

Investigative Study of Structural morphology of Polypropylene and BaCo₃ – Nanoparticle Composites

P.S.V.Shanmukhi¹, Dr.K.Chandramouli², Dr.P.V.S.Machiraju³

1 & 2. Department of Engineering Physics, A.U. College of Eng. (A) Andhra University, Visakhapatnam-530003, A.P, India

3. Department of Chemistry, Pragati Engineering College (A), Surampalem, -523437, A.P. India.

Abstract

The aim of the present study is to introduce nano particle BaCo₃ (NPBC) in isotactic polypropylene (ipp) with filler contents percentages of 1%, 3%, 5% & 10% wt. respectively and to verify the effect of nanoparticle BaCo₃ on morphological properties of injection molded iPP. Melt mixing technique is used for the fabrication of nano particle composites, where BaCo₃ nanoparticle powder is mixed with PP and heated at a temperature of 200^oc for 15 minutes and dried. The solidified products were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) for structural conformation. It has been concluded that with an increase in the filler loadings, the width of a strong peak of PP i.e.; (221) decreased up to 5% weight of PP then after it increased, which results in increase of the percentage of crystallinity of the nanocomposite up to 5% weight of the filler loadings after that the decrement is due to the agglomeration of BaCo₃ nano particles in the host PP matrix.

Keywords X-ray diffraction (XRD), scanning electron microscope (SEM), isotactic polypropylene (ipp), Nanoparticle Barium carbonate (NPBC), Polypropylene (PP), nanocomposites.

I. INTRODUCTION

The process of toughening polymers which exist as semi crystalline polymers with the addition of inorganic filler involves stress concentration, debonding of polymer [1]. In the formed composite the filler acts as stress concentrator in the matrix due to deformation and difference between elastic behaviours of different phases. Recently the polymer nanocomposites have attracted attention due to their significant improvement in mechanical characteristics, thermal stability and electrical properties over the matrix polymers [2]. The effects of filler nanoparticles on these properties have been extensively investigated. It has been identified that the addition of nanoparticles with a few percentages by weight can result in significant improvement in physical and chemical properties [3]. However the advantages are associated only when filler nanoparticles are dispersed homogeneously and do not aggregates in the polymer matrix [4]-[5]. Literature survey revealed that several researchers attempted to modify polymer materials by filling with

nano metric inorganic rigid particles, previous research studies revealed that calcium carbonate (CaCo₃) as one of the most commonly used inorganic filler in polymers like polypropylene[6],[7]. The studies also reported their wide range of applications like sewer pipes, garden furniture, breathable films, etc; it has also been reported that addition of CaCo₃ nanoparticles could improve the thermal and mechanical properties of polypropylene (PP) [8].

The objective of the present study is to introduce nano particle BaCo₃ (NPBC) in isotactic polypropylene (ipp) with filler contents percentages of 1%, 3%, 5% & 10% respectively and to verify the effect of nanoparticle BaCo₃ on morphological properties of injection molded iPP.

II. MATERIAL AND METHODS

The powdered form of nano particle BaCo₃ and NPBC+PP nanocomposites with NPBC filler loadings of 1%,3%,5% & 10% weight of polypropylene were prepared to verify the effect of filler content and to investigate the relationships between isotactic polypropylene and Barium carbonate nanoparticle combinations. The polymer matrix material that used in this study is a commercial grade isotactic polypropylene supplied by SIGMA-ALDRICH, USA.

A. Preparation of BaCo₃ nano Powder

0.1M BaCo₃ (100ml) aqueous solution was mixed with of Sodium bicarbonate (100ml) and stirred for 2 hours and washed with water for four times using centrifuge at 5000 rpm and dried at 60^oC to obtain the required nanoparticle BaCo₃ powdered form. It has been confirmed by Scherrer's formula that the average particle size of BaCo₃ is in nano metric scale.

B. Preparation of BaCo₃ +Polypropylene Nanocomposites

The choice of processing technique plays an important role to achieve the desired improvement in the properties of interest [9]. The efficiency of processing techniques is to disperse the filler which has very strong tendency to agglomerate due to their high surface energies [10]. The two common melt processing techniques employed to produce nanocomposites are melt- mixing using internal mixer and melt-extrusion using a twin-screw extruder. It has

been reported that nanocomposites of PP with nano-sized CaCO_3 have been successfully prepared via melt-mixing by Chan et, al [2]; The good filler dispersion obtained by using the internal mixer has resulted in significant improvement in modulus and impact strength with only slightly lowering of the tensile strength. For higher filler loadings more than 10% weight of PP, the extrusion technique is more effective to disperse the nano filler resulting in better impact properties [11]. Since our composites are up to 10% weight. of polypropylene only, ie; the filler loadings are $\leq 10\%$ wt. of PP, the internal mixer method is employed.

In the present technique 10 gm of PP was heated at 200°C for 15 minutes and BaCO_3 nano powder with various concentrations of 1%,3%,5% and 10% weight. of PP were mixed. The resultant mixtures were stirred for 15 minutes, it is cooled for solidification. The solidified products were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) for structural conformation.

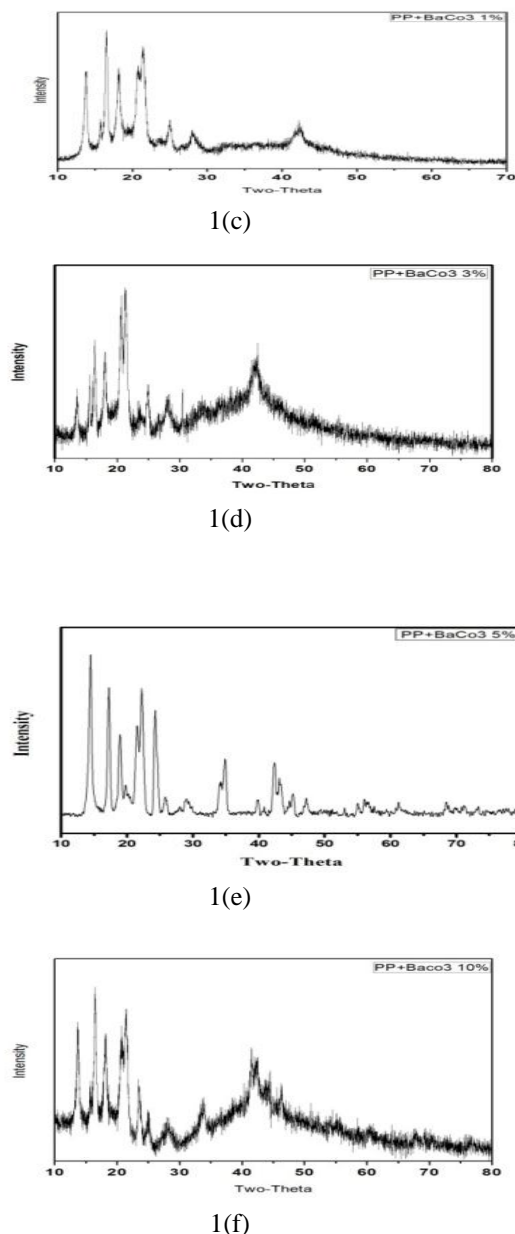
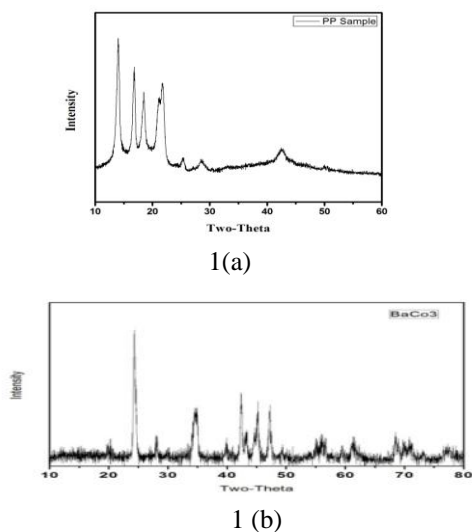
III. RESULTS

A. Characterization of PP+NPBC Composites

1) X-ray Diffraction (XRD) Measurements

XRD measurements are performed on Bruker’s AXS Model D8 Advanced Powder X-ray Diffractometer instrument operated with copper (Cu) of K_α radiation as X-ray source with wavelength of $\lambda=1.45\text{\AA}$ for the analysis of the phase of the products. The XRD diffractograms of pure PP, pure BaCO_3 and nano composites of PP filled with BaCO_3 nanoparticles with filler loadings of 1, 3, 5, 10% weight of PP are given in figures 1(a) to 1(f) respectively. The peak identification of the nanocomposites was performed by using X-ray diffraction (XRD).

Fig.1: XRD diffractograms of (a) pure PP (b) pure BaCO_3 (c) PP+1% BaCO_3 (d) PP+3% BaCO_3 (e) PP+5% BaCO_3 & (f) PP+10% BaCO_3 .



The average crystallite size of the BaCO_3 was measured by x-ray line broadening technique employed by Scherrer formula. There are strong peaks of orthorhombic structure of BaCO_3 in this XRD pattern due to drastic increase on the temperature [12]. The Bragg’s peaks of the crystallized powders correspond to each sample agree well with the reflections of pure orthorhombic BaCO_3 single phase (witherite) with $a=5.314\text{\AA}$ and $b=8.904\text{\AA}$ [13]. XRD patterns of all present samples of nanoparticle Barium carbonate polypropylene (NPBC+PP) show that intensities of basic peaks of the (111), (002), (221) and (131) planes are more than the other peaks[14]. The crystallite size was estimated from the broadening peaks using Scherrer’s formula

$$d_{\text{XRD}} = \frac{k\lambda}{\beta \cos\theta}$$

Where ‘ θ ’ is the Bragg’s angle of diffraction line; in fact ‘ 2θ ’ must be substituted directly instead of θ in

the formula. ‘k’ is the shape factor taken as 0.94 assuming that the crystallites are spherical in shape. ‘λ’ is the wavelength of incident X-rays ($\lambda = 1.54056 \text{ \AA}$ for K_{α} of ‘Cu’) and ‘β’ is the full – width at half maximum (FWHM)[14]. From XRD patterns and Table-1, it may be concluded that with an increase in the filler loadings, the width of a strong peak of PP i.e.; (221) decreased up to 5% weight of PP then after it increased, which results in increase of the percentage of crystallinity of the nanocomposite up to 5% weight of the filler loadings after that the decrement is due to the agglomeration of BaCo_3 nanoparticles in the host PP matrix. The details of XRD patterns of BaCo_3 nanoparticles with various percentages viz; 1%, 3%, 5% and 10% wt. of PP are presented in table-1.

lattice strain is very less at the filler loading of 5% weight of NPBC. It shows there are a good crystalline formation and good nanoparticle dispersion in the nanocomposite of PP+5% BaCo_3 when compared to other composites.

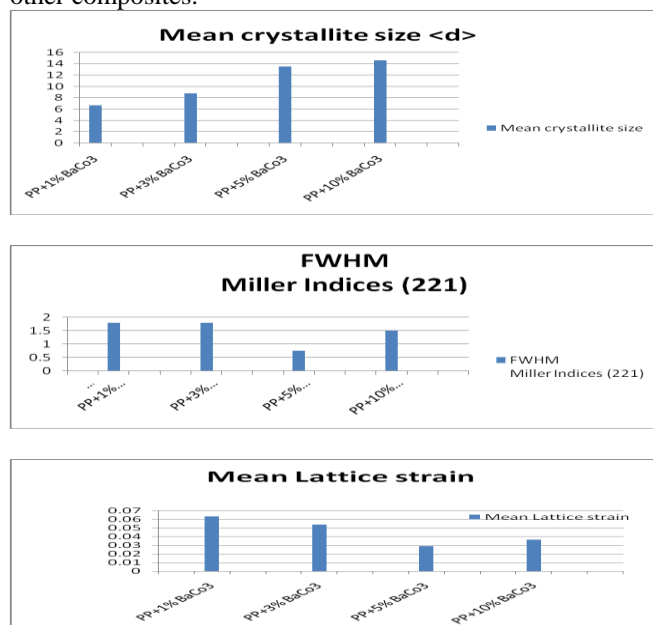


Table-1: Details of XRD patterns of nano composites in different crystallography orientations with different filler loadings of PP.

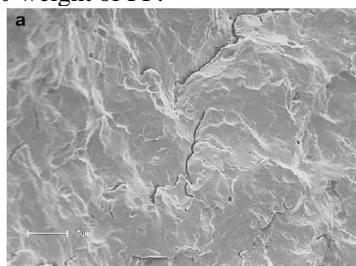
Sample (composite)	Miller Indices (hkl)	2 θ	FWHM	d (nm)	Mean crystallite size $\langle d \rangle$ (nm)	Lattice Strain	Mean Lattice strain
PP+1% BaCo_3	(111)	25	0.8955	9.49	6.73	0.0176	0.0637
	(002)	28.507	1.492	5.74		0.0256	
	(221)	41.79	1.791	4.96		0.0205	
PP+3% BaCo_3	(111)	25	0.597	14.24	8.787	0.0118	0.0538
	(002)	27.388	1.194	7.16		0.0214	
	(221)	41.47	1.791	4.96		0.0206	
PP+5% BaCo_3	(111)	24.4	0.597	14.23	13.567	0.012	0.0288
	(130)	34.701	0.5970	14.56		0.0083	
	(221)	41.79	0.746	11.91		0.0085	
PP+10% BaCo_3	(111)	23.507	0.2985	28.41	14.68	0.0063	0.0363
	(130)	34.104	0.8955	9.7		0.0127	
	(221)	41.194	1.4925	5.94		0.0173	

The mean crystallite sizes ($\langle d \rangle$) for the samples as determined by the Scherrer’s formula are presented in table-1. The average values of d_{nm} indicate the mean crystallite sizes are in nano metric orders. The values determined by Scherrer’s formula and XRD generated data also confirms the composite materials are in nano metric sizes. Increase in average crystallite sizes with increase in the percentage of filler content confirms the formation of crystalline structure in the polymer composite. It is also observed from the data given in the Table-1, the

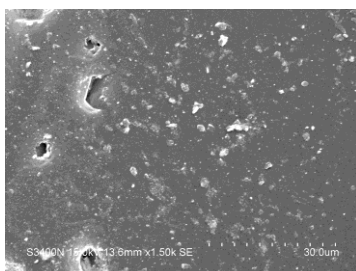
2) **Surface Morphology**

Scanning electron microscopy (SEM) is employed to study the morphology to investigate the impact fracture surfaces of the nanocomposites by Hitachi Model S4700. The dispersion of nanoparticles will have a significant effect on the mechanical properties of the nanocomposites [15]-[16]. The morphology of nanocomposites is evaluated by scanning electron microscopy (SEM) to observe the distribution of nanoparticles within the materials. SEM images of 1%, 3%, 5% & 10% weight of PP are

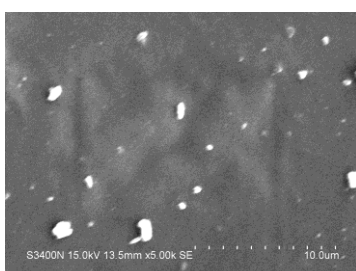
presented in figures from 2(a) to 2(e), which depict the micro graphs of a fractured surface of the nanocomposites for the filler contents. The fractured surface of pure PP is smooth and featureless[17], but fairly good nanoparticle dispersion is seen in the micro graphs of pp with filler loadings of 1%, 3%, 5% & 10% weight of PP.



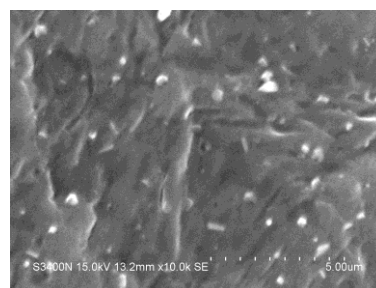
2(a) SEM Image of Pure PP



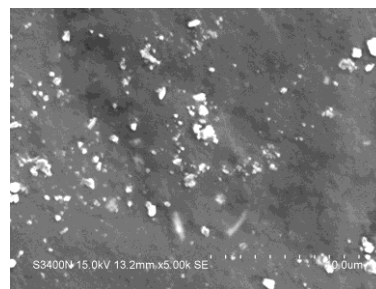
(b) SEM Image of PP+1% BaCO₃ (NPBC)



2 (c) SEM Image of PP+3% BaCO₃ (NPBC)



2(d) SEM image of PP+5% BaCO₃ (NPBC)



2 (e) SEM image of PP+10% BaCO₃ (NPBC)

The dispersion is found to be better for nanocomposites containing 5% w/w BaCO₃ nano particles. With filler content of 10% w/w, aggregates of nanoparticles are found. The SEM images were analysed and observed crystallite sizes were compared with the results obtained from XRD (Scherrer's formula). The average values of crystallite sizes calculated from XRD range from 6-14 nm are in good agreement with the values as seen from SEM micro graphs of NPBC with small differences. This difference in the sizes reveals the fact that: the SEM shows the sizes of clusters or the aggregates of particles where as in XRD the peaks are due to the diffraction of X-rays by the nanoparticles.

IV. CONCLUSIONS

PP+BaCO₃ nanoparticle composites with various filler loadings of 1,3,5, and 10% weight of PP have been successfully synthesized and structurally characterized. They can be utilized in several thermo plastic applications by examining the composites with thermal, mechanical and electrical studies.

REFERENCES

- [1] Daniel Eiras, Luiz Antonio Pessan. "Mechanical Properties of Polypropylene/Calcium Carbonate Nanocomposites", *Materials Research*, Vol. 12, No. 4, 517-522, 2009.
- [2] Y.Lin, H.Chen,C.M.Chan, J.Wu, "Nucleating effect of calcium state coated CaCO₃ nanocomposites on polypropylene", *J.Colloid interface Sci*; 354(2), pp.570-576, 2011.
- [3] S.Karamipour, H.Ebadi-Dehaghani, D.Ashouri, S.Mousavian, " Effect of nano-CaCO₃ on rheological and dynamic mechanical properties of polypropylene: Experiments and models," *Polym.Test*;30,pp.110-117,2011.
- [4] A.Kiss, E.Fekete, B.Pukansky, " Aggregation of CaCO₃ particles in polypropylene composites: Effect of surface coating," *Compos. Sci. Technol*; 67,pp.1574-1583,2007.
- [5] Thio Y.S; Argon A.S; Cohen R.E; Weinberg M.: Toughening of isotactic polypropylene with CaCO₃ particles. *Polymer*,43,3661-3674(2002).
- [6] J.Z.Liang, " Evaluation of dispersion of nano-CaCO₃ particles in polymer matrix based on fractal method." *Compor. Part A: Appl.Sci. Manuf*; 38(6) PP. 1502-1506,2007.
- [7] B.Shentu, J.Li, Z.Weng, "Effect of oleic acid-modified nano-CaCO₃ on the crystallization behavior and mechanical properties of polypropylene", *Chinese J.chem. Eng*; 14,PP.814-818,2006.
- [8] Z.Zhang, e.Wang, Y.Meng, K.Mai, " Sinergistic effects of toughening of nano-CaCO₃, and toughness of β -polypropylene", *compos, Part A : Appl. Sci.Manuf*; 43(1), 189-197, 2012.
- [9] Jordan J; Jacob K.I; Tannebaum R; Sharaf M.A; Jasiuk I.: Experimental trends in polymer nanocomposites – A review. *Material Science and Engineering.A*,393,1-11 (2005).
- [10] Krawczak P.: Compounding and processing of polymer nanocomposites: From scientific challenges to industrial stakes. *Express Polymer Letters*, 1, 188 (2007).
- [11] M.Y.A.Faud, H.Hanim, R.Zarina, Z.A. Mohd.Ishak, Azman Hassan, " Polypropylene/ Calcium carbonate nanocomposites- effects of processing techniques and

- maleated polypropylene compatibiliser,” Express Polymer Letters Vol.No.10(2010) 611-620.
- [12] Amir Zelati, Ahmed Amirabadizadeh, Ahmed Komany, “ Preparation and characterization of Barium Carbonate Nanoparticles”, International journal of chemical Engineering and Applications, vol.2,No.4, (2004).
- [13] M.M.Bagheri-Mohagheghia, N.Shahtah masabia, M.R.Alinejada, A.Youssefic, M.Shokooh-saremi.“The effect of post-annealing temperature on the nano-structure and energy level gap of SnO₂ semi conducting oxide nano particles synthesized by polymerizing-complexing sol-gel method”. Physica B 403 (2008)2431-2437.
- [14] P.Klug, I.E.Alexander, “Diffraction Procedures for Polypropylene and Amorphous materials,” Wiley, New York ,1954.
- [15] P.Mareri, S.Bastide, N.Binda, A.Crespy, “ Mechanical behavior of polypropylene composites containing mineral filler: Effect of filler surface treatment,” Compos.Sci.Technos; 58,pp.747-752, 1998.
- [16] J.Z.Liang, “Evaluation of dispersion of nano-CaCO₃ particles in polypropylene matrix based on fractal method.” Compos.Part A: Appl. Sci. Manuf; 38(6).pp. 1502-1506,2007.
- [17] C.M Chan, J Wu, J.X. Li, Y.K. Cheung, “Polypropylene/calcium carbonate nanocomposites,” polymer , 43, pp. 2981-2992,2002.