Mechanical Properties and Morphological Characteristics of Polypropylene Ternary Nanocomposite (PP-LS-MWCNT) for Industrial Applications

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Abstract

Polymer nanocomposites are credited with better properties compared with the conventional composite made from microfillers and have found potential applications in civil constructions and fabrication of process vessels. Dispersion of multiple fillers in polymer matrix has become a subject of interest as it addresses most of the common shortcomings observed in the binary composite and enhances the development of composites with multifunctional properties. Polypropylene (PP) ternary nanocomposites of layered silicate (LS) and multiwall carbon nanotubes (MWCNT) have been prepared at a pre-determined percentage (3%) layered silicate while the MWCNT loadings were varied between 0.1 and 0.7%. The investigation focused on the effect of MWCNT loadings on the binary precursor (PP/LS) measured in terms of tensile strength and Young's modulus. The degree of enhancement was compared with the level of dispersion measured by wide angle X-ray diffraction (WXRD) and complemented with the morphological characterization using transmission and scanning electron microscope (TEM and SEM) respectively. The results show that the Sample 1 with 0.17% MWCNT displayed highest enhancement of 52.30MPa and 1759.32MPa for tensile strength and elastic modulus respectively compared with Sample 2 and 3 with higher MWCNT content that gave 48.19 and 1679.26MPa and 47.43 and 1726.14MPa for tensile strength and Young's modulus respectively. WXRD gave up to 28Å and 20.11Å in the clay layer distance within the composite and LS respectively, indicating intercalation in the composite system. TEM images show clearly well distributed fillers in Sample 1 with 0.17% MWCNT, partly distributed in Sample 2 with 0.45% and array of network of carbon nanotubes in Sample 3 with 0.16% MWCNT. These results were complemented with SEM images which show that the composites developed are combination of exfoliation, intercalation and some micromixing.

Key words: Polypropylene ternary Nanocomposites layered silicate (LS) multiwall carbon nanotubes (PP-LS-MWCNT), tensile properties, morphological characterization,

1. Introduction

Polypropylene-clay (PP/Clay) nanocomposites have been experimented and credited with better properties compared to conventional composites made from fillers at micro dimensions. These micro-fillers range from particulate types such as glass, talc, calcium carbonate, activated carbon to wide varieties of fibres of agricultural origin such as sisal, jute, and cotton due to their renewability and biodegradability [1]. Polymer nanocomposites are new class of materials which show improved properties at very low filler loadings compared to the conventional micro-composites [2]. The most abundant filler that are commonly in use is clay (layered silicate) due to its environmental friendliness as well as being less expensive. However despite the level of improvement achieved in

PP/Clay nanocomposites which include; mechanical, thermal stability and flame retardant enhancement, a lot of shortcomings have been reported. This is because practically all composites prepared from organophilic clay and a polypropylene homo- or copolymer, do not show improvements to an extent to satisfy the requirements of most applications in terms of mechanical properties because complete dispersion of the silicate is never achieved in the polypropylene matrix [3]. Other drawbacks associated with PP/Clay nanocomposite is property trade- off such that strength will be traded for elastic modulus or flame retardant property will be obtained at the cost of optical clarity. All these aforementioned shortcomings have called for series of research such that polymer composite of a very good mechanical properties could be produced.

However, with the introduction of polypropylene ternary nanocomposite using both the organo-modified nanoclay and carbon nanotube (CNT) with a view to reduce the quantity of layered silicate and complement it with CNT, most of the associated problems could be addressed [4]. As a result, the properties of the polymer composite can now be tailored towards a specific area of application at predetermined percentage filler loading of both the clay and CNT.

The degree of mixing (intercalation or exfoliation) is the major parameter used to describe the performance of polymer nanocomposite and this could be described in connection with the expected properties. The most common and reliable method of obtaining the structural information is through X-ray diffraction scattering and the most commonly used is wide angle (WAXRD) and the newer is small angle X-ray scattering machine (SAXRD). It is a common practice to use scattering angle $2\Theta = 2^o$ as a boundary between these two, but SAXRD usually provide reliable scattering profile down to $2\Theta = 1^o$ [5]. However, it is relatively difficult to describe nanocomposite structures with only one equipment because sometimes it could be misleading due to the complexity in the polymer/filler dispersion [6]. As a result transmission electron microscope is usually used to complement the results of XRD.

Therefore, in order to study the effect of double fillers (Clay and CNT) in polypropylene matrix, this paper investigated the correlation between the morphological properties by XRD and TEM with the mechanical properties specifically tensile strength and the Young's modulus of the ternary nanocomposites produced. The effect of CNT percentages on the binary precursor (polypropylene layered silicates) was understudied and the final product characterized. This study will serve as a basis for development of ternary nanocomposite using various matrices such as polyethylene, polycarbonate and rubber.

2. Materials and Methods

2.1 Materials

A commercial polypropylene homopolymer with an MFR > 3g/10min supplied was used. Maleic anhydride grafted polypropylene (MAgPP oligoma) (Polybond 3200) with 1.2 wt% MA was used as compatibilizer. Multiwall carbon nanotubes with outer diameter ranges between 10-20nm, length ~30µm and 95% purity was manufactured by Zyvex Instrument, Germany and supplied by Cahaya Bhd SDN, Malaysia. Bentonite clay manufactured by across organics was modified in our laboratory using octadecylamine salt.

2.2 Preparation of Ternary Nanocomposites

Ternary nanocomposite production was carried out using melt mixing method in a hakee mixer (Type Rheomix 600P) by employing two batches system. First batch involved the production of PP/Clay composite using 3% layered silicate in the presence of MAgPP (9%) [7] as compatibilizer in a twin screw extruder (Type 002-4818). The second batch system involved the introduction of multiwall carbon nanotubes in the predetermined quantity. The entire mixture was allowed to mix for a period of 12 minutes before homogeneity was attained. The MWCNTs percentage was varied between 0.1 to 0.7% of PP/Clay according to Salawudeen et al, 2011 [7]. The final nanocomposite was manually pelletized, hot pressed and molded into dumb bell shape according to ASTM D638 standard.

2.3 Characterization

Tensile properties (tensile strength and Young's modulus) were determined using universal tensile machine (LYLOYD Instruments, Type 1025) at room temperature following ASTM D638 standard procedure and each of the composite samples were morphologically characterized using wide angle XRD (Shimadzu X-ray diffractometer (LabXRD-6000) with Cu Kα radiation of wavelength = 1.541 Å at a step size of 0.0200 deg and a scan range of 2.00 to 10.00 deg.) and TEM (Type JEOL model JEM-2100).

3. Results and Discussions

3.1 Tensile properties ternary nanocomposites.

Tensile strength (T/S) and Elastic modulus (E/M) are among the most important properties used to determine the quality of polymers and their composites [8] and it has been used in this work for the same purpose. Table 1 show the T/S and E/M of the selected ternary nanocomposites prepared under different process conditions as determined by Salawudeen et al, [7]. The highest tensile properties were obtained in sample 1 when the filler (MWCNT) content was 0.17%, melting temperature of 165°C and mixing speed of 119 rpm. Comparing this result with samples 2 and 3 with 0.45 and 0.71% MWCNT loadings and very closed process conditions (151°C melting temperature and 121rpm mixing) and (153°C and 121rpm) for samples 2 and 3 respectively, it is observed that tensile properties enhancement favored sample 1 with low percentage MWCNT. However, comparing samples 2 and 3, though tensile strength is favored with lower MWCNT but sample 3 with higher MWCNT is favored in terms of Young's modulus.

Table 1 Tensile Properties of the Selected Ternary Nanocomposites

Sample No	Process Parameters			Experimental Results	
	CNT (%)	Temperature (°C)	Mixing Speed (rpm)	T/S (MPa)	E/M (MPa)
1	0.17	165	119	52.30	1759.32
2	0.45	151	121	48.19	1679.26
3	0.61	153	121	47.43	1 726.14

The highest properties enhancement observed in sample 1 with the least MWCNT may be as a result of uniform distribution of the filler and less agglomeration that facilitated good load distribution between the fillers and the matrix. However, slight reductions observed in samples 2 and 3 with 0.45 and 0.61wt% MWCNT respectively may be due to the interaction between the CNTs themselves which may have led to the formation of more and larger agglomerates which in turn act as stress concentrators and ultimate failure points of the final nanocomposites [9]. While increase in modulus enhancement observed in sample 3 compared to sample 2 could be as a result of higher viscosity due to higher MWCNT loading. This is in agreement with Einstein postulate which state that the effect of filler on modulus is proportional to that on viscosity and this is represented mathematically thus:

$$\eta = \eta_s \left(1 + 2.5V_r\right) \tag{1}$$

where η represents the viscosity of the composite, η_s represents the viscosity of the matrix and V_r the filler volume fraction. The viscosity terms in Equation 1 can be replaced by the modulus term E as shown in equation 2 following Einstein's theory:

$$E = E_s \left(1+2.5V_r\right) \tag{2}$$

E and E_s represent the modulus for composite and matrix respectively.

3.2 Morphological characterization of ternary nanocomposites

In order to justify the nature of the composite in terms of dispersion, the filler's distribution within the polymer matrix was studied by using wide angle X-ray diffraction (WAXD), Transmission electron microscope (TEM), and Scanning electron microscope (SEM). It was reported by Koo [6] that both XRD and TEM are very useful imaging techniques which allow the screening of formulations, distinguishing of compositions that exhibited either favorable or unfavorable filler dispersion in polymer/ filler blends and provide guidelines in the scale-up of favorable compositions.

3.3 X-ray Diffraction

Figure 1 displays the wide angle X-ray diffraction patterns for the three selected validated samples (Samples 1, 2 and 3), sample 4 (master batch or intermediate product) and sample 5 (pure and unblended polypropylene). The aim was to determine the degree of nanodispersion and at the same time to determine the effect of secondary filler (MWCNT) on the structure of the PP/Clay and to see if there is any interaction between the two nanofillers within the matrix. It can be observed from the diffraction patterns as shown in Figure 1 that pure polypropylene (sample 5) shows no diffraction peak most especially between 2 and 3 degrees where major peaks appeared for the nanocomposite samples. This signifies lack of inclusions or fillers in the polypropylene matrix. However, the minor peaks that appear in the higher degrees could be as a result of the compatibilizer (MAgPP) or other impurities from the process equipment. The presence of nanofillers is shown clearly by the XRD trace of the layered silicate polypropylene nanocomposite (PP/Clay) of 3% clay content and 9% MAgPP by diffraction peaks (Sample 4). The interpretation is that the nanocomposite of PP/Clay master batch is not fully exfoliated but rather intercalated or the combination of the two. Similar occurrences have been reported in literatures by many researchers when dealing with PP/Clay nanocomposite [10]. Similarly, samples 1, 2 and 3 that were prepared with 0.17, 0.45 and 0.61% MWCNT inclusions shows the major diffraction peaks within the lower angles. This suggests that the addition of MWCNT did not disrupt the existing structure of PP/Clay composites as expected but rather additional peaks were created in the higher degrees due to its addition. This could be as a result of impurities deposited in it from the metal catalyst or substrate during production [11].

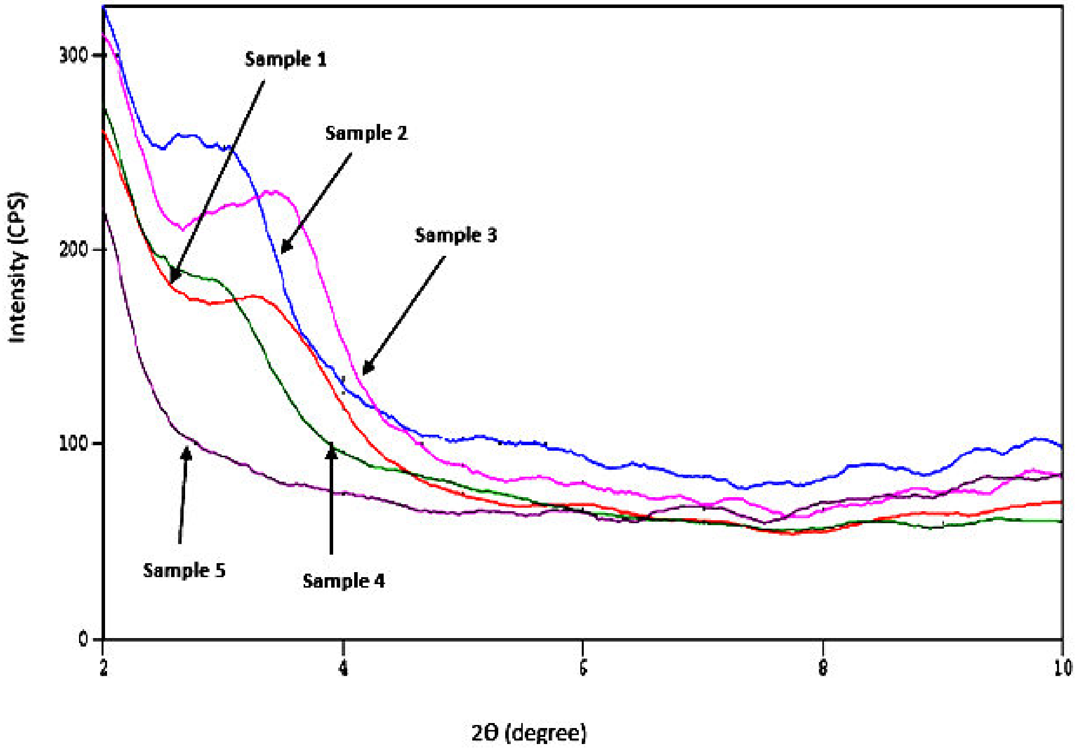

Figure 1 XRD Patterns of Sample 1 (0.7% MWCNT), Sample 2 (0.45% MWCNT) and Sample 3 (0.61MWCNT) Compared with Sample 4 (PP/Clay) and Sample 5 (Pure PP)

In order to compare the position of the selected peaks of the modified clay and the nanocomposites prepared, the location of the peaks in the X-ray patterns were analyzed. The diffraction peak of the modified clay is 2Θ = 4.6 degrees while those of the nanocomposites as shown in Figure 1 are located at 3.44, 3.08, 3.43 and 3 degrees for sample 1, 2, 3 and 4 respectively (Figure 1). Based on the analysis, it is obvious that all peaks of the nanocomposites appeared to have shifted to lower angle when compared to that of the modified clay. These show expansions in the d-spacing (interlayer distance between the clay galleries) due to intercalation of polymer between the galleries of the clay. Similar result was obtained by Garcia-Lopez et al, [2] who observed an expansion in the intergallery spacing as diffraction angle shifted to lower angle.

The summary of the resulting d-spacings and the diffraction angle of samples 1, 2, 3, 4 and the modified clay determined from XRD patterns using Bragg's law (Equation 3) are shown in Table 2.

$$n\lambda = 2d\sin\Theta \qquad (3)$$

where n, λ, d and Θ are integer, wave length, layer distance (d-spacing) and diffraction angle respectively.

The expansion in the d-spacing is obvious by comparing that of the modified clay with the final d-spacing after nanocomposite preparation. The analysis of the results show that while that of the modified clay is fixed at 20.11Å, the interlayer distance after nanocomposite preparation are; 25.63, 28.65, 25.70 and 28.88Å for sample 1 with

MWCNT content of 0.17wt%, sample 2 with MWCNT content of 0.45wt%, sample 3 of MWCNT content of 0.61wt% and the master batch with 0wt% MWCNT. This increase is as a result of the intercalation of PP and functionalized PP between clay platelets [12]. It was also observed from Table 2 that there were slight differences in the d-spacing in sample 1, 2 and 3 relative to sample 4 with no MWCNT due to the presence of the secondary fillers. The difference in the layer distance (d) between samples 1 to samples 3 shows that the more the percentage MWCNT the higher the layer distance. Hence, sample 3 with 0.61% MWCNT has higher layer distance than sample 2 with 0.45% and sample 1 has the least.

Table 2 Properties of the Selected Strongest Peaks

Nanocomposites	**MWCNT (%)**	**2ω (degree)**	**Layer distance (d) (Å)**
Sample 1	0.17	3.445	25.626
Sample 2	0.45	3.081	28.647
Sample 3	0.61	3.435	28.701
Sample 4	0	3.056	28.881
Modified Clay	0	4.4	20.111

3.4 Transmission electron microscopy analysis

Many researchers have pointed out that the use of X-ray diffraction patterns can sometimes be misleading most especially where a mixture of exfoliation and intercalation is present [13; 3]. As a result, to further investigate the degree of filler dispersion in the polypropylene matrix, transmission electron microscopy (TEM) analysis of the three selected samples prepared under different process parameters [melting temperature (^{o}C), MWCNT content (%) and mixing speed (rpm)] were conducted. The TEM images (50000X magnifications) are presented in Figure 2. It is evident from Figure 2 that the fillers are fairly well distributed in sample 1 and high concentration of MWCNT clustered the entire matrix in sample 3. Sample 2 did not show clearly the distribution of the fillers, however, some agglomerates are indicatives. Based on TEM and XRD analysis, it can be inferred that the ternary nanocomposites prepared is a combination of both intercalation and exfoliation with some micromixing since XRD showed a distinctive increase in d-spacings of the clay within the matrix and some agglomerations are still obvious in TEM images.

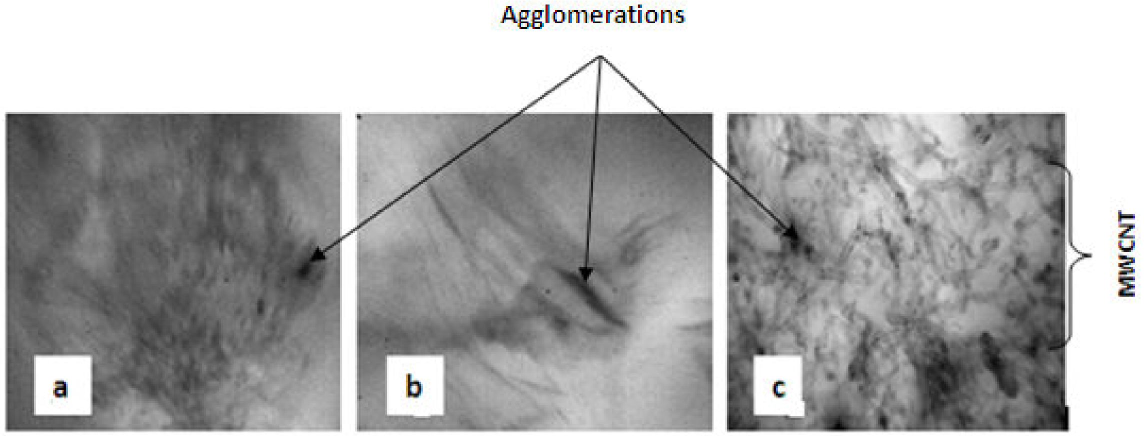

Figure 2 TEM Images of Samples 1 (a), 2 (b and 3 (c) as seen under TEM at 50000X maginification

3.4 Scanning Electron Microscopy

The morphology of the ternary nanocomposites was further investigated by using scanning electron microscopy (SEM) with a very low magnification (5000X). This was carried out to observe the wetting of the nanotubes by the polymer matrix especially in cases of applied coating phase [14] and at the same time to see the micro dispersion of the fillers. Such result will complement that of XRD and TEM discussed above. Figure 3 shows the SEM image of ternary nanocomposite sample 1, sample 2 and sample 3 prepared with 0.17, 0.45 and 0.61% MWCNT respectively. It is evident from sample 1 that the fillers are wetted by the polymer matrix and that only those that are dispersed at micro-scale or agglomerates are visible to the naked eyes. The distribution of the filler aggregates within the matrix are indicative due to low magnification of 5000 X used compared to TEM images observed at a very small area with a magnification of 50000X. The existence of good load transfer between the polymer matrix, nanoclay, and the MWCNT are evident from the image because the fillers are homogeneously distributed despite low percentage (0.17%).

Samples 2 and 3 however, have more MWCNT with highest percentage in 3. The clay agglomerates are very conspicuous and surrounded by MWCNT patches as shown in Figure 1 but are more obvious in Sample 3 due to a very high concentration of MWCNT used. Sample 3 has a slightly reduced tensile strength (47.43MPa) compared to sample 2 (48.19MPa) but enjoyed higher stiffness measured in terms of Young's modulus of 1726.14 MPa compared to sample 2 with lower MWCNT (Table 1). All these observations show that the composites are not fully exfoliated but rather a combination of exfoliation, intercalation and even micromixing.

When the mechanical properties of the sample that gave the best result (Sample 1), was compared with PP/Clay and virgin polypropylene used in this work, maximum of 26.20 and 42% enhancement in tensile strength and elastic modulus respectively was achieved when compared with PP/Clay and 57 and 63% respectively when compared with virgin PP. This is a significant achievement because the ternary nanocomposite developed will address most of the associated problems peculiar to both PP/Clay and PP/MWCNT if the fillers are applied at higher percentage. Such nanocomposites will find wider application

in various engineering fields such as in the fabrication of bioprocess equipment (bioreactor), bioenvironmental equipment (composite septic tank), electronic devices and even in biomedical materials like prosthesis for amputees.

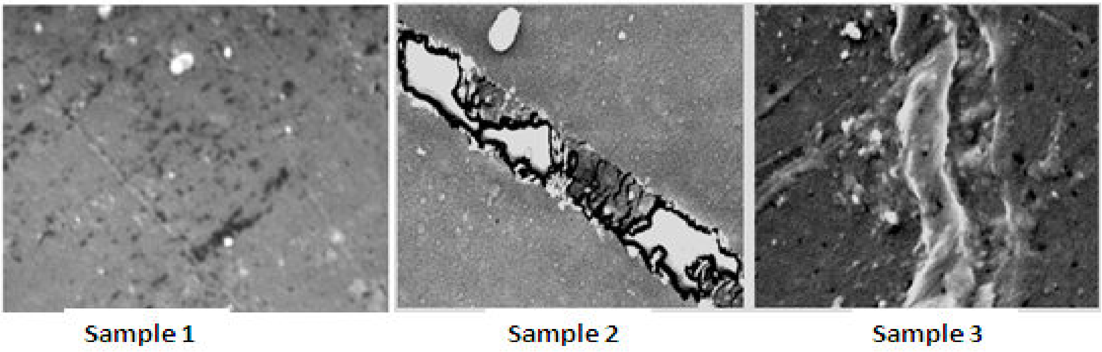

Figure 3 SEM Images of Sample 1, 2 and Sample 5 (Magnification 5000X)

4. *Conclusion*

Polypropylene ternary nanocomposite which comprises of polypropylene Homopolymer, organically modified clay and multiwall carbon nanotube have been prepared by melt mixing method using hakee mixer. Three selected samples prepared under different process conditions (Mixing speed, melting temperature and percentage carbon nanotubes) were analyzed for their tensile properties, specifically tensile strength and elastic modulus and then morphologically characterized using XRD, TEM and SEM. The results show that sample 1 with 0.17% MWCNT loading, prepared under 165°C melting temperature and 119 rpm mixing speed was better enhanced compared with samples 2 and 3 of which comprised 0.45 and 0.67% MWCNT respectively and prepared under melting temperatures of 151 and 153°C respectively at 121 rpm mixing speed. The characterization of the selected nanocomposites samples by using XRD, TEM and SEM showed that the nanocomposites structure are made up of both intercalation, exfoliation combined with micromixing. However, the distribution of the fillers favored the composite with lower MWCNT loading of 0.17wt% compared to those with 0.45 and 0.61wt% as seen under TEM and SEM. This justified the better enhancement in the optimized nanocomposite samples.

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