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The Morphological and Rheological Behavior of Calcium Carbonate Nanoparticles Filled Virgin and Waste Polypropylene

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Abstract: This study investigated the morphological and rheological properties of Calcium Carbonate ($CaCO_3$) nanoparticles reinforce virgin Polypropylene (PP) and its waste. PP and $CaCO_3$ nanoparticles in the content of (3, 5, 7 and 10 wt.%) were mixed by melt extrusion in a twin screw extruder at different screw speeds 25 and 50 rpm at 190°C. Different microstructure and morphological techniques (X-ray diffraction and field emission scanning electron microscopy) were used to evaluate the effect of the additive percentage ($CaCO_3$) and the processing condition (screw speed) on the microstructure of the nanocomposite. The rheological behavior (Melt Flow Rate (MFR) and Melt Volume Rate (MVR)) is tested using Melt Flow Index (MFI) device. MFR of the new modified composite are tested due to the nanoparticles concentration, loads, temperatures and rotating speed while MVR was tested at different $CaCO_3$ nanoparticles percentage at 2.16 kg. Shear rate and viscosity are predicted according to the MFR values. The results shows that the crystallinity was increasing with the $CaCO_3$ nanoparticles percentage increasing while the results of FESEM show that $CaCO_3$ nanoparticles distribution in PP matrix at 25 rpm is more homogenous and less agglomeration than at 50 rpm. The value of MFR and MVR were increasing for virgin PP while decreasing for waste PP at 25 and 50 rpm.

Key words: Virgin and waste PP, $CaCO_3$ nanoparticles, twin screw extruder, morphology, rheological properties, flow behavior

INTRODUCTION

Polypropylene (PP) is a polymer widely used for medical, constructions, automotive components, electronic applications due to its good performance, high strength to weight ratio and excellent processing properties as well as low cost. After each melting process the properties of PP drop to a certain limit. Nanoparticles $CaCO_3$ are mixed with PP to improve mechanical and electrical properties, heat resistance, radiation resistance, rheological and physical properties as a result of the nanometric scale dispersion of the filler in the matrix. The nanocomposite produced can be used in specific field due to change in internal structure between chains and nanoparticles. Plastics are considered extremely effective materials to recycle for two primary reasons. Firstly, there is a demand to use more and more plastics in our everyday life. Therefore, the demand for raw materials will increase and recycled plastics will serve as a necessary source. Secondly, the recovery processes comply with the environment guidelines that promote the reduction of waste arising at the source and the recycling of materials. The possibility of using recycled materials to manufacture relatively good article depends on the rheological and mechanical behavior of the recycled polymers. Therefore, it is essential to understand these fundamental concepts in order to make the acceptable product according to Hani *et al.*

Many nanometer sized fillers have been commercially produced and they represent a new class of alternative fillers for polymers. Several researchers attempted to modify polymeric materials by filling with nanometer inorganic rigid particles and discussed the dispersion property as well as its mechanisms such as mica, talcum powder, organ clay, carbon nanotube and so on according to Liang (2007), Shentu *et al.* (2006) and Hanim *et al.* (2008). Among these fillers, Calcium Carbonate ($CaCO_3$) is one of the most commonly used inorganic fillers in polymer. It based fillers have extensively been used because of their low-cost and availability. These fillers are generally much less expensive than polypropylene resin itself and these fillers reduce the costs of the compound formed with polypropylene and also increase the stiffness according to Zhang *et al.* (2012, 2004).

The incorporation of nanoparticles have been attracted much interesting in scientific field because of the possibility of use low contents of fillers with great

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increases in both impact and tensile properties according to Xie *et al*. (2004), Chan *et al*. (2002) and Zuiderduim *et al*. (2003). Studies have shown that the large surface area possess by these nanofillers promotes better interfacial interactions with the polymer matrix compared to conventional micrometer size particles, leading to better property enhancement according to Gao (2004).

Through further investigations, however, the usage of $CaCO_3$ as a toughening agent is a new concept which is relatively well known to impart high impact properties and deformability, though at the cost of the strength of PP. There are a few works that have reported regarding the ability of $CaCO_3$ to act as toughening agent, the most recent one being Zuiderduin *et al*. (2003) which confirmed that $CaCO_3$ has indeed the ability to not only increase the stiffness but also the toughness of PP according to Samsudin (2008).

Molten polymers have very high viscosity values and present shear thinning behavior as the rate of shearing increases, the viscosity decreases, due to alignments and disentanglements of the long molecular chains. In addition to the viscous behavior, molten polymers exhibit elasticity. These include stress relaxation, normal stress differences and swelling according to Gao (2004). The ease of melt flow depends upon the mobility of PP molecular chains and forces holding the molecules together. As the free volume increases with temperature, PP molecules occupy more space due to an increase in the distance between them making it easier to slide among each other with the introduction of high shear rate will eventually reduce the PP matrix viscosity significantly according to Ariff *et al*. (2012).

The $CaCO_3$ act as lubricant factor inside the structure of PP and the spherical nanoparticles behave as ball bearings, reducing the interlayer interaction of melts. The increasing in MFR rate can facilitate the injection and extrusion process parts and can lead to the reduction of energy consumption of molding process according to Ariffin *et al*. (2009). The ratio between MFR at higher load and MFR at lower load called broadness molecular weight distribution. The higher value of this called Broadness Molecular Weight Distribution (BMWD) which represents polymers with varying length the lower value called Narrow Molecular Weight Distribution (NMWD) according to Shenoy and Saini (1996). The polymer with NMWD may be assumed to have a similar degree of entanglement while BMWD the longer chain molecules appear to form protective network around their shorter parts according to George Godwin Ltd. (2003).

The aim of this research is to mix virgin PP and its waste with $CaCO_3$ nanoparticles in the content of (3, 5, 7 and 10 wt.%) by using twin screw extruder at different screw speed 25 and 50 rpm at 190°C, the effect of these nanoparticles content, loads, temperature and rotating speed on the rheological behavior of the producing nanocomposite was investigated. The relationship between structure of nanocomposite with the rheological and physical properties are studying. MFR and MVR behaviors of VPN and WPN are tested also the viscosity and shear rate of nanocomposite are predicated.

MATERIALS AND METHODS

The materials used were polypropylene homo-polymer, 575-S (MFR = 8.3 g/10 min) was supplied by Subic company and calcium carbonate nanoparticles were supplied by (Shijiazhuang Sun power Technology Co., Ltd., Chain) with particle size about (15.88 nm) and density 2.71 g/cm^3.

Preparation of the nanocomposite: PP pellets and $CaCO_3$ immersed in alcohol solution and mechanically mixed. The mixing process is performed using twin screw extruder (SLJ) and design with the screw speed rang 0-320 rpm and screw diameter is 30 mm, the power of main motor and heating 4 and 3 kW, respectively. The extruder dimensions (1.8*0.6*1.5 m), weight 450 kg and output (20 kg/h. The virgin PP/$CaCO_3$ nanoparticles, waste PP/$CaCO_3$ nanoparticles mixing in the twin screw extruder at 25 and 50 rpm and 190°C.

Characterization of $CaCo_3$ nanoparticles and nanocomposite

$CaCO_3$ nanoparticles

AFM: AFM conducted by tapping mode (AA3000) is used to measure the particle size and the morphology of

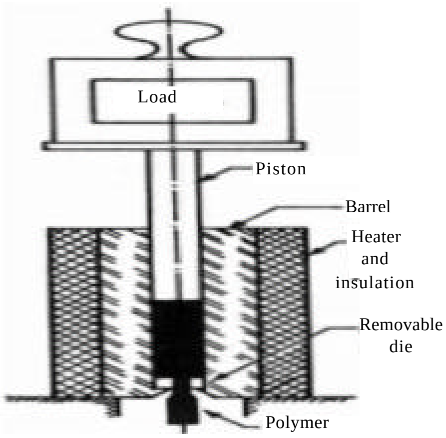

Fig.1: Schematic diagram a constant plunger of melt flow index

$CaCO_3$ nanoparticles in two and three dimensions. The $CaCO_3$ nanoparticles were dispersed in alcohol by using ultrasonification at 40°C for 30 min and the applied energy is 30% of the total energy 1200 W then using the standard method for testing thin film.

XRD: The XRD (Rigaku Diffract meter) with Cu Kα radiation at 30 mA and 40 kV from 10-40θ at scanning speed of 2°/min was used to show the effect of nanoparticles percentage and processing condition on crystallinity level of nanocomposite also to check the composition, crystalline size of $CaCO_3$ nanoparticles based on Scherer equation 1 as shown:

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

Where:

D = The crystallite size
λ = Diffraction wavelength equal (0.1541 nm)
β = The corrected FWHM

Nanocomposite

FESEM: The surface morphology and distribution of nanoparticles through virgin and waste PP were performed on small pieces taken from the impact samples using a low voltage FESEM (Model MIRA 3 XM4, USA). The fracture surfaces of impact samples were coated with a thin layer of gold before test. The photographs were taken at 5.00 x magnifications.

Rheological properties (MFR and MVR): Melt indexer type (Shi Jia Zhuang Zhong Shi Testing Machine Co., Ltd.,) according to the standard of (ISO1133:2005) was used to measure the (MFR and MVR) of nanocomposite through capillary die with Diameter (Dc is 2.095 mm) and the ratio of the die Length (L) to capillary die is (8/2.095) (Fig. 1).

RESULTS AND DISCUSSION

$CaCO_3$ nanoparticles

AFM: The principle of AFM is based on mechanical contact between the sample and tip, therefore, the measurement of particles in nanometer scale is strongly affected by sample-tip interaction. Figure 2a shows the topography of the surface of the thin film prepared of $CaCO_3$ nanoparticles dispersion in the alcohol solvent by using ultrasonic device. The particle size is bigger than that in origin specification sheet due to agglomeration of nanoparticles, however, the range of particle size in nanometer scales in one dimension and >0.1-0.3 μm in the other dimension.

Figure 2b indicates the surface topography in bulk solution (3-D), its approximately not the best way to assess nanoparticles size but particles size distribution extracted from the images can produce accurate information as show in Fig. 2c.

With increasing Nanoparticles (NP) depositions an overall increase in particle size is observed. This suggests that the NP is transitioning from individual entities on the surface into larger aggregate structures with additional NP.

XRD: Figure 3a show the standard XRD of $CaCO_3$ nanoparticles which used to compare with the using $CaCO_3$ nanoparticles. The XRD pattern at Fig. 3b illustrates that the used nanoparticles from (Shijiazhuang Sun power Technology Co. Ltd., Chain) are calcium carbonate by analyzing it and comparing with the standard $CaCO_3$. The diffraction patterns consist of the main diffraction peaks at around 2θ (24.5, 29.5, 37, 39.5, 43, 48, 49.5 and 57°). The three main diffraction peaks 104 reflection of calcite and the 110 reflection of vaterite, this results have good agreement with the results of Abdullahi Shafiu, the average size of $CaCO_3$ based on Eq. 1 at the main beaks 29.4 is approximately 44 nm.

Crystallinity of nanocomposite: Figure 4 shows the crystallinity level of neat PP and the nanocomposite with (5 and 10 wt.% $CaCO_3$) at 25 and 50 rpm. The neat PP presents peaks characteristics of α phase in 2θ values of 13.1, 16.4 and 18.2° representing the crystallographic planes 110, 040 and 130, respectively which confirm with the results of Motsoeneg (2012). For the nanocomposite the same planes appeared in 2θ values 14.2, 16.9 and 18.7°. The nanocomposite shows sharp and highly intense peaks while neat PP shows less intense peaks, this may due to the development of crystallinity in the polymer. The crystallinity increase with $CaCO_3$ content increasing, this is due to $CaCO_3$ nanoparticals filled the hole and oriented the chain, so, the crystallinity increasing. At 25 rpm the crystallinity level is higher than that at 50 rpm due to the high uniformity distribution and less agglomeration of $CaCO_3$ nanoparticles at low speed as shown in Fig 5-7.

Figure 5 indicates the crystallinity levels of neat waste PP and its nanocomposite of (3 and 10 wt.% of $CaCO_3$ at 25 and 50 rpm. The crystallinity level for virgin PP nanocomposite is higher than for waste PP nanocomposite at 25 and 50 rpm because nanoparticles may be not filling the hole completely in addition to contamination effect.

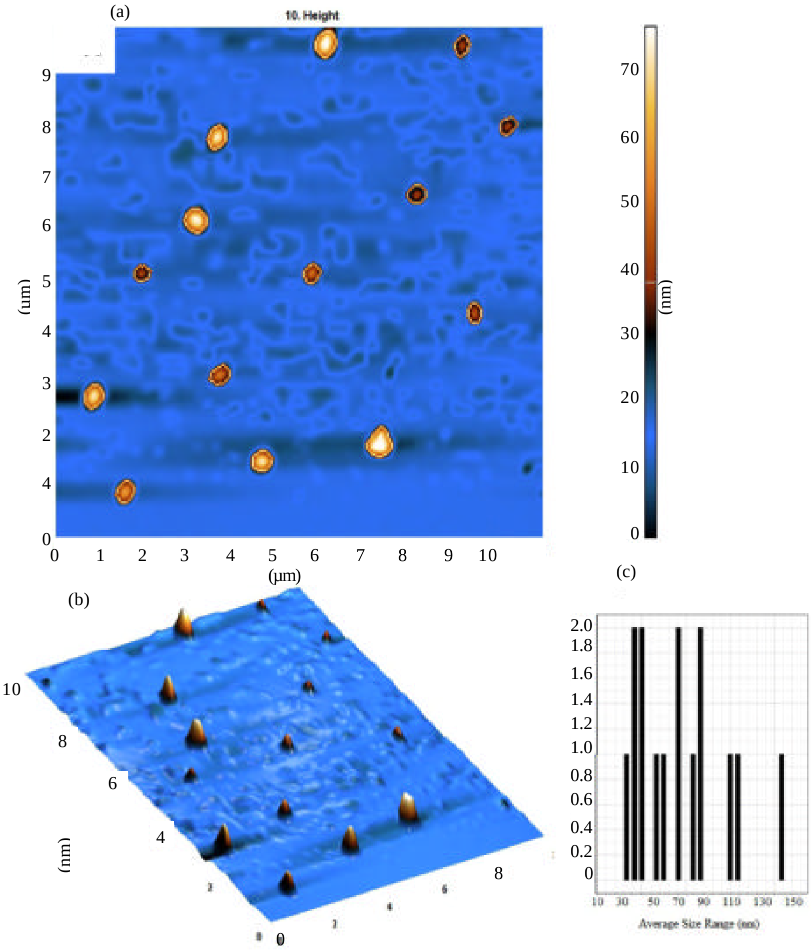

Fig. 2: The topography of the evaporated $CaCO_3$ nanoparticles solution: a) 2-D particles size; b) 3-D and c) Particle size distribution

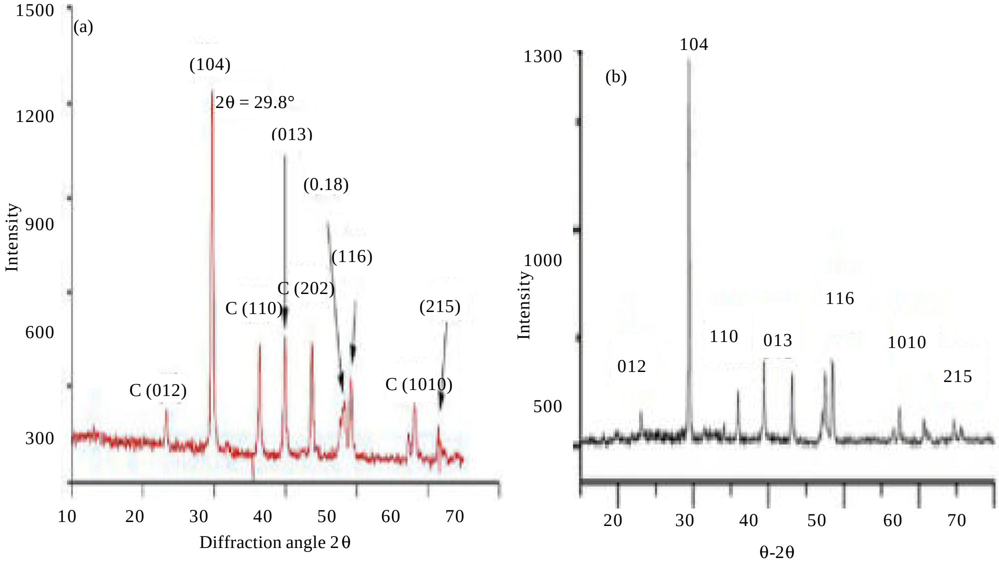

Fig. 3: a) Standard X-ray Diffraction of $CaCO_3$ nanoparticles (Kamba *et al*., 2013) and b) X-ray diffraction of the used $CaCO_3$ nanoparticles

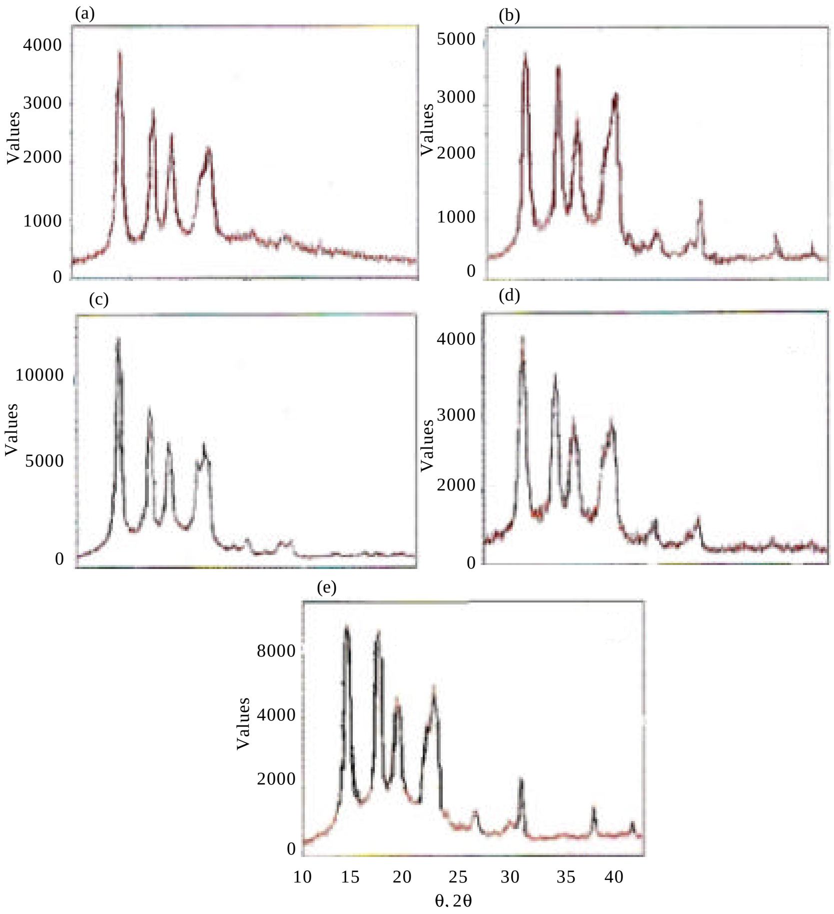

Fig. 4: XRD: a) pure virgin PP; b) 5% $CaCO_3$; c) 10% $CaCO_3$ at 25 rpm; d) 5% $CaCO_3$, and e) 10% $CaCO_3$ at 50 rpm for virgin PP nanocomposite

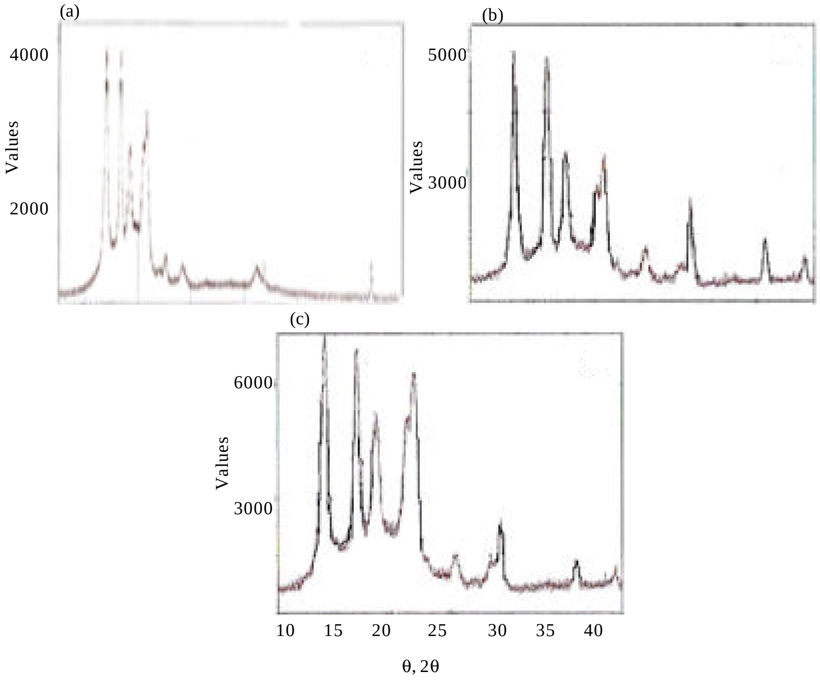

Fig. 5: Continue

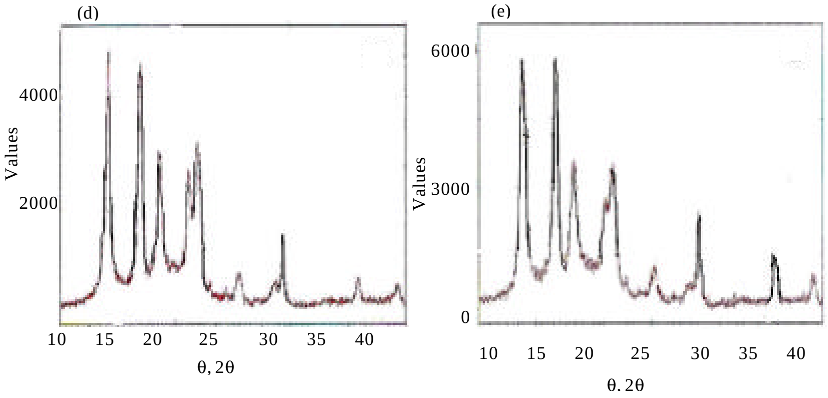

Fig. 5: XRD: a) pure waste PP; b) 5% $CaCO_3$; c) 10% $CaCO_3$ at 25 rpm; d) 5% $CaCO_3$, and e) 10 % $CaCO_3$ at 50 rpm for waste PP nanocomposite

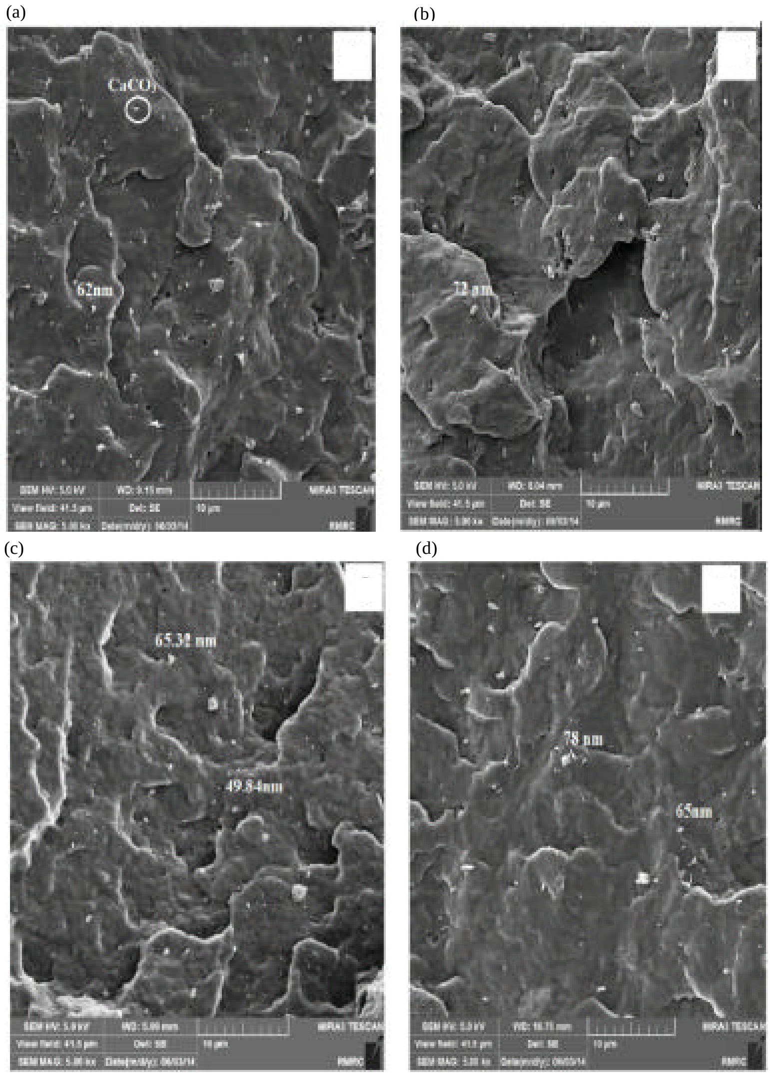

Fig. 6: The micrographs of the nanocomposite: a, b) (3 and 10 wt.%) nano $CaCO_3$ filled virgin PP; c, d) (3 and 10 wt.%) of $CaCO_3$ nanoparticles filled waste PP at 25 rpm

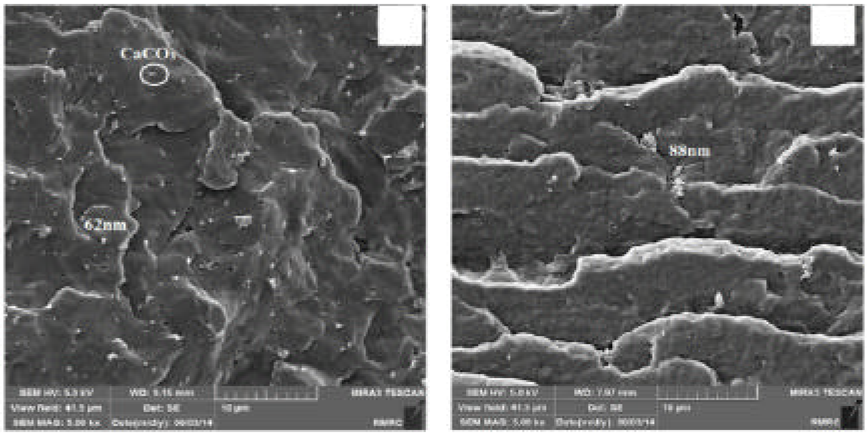

Fig. 7: The micrographs of the nanocomposite of 3% $CaCO_3$ nanoparticles filled virgin PP; a) At 25 rpm and b) At 50 rpm

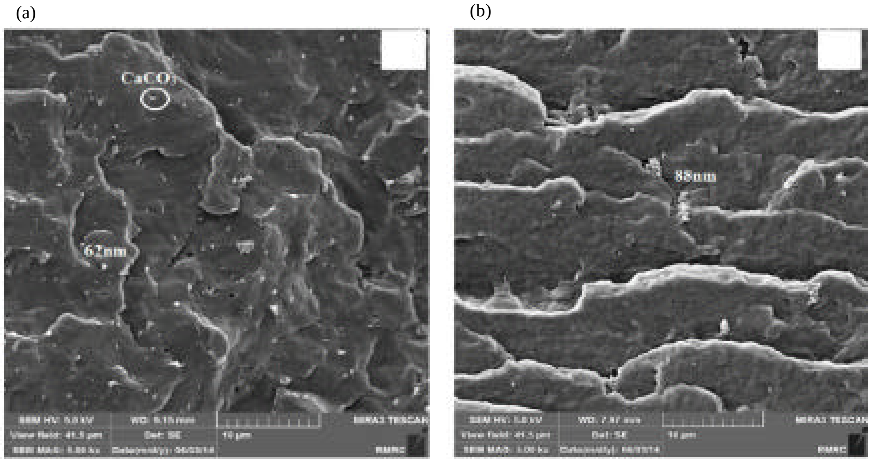

Fig. 8: The micrographs of the nanocomposite of 10% $CaCO_3$ nanoparticles filled virgin PP; a) At 25 rpm and b) At 50 rpm

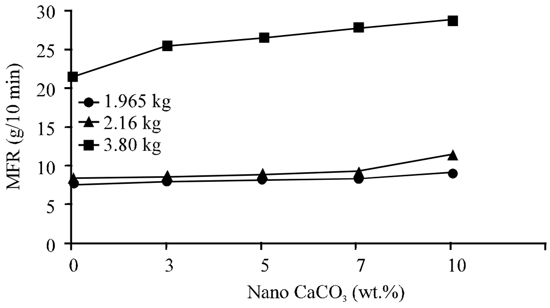

Fig. 9: The MFR behavior of virgin PP nanocomposite with different loads at 25 rpm and190°C

FESEM: The evaluation of filler dispersion is important because only well dispersed nanoparticles can lead to the expected improvement in mechanical properties. For the nanocomposite to have good impact toughness, the filler dispersion in the polymer matrix must be very uniform to avoid creation of crack-initiating at large agglomerates. Figure 6 shows the fracture surfaces of samples containing 3 and 10 wt.% of nanoparticles $CaCO_3$ filled virgin and waste PP at the speed of 25 rpm. In these photos, the main difference is the dispersion of the nanoparticles. At low filler content good dispersion observed therefore will generate desired stress distribution from the matrix to the filler throughout the tensile loading but at high loading weight, sample exhibits a structure having large aggregates which act as stress concentrators.

Figure 7 and 8 show the samples containing 3 and 10 wt.% of $CaCO_3$ nanoparticles type filled virgin PP processed at different screw speeds, 25 and 50 rpm, respectively. Better nanoparticles dispersion is achieved at the speed of 25 rpm while at 50 rpm nanoparticles not dispersed well and large aggregates are observed therefore, all properties of nanocomposite of 25 rpm is higher than at 50 rpm.

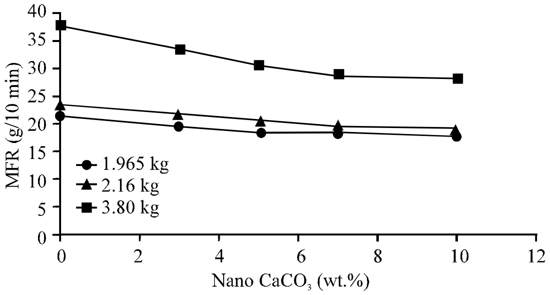

Fig. 10: The MFR behavior of waste PP nanocomposite with different loads at 25 rpm and190°C

Rheological properties

Melt flow rate

CaCO$_3$ nanoparticles percentage and loads effect: The rheological behavior of virgin and waste PP and its nanocomposite depend on the microstructure, physical, chemical properties, flow behavior, deformation rate and boundary condition.

Figure 9 indicates the MFR of different compounds of virgin PP nanocomposite at different CaCO$_3$ nanoparticles percentage, different loads at 25 rpm. The results show that the increasing in MFR at 2.16 and 1.965 is approximately the same up to 5% CaCO$_3$ after that the difference becomes clear. The MFR at 3.80 kg is higher than that at 2.16 kg by about 200% due to load increasing and viscosity decreasing, the MFR increasing with CaCO$_3$ nanoparticles content increasing at different loads because the presence of CaCO$_3$ nanoparticles in the molten PP has a rolling effect which facilitates sliding of melt on the cylinder wall of MFR tester, spherical nanoparticles serve as ball bearings, reducing the interlayer interaction of melts this results have good agreement with the results of Karim.

Figure 10 shows that the MFR of waste PP nanocomposite at 25 rpm decreases with the CaCO$_3$ nanoparticles percentage increasing, MFR value is still higher than that of waste PP this due to the polymer chain degradation which correlates with the molecular weight and chain length decreasing thus the viscosity decreasing.

Temperature effect: MFR increase with increasing temperatures for 3% of CaCO$_3$ nanoparticles at 2.16 kg and 25 rpm because when heat is supplied to a polymer the molecules vibrate more rapidly and there is an increase in Brownian motion and free volume thus the chain is easy movement in free volume therefore viscosity decrease and MFR increase.

Viscosity

CaCO$_3$ nanoparticles percentage and load effect: The viscosity inversely changes with shear rate and MFR, the magnitude of viscosity can be predicted according to the Eq. 2 (Shenoy and Saini, 1996):

$$\eta = 4.98*10^4\rho L/MFR \tag{2}$$

The viscosity of virgin PP and waste PP nanocomposite is higher than that at difference of MFR because as a results of rotation speed increasing. The viscosity of waste PP is lower than that of virgin PP due to chain degradation during process and lower MW.

Temperature effect: It was found that the viscosity decreases when temperature increasing for nanocomposite of 3% of CaCO$_3$ reinforced virgin and waste PP. There are many theories dealing with the viscosity-temperature relationship in liquids and polymers melts which use the concept of free volume and equations derived from this concept have been used in the description of the behavior of polymer solutions. In this research, the correlation between viscosity and temperature for nanocomposites are tested. The results have a good agreement with the Arrhenius law as follows according to Gupta and Yaseen (1997):

$$\eta = \eta_o e^{-Ea/RT} \tag{3}$$

Where:

η_o = A pre-exponential constant
Ea = The apparent energy of activation
R = Gas constant (J/mol.k)
T = Temperature (K)

Shear rate: The shear rate is directly changed with the MFR and it can be predicated from the following formula Eq. 4:

$$\gamma^{\bullet}_{w} = (1760/\rho)*AMFR \tag{4}$$

The shear rate at capillary wall at 2.16 kg and 230°C for VPN and WPN according to CaCO$_3$ nanoparticles percentage. The shear rate of WPN is very high as compared with the VPN at 25 and 50 rpm due to chain session and reduces in molecular weight therefore, the viscosity reduced. The MFR increase with loads increasing also MFR proportional with the shear rate according to the Eq. 5, so, the viscosity inversely change with shear rate which increase the shear thinning effect. This behavior approximately fit with power law (or Ostwald) non-Newtonian Viscosity Model. The power law model takes the form Eq. 5:

$$\eta = K\gamma^{\bullet n-1} \tag{5}$$

Where:

η = Viscosity (pa.s)

$\gamma^{\bullet}$ = The shear rate (sec^{-1})

Melt volume rate: Figure 15 and 16 show the MVR results for virgin PP and its waste due to the $CaCO_3$ nanoparticles content at constant time and distance equal 6. The results show that the MVR increasing with nano $CaCO_3$ percentage increasing for virgin PP nanocomposite but decreasing for waste PP nanocomposite at 25 and 50 rpm. MFR and MVR inversely change with viscosity and $CaCO_3$ nanoparticles act as lubricant therefor viscosity decreasing while MVR increasing.

CONCLUSION

The agglomeration of $CaCO_3$ nanoparticles increases with screw speed and nanoparticles percentage increasing. There are a relationship between dispersion of nanoparticles and the crystallinity and rheological properties for both virgin and waste PP nanocomposite, the higher levels of nanoparticles dispersion and less agglomeration giving higher level of crystallinity and lower MFR value. MFR results strongly connected with the density, MW, viscosity and shear rate. The behavior of MFR at 25 is more smooth and higher than at 50 rpm except at higher loads. The MFR at 50 rpm of WPN is more fluctuated due to non-homogeneous mixing. The crystallinity level increase with nano $CaCO_3$ percentage increasing for both virgin and waste PP but the crystallinity of VPN is higher than that of WPN.

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