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Nanocomposites of Calcium Carbonate and Polyethylene: Preparation and Characterization

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Calcium carbonate (nano sized) was synthesized by In-situ deposition technique and its size (35 to 60 nm) was confirmed. Composites of the filler CaCO3 (conventional and nano) and the matrix polyethylene (LLDPE) were prepared with different filler loading (1-5 wt. %). The variation of torque was studied for these formulations using a Brabender torque rheometer. In addition, mechanical properties and crystallization behavior of the nano and conventional composites were also studied. A marginal effect of nano CaCO3 on the magnitudes of torque was observed; however, the tensile strength of LLDPE-nanocomposites filled with low contents (1 and 2 wt. %) of calcium carbonate was higher than that filled with corresponding conventional calcium carbonate-LLDPE composites. The crystallization peak temperature for these nanocomposites showed a significant increase. This change is accounted in terms of the uniform dispersion of nano calcium carbonate particles or more particles per unit wt. at lower wt. % as compared to the higher wt. % of nano calcium carbonate. WAXD showed flocculation of calcium carbonate nanoparticles on the surface of the LLDPE nanocomposites. Tensile fractured surfaces, studied using the scanning electron microscope (SEM), showed uniform dispersion of nanoparticles for 1 wt. than 3 & 5 wt. % filler loading.

Keywords: Nanoparticles, calcium carbonate, polyethylene, Brabender torque rheometer.

1. Introduction

Recently organic – inorganic nanocomposites have been in the spotlight as a promising class of materials because of their advantages and unique properties synergistically derived from the nano-scale structure. These nanocomposites exhibit improved mechanical properties, low thermal expansion coefficient, high barrier properties, flame retardancy, and solvent resistance. Further, these benefits can be achieved even at very low loading level in comparison to conventional polymer composites [1]. However, the type of the structures and properties of nanocomposites are not fully under control as has been discussed in a recent review [2]. This unpredictability about structure and properties seems to originate from the unusually large surface area of the nanoparticles. Thus, many studies on the preparation, structure and physical, mechanical and thermal properties of polymer layered silicate nanocomposites have been made.

It is known that the mechanical properties of composites are, in general, strongly related to the aspect ratio of the filler particles. Based on this reasoning, layered silicates, such as montmorillonite which has a fairly large aspect ratio, have been extensively studied in recent years. Nanocomposites prepared with montmorillonite show improved strength, modulus, heat distortion temperature and barrier properties. In spite of many attractive improvements in physical and mechanical properties of the polymer/ (intercalated or exfoliated) clay nanocomposites, a significant drawback – low fracture toughness – has greatly limited their engineering applications. We know of no convincing evidence in the open literature reporting enhanced fracture toughness for polymer/clay composites. In most cases, a dramatic decrease in toughness due to the addition of clay has been reported. This represents a major challenge to researchers in the field of polymer toughening [3].

Other nanoparticles, such as silica and calcium carbonate, have been used to prepare nanocomposites. Among them, calcium carbonate has been one of the most commonly used inorganic fillers for thermoplastics, such as poly (vinyl chloride) and polypropylene (PP). Historically it has been used to merely reduce the cost of resins. The particle size of most commercially available $CaCO_3$ varies from 1 to 50 µm. The results of numerous studies have indicated that the improvement in the mechanical properties of micron-sized- $CaCO_3$ – filled composites. The use of nano-$CaCO_3$ particles may bring new insights in the study of polymer filler interactions, because of the dramatic increases in the interfacial area between the filler and polymer. In addition, when surface smoothness and high gloss are required, micron size $CaCO_3$ can not be used. Nano-$CaCO_3$ particles can be good filler that can provide surface smoothness and high gloss. In addition, the mechanical properties of nano-$CaCO_3$ filled composites, which may be very different from those of the micron sized – $CaCO_3$ filled composites, have been rarely studied [4,5].

In the present study, linear low-density polyethylene (LLDPE) was selected as the matrix for making nanocomposites as it is the most widely used polyolefin polymer because of its low density, low cost, excellent processability and high chemical resistance. The nanoparticles of $CaCO_3$ were synthesized using In-situ deposition [6-8] technique and their particle size was confirmed. The melt mixing of LLDPE with nano and conventional $CaCO_3$ was carried out using Brabender Plastograph EC, which gave data on rheological behavior. The composites so formed were tested for physical, mechanical, thermal and structural properties [9-26].

2. Experimental Section:

2.1 Materials

Calcium chloride and potassium carbonate, of analytical grade and poly (ethylene glycol)

(PEG; MW 6000 g.) were procured from s. d's. Fine Chem., Ltd. Mumbai, India and used for the synthesis of nanoparticles of calcium carbonate. The linear low density polyethylene (LLDPE), of grade F 19010 having MFI 0.9 g/10, was obtained from Reliance Industries Ltd., Mumbai, India, as a matrix. Conventional $CaCO_3$ (3 μ) was used as a comparison filler without any treatment.

2.2 Preparation of nanoparticles:

The nanosized calcium carbonate filler particles were synthesized using in situ deposition technique by refereeing literature reported method [4-6]. The detail description of the preparation of nano calcium carbonate was reported in our previous article [27, 28].

2.3 Preparation of Composites:

The composites of LLDPE with nano and conventional calcium carbonate were prepared using a Brabender Plastograph EC equipped with an electrically heated mixing head (W 50 EHT mixer) having 55 cm^3 volume capacity and two non-interchangeable rotors. The processing temperature, rotor speed, and blending time were set at 180 ^{0}C, 40 rpm, and 10 min, respectively. The sample volume of each blending was kept at 90 % of the volume capacity of mixer to study the variation in torque of composites of nano and conventional fillers. The compounds of the composites were obtained in the form of lumps. These lumps were then crushed to get coarser particles (approx 3-4 mm size) of composites, suitable for injection moulding of tensile and impact specimens.

2.4 Characterization

The structure of the PE-$CaCO_3$ nanocomposites were characterized by WAXD and SEM. WAXD was performed on a X'pert–Pro PANAlytical (Philips) diffractometer using Cu Kα radiation at a generated voltage of 40 kV and current of 30 mA at 25 ^{O}C. The diffraction patterns was continuously scanned from $2\theta = 0^O$ to 40^O in 0.01^O steps.

To study the dispersion of filler and morphology of the composites, a tensile fractured surface was coated with platinum and observed in a JEOL 6360 scanning electron microscope (SEM) at an acceleration voltage of 10 kV with EDS at a room temperature.

A Shimadzu DSC-60 (Japan) was used for the calorimetric studies. The composites is prepared in the mixer were heated from room temperature to 250 ^{O}C at the rate of 5 ^{O}C/min. under nitrogen atmosphere. The melting temperature was taken as the temperature corresponding to the peak in heat flow during heating.

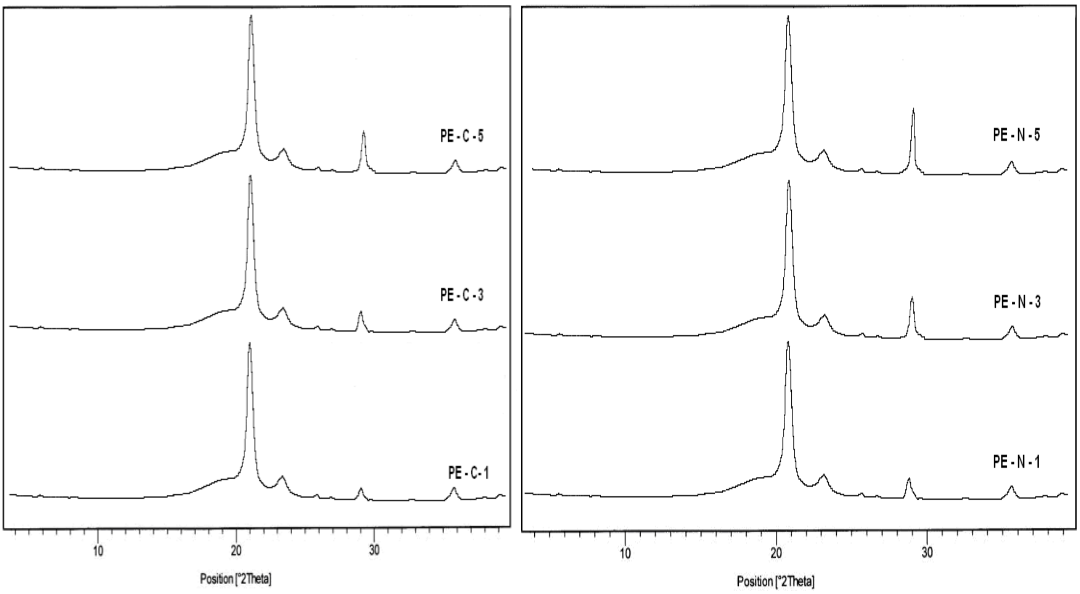
Tensile strength was determined by subjecting dumb-bell shaped specimens (in accordance with ASTM D – 638) to a Universal Testing Machine (UTM 2302, R & D Equipment, Mumbai, India). The specimens were conditioned at 25 ^{o}C for 24 hours prior to subjecting to the tensile testing. A load cell of 3000 kg and a crosshead speed of 50 mm/min. was employed.

3. Results and discussion

3.1 Particle Size

The average particle size of the nano calcium carbonate was in the range of 35 to 60 nm, as verified by the TEM micrograph of the $CaCO_3$ nanoparticles and was reported elsewhere by authors [27] the same nano particles were used for the preparation of nanocomposites.

3.2 Wide Angle X-ray Diffraction Studies (WAXD)



(a) (b)

Figure 1. WAXD of a) PE – conventional $CaCO_3$ b) PE - nano $CaCO_3$ composites at 1, 3 and 5 wt. % of filler

The WAXD analysis of LLDPE – $CaCO_3$ composites (Fig.1, a and b) showed no significant changes in the position of peaks. The main diffraction peaks evident in the LLDPE - $CaCO_3$ composites are at $2\ \theta_1 = 21.3^0$ and $2\ \theta_2 = 23.7^0$ corresponding to the 110 and 200 diffraction planes, characteristic peaks of those polyethylene with the $2\ \theta_1 = 21.3^0$ possessing higher intensity. However, at $2\ \theta_3 = 29.0^0$ and $2\ \theta_4 = 36.0^0$ are from the filler. It is evident that there is no indication for complete and uniform dispersion of the nano and conventional calcium carbonate. On the contrary, on varying the concentration of calcium carbonate from 1 to 5 % increases the intensity of the $CaCO_3$ peaks. However, the peaks corresponding to LLDPE appeared unaffected, which means that the presence of the inorganic material did not alter the crystalline structure of LLDPE. These results verify that the mixing of LLDPE with inorganic material lead to a phase separated system due to the non-polar character of LLDPE. It is clear from preparation of LLDPE – $CaCO_3$ composites that one has to modify the interactions between the polymer and the inorganic surfaces.

3.3 Scanning Electron Microscopy (SEM) Studies

To validate the WAXD results, the tensile fracture surface of samples were scanned by SEM. Fig. 2 shows the SEM micrographs of LLDPE – $CaCO_3$ conventional(a-c) and nanocomposites (d-f) with $CaCO_3$ content of 1, 3 and 5 wt. %. The study of SEM micrographs revealed that all the samples contain agglomerates, the size of which varied with the calcium carbonate content.

For the content of conventional calcium carbonate at 1 and 3 wt. % the composites of LLDPE exhibited a few agglomerates with particle size of less than 600 nm and a few large agglomerates of size 1-2 μm. The composite of 5 wt. % showed agglomerates of more than 5 μm size. Similar results were observed for nano calcium carbonate composites too. This result indicated that the shear force applied by Brabender mixer was not sufficient to break down all the $CaCO_3$ aggregates during melt mixing and the flocculation of nano-$CaCO_3$ was observed on the matrix.

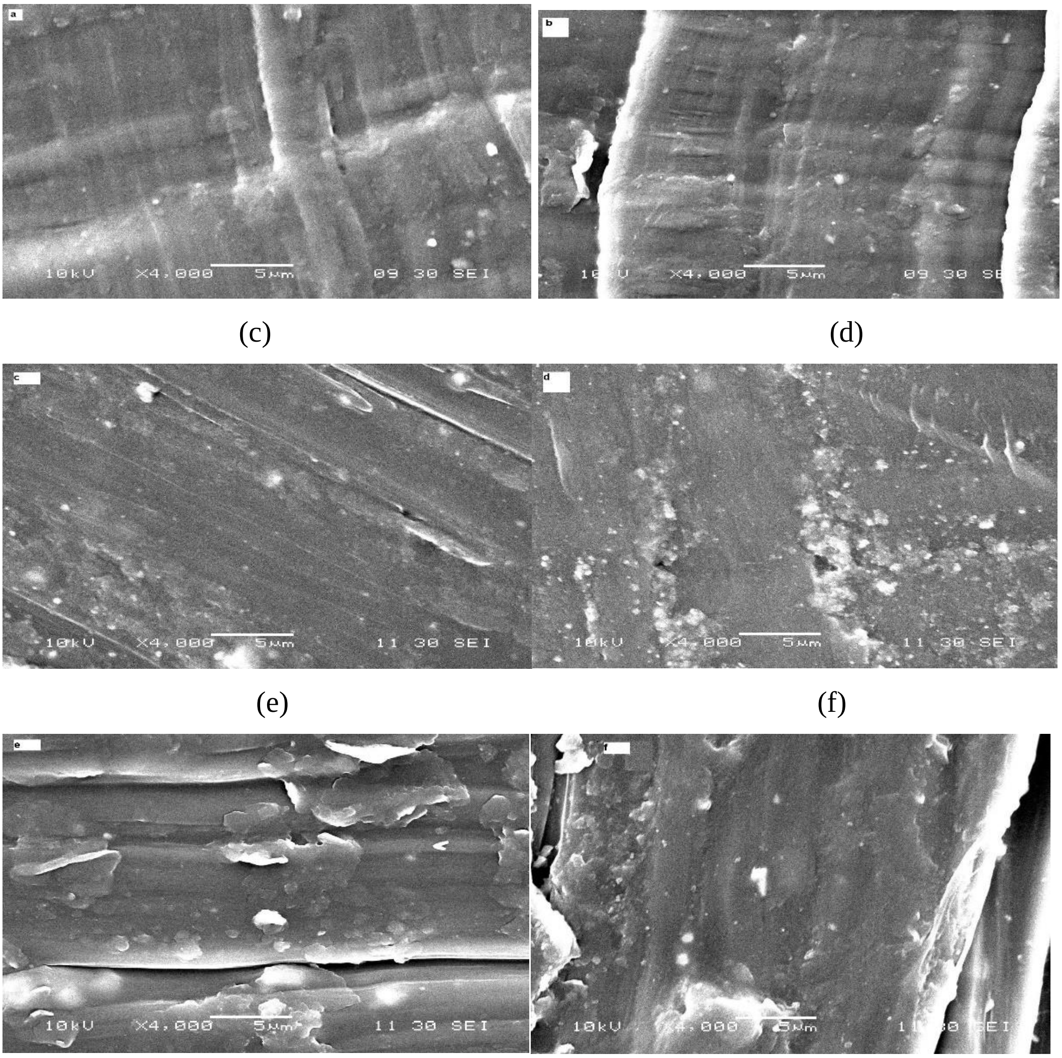

(a) (b) (c) (d) (e) (f)

Figure 2 SEM micrographs of fracture surfaces: a-c) LLDPE – conventional $CaCO_3$ composites and d-f) LLDPE –nano$CaCO_3$ composites at 1, 3, 5 wt. % of filler.

3.4 Tensile Strength

The tensile strength of the composites of conventional and nano calcium carbonate is shown in Fig. 3. The tensile strength of LLDPE-nanocomposites filled with low contents (1 and 2 wt. %) of nano calcium carbonate is higher than that of the corresponding conventional calcium carbonate-LLDPE composites. The tensile strength however decreased rapidly from 2 to 5 wt. % filler in the nanocomposites; the reason is that the dispersion of calcium carbonate is very difficult at high content as nanoparticles with high surface energy were prone to agglomerate. The agglomerated sites in the composites were easy to debond from the matrix, and debonded nanoparticles did not bear any fraction of external load so the tensile strength decreased, especially in the case of composites of 3 – 5 % filler loading. It appears that the chances of agglomeration becomes greater as the filler content (%) increases, under similar torque conditions.

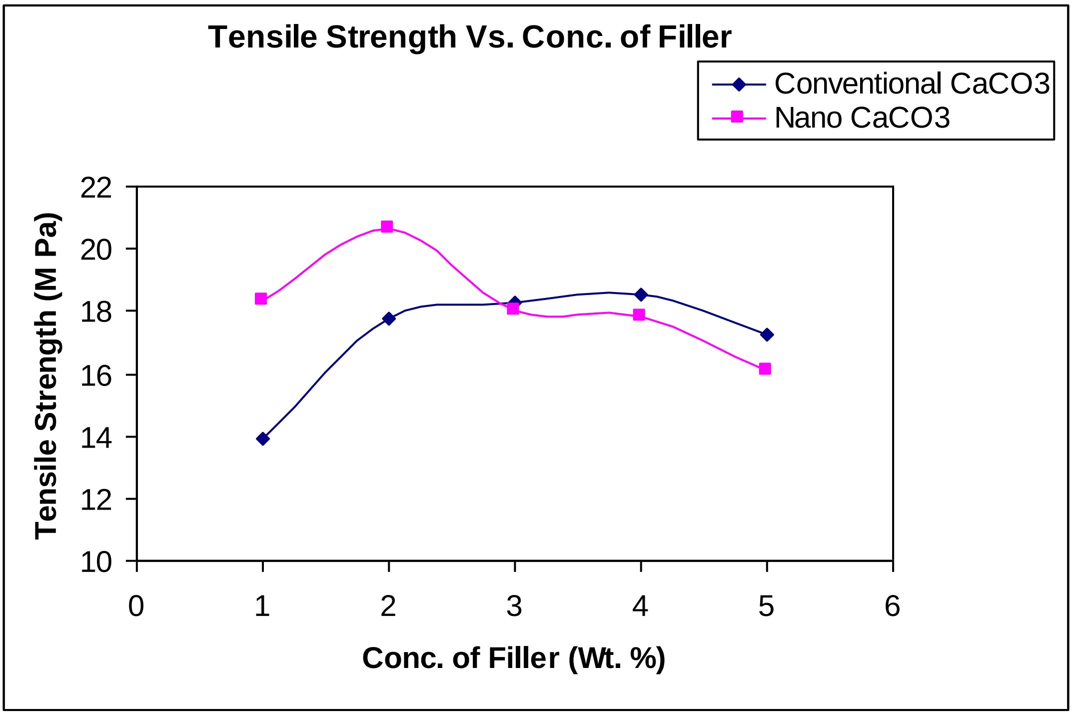


Figure 3 Tensile strength of composites (both nano and conventional) with the variation of filler content (1 to 5 %)

3.5 Torque measurement

The maximum torque (Nm) recorded during the melt mixing of the LLDPE-conventional calcium carbonate compounds was found to be greater than that of nano compound. (Fig.4). It was observed that the torque of all compounds decreased marginally with increasing concentrations. Although the applied shear force was same in both the cases, comparatively lower increments of magnitudes of torque values were observed in nanocomposites; this indicated that nanoparticles having stronger tendency to agglomerate due to the relatively higher surfaces energies associated with nanoparticles.

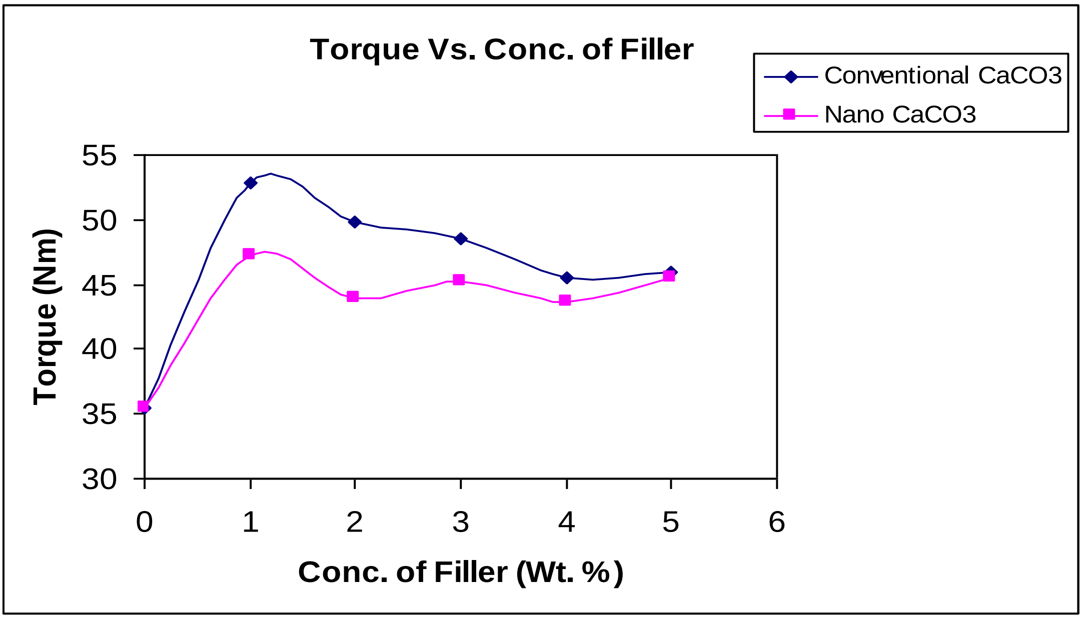


Figure 4 Torque (Nm) analysis of composites

3.6 DSC Thermograms of composites

The DSC heating thermograms of the composites in heating mode are presented in Fig. 5 for odd % of filler content (conventional as well as nano). The DSC results in terms of melting temperature (T_m), heat of fusion (ΔH) and temperature at DSC peak for conventional and nanocomposites of $CaCO_3$ are summarized in Tables 1 and 2, respectively.

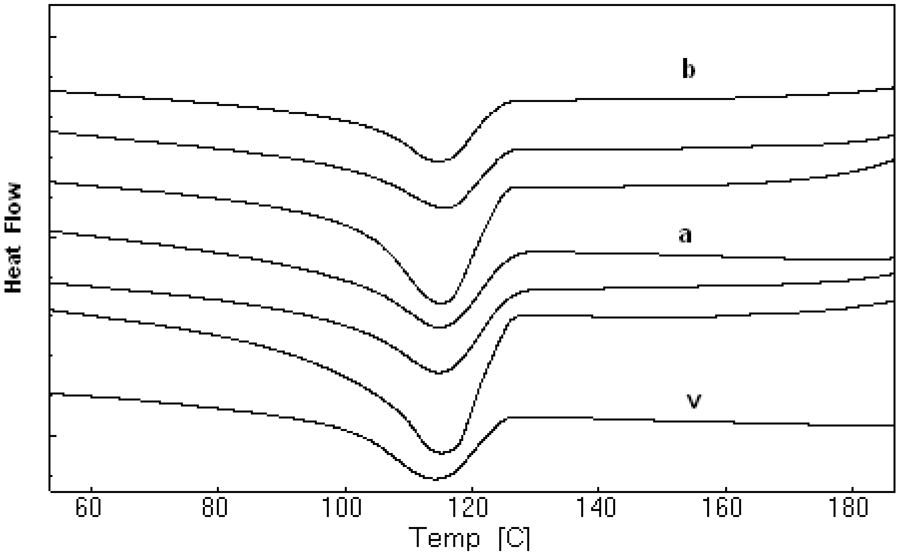


Figure 5 DSC thermograms of a) LLDPE conventional $CaCO_3$, b) LLDPE – nano $CaCO_3$

composites at 1, 3, 5 wt. % and v) virgin polyethylene

Table 1: DSC results of LLDPE – conventional$CaCO_3$ composites.

Sample Type commercial-$CaCO_3$ (wt %)	Melting Temperature T_m (^{0}C)	Heat of Fusion (ΔH) (J/g)	Temperature at DSC Peak (^{0}C)
0	110.2	100. 2	115.6
1	104.0	31.5	113.7
3	105.7	33.9	115.7
5	109.0	48.7	115.3

Table 2: DSC results of LLDPE – nano $CaCO_3$ composites.

Sample Type nano-$CaCO_3$ (wt %)	Melting Temperature T_m (^{0}C)	Heat of Fusion (ΔH) (J/g)	Temperature at DSC Peak (^{0}C)
0	110.2	100. 2	115.6
1	107.3	71.9	114.3
3	108.5	59.7	115.7
5	109.6	35.7	115.1

The DSC data shows that there is hardly any effect of filler on melting temperature of the composites. The nanocomposites containing 1 % $CaCO_3$ showed the lowest value (104^{0}C) while the heat of fusion of all the composites (nano and commercial) have shown lower than neat LLDPE.The heat of fusion of microcomposites increased with the increases in filler content, however, reversed trend was observed in case of nano composites. The heat of fusion is a measure of crystallinity and it is evident from the data that the composites containing 1 % nanofiller showed highest heat of fusion compared to the other, showing highest crystallinity among all other composites. This crystalline behavior was also reflected in higher values of tensile strength compared to the other composites.

4. Conclusions

The achievement of high degree of exfoliation of inorganic nanoparticles in non-polar polymer matrix, such as polyethylene (PE) and polypropylene (PP) is difficult. The chemical incompatibility between these two components hinders the uniform dispersion of the individual nanoparticles. Occurrence of particulate agglomerates and aggregates which are unable to break by applied shear forces resulted in flocculation of calcium carbonate nanoparticles on the surface of matrix. Highly agglomerated particles are seen on the surface regions as evident from the SEM and WAXD analysis of composites, showing their inability for uniform mixing in a non polar matrix. There was no significant increment in the magnitude of torque exerted by nanocomposites while compounding on Plastograph EC (Brabender). The addition of nano calcium carbonate has shown very marginal increase in melt temperature with increasing filler loading compared to microcomposites, however, an opposite trend is observed in the result of heat of fusion i.e. it decreases with increasing filler content.

It could be concluded that the uniform dispersion of fillers is an important aspect of nanocomposite research. Further, it may be concluded that the modification in the surface of nanoparticles or increase in shear forces may highly influence the properties of nanocomposites.

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