

Study The Effect OF CaCO₃ Nanoparticles on The Mechanical Properties of Virgin and Waste Polypropylene

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Abstract. This paper study the effect of the calcium carbonate (CaCO₃) nanoparticles on mechanical and physical properties of virgin and waste polypropylene (pp). 3, 5, 7 and 10 (wt. %) of CaCO₃ nanoparticles are mixed with each of virgin and waste pp. These mixture are blended in co-rotating twin screw extruder at 190 °C and different screw speed (25 and 50 rpm). Different mechanical and physical technique are used to evaluate the characteristics of polymer nanocomposites ex: Tensile strength, elastic modulus, impact strength, hardness and density. The results of virgin pp./ (CaCO₃) showed that The tensile strength decreasing with nano (CaCO₃) concentration for virgin pp., while for waste increasing at 5% and then decreasing gradually. The impact strength increasing with nano CaCO₃ concentration increasing. The hardness and density increasing with the increasing of the nano CaCO₃ concentration for two type of pp.

Nearly all the mechanical properties were found to increase with the processing speed of 25 rpm. In this studies, it was seen that the highest processing speed of 50 rpm does not give the material performance enhancements due to higher shear intensity which causes defect points in the structure. Also the time is smaller at high screw speeds, so there is not enough time for good dispersion to occur.

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 such as low cost, while home appliances and industrial applications attributed to their high impact strength and toughness when filler has incorporated. After each melting process the properties of pp. drop to a certain limit. CaCO₃ nanoparticles are mixed with pp. to improve the rheological, mechanical, thermal and physical properties. The nanocomposite produced can be used in specific field due to change in internal structure between chains and CaCO₃ nanoparticles.

Recycling has been practiced for many years by industries without any great accuracy. The new environmental, economic have induced the scientific community to increasingly deal with polymer reprocessing and sustainability. Numerous academic research works have become more and more interested in the recycling of the widespread polyolefin as polyethylene (PE) and polypropylene (PP) [1].

One problem with recycled resins is that tensile toughness and impact strength usually decrease during recycling so that requires additives. Nano sized additives can confer significant property improvement with very low loading levels compared to traditional micro sized additives, which require much higher loading levels to achieve similar performance [2].

The mechanical properties of thermoplastic resins are sometimes unsuitable for specific applications. To overcome this, several fillers are added to impart better properties to the end material [3]. The incorporation of nanoparticles have been attracted much interesting in scientific field because of the possibility of use low contents of fillers with great increases in both impact and tensile properties [4].

Polymer nanocomposites are used as engineering materials, owing to their improved mechanical and electrical properties, heat resistance, radiation resistance, and other properties as a result of the nano metric scale dispersion of the filler in the matrix [5].

Manias defined nanocomposites as multi-phase solid materials where one of the phases has one, two or three dimensions of less than 100 nano meters (nm) or structures with nano-scale repeat distances between the different phases that make up the material[6].

A wide variety of natural minerals have been introduced as fillers since 1930 in thermoplastic polymers to reduce the cost of the end product [7].

Studies have shown that filler loads play an important role in modifying the properties of polymers and found that its addition offers an effective means for improving the mechanical properties of polymeric materials [8] .

The effects of filler on the mechanical and physical properties of the composites strongly depend on its shape, particle size, aggregate size, surface characteristics and degree of dispersion. Nucleating agents can be divided into two types: inorganic and organic. Inorganic nucleating agents include talc, mica, barium sulfate (BaSO_4) and calcium carbonate (CaCO_3) [9] .

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. It has been reported that the addition of CaCO_3 nanoparticles could improve the thermal and mechanical properties of polypropylene (PP) [10].

Fundamentally, the mechanical properties of nanocomposites are strongly influenced either by type and composition of the matrix and the fillers or by the preparation conditions [11].

The main condition to achieve the desired performance of the nanocomposites is the good dispersion of the nanoparticles. This can be a difficulty problem to overcome due to the strong tendency of agglomeration of the nanoparticles, which can be explained by their small particle diameter, i.e., high surface energy[13]. Many strategies have been used to solve this problem, the most commons are the surface treatment of the nanoparticles in order to reduce the surface energy and in some cases to increase the compatibility with the matrix , so the achievement of good dispersion of the nanoparticles seems to be strongly dependent on the mixing or residence time [12], and the use of different techniques of mixing, in-situ polymerization, solution and melt processing. Among these techniques, melt processing is considered one of the most interesting methods being the most economical, flexible for formulation and involves compounding and fabrication facilities commonly used in commercial practice[13]. On the other hand by extrusion process, higher screw speed rotation leads to bad dispersion and impact resistance[14].

Recently, nanocomposites based on PP matrix constitute a major challenge for industry since they represent the route to substantially improve the mechanical and physical properties of PP [15]. In this study, the aim is to produce nanocomposite materials from virgin and waste pp. as the matrix with the addition of CaCO_3 nanoparticles as the filler, and observe the effects of nanoparticles content and processing speed on sample properties, e.g. mechanical, and physical properties. The nanoparticles content (3,5,7,10 %wt.) by using co- rotating twin screw extruder at speed of 25 and 50 rpm and at 190°C.

Materials and method:-The materials used in this work are polypropylene homo-polymer, Subic 575-S (MFI= 8.3 g/10 min),and calcium carbonate nanoparticles CaCO_3 The characterization of CaCO_3 is illustrated in Table (1).

Table (1):The specifications of nano CaCO₃

Specification	Results
CaCo3 %	98.55
Whiteness	95.45
Moisture %	0.11
Hydrochloric acid insoluble matter %	0.16
Fe %	0.01
PH	9.02
325 mesh sieve residue %	0.00
Particle size D97(um)	15.88
Loss on Ignition %	43.20
Hard salt (As) %	0.00019
Heavy metals aluminum (Pa) %	0.0018

Nanocomposites samplesPreparation

The melt blending of nanoparticles and PP. pellets were carried out by a co-rotating twin screw extruder (model SLJ) [crew speed is (0-320) rpm and diameter is 30mm,main motor (4KW),Heating power is (3KW). The extruder dimensions (1.8m*0.6m*1.5m), weight (450Kg), output (20Kg/h)]. The pp./CaCO₃ nanocomposites (PNC) were prepared in the following procedure:-

- 1- The virgin and waste of pp. are mixing with CaCO₃ nanoparticles according to the mentioned ratios.
- 2- The mixture produce are wetting by using acetone solvent .
- 3- Each of virgin pp./CaCO₃, waste pp./CaCO₃ mixture blended in twin screw extruder at 190°C and the screw speed is (25 and 50 rpm) respectively.

Mechanical properties

Tensile:- Instron 5556 Universal Testing Machine in accordance to ASTM D-638 IV, as shown in (Fig. 1) is used to perform tensile test. For each PNC, 2 samples were tested and the mean values were considered. The crosshead speed was 5 mm/min. The load was applied (5KN). The sample are cutting to require shape by CNC machine .

Impact strength:- CEAST Resil impact instrument according to ASTM D-256, at ambient temperature is used to analyze the effect of adding CaCO₃ nanoparticles on impact strength of polymer nanocomposites.

Hardness test was performed on the sample using ASTM D-2240 standard at room temperature in order to analyze the effect of adding CaCO₃ nanoparticles on the hardness of polymer nanocomposites. For each compound, 4 samples were tested and the mean values were considered. The standard samples dimensions are shown in Table (2).

Density test is performed using (Matsu Haku HIGH Precision DENSITY TESTER GP-120S D=0.0001 g/cm³). Which contain water at room temperature and the measuring based on the following formula :-

density = weight of the polymer in air – weight of the polymer in water



Fig. 1: Tensile test device



Fig .2: Impact test instrument

Table(2):Standard samples dimensions.

No.	Property	Sample	ASTM
1	Tensile		D 638 IV
2	Impact		D 256-87
3	Hardness		D 2240

Results and discussion

Mechanical: Calcium carbonate nanoparticles were added to PP homo-polymer and its waste in order to achieve better impact resistance and reinforcement of the matrix, so it is convenient to study the stress-strain behavior of virgin and waste PP and its nanocomposites. Moreover the analysis of the tensile mechanical properties, yield stress and elastic modulus, can be related to nanoparticles dispersion.

The effects of particle loading on the elastic modulus of virgin and waste pp. at (25 and 50 rpm) are given in (Fig. 3, 4). The results showed that the elastic modulus gradually increases with increasing

content of nanoCaCO₃ for different screw speed (25 and 50 rpm) for both virgin and waste pp. The elastic modulus for waste pp. is higher than that for virgin pp. for two screw speed (25 and 50 rpm) due to strong interaction between the polymer and filler, because of high surface contact area which is a result of the small particle diameter. It was described in the literature that the elastic modulus of polymeric composites depends, on surface contact area of the filler not on its surface treatment this good agreement with [1,8]

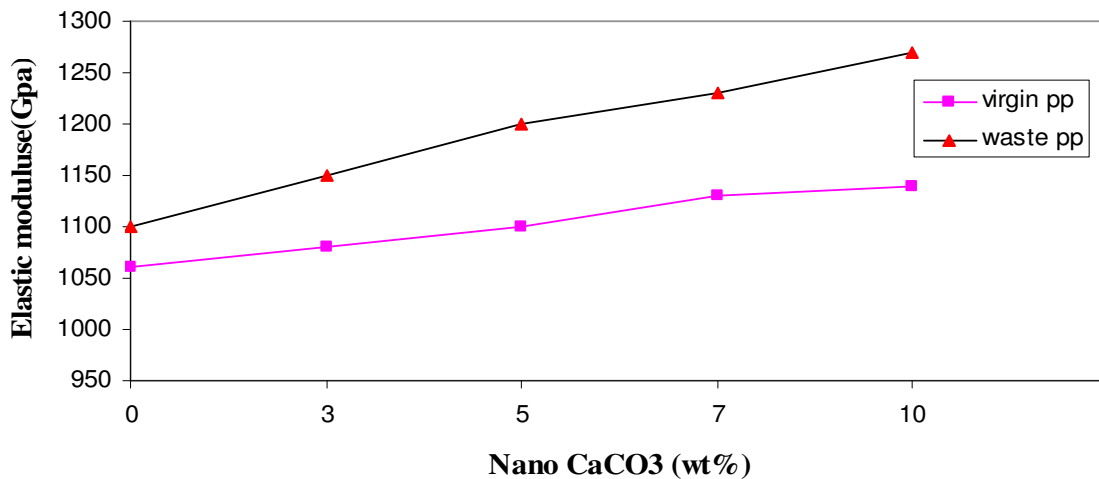


Fig. 3: Modulus of Elasticity of Virgin PP and its Waste With Different Nano CaCO₃ Percentage at (25 rpm).

The elastic modulus at 25 rpm is higher than that of 50 rpm, due to that the screw speed actually has important effect on the dispersion mechanism of nanoparticles in polymer. Higher rpm implies higher shear intensity, but lower residence time in the barrel so that nano CaCO₃ at 50 rpm don't distribute homogenously and filled the holes uniformly in polymer matrix.

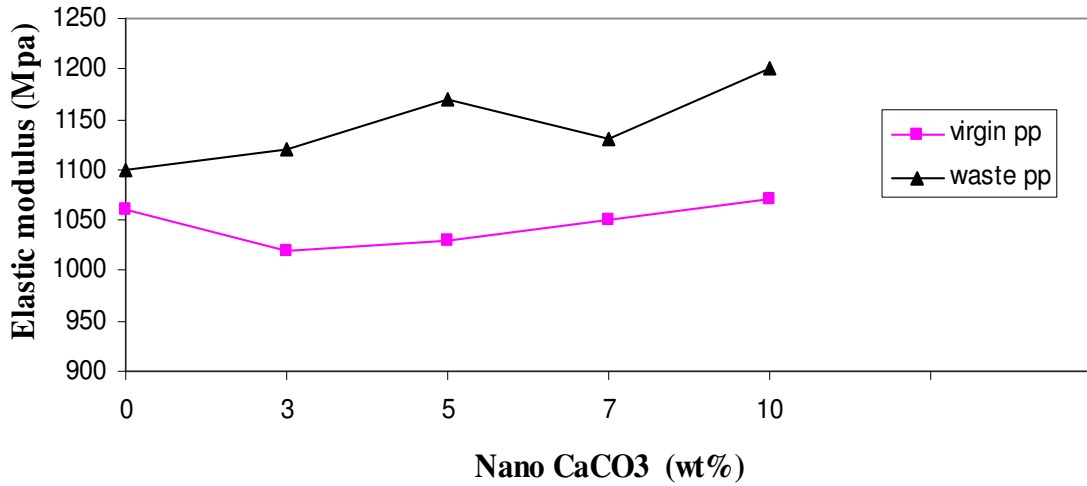


Fig. 4 :Modulus of Elasticity of Virgin PP and its Waste With Different Nano CaCO₃ Percentage at (50 rpm).

(Fig, 5, 6): Show that the pure waste pp. have lower tensile strength than pure virgin pp. due to repeat melting processes, each melting processes reduce the molecular weight and the secondary force between molecules this agreement with [16]. The tensile strengthslightly decreases with the CaCO₃ nanoparticles percentage increasing at 25 and 50 rpm . In general the decreasing in tensile strength is properly due to the poor interfacial adhesion between the CaCO₃ surface and the PP matrix, resulting in poor stress transfer across the interface, this agreement with[1,4]

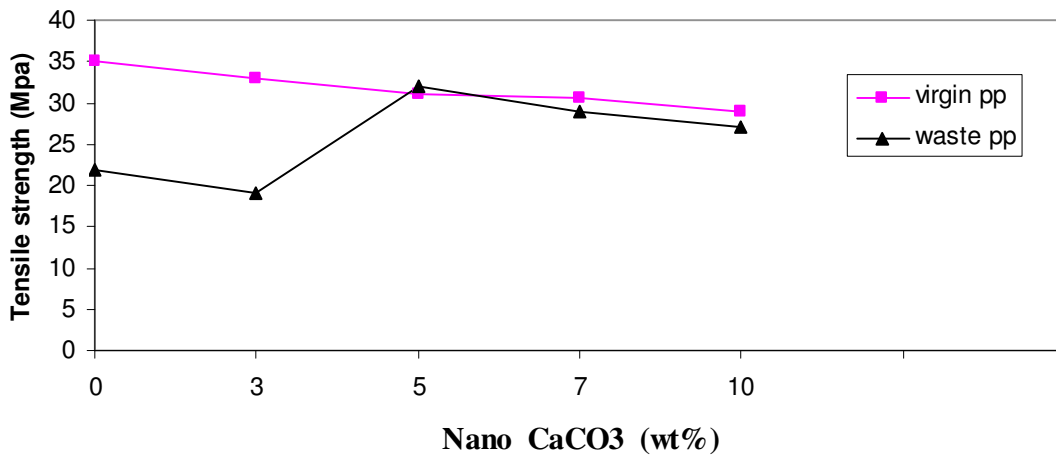


Fig. 5:Tensile Strength Behavior For Virgin pp. and its Waste With Different Nano CaCO₃ Percentage at (25 rpm).

The tensile strength for waste pp. in (Fig. 5) indicates non-stable behavior. At 3% nanoCaCO₃ the tensile strength decreasing , while at 5% the tensile strength reach the maximum value and then decreasing at 7% and 10% gradually

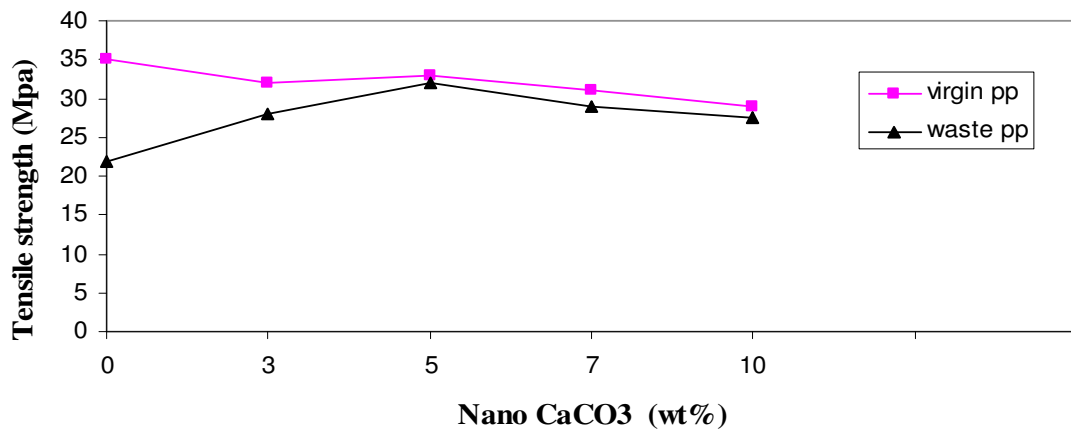


Fig. 6: Tensile Strength Behavior For Virgin pp. and its Waste With Different Nano CaCO₃ Percentage at (50 rpm).

Fig. 6: The tensile strength of waste pp. increase up to 5% then decrease slightly up to 10%, in general the tensile increasing with nano CaCO₃ concentration increasing.

Impact strength: The results of nanocomposite at (25 and 50 rpm) at (Fig. 7, 8) shown that the impact strength of nanocomposites gradually increases with increasing content of fillers for both virgin and waste pp. The impact strength of pure waste is lower than pure virgin pp. because the reduction in chain length which occur during multi-melting processes this a good agreement with [16].

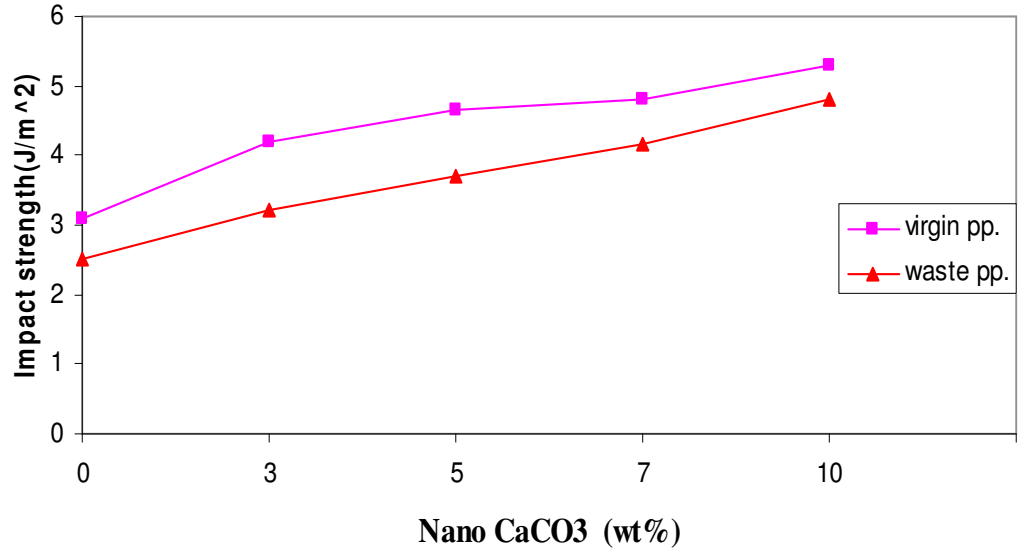


Fig. 7: Impact Strength Behavior For Virgin pp. and its Waste With Different Nano CaCO₃ Percentage at (25 rpm).

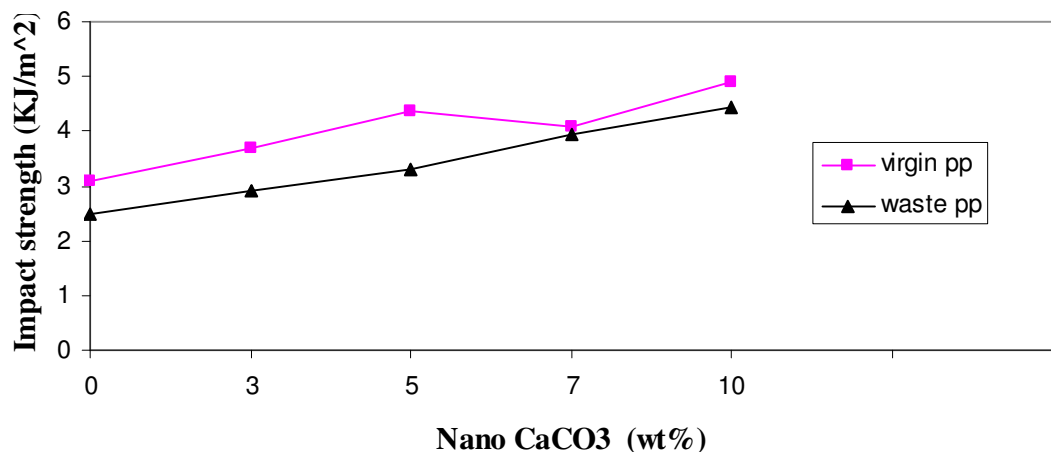


Fig. 8: Impact Strength Behavior For Virgin pp. and its Waste With Different Nano caco3 Percentage at (50 rpm).

Addition of nano-CaCO₃ increases the impact strength significantly. This may be explained by the fact that the presence of nano-CaCO₃ in the PP matrix lead to a more uniform distribution of impact energy . Kemal et al. reported that the raise of toughness and impact energy may be attributed to enhanced micro-void formations initiated by nanoparticles, The presence of nano-CaCO₃ may possibly facilitate the mobilization of macromolecular chains and improve the ability of matrix polymer to adapt to deformation and hence to increase the ductility and impact strength of composites, this agreement with[3,14].

Density: Density results for nanocomposites at (25 and 50 rpm) are shown in (Fig. 9, 10). The density gradually increases with increasing content of fillers for different screw speed (25 and 50 rpm) for two type of pp. This is due to higher density of CaCO₃ nanoparticles (2.71 g/cm³). The density of PNC at 25 rpm is higher than that at 50 rpm due to the better distribution of CaCO₃ nanoparticles throughout polymer matrix at low speed. The period of time during low speed rotating is higher than at high speed. The difference in density at 25 rpm is approximately the same , the behavior in Fig. 9 unlike the behavior which occur in Fig. 10.

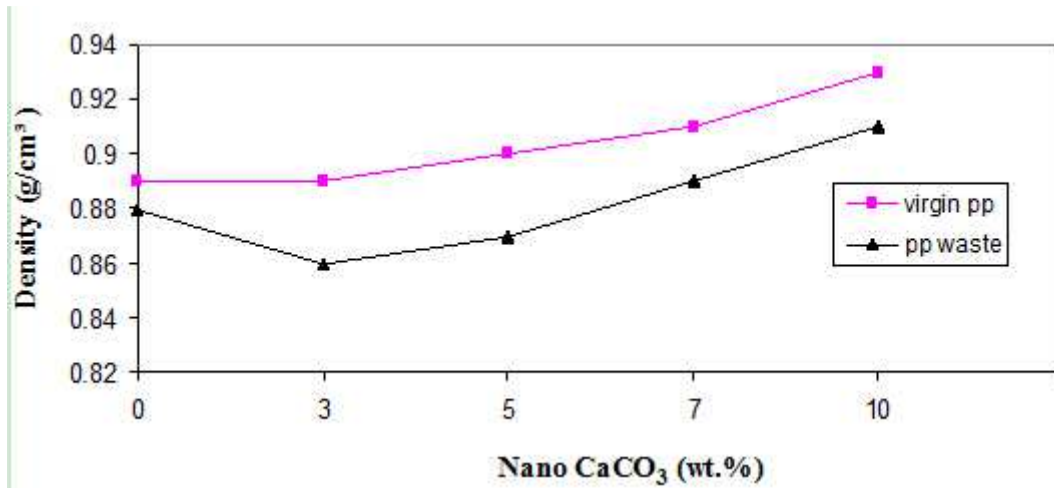


Fig. 9: The Density Behavior of Virgin pp. and its Waste With Different Nano CaCO₃ Percentage at (25 rpm).

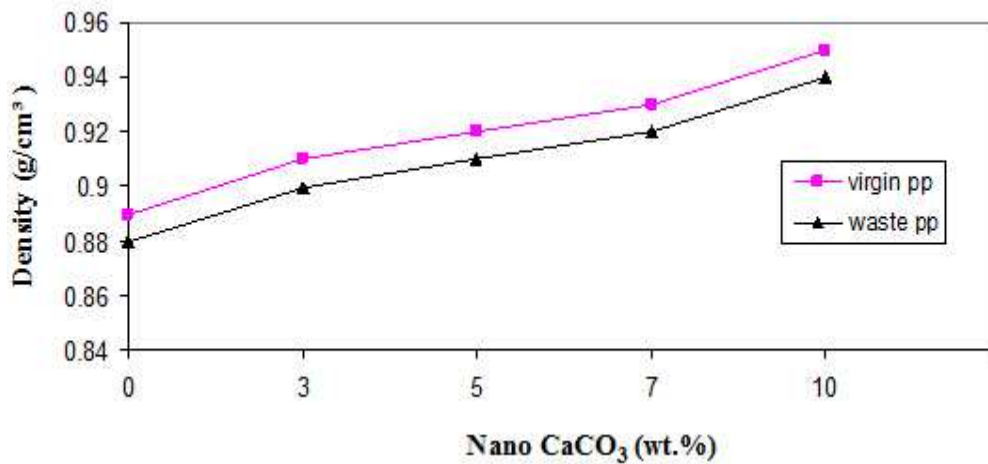


Fig. 10: The Density Behavior of Virgin pp. and its Waste With Different Nano CaCO₃ Percentage at (50 rpm).

Hardness: Shore D hardness for nanocomposites at (25 and 50 rpm) were shown in (Fig. 11, 12). The results showed that the hardness of virgin pp. and its waste slightly increases with increasing content of nanoparticles for different screw speed (25 and 50 rpm) due to the CaCO₃ nanoparticles fill the holes and act as fillers.

The hardness of virgin and waste pp. at 25 rpm is higher than that of 50 rpm, because higher residence times due to low screw speed led to better distribution of nanoparticles through polymer matrix.

The increasing in hardness consist of two stage. The first one ends at 5% and the second stage starts at 5% and ends at 10%.

The slope and magnitude of the second stage is higher than that of first stage due to the CaCO₃ nanoparticles percentage increasing.

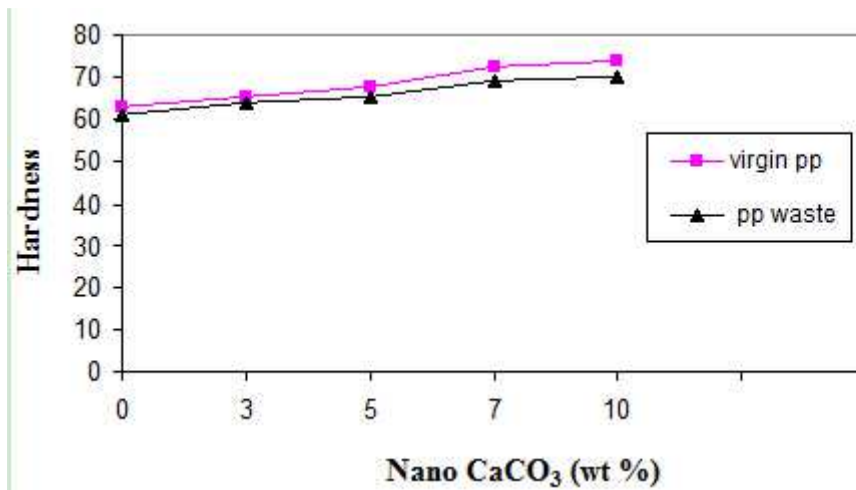


Fig. 11:-The Hardness Behavior of virgin pp. and its waste with Different nano CaCO₃ Percentage at (25 rpm)

The hardness increasing in (fig. 11) is more smooth than at (fig. 12) due to lower screw speed and the more homogenous nanocomposites.

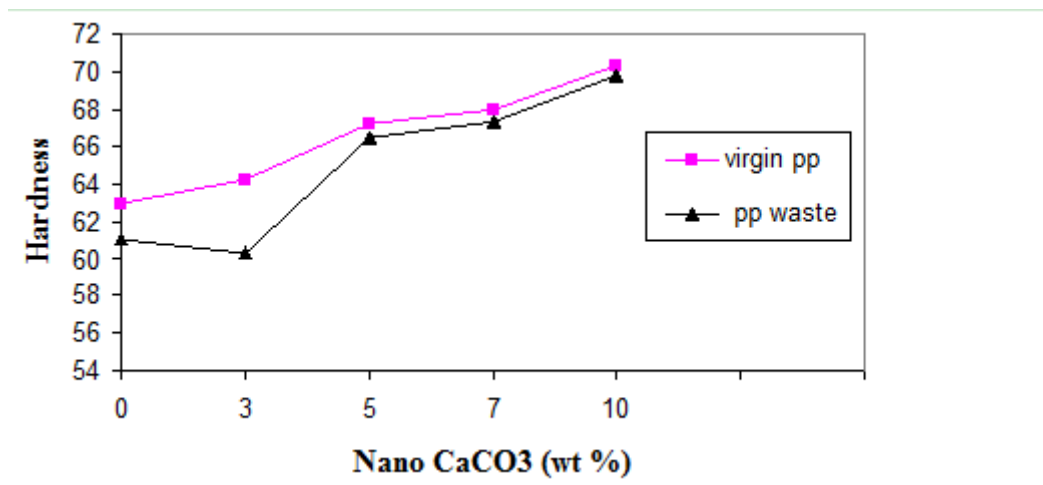


Fig. 12:-The Hardness Behavior of virgin pp. and its waste with Different nano CaCO₃ Percentage at (50 rpm)

Conclusion

From this study, it can be conclude that

The tensile strength , impact strength , density and hardness of pure waste pp. are lower than that of pure virgin pp. due to multi-melting processes which performed to the waste pp. After each melting process the molecular weight or chain length reduce by half , because of shear and extensional stress. In general elastic modulus , hardness , impact strength and density are increasing with nano CaCO₃ concentration increasing for virgin and waste pp. At 25 rpm the shifting in the value of all properties is approximately constant , while at 50 rpm the shifting is change due to betterdistribution of CaCO₃ nanoparticles at 25 rpm. The nanocomposites of virgin pp./CaCO₃ indicate decreasing in tensile strength while this value increasing for waste pp./CaCO₃ nanocomposites at 25 and 50 rpm.The tensile strength of waste pp. is a very important result.

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