 5 to 60° (2θ) consecutively. Start: 10.000 ° - End: 60°, Step: 0.02°, Step time: 0.3s, wavelength: 1.5406m and Temperature: 25°

The crystallite size was obtained from the measured width of the X-ray diffraction line.

The Scherrer formula for the calculation of crystallite size (grain diameter) D, of the sample is

$D = \frac{k\lambda}{\beta Cos\theta}$ …….…………………………………………... (1)

Where, D is the crystallite size, K is a constant varies with crystallite shape but usually nearly equal to 0.94, λ is the wavelength of source radiation and β is full-width at half maximum (FWHM) of the peak, in radians and θ is the Bragg's angle The crystallite size calculated using Scherrer formula for the prominent peaks in the diffraction pattern for both sample PP: $CaCO_3$ is same.

The percentage crystallinity $(X_C) = \frac{I_c}{I_c + I_a}$ x 100 ………………………… (2)

The crystanillity index $(I_x) = \frac{I_c - I_a}{I_c}$ x 100 ……………………………... (3)

Where I_c and I_a are the intensities of the crystalline and the amorphous region (prominent peaks) respectively.

From the observed results, the XRD patterns (prominent peak) of sample PP: $CaCO_3$ and PP: CNSP represented that the both composites material have more of amorphous region than crystalline region that is, the incorporation of the two fillers in to the neat Polypropylene decreased the crystallinity of the polypropylene and the crystallinity decreases with increasing fillers lording. In Figure 4-8, XRD patterns for unfilled PP, filled PP: $CaCO_3$ and PP: CNSP show strong diffraction peaks at 19.5208^o, 33.6130^o, 19.2451^o, 19.3648^o, 29.5839^o, 31.4316^o, 24.0683^o, 29.5125^o, 23.9400^o, 19.3631^o, 24.1144^o, 33.4794^o and 19.3889^o, 33.5275^o, 28.8550^o respectively. The patterns show sharp and well defined peaks, indicating the crystallinity of the composites produced (see figure 4-8). Intensity of diffraction peaks for the composites PP: CNSP is lower than both of the pure PP and PP: $CaCO_3$ of composites. This implies that the intensity depends on the composition of the composites.

4. Conclusion

The present study has generally also investigated the effect of the filler content in the polypropylene on the morphological properties of PP, PP: $CaCO_3$ and PP: CNSP and the results revealed that the crystallinity of the neat polypropylene deceased with increasing filler loads (both $CaCO_3$ and CNSP) and that both 60g PP: 40g $CaCO_3$, 60g PP: 40g CNSP and 50g PP: 50g$CaCO_3$, 50gPP: 50g CNSP are completely compatible at which there are no phases that are grossly separated.

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