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The Effects of Adding Nano-Calcium Carbonate Particles on the Mechanical and Shrinkage Characteristics and Molding Process Consistency of PP/nano-CaCO₃ Nanocomposites

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1. Introduction

The performance characteristics of plastic injection molded parts are depended upon the compositions of processing raw materials, parts and molds design specifications as well as the processing conditions. By appropriate incorporation of additives into a polymer matrix, it is possible to achieve the desired characteristics in the molded parts. Polypropylene (PP) is a semi-crystalline thermoplastic and is widely used for general applications. PP possesses the advantages of processing ease, very resistant to moisture absorption, and good chemical resistance to solvents. However, its applications as an engineering thermoplastic are limited due to its high shrinkage rate and relatively poor impact resistance at room or low temperatures (Lam et al., 2009).

Recent developments in fillers and reinforcements technology have made it possible to enhance the properties and applications of PP. In formulating different compositions of materials, it is essential to bring into account the cost effectiveness, adding value, ease of processing and wide range of applications. Types, shapes, concentrations and dimensional conditions of fillers and reinforcements may directly affect the processing ease, production consistency, molding cycle time, parts dimensional conditions, mechanical, thermal as well as tribological properties. Platelike and layered particles may lead to poor impact strength, and the impact resistance is in reverse proportion to particle size (DeBoest, 1988; Mohd Ishak et al., 2008). These fillers may act either as sites of stress concentration or micro cracks initiator. Micron-sized spherical fillers such as CaCO₃ have marginal influence on the impact resistance (DeBoest, 1988). While nano-sized CaCO₃ may act as a nucleating agent (Avella et al., 2006) and impact modifier (K. Yang & Q. Yang, 2006) in a polymer matrix. 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. The nanoparticles may also initiate micro-void formations which locally deform the matrix surrounding the particles and initiate mass plastic deformation and, in consequence, increase the toughness and impact energy (Kemal

et al., 2009). Stiffness or Young's modulus can be readily improved by adding either micro- or nano-particles since rigid inorganic particles generally have a much higher stiffness than polymer matrices. However, strength strongly depends on the stress transfer between the particles and the matrix. For well-bonded particles, the applied stress can be effectively transferred to the particles from the matrix; this clearly improves the strength (Fu et al., 2008).

Due to its non-polar chemical structure, PP interacts poorly with the typically polar fillers such as CaCO_3 , and optimum dispersion is normally difficult to achieve. Compatibilisers are frequently used to improve the interfacial adhesion between CaCO_3 and PP, in order to gain the envisaged enhancement in mechanical properties (Fuad et al., 2010). Bi-functional molecules such as maleic-anhydride grafted PP (PP-g-MAH) are commonly used as compatibilisers for PP and CaCO_3 (Roberts & Constable, 2003).

The crystallographic morphology of PP matrix can be noticeably altered by the presence of nano- CaCO_3 because of its nucleating effect (Lin et al., 2011; Zhang et al., 2004). The coated CaCO_3 nanoparticles affect the crystallization of PP in two ways: by serving as heterogeneous nucleation sites and also by reducing the spherulitic growth rate due to block the diffusion of polymer chains. Heterogeneous nucleation is, however, the dominating step controlling the crystallization rate of the PP/ CaCO_3 nanocomposite blends (Lin et al., 2011).

Besides mechanical properties, thermal contraction and uniformity of molded samples may also be influenced by different concentrations of the nano- CaCO_3 in PP matrix. The objective of this research is to determine mechanical performances, shrinkage behavior and at the mean time the injection molding consistency of PP filled with nano- CaCO_3 particles. In this research, PP/nano- CaCO_3 polymer nanocomposites of different compositions were prepared by using a twin-screw extruder. PP-g-MAH compatibiliser was applied to improve the interfacial interaction between nano- CaCO_3 and PP, and to extend the dispersion of nanoparticles in polymer matrix. An injection molding machine was employed to produce the standard specimens. The melt pressure inside the mold cavity was measured during the injection molding process of PP- CaCO_3 nanocomposites to assess the production consistency. Dimensional conditions of different samples were characterized in order to determine the effect of nano- CaCO_3 inclusion on the shrinkage rates. Morphology was observed and tensile, flexural and impact properties were examined to ascertain the influence of nano- CaCO_3 on the mechanical performances.

2. Experimental procedures

2.1 Material used, compounding and sample preparation

Polypropylene (PP500P, SABIC) has melt flow rate of 3.1 (2.16 kg at 230 °C) and density of 905 kg/m³ was used as matrix resin. Nano-sized synthetic ultrafine surface treated precipitated calcium carbonate (Socal 312, Solvay, France) with mean particle diameter of 70 nm used as filler phase. PP-g-MAH compatibiliser (Priex 20097, Solvay, France) with a maleic anhydride content of 0.05 wt % and MFI of 15 (2.16 kg at 230 °C) was employed to promote the interfacial interaction between nano- CaCO_3 and PP, and to extend the dispersion of nanoparticles in polymer matrix. Compounds used as processing materials are listed in the table 1.

Material	PP (wt%)	nano-CaCO ₃ (wt%)	PP-g-MAH (wt%)
PP	100	0	0
P5	94	5	1
P10	88	10	2
P15	82	15	3

Table 1. List of various compounds used in the experimentations

The neat PP and PP-g-MAH were dried in a vacuum oven at 80°C for 6 hours. Melt extrusion technique was applied to produce different compositions of PP/nano-CaCO₃ by a ZSK-25 (Coperion Werner Pfliederer-Germany) co-rotating twin-screw extruder (D= 25 mm, L/D = 40) with a barrel temperature profile ranging from 160°C near the hopper to 200°C at the die and a screw speed of 400 rpm.

Molded samples utilized throughout the experimentations comprised standard tensile (ASTM D-638), flexural (ASTM D-790) and impact (ASTM D-256) specimens. An advanced microprocessor control injection molding machine (Poolad-110/380) with clamping force capacity of 110 tones and shot size capacity of 268 grams was employed to produce corresponding samples. The reciprocating screw diameter was equal to 45 millimeters and the ratio of screw length to diameter was 20. The values of molding parameters settings for standard tensile, flexural and impact specimens are given in table 2. The values of different settings were obtained on the basis of dimensional conditions of molds cavities and feed channels and in a manner to produce samples free of defects.

Molding Parameter	Unit	Value for tensile specimens	Value for Flexural and impact specimens
Nozzle Temperature	°C	180	180
Mold Temperature	°C	40	40
Injection Pressure	MPa	57	89
Injection Speed	cm ³ /s	68	68
Holding Time	s	8	15
Holding Pressure	MPa	32	63
Screw feeding speed	rpm	108	108

Table 2. The values of molding parameters settings for standard tensile, flexural and impact specimens

2.2 Characterization

2.2.1 Molding process consistency

The uniformity of injection molding process of different compounds was characterized by melt pressure measurement inside the mold cavity. A piezo-electric sensor (9221 AA0.6, Kistler, Switzerland) incorporated inside the tensile mold cavity and located behind and in contact to the ejector pin to measure the force exerted to the pin by melt pressure during the cyclic molding process against the time. The influence of nano-CaCO₃ inclusion in the PP

matrix resin on the sameness of pressure-time profiles and hence the variation of molding process was investigated. Two variables encompassing the maximum force and the force-time integral were chosen as the control parameters to assess the consistency of injection molding process during the molding cycles. For each compound, 10 samples were examined and the mean values of control parameters were considered.

2.2.2 Dimensional conditions

Standard tensile specimens (ASTM D-638) of PP with different contents of nano-CaCO₃ were molded and employed to analyze the dimensional conditions and shrinkage rates. Figure 1, indicates the reference dimensions and their locations for shrinkage estimation of corresponding molded parts. The reference dimensions of matching cavity including cavity length, width and depth were equal to the 165.83, 19.10 and 3.20 millimeters respectively. The molded parts reference dimensions including parts length, width and thickness were measured with 0.01 mm accuracy after passing two weeks of molding. The differences of cavity dimensions and molded parts dimensions were considered as shrinkage values. For each compound, 5 samples were tested and the mean values were taken into account.

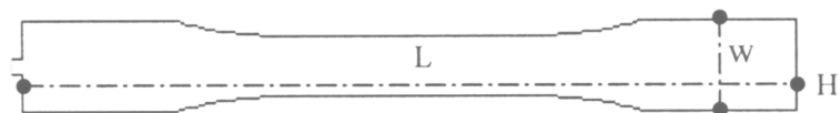


Fig. 1. Reference dimensions and their locations for shrinkage assessment of part length (L), part width (W) and part thickness (H)

2.2.3 Mechanical properties

Tensile, flexural and impact tests were performed based on the ASTM D-638, ASTM D-790 and ASTM D-256 standards respectively in order to analyze the effect of adding nano-CaCO₃ particles on the mechanical performances of PP/CaCO₃ nanocomposites. For each compound, 5 samples were tested and the mean values were considered. The specifications of testing equipment and conditions are presented in table 3.

Tensile test	
Manufacturer: Zwick/Roll	Model: TIFR010THA50
Load range: 0.5 g to 3000 kg	Adjusted load sensitivity: 0.5 g
Speed range: 1 to 200 mm/min	Adjusted crosshead speed: 50 mm/min
Impact resistance test	
Manufacturer: Gotech	Model: GT-7045-I
Capacity: 100 kg-cm	Test type: Izod-type
Flexural strength test	
Manufacturer: Gotech	Model: GT-7010A2
Load range: 3000 kg	Speed range: 10 to 200 mm/min
Extension range: 10.00 mm	Span: 30.00 mm
End point: 7.00 mm	Adjusted speed: 10 mm/min

Table 3. The specifications of mechanical properties testing equipment and conditions

2.2.4 SEM

A scanning electron microscope (Tescan VegaII) was employed to observe the dispersion of nano-CaCO₃ particles in PP matrix in the fracture sections of impact specimens. Prior to SEM observations, the samples were made conductive by gold sputtering.

3. Results and discussions

3.1 Melt flow rate

Figure 2, indicates the melt flow rates of different compounds of PP/nano-CaCO₃ with respect to the nano-CaCO₃ contents.

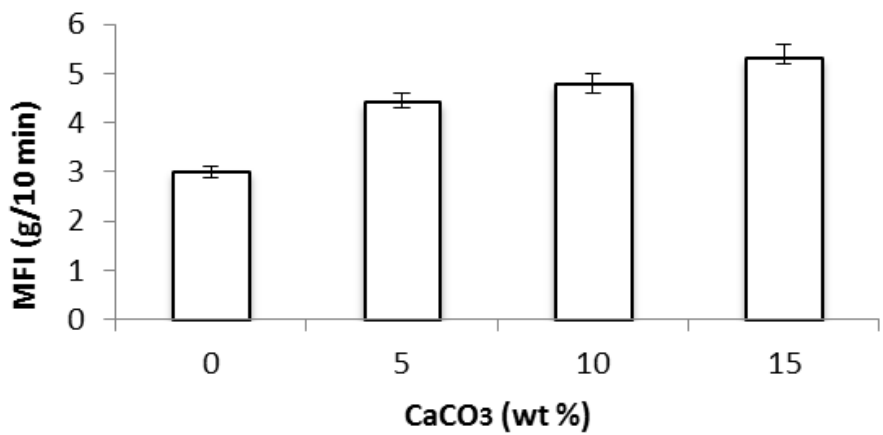


Fig. 2. Melt flow rate versus nano-CaCO₃ contents

Inclusion of nano-CaCO₃ considerably raised the melt flow rate. The presence of nano-CaCO₃ in the molten PP has a rolling effect which facilitates sliding of melt on the cylinder wall of MFI tester (Jiang & Huang, 2008). According to Xie et al., spherical nanoparticles serve as ball bearings, reducing the interlayer interaction of melts (2004). The increment of MFI rate can facilitate the injection molding of thin-walled parts and can lead to the reduction of energy consumption of molding process.

3.2 Injection molding uniformity

The results of melt pressure measurement during the molding cycles for different compounds are indicated in table 4 and figure 3.

Material	Integral (N-s)		Max. Force (N)	
	Ave. Value	Std Dev.	Ave. Value	Std Dev.
PP	4953.29	133.30	843.28	8.75
P5	4923.87	138.26	820.49	11.20
P10	4894.25	50.45	826.49	7.49
P15	4468.54	52.53	800.05	4.46

Table 4. The magnitudes of control parameters and their deviations during the molding process

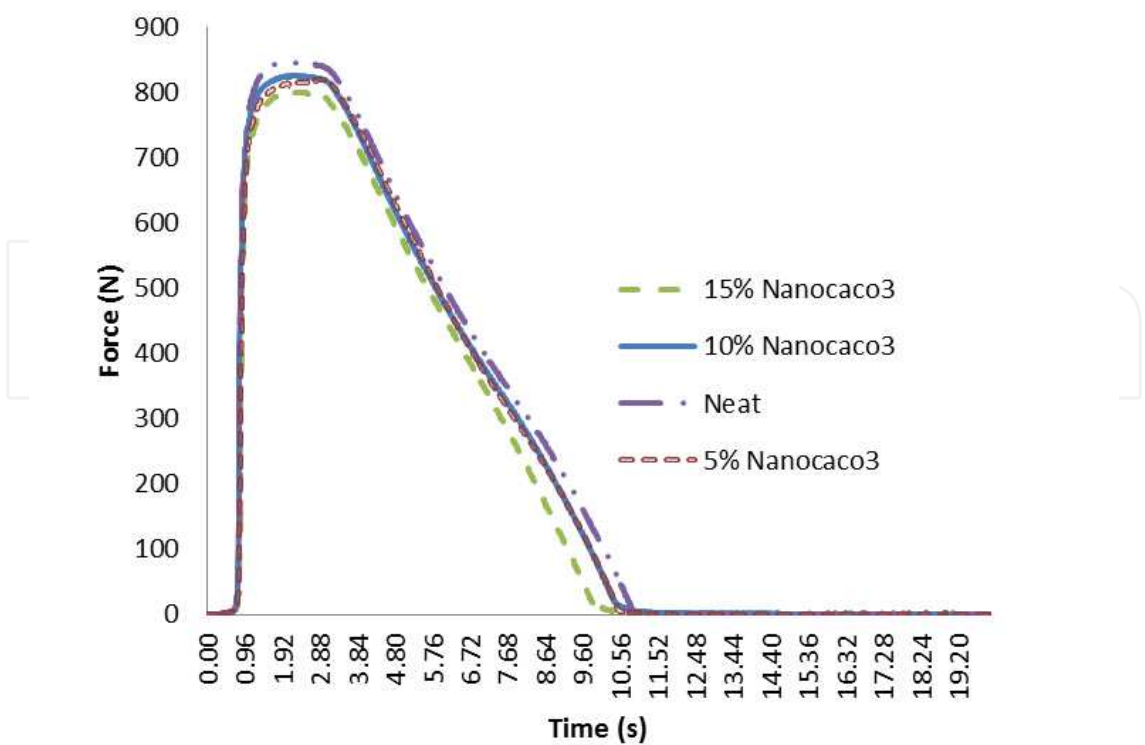


Fig. 3. Force-time traces of different compounds

As the nano-CaCO₃ loading was increased, the maximum force and the force-time integral were decreased. This may be attributed to the influence of nano-CaCO₃ on melt fluidity and crystallization behavior of PP matrix. By incorporating higher loading of nano-CaCO₃ (10 and 15 wt%), the deviation of molding process was significantly declined. By adding 15 wt% of nano-CaCO₃, the maximum force standard deviation dropped from 8.75 to 4.46 (N) and the force-time integral standard deviation declined from 133.30 to 52.53 (N-s). According to the figure 3, by increasing the nano-CaCO₃ content in the PP matrix, a change in the slope on the right side of force-time profile is observed. This may possibly be related to the increase of PP crystallinity and, in consequence, higher thermal contraction of melt during the molding process, as a result of nano-CaCO₃ presence.

3.3 Shrinkage behavior

Table 5, indicates the shrinkage rates along the flow, across the flow, and along the thickness of molded parts with respect to the amount of nano-CaCO₃ content.

nano-CaCO ₃ (wt%)	Ave. Shrinkage along the flow (%)	Ave. Shrinkage across the flow (%)	Ave. Shrinkage along the flow thickness (%)
0	1.64	1.74	5.00
5	1.42	1.50	4.93
10	1.51	1.65	4.87
15	1.53	1.64	4.62

Table 5. Effect of nano-CaCO₃ concentration on the shrinkage of PP/nano-CaCO₃

The neat PP possessed the highest shrinkage rate. The inclusion of nano-CaCO₃ reduced the thermal contraction because of its filling effect and its lower thermal contraction. The molded samples with concentration of 5 wt% nano-CaCO₃ possessed the lowest shrinkage along the flow and across the flow directions. Addition of higher values of nano-CaCO₃ (10, 15 wt%) to the PP, elevated the shrinkage rates along and across the flow directions. Nano-CaCO₃ has nucleating effect and can lead to the increment of crystallization rate in the PP matrix (Chan et al., 2002; K. Yang & Q. Yang, 2006). Addition of higher values of nano-CaCO₃ (10, 15 wt%) to the PP, slightly increased the tendency of non-isotropic thermal contraction along and across the flow directions. This can possibly be related to increment of PP crystallinity as a result of higher loadings of nano-CaCO₃, and non-isotropic crystal growth of PP Matrix.

3.4 Morphology

Figure 4, indicates the presence and distribution of nano-CaCO₃ (5 and 15 wt%) in the PP matrix in the cross sections of impact test samples. Higher concentration of nano-CaCO₃ particles is observed in the PP matrix with higher content, i.e. 15wt%, of nano-CaCO₃. Due to the surface modification of nano-CaCO₃ and application of PP-g-MAH compatibiliser, relatively good dispersions of nanofillers were achieved. According to figure 4-b, more tendency to agglomerate is observed at 15 wt% loading of nano-CaCO₃.

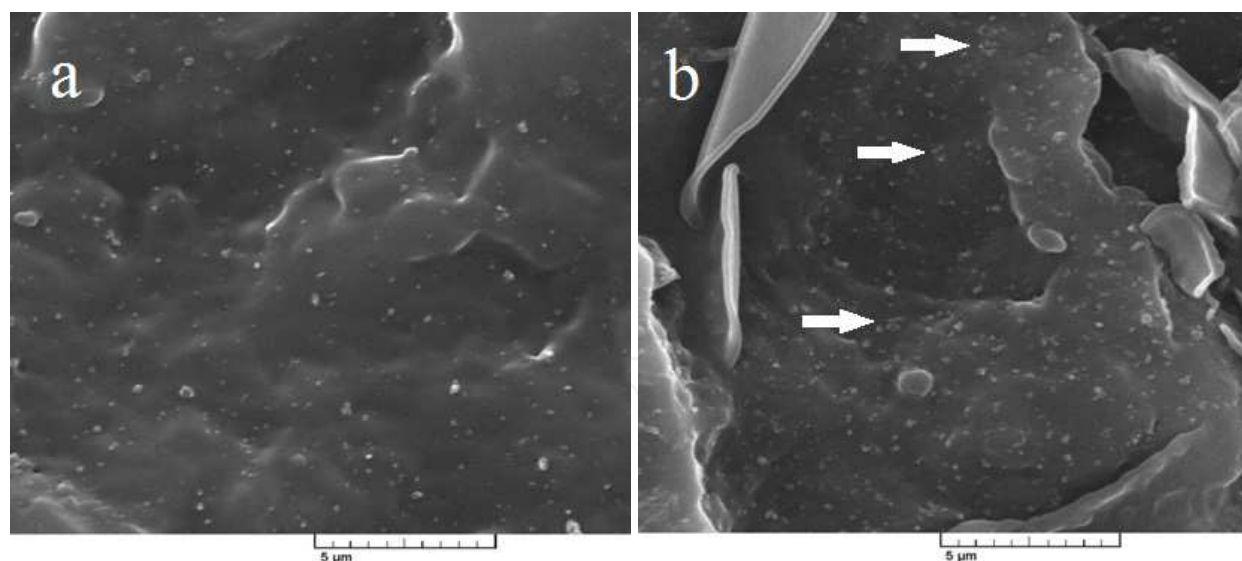


Fig. 4. Morphologies of PP/nano-CaCO₃ at two loadings of (a) 5 and (b) 15 wt% of nano-CaCO₃

3.5 Mechanical properties

The tensile tests results of various compounds of PP/nano-CaCO₃ are indicated in Table 6 and Figures 5 and 6.

Material	Ave. Elastic modulus (Mpa)	Ave. Tensile Strength (Mpa)	Ave. Strength at break (Mpa)	Ave. Elongation at break (%)
PP	960.17	36.04	19.81	75.03
P5	971.65	35.67	11.62	122.88
P10	983.94	34.64	6.81	161.29
P15	990.41	33.80	7.58	118.87

Table 6. The results of tensile tests

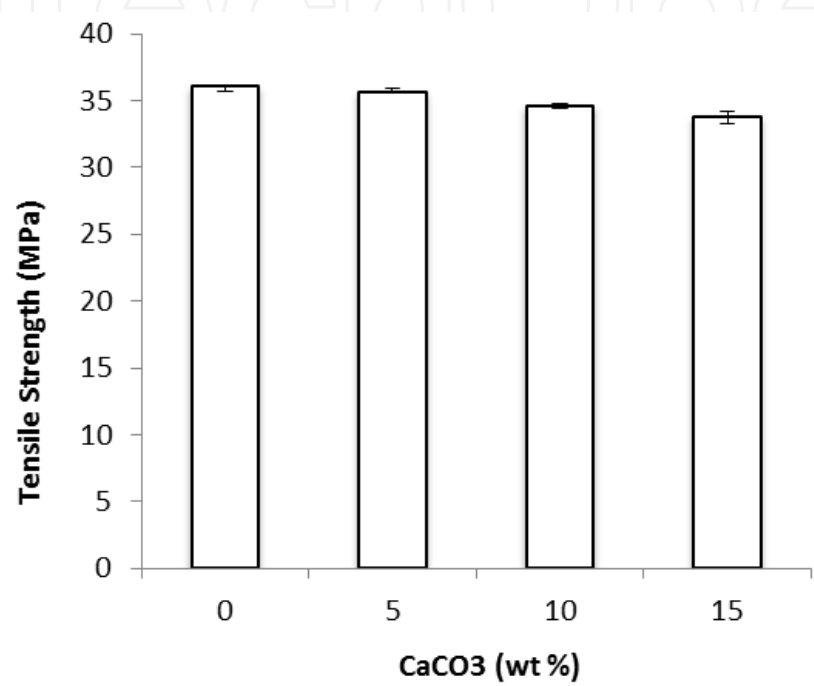


Fig. 5. Tensile strength of PP/nano-CaCO3 against nano-CaCO3 content

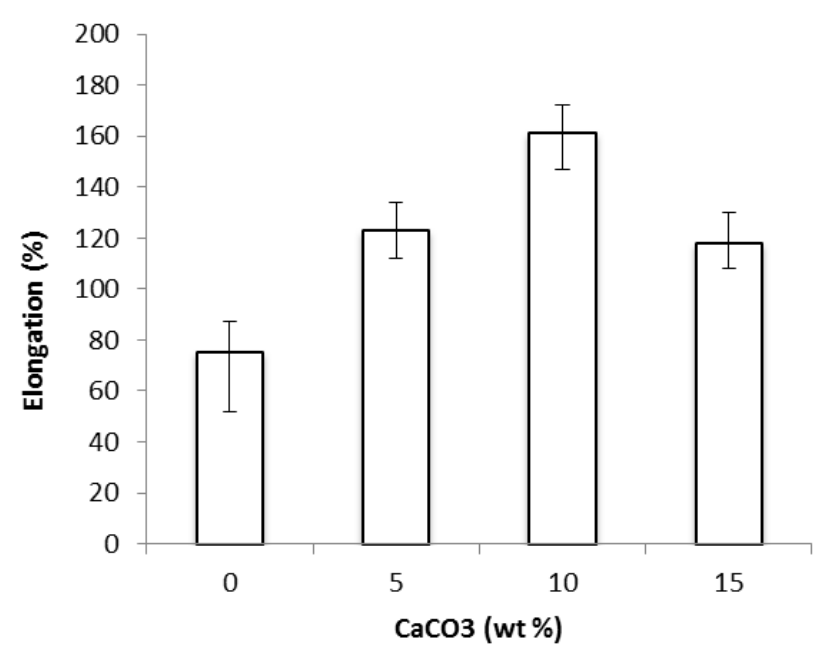


Fig. 6. Elongation of PP/nano-CaCO3 against nano-CaCO3 content

Figure 7, Compares the stress-strain characteristics of median specimens of different compounds.

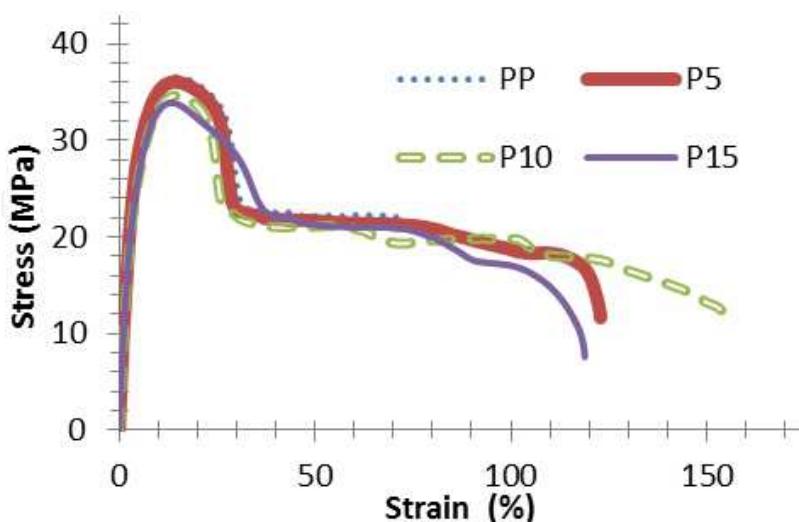


Fig. 7. The influence of adding nano-CaCO₃ on the stress-strain behavior of PP/nano-CaCO₃

The results of tensile tests revealed that the inclusion of nano-CaCO₃ slightly increased modulus and decreased tensile strength and significantly increased the elongation at break. Addition of rigid particles to a polymer matrix can easily improve the modulus since the rigidity of inorganic fillers is generally much higher than that of organic polymers (Fu et al., 2008). The reduction of tensile strength may be attributed to the weakly bonded nanoparticles which promote matrix yielding (Kemal et al., 2009). According to Zhang et al., when CaCO₃ particles were introduced, small and imperfect spherulites formed. The reduction of spherulite size and the disappearance of sharp interfaces among spherulites favored the increase of elongation at break for the PP/CaCO₃ composites (2004). Xie et al. reported that the increases in elongation at break can be attributed to ellipsoidal voids formation in the matrix surrounding the particles, allowing ductile pull out (2004). At high fraction of nano-CaCO₃ (i.e. 15 wt%), the elongation at break was declined. This result is consistent with the morphology of corresponding compound which shows agglomeration sites of nano particles in the PP matrix as presented in figure 4-b.

Figure 8 depicts the results of flexural tests.

The incorporation of nano-CaCO₃ led to the elevation of flexural strength in PP/nano-CaCO₃ compounds. This may also be related to the nucleating effect of nano-CaCO₃ in the PP matrix. Figure 9 shows the impact tests results.

Addition of nano-CaCO₃ elevated 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. Additionally, the presence of nano-CaCO₃ may influence the crystallization behavior by reducing the spherulites size and subsequently alter the impact strength. Kemal et al. reported that the raise of toughness and impact energy may be attributed to enhanced micro-void formations initiated by nanoparticles, which locally deform the matrix surrounding the particles and initiate mass plastic deformation (2009).

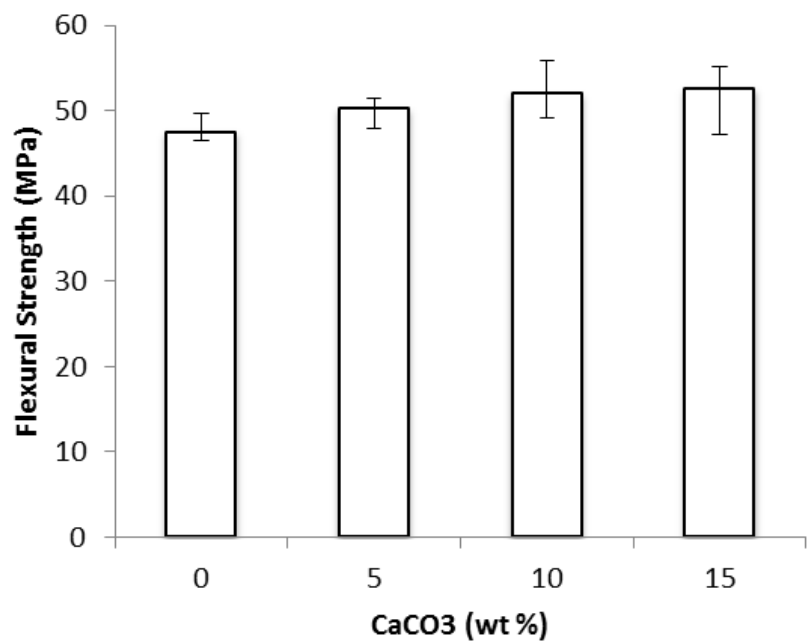


Fig. 8. Flexural strength of PP/nano-CaCO3 versus nano-CaCO3 content

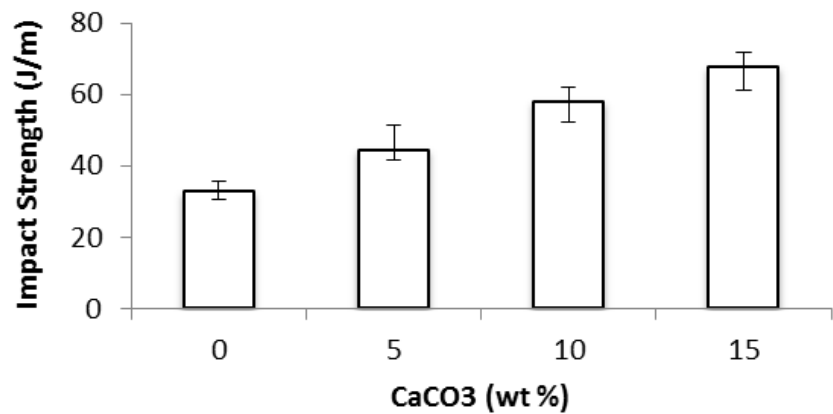


Fig. 9. Impact strength of PP/nano-CaCO3 versus nano-CaCO3 content

4. Conclusion

In this study the influences of nano-CaCO3 on the production consistency, shrinkage and melt flow rates, as well as mechanical properties of PP/nano-CaCO3 nanocomposites were experimentally investigated. PP-g-MAH compatibiliser with a maleic anhydride content of 0.05 wt% was employed to improve the interfacial adhesion between nano-CaCO3 and PP and to extend dispersion of nanoparticles in polymer matrix. Inclusion of nano-CaCO3 raised the melt flow rate as high as 77%. By incorporating higher loading of nano-CaCO3 (10 and 15 wt%), the deviation of molding process was significantly declined. The molded samples with concentration of 5 wt% nano-CaCO3 possessed the lowest shrinkage along the flow and across the flow. The results of tensile tests revealed that the inclusion of nano-CaCO3 slightly increased modulus and decreased tensile strength and significantly increased the elongation at break. At high fraction of nano-CaCO3 (i.e.15 wt%), the elongation at break was declined. Addition of nano-CaCO3 elevated the impact strength as

high as 107%. The nano-sized feature, shape and dispersion conditions of nano-CaCO₃, played important roles in determining the performances of PP/nano-CaCO₃.

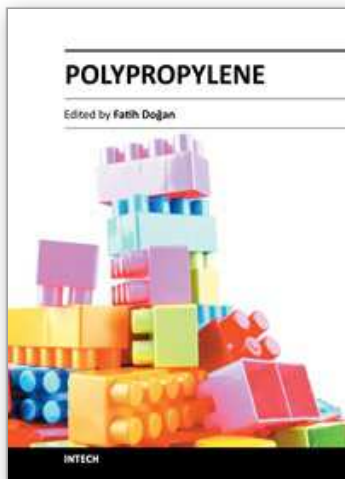
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This book aims to bring together researchers and their papers on polypropylene, and to describe and illustrate the developmental stages polypropylene has gone through over the last 70 years. Besides, one can find papers not only on every application and practice of polypropylene but also on the latest polypropylene technologies. It is also intended in this compilation to present information on polypropylene in a medium readily accessible for any reader.

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