Rheological behavior of waste Polypropylene reinforced with zinc oxide nanoparticles

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Abstract

The present paper investigates the influences of ZnO nanoparticles on the rheological behavior of waste polypropylene. The adding of nanoparticles to the waste plastic produces significant changes in its properties. Waste PP mixed with 3, 5, 7 and 10wt% of ZnO nanoparticles using twin screw extruder. The mixing process starts with sonication of nanoparticles in alcohol to get better particles distribution. X-ray Diffraction and field emission scanning electron microscopy are used to evaluate the effect of the ZnO nanoparticles percentage on the microstructure and morphology of the nanocomposite. Various rheological properties such as melt flow rate MFR and melt volume rate MVR are examined, also the solid and melt density are studied. The results of XRD test show that the crystallinity level increases with ZnO nanoparticles percentage increasing while the results of FESEM show that the sonication process and twin screw extruder reduces the agglomeration of ZnO nanoparticles in polypropylene matrix gradually. The results of rheological test show that an improvement in the viscosity of nanocomposite due to the decreasing in MFR and MVR with the increasing in ZnO nanoparticle percentage. Signification difference between solid and melt density was observed.

Keywords: Waste polypropylene, ZnO nanoparticles, MFR and MVR, flow behavior, twin screw extruder.

1 Introduction:

Degradation of thermoplastic polymer after each melting process becomes essential problem to deals with the recycling of these materials. Wide use of polymeric materials creates problem of growing quantity of waste and possibility of using recycled materials is limited because of poor properties of recycled plastics to virgin ones. One of the possibilities to improve the properties of plastic products is using diverse fillers like $CaCO_3$, TiO_2 and ZnO [1].

Recycling of plastic materials is strategically very important for the environmental policy of industry. This is especially true for high consumption plastics as polypropylene (PP). The key factor to the success of PP is its versatility, which is due to the fact that the structure and properties of PP can be design to satisfy the requirements [2].

Polypropylene is a trading widely used thermoplastic polymer, which offers best price/performance characteristics among all thermoplastics. It's having useful properties include high thermal stability and good mechanical properties, dimensional stability, low density, better process ability, high water permeation resistance, and resistance to corrosion [3]. A great volume percent of PP blends used in fibers and fabrics technology and composites which used in a wide range of applications such as automotive parts, extruded profiles, cable insulation, footwear, medical syringes and packaging industry[4].

In recent years, the incorporation of nanoparticles in PP matrix has generated extreme importance among polymer scientists due to its promising industrial applications in many aspects of technology. Nanocomposite with good filler dispersion offer significant improvements in mechanical, thermal, electrical, optical and physicochemical properties even at relatively low filler content [5].

Nanocomposite are a new class of mineral-field plastics that contain relatively small amounts (<10%) of nanometer-sized clay particles [6]. The particles, due to their extremely high aspect ratios (about 100-15000), and high surface area (in excess of 750-800 m^2/g) promise to improve structural, mechanical, flame retardant, thermal and barrier properties [7].

ZnO is one of multifunctional compound has down increasing attention in recent year due to its prominent properties such as chemical stability, high luminous transmittance, high catalyst activity, effective antibacterial, intensive ultraviolet and infrared absorption, high melting temperature, non-toxic . The advance of ZnO nanoparticles could improve mechanical and optical properties of polymer matrix [8].

The enhanced properties are due to the effects of nanoscale structure and interaction of fillers with polymers. The size and structure of the dispersed phase significantly influence the properties of polymer nanocomposite [9] .The key factors for the preparation of improved performance are the fine and a homogeneous dispersion of the nano powders and a strong interface adhesion between matrix and nanofillers [10].

Rheology is a branch of physics that deals with the deformation and flow of matter under stress. It is particularly concerned with the properties of matter that determine its behavior when a mechanical force is exerted on it. Rheological properties have important implications in many and diverse applications [11]. The relationship between the structure and rheology of a polymer is of practical interest for two reasons: firstly, rheological properties are very sensitive to certain aspect of structure and they are simpler to use than analytical methods, such as nuclear magnetic resonance. Secondly, it is the rheological properties that govern the flow behavior of polymers when they are processed in the molten state [12].

In 2011, Mohagheghian Majid and et al, [13] study the effect of effect of nano-ZnO on rheological and dynamic mechanical properties of polypropylene. Three polypropylene (PP)/zinc oxide nanocomposite containing 5, 10 and 15 wt. % nanoparticles were prepared through melt-blending. Dynamic rheometry using a parallel plate rheometer showed that the rheological moduli of the nanocomposite increased with increase in nanofiller concentration. There was an increase in complex viscosity of the nanocomposite with increasing the nanofiller concentration.

This article aims to produce nanocomposite materials from waste polypropylene as matrix with the addition of ZnO nanoparticles as filler with the ratio (3, 5,7,10 wt. %) using rotating twin screw extruder at 25 rpm and 190 °C. Also observe the effects of nanoparticles concentration on the MFR, MVR, viscosity solid and melt density. The viscosity and melt density behavior used to predict the improvement in the materials properties and the exact manufacturing process conditions.

2 Materials and Methods:

Waste polypropylene (G-801) has melt flow rate of 23 g/10min and density of (902-906) kg/m^3 was used as matrix resin. ZnO nanoparticles provided from Shijiazhuang Sun power Technology Co., Ltd, China are used as reinforcing phase, the main specifications of these nanoparticles are particle size 40nm and density of $3.6 g/cm^3$.The modified composite of waste polypropylene pellets and ZnO nanoparticles are prepared in two stages the first one mix the ZnO nanoparticles in alcohol using ultrasonic power at 30min, 40ºC and the applied energy is 450watt to reduce the agglomeration. The second stage using a rotating twin screw extrude at 25 rpm and 190ºC to mix the ZnO nanosolution with the waste PP. ZnO /waste PP nanocomposite produce as sheet with thickness of 1mm. The colour of sheet approximately is yellow.

3 Characterizations:

3.1 Nanoparticles:-

Atomic Force Microscopy (AFM) version AA3000 was used to check the morphology and particle size. The ZnO nanoparticles are dispersed in alcohol by using ultrasonic device under the condition (30min, 40°C and 480 watt), then using the standard method for testing the thin film of nanosolution.

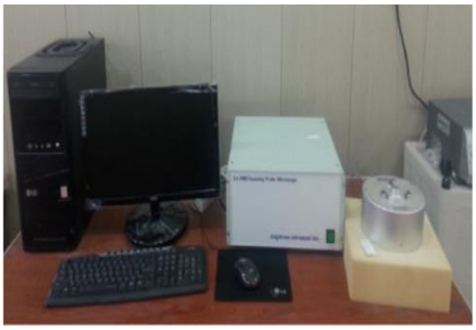

Figure 1: Atomic force microscopy

X-Ray Diffraction (XRD) was used to show the crystallinity levels of nanocomposite and check the composition, crystallite size of ZnO nanoparticles based on Scherer equation was determined:-

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

D is the crystallite size, the λ diffraction wavelength equal 0.1541 nm, β is the Full With at Half Maximum must be in rad and θ is the diffraction angle.

3.2 Polymer Nanocomposite:-

The surface morphology and distribution of nanoparticles through the waste polypropylene was tested by Field Emission Scanning Electron Microscopy (FESEM), (model MIRA 3 XM4, USA).

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 waste polypropylene and its nanocomposite through capillary die with diameter Dc is 2.095mm and length of capillary die is 8mm. The MFR was tested with different concentration of ZnO nanoparticles and different loads at 230ºC**,** also 3wt% nanocomposite tested with different temperature at 2.16 kg. The MVR was examined at different concentration of ZnO nanoparticles at 2.16 kg and 230 ºC. The viscosity can be calculated from the following equations [12]:-

$$\eta = = \frac{\pi * \Delta P R^4 * \rho}{8 * L * MFR} \quad (2)$$

$$\eta = \frac{\pi * \Delta P R^4}{8 * L * MVR} \quad (3)$$

Where:-η:- the viscosity(pa.s), ρ:-the density(kg/m^3), and L:- the capillary length(m)

Solid Density was tested at room temperature using (Matsu Haku HIGH Precision DENSITY TESTER GP-120S D=0.0001 g/cm^3), while the **melt density** is determined according to the following formula [14]:-

$$\textbf{Melt density } (\rho') = \frac{MFR}{MVR} \quad (4)$$

The MFR and MVR with different nanoparticles concentrations at 2.16 kg and 230 ºC were used to calculate the melt density.

4 Results and Discussion

4.1 Nanoparticles distribution evaluation:-

Figure (1) shows the topography of the surface of the thin film prepared of ZnO nanoparticles dispersion in the alcohol solvent using ultrasonic device. It is illustrate the effect of sonication process to produce a good dispersion and reduce the agglomeration of nanoparticles. Nanoparticles with almost spherical shape and 20-90 mean diameter is present in figure (1.A). Needle shape with the nanoparticles is obtained in figure (1,B). It's very clear in figure (1,C) the nanoparticles size in nano-scale range.

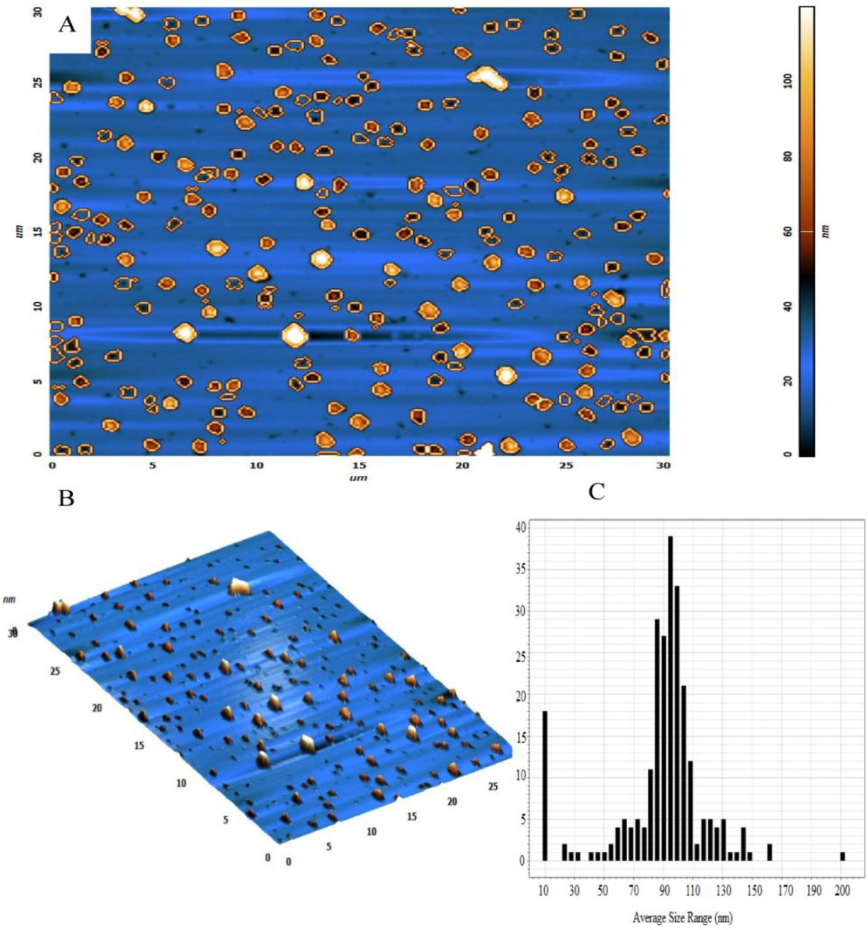

Figure 1: AFM images for morphology of ZnO nanoparticles (A) 2-D particles size (B) 3-D particles size(C) particle size distribution

Another inspection to evaluate the size of nanoparticles is XRD based on Scherer equation. Figure (2): shows the XRD for standard ZnO nanoparticles which was used to compare with the used ZnO nanoparticles. The XRD pattern at Figure2 illustrates that the used nanoparticles are approximately indicate the same of standard ZnO. The diffraction patterns of used ZnO consist of the main diffraction peaks at around 2θ (31.6º, 34.4º, 36.2 º, 47.5º, 56º, 62º, 66.3 º, 67.8 º, 69 º, 72.5 º, 76.9 º), and the main peak at 2θ=36.2º, this results agreement with the standard XRD peaks of ZnO nanoparticles. The data in Fig.(3) are used to calculate the average crystallite size of used ZnO nanoparticles which is approximately 65nm in figure (3).

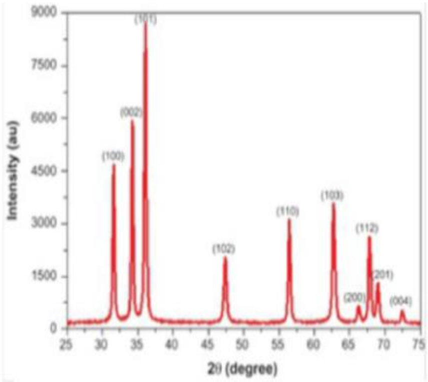

Figure 2: Standard XRD for ZnO nanoparticles

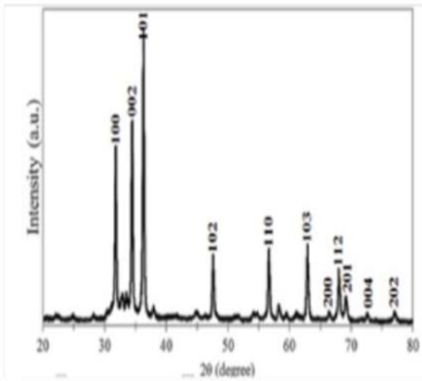

Figure 3: XRD for Used ZnO Nanoparticles

4.2 Nanocomposite:-

4.2.1 Structure:-

The crystallinity level was measured using XRD test according to the sharpness and the intensity of the appearing peaks. Figure (4) shows the crystallinity levels of waste polypropylene and its nanocomposite with 5 and 10 wt% of ZnO nanoparticles. It's very clear that the crystallinity level increases with nanoparticle percentage increasing and a new beaks appear at 2θ (30º -40º) which mean the existence of ZnO nanoparticles through the polypropylene matrix and acts as filler. The increasing of crystallinity level is very important in the improvement of nanocomposite properties.

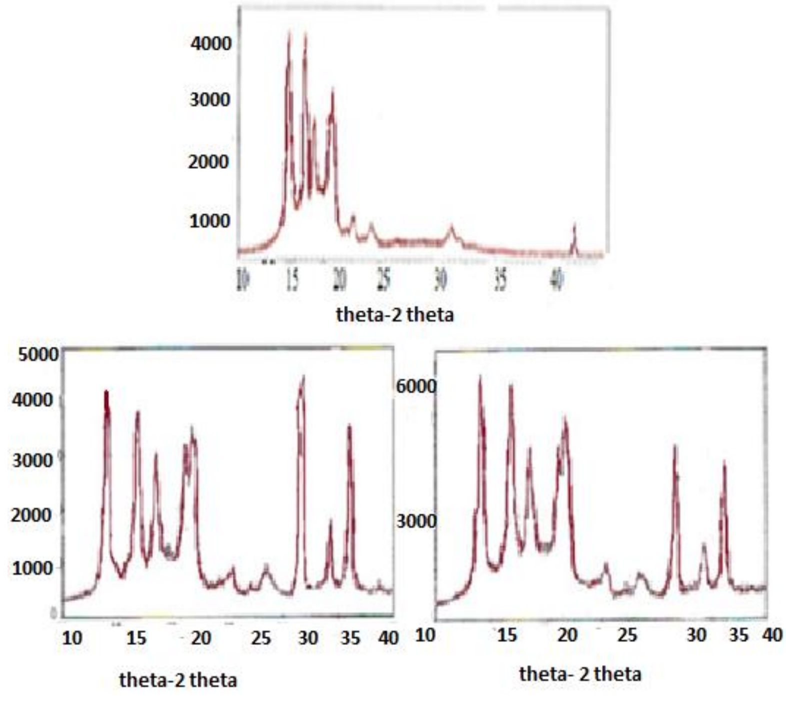

Figure 4: The crystallinity level of nanocomposite: (A) waste PP (B) 5% ZnO nanocomposite (B) 10%ZnO nanocomposite

The dispersion of the nanoparticles will have a significant effect on the properties of the nanocomposite. The morphology of nanocomposite was tested by FESEM to observe the distribution of nanoparticles within the polypropylene matrix. Figure (5) shows the micrographs of a fractured surface of Charpy impact of waste PP composite filled with 3 and 10 wt. % of ZnO. It was obvious that, the fracture surface of the nanocomposite sample was smooth and the agglomeration increases with nanoparticles content increasing because of high specific surface area. The good dispersion of nanoparticles produces strong interaction between nanoparticles and polymer matrix.

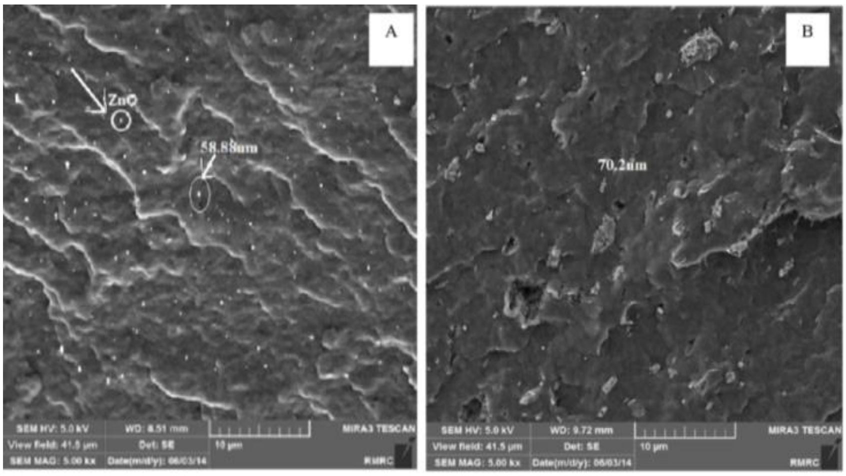

Figure 5: The images of the Nanocomposite: A and B (3and10 wt. %) ZnO nanoparticles filled waste PP.

4.2.2 Rheological properties:-

MFR:-The MFR values of waste PP nanocomposite at different ZnO nanoparticles percentage and different loads are shown in figure (6). The MFR slightly decreases with ZnO nanoparticles percentage increasing due to viscosity increasing. The MFR values increasing with loads increasing and it's proportional to the shear rate and inversely change with the viscosity. Therefor the shear rate increases with the viscosity decreasing. This phenomena is present in the non-Newtonian polymer flow which is called shear thinning effect. This behavior can be used as indicator to predicate many other structures, thermal and mechanical properties.

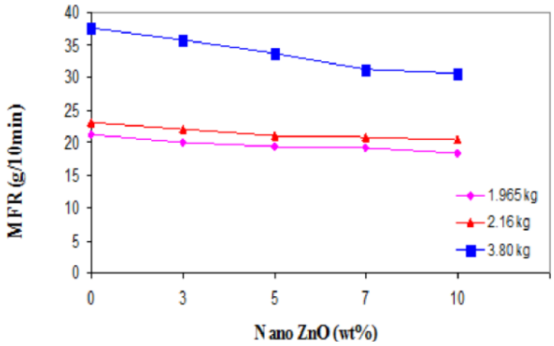

Figure 6: The MFR behaviour of waste PP nanocomposite with different loads and ZnO nanoparticles percentage at 230 ºC.

Melt Volume Rate (MVR):-

Figure (7) Shows MVR value for waste PP nanocomposite due to ZnO nanoparticles content at constant time and distances is 6mm. It can be seen that the MVR decreasing with ZnO nanoparticles percentage increasing because the chains motion. The MFR and MVR inversely change with viscosity.

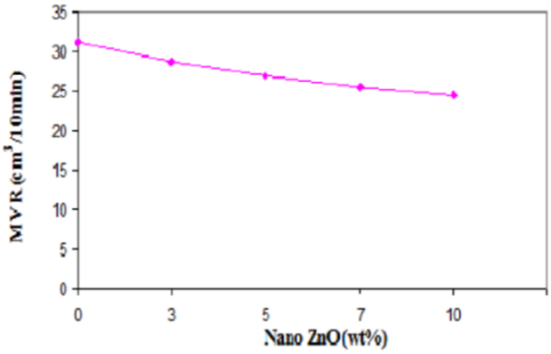

Figure 7: The MVR behaviour of waste PP nanocomposite with different ZnO nanoparticles percentage at 2.16 kg and 230°C

Density: density results for waste PP nanocomposite are shown in figure (8). The solid and melt density gradually increases with ZnO nanoparticles percentage increasing, this is due to higher density of ZnO nanoparticles 3.6 g/cm³.

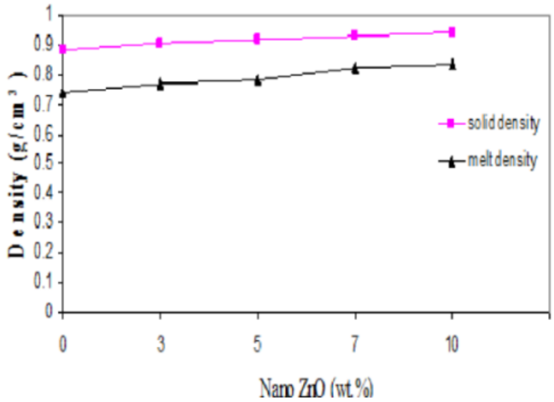

Figure 8: The solid and melt density behaviour of waste PP nanocomposite with different ZnO nanoparticles percentage.

The melt density is less than the solid-state density by about 20%, due to the change in volume between solid and melt state. The melt polymer has higher volume than that of solid polymer. The melt density is a very important data for numerical simulation study of rheological and flow behaviour of polymer melts. The polymer process strongly depends on melt density which effects on the manufacturing operation. The use of melt density instead of solid density produce accurate results in numerical study and reduces cost in the manufacturing process.

The viscosity, shear rate and the molecular weight can be calculated using MFR, MVR and melt density. Also the condition and behaviour of polymer structure may be predicated.

Viscosity:-There are many factors influence on polymer melt viscosity such as MFR, MVR, shear rate and polymer structure etc. Figure (9) shows the effect of ZnO nanoparticles on the viscosity of waste PP.

The results show that the viscosity increasing with the ZnO nanoparticles percentage increasing because that the interaction between nanoparticles and the chains of waste PP polymer may be increases the viscosity and reduces the flexibility of chains movement. The increasing of viscosity confirmed with the MFR decreasing. The viscosity inversely changes with shear rate which increase the shear thinning effect.

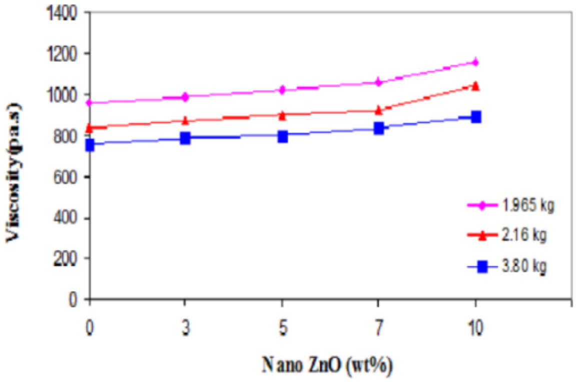

Figure 9: The Viscosity behaviour of nanocomposite at different ZnO nanoparticles percentage and different loads at 230 ºC.

Figure (10) show the calculated viscosity of waste PP as a function of ZnO nanoparticles from MVR test at 2.16 kg and 230 ºC. The value of the viscosity in figures (9 and 10) is approximately the same. The increasing of viscosity qualifies the material to be used in specific application, due to signification change in thermal, mechanical and structure properties [15].

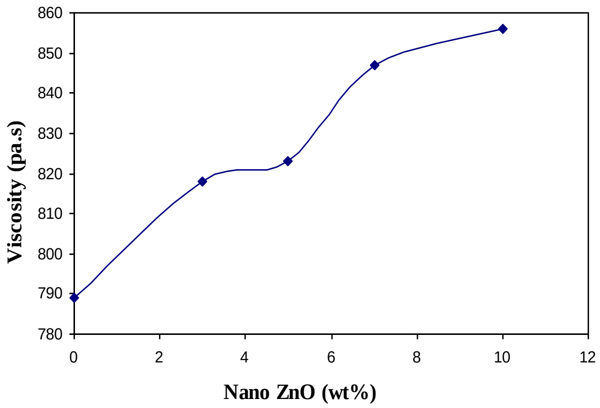

Figure 10: The Viscosity behaviour of nanocomposite at different ZnO nanoparticles percentage at 2.16 and 230 ºC.

5 Conclusions:-

The using of ultrasonic and twin screw extruder device are very important techniques to produce better distribution and less agglomeration of nanoparticles in polymer matrix. The uniformity of nanoparticles distribution strongly effect on rheological and physical properties of melt nanocomposite. The value of MFR and MVR play very important role in determining the viscosity and melt density. The MFR decreases with ZnO nanoparticles, and increasing with temperature and loads increasing. The MVR decreases with ZnO nanoparticles concentrations increasing. The viscosity increases with MFR and MVR decreasing. The increasing in viscosity may be attributed to the interaction forces between the ZnO nanoparticles and waste PP chains. According to the rheological analysis, the increasing in viscosity leads to change in the properties of the new nanocomposite to the opposite direction whether the viscosity is decreases. The melt density produce is lower than that the solid density. The increasing of density is compatible with calculating viscosity increasing. The viscosity and melt density together used to control the final properties of products and the manufacturing processes conditions.

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