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

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Abstract:-This work investigated the morphological and rheological behavior of calcium carbonate ($CaCO_3$) nanoparticles reinforces virgin polypropylene and its waste. The reductions   in the global properties especially the rheological behavior as a result of structure degradation are essential issue in reusing the waste thermoplastic polymer. The mixing of nanoparticles with polymer melts giving significant changes in the flow and physical properties. $CaCO_3$ nanoparticles are mixed in different concentrations 3, 5, 7 and 10wt % with the virgin polypropylene and its waste by melt compounding in a twin screw extruder at different screw speeds (25and 50) rpm and 190°C. Different microstructure and morphological techniques (X-ray Diffraction and field emission scanning electron microscopy) were used to evaluate the effect of the $CaCO_3$ nanoparticles concentrations on the microstructure of the nanocomposite, also melt flow rate (MFR) and melt volume rate (MVR) were tested using melt flow index (MFI) device. MFR of the polymer nanocomposite was examined due to the nanoparticles concentration, loads, temperatures and rotating speed changes, while MVR was tested at different $CaCO_3$ nanoparticles concentrations at standers load (2.16kg). Shear rate and viscosity were predicted according to the MFR values. The results show that the crystallinity level was increasing with the $CaCO_3$ nanoparticles percentage increasing for virgin and waste polypropylene. The $CaCO_3$ nanoparticles distribution in polypropylene matrix at 25 rpm is more homogenous and less agglomeration than at 50 rpm.

Keywords: polypropylene, $CaCO_3$ nanoparticles, twin screw extruder, microstructure, flow behavior, nanocomposite.

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 (J.Z. Liang, 2007).

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 recycling processes reduce the effect of waste on the environment and human health. 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 (Hani E. *et al*., 2002).

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 (J.Z. Liang, 2007, Bao-Qing *et al.,* 2006, Hanim R. Zarina *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 (C. D. Han *et al.,* 1981, Xiao-lin *et al.,* 2004, Chi-ning *et al.,* 2002).

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 Mohd Shamsul and Farid Samsudin (2008) and (Zulkifli *et al.,* 2012). 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) A.V. 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 (Gorgy Godwin, 2003).

Pitt Supaphol et al.(2004) had carried out a study on the effect of surface modification type (stearic acid coated and paraffin-coated) on the flow behavior of $CaCO_3$ filled syndiotactic polypropylene (sPP). It's found that both type of surface treatment had reduced the shear viscosity of filled system compared with untreated $CaCO_3$ and this trend elucidates an improvement of filler distribution in the sPP matrix.

Haydar U Zaman and MDH Beg (2014) studying the effect of $CaCO_3$ nanoparticles on the thermal, mechanical and rheological properties of polypropylene. It has found that the viscosity increases with filler content increasing especially at low shear rates.

In this work virgin polypropylene and the waste are mixing with the $CaCO_3$ nanoparticles at different concentration 3, 5, 7 and 10 wt. % using twin screw extruder at different screw speed (25 and 50) rpm and 190°C. The effect of $CaCO_3$ 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 virgin and waste polypropylene nanocomposite are tested; also the viscosity and shear rate of nanocomposite are predicated.

Methodology Work:-

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

Samples Preparation:- polypropylene granules and $CaCO_3$ nanoparticles were immersed in alcohol solution and mechanically mixed. The mixing process was performed using twin screw extruder (SLJ) with the specifications of screw speed

rang (0-320) rpm and screw diameter is 30mm, the power of main motor and heating (4KW and 3KW) respectively. The extruder dimensions (1.8m*0.6m*1.5m), weight (450Kg), and output (20Kg/h). The mixing process was performed at (25 and 50 rpm) and 190°C.

Characterization:-

$CaCO_3$ Nanoparticles:-

AFM version (AA3000) tapping mode is used to measure the particle size and the morphology of $CaCO_3$ nanoparticles in two and three dimensions. The $CaCO_3$ nanoparticles were dispersed in alcohol using ultrasonic at 40°C for 30 min and the applied energy is 500 watt. The standard method for testing thin film is adopted.

The another techniques to characterize the nanoparticles is X-ray diffraction (Rigaku Diffract meter) with Cu Kα radiation at 30 mA and 40 KV at scanning speed of 2°/min. The crystalline size of $CaCO_3$ nanoparticles are determined based on Scherer equation:-

$$D=0.9\lambda/\beta \cos\theta \tag{1}$$

Where D is the crystallite size, the λ diffraction wavelength equal (0.1541 nm), β is the corrected FWHM. Also XRD used to show the effect of $CaCO_3$ nanoparticles concentration and processing conditions on the crystallinity level of the new nanocomposite from the intensity of the main peaks of polypropylene.

Nanocomposite:-

Nanoparticles distribution:-

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 Field Emission Scanning Electron Microscopy 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 at5.00x magnifications.

Rheological Properties (MFR and MVR)

Melt indexer type (SHI JIA ZHUANG ZHONG SHI TESTING MACHINE CO., LTD) according to the Standard of (ISO١١٣٣:٢٠٠٥) was used to measure the MFR and MVR of polypropylene and its nanocomposite for both virgin and waste

through capillary die with diameter (Dc is ٢.٠٩٥mm) and the ratio of the die length (L) to diameter is (8/2.095), the melt indexer shown in **Fig.1.**

Results and Discussion

The Microstructure:-

The principle of AFM is based on mechanical contact between the sample and tip; therefor the measurement of particles in nanometer scale is strongly affected by sample-tip interaction. **Fig. 2, A:** Shows the topography and particles size of $CaCO_3$ nanoparticles in 2- D. The particle size is bigger than that in origin specifications sheet due to agglomeration of nanoparticles. However the range of particle size in nanometer scales. **Fig. 2, B:** shows the topography of $CaCO_3$ nanoparticles in bulk solution (3-D). The 3-D topography image approximately not the best way to assess nanoparticles dimensions, but particles size distribution extracted from the images can produce accurate information as show in **Fig. 2,C.** 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 is another important technique, the simplest and most widely used for estimating the average crystallite size of nanoparticles according to Scherrer equation. **Fig.3, A: -** shows the standard XRD of $CaCO_3$ nanoparticles which used to compare with the $CaCO_3$ nanoparticles that are using in this work. The X-ray diffraction pattern at **Fig.3, B: -**illustrates that the used nanoparticles 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 result have good agreement with Abdullahi Shafiu (2013). The grain size was calculated at FWHM (0.3) of main peak (29.4º) are 44nm.

The crystallinity level was examined according on sharpness and the intensity of the appearing peaks. **Fig (4):** shows the crystallinity level of virgin PP and its nanocomposite with (5and 10 wt. % $CaCO_3$) at 25 and 50 rpm. The polypropylene peaks characteristics of α phase in 2θ values of 13.1º, 16.4º and 18.2º 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 14.2º, 16.9º and 18.7º. The nanocomposite shows sharp and highly intense peaks while polypropylene 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. 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(7).

Fig. 5:-indicates the crystallinity levels of waste PP and its nanocomposite of (3 and 10wt. % of $CaCO_3$ at 25 and 50 rpm. The crystallinity level for virgin polypropylene nanocomposite is higher than for waste PP nanocomposite at 25 and 50 rpm because nanoparticles may be not filling the hole completely.

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

Fig.7 and 8: show the FESEM image of samples containing 3and 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 25 rpm. At 50 rpm nanoparticles with large aggregates are observed. The properties of nanocomposite at 25 rpm are higher than that at 50 rpm.

Rheological Properties:-

The rheological behavior of virgin and waste polypropylene and its nanocomposite depend on the microstructure, physical and chemical properties, flow behavior, deformation rate, boundary condition and die geometry. **Fig.9:** indicates that the MFR of different compounds of virgin polypropylene nanocomposite at different $CaCO_3$ nanoparticles percentage, different loads at 25 rpm**. The increasing in

MFR value at 2.16 and 1.965 is approximately the same up to 5% CaCO$_3$, after that the difference becomes clear due to the load increasing. The MFR values at 3.80 kg are higher than that at 2.16 kg by about 200% due to the viscosity decreasing. The value of MFR increasing as CaCO$_3$ nanoparticles content increasing at different loads the presence of nanoCaCO$_3$ in the molten polypropylene has a rolling effect which facilitates sliding of melt structure. Spherical nanoparticles serve as ball bearings, reducing the interlayer interaction of melts this results have good agreement with the results of (Karim, et al., 2009).

Fig.10:- Shows that the MFR for waste polypropylene nanocomposite at 25 rpm decreases with the CaCO$_3$ nanoparticles percentage increasing, MFR value is still higher than that of virgin polypropylene nanocomposite this due to the polymer chain degradation, then the molecular weight, chain length and viscosity decreasing.

Figs. 11 and 12: show the MFR of virgin and waste polypropylene nanocomposite with different CaCO$_3$ nanoparticles percentage at 50rpm. The MFR values increasing at different loads for virgin polypropylene while decreasing for waste polypropylene nanocomposite. The MFR values at 25 rpm are less than that at 50 rpm due to lower rotating speed. In general, at 25 rpm the dispersion is highest and the agglomeration of nanoparticles is small, thus the viscosity is highest and MFR is lowest as compared with 50 rpm. The results of viscosity show that the viscosity decreases with the MFR increasing, due to the scission of the chains during the melting processes. The magnitude of viscosity can be predicted according to the formula below A.V. Shenoy and Saini (1996):

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

The viscosity of virgin polypropylene and the waste at **Table (1)** is higher than that at **Table (2)** due to higher difference of MFR because of rotation speed increasing. The viscosity of waste is lower than that of virgin polypropylene due to chain degradation during process and lower Mw. The shear rate is directly changed with the MFR and it can be predicated from the following formula (Nizar Jawad *et al.,* 2013):-

$$\gamma^{\cdot}_{w} = (1760/\rho) * MFR \tag{3}$$

Table 4 and 5: show the shear rate at capillary wall at 2.16kg and 230 ºC for virgin and waste polypropylene nanocomposite according to CaCO$_3$ nanoparticles

percentage. The shear rate of waste polypropylene is very high as compared with the virgin at 25 and 50 rpm due to the chain session and the reducing in molecular weight. The MFR proportional with the shear rate according to the eq. (3),so the viscosity inversely change with shear rate which increases the shear thinning effect of polypropylene. This behavior approximately fit with Power Law or Ostwald non-Newtonian viscosity model. The Power Law model takes the form M.H. Allouche and et al, 2015:

$$\eta = K \, \gamma^{\cdot \, n-1} \tag{4}$$

Where:- η is viscosity (pa.s), $\gamma\cdot$ is the shear rate (s^{-1}).

Fig.13 and 14: Show that the MFR increases with the temperatures increasing for 3% of $CaCO_3$ nanoparticles at 2.16kg and 25 rpm, when heat is supplied to the polymer the molecules vibrate more rapidly so that the Brownian motion and free volume of the chain increases, this produced decreasing in viscosity and increasing in MFR. The data in Figs.(13and 14) are used to calculate the value of viscosity, it was found that the viscosity decreases when temperature increasing as shown in **Table (3)** for 3% of $CaCO_3$ nanoparticles for virgin and waste polypropylene.

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 work, the correlation between viscosity and temperature for VPN composites are tested. The results in these figures have a good agreement with the Arrhenius law as follows Gupta, and Yaseen (1997):-

$$\eta = \eta_\circ \, e^{-Ea. /RT} \tag{5}$$

Where $\eta_\circ$ is a pre-exponential constant and *EA* is the apparent energy of activation.
R is gas constant (J/mol.k), T is temperature (K).

Figs. 15 and 16: Show the MVR results for virgin and waste polypropylene nanocomposite, the test is performed at constant time and the distance equal 6mm.The MVR increasing with $CaCO_3$ nanoparticles percentage increasing for virgin polypropylene nanocomposite while decreasing for the waste at 25and 50 rpm. MFR and MVR inversely change with the viscosity.

Conclusions:-

The agglomeration and homogeneous distributions of nanoparticles in the polymer matrix are very important issue which has significant effect in the improvement of the final properties of the polymer matrix. The rotation speed of the screw extruder is important factor which effect on the nanoparticles distribution; the lower speed produces good nanoparticles distribution and less agglomeration through polymer matrix. There are a relationship between dispersion of nanoparticles, the crystallinity level and the rheological properties for both virgin and waste polypropylene nanocomposite. The higher level of nanoparticles dispersion and less agglomeration gives higher level of crystallinity and lower MFR values. 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 waste polypropylene is more fluctuated due to non-homogeneous mixing. The crystallinity level increase with $nanoCaCO_3$ percentage increasing for both virgin and waste polypropylene but the crystallinity of virgin is higher than that of waste polypropylene nanocomposite.

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Table (1): The Viscosity value for VPN and WPN at 2.16 Kg at 25 rpm and 190 ºC

(CaCO$_3$) (Wt. %)	Viscosity of VPN (pa.s)	Viscosity of WPN (pa.s)
0	3250.00	888.23
3	2093.40	938.36
5	1150.21	948.80
7	1116.95	990.39
10	1100.50	1000.02

Table (2): The Viscosity value for VPN and WPN at 2.16 Kg at 50 rpm and 190 ºC

(CaCO$_3$) (Wt. %)	Viscosity of VPN (pa.s)	Viscosity of WPN. (pa.s)
0	3250.00	888.23
3	1988.50	922.60
5	1030.25	939.95
7	1100.00	984.20
10	988.56	999.59

Table 3: Viscosity Behavior with Different Temperature for 3% CaCO$_3$ at 2.16 kg and 25 rpm

Temperature (ºC)	Viscosity of VPN (pa.s)	Viscosity of WPN (pa.s)
225	2175.5	1140.63
230	2093.4	938.36
235	2045.32	920.54
240	1987.6	887.6

Table (4): The shear rate value for VPN and WPN at 2.16 Kg at 25 rpm and 190 ºC

(CaCO$_3$) (Wt. %)	$\gamma^{\cdot}_w$ of VPN (S^{-1})	$\gamma^{\cdot}_w$ of WPN (S^{-1})
0	16400	64000
3	16632	42044
5	17026	39261
7	17259	37074
10	25103	35199

Table (5): The shear rate value for VPN and WPN at 2.16 Kg at 50 rpm and 190 ºC

(CaCO$_3$) (Wt. %)	$\gamma^{\cdot}_w$ of VPN (S^{-1})	$\gamma^{\cdot}_w$ of WPN (S^{-1})
0	16400	46000
3	17323	44267
5	18480	40108
7	23029	37907
10	23953	36539