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Structural, Morphological Properties of Polypropylene/Strontium Carbonate (Srco₃) Nanocomposites

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ABSTRACT

The present study aimed to investigate the effect of incorporated nanoparticles of Strontium carbonate $(SrCO_3)$ on structural and morphological properties of thermoplastic polymer matrix polypropylene (PP). Strontium carbonate nanoparticles were synthesized and reinforced in polypropylene matrix in order to prepare PP/SrCO₃ nanocomposites with filler loadings of 1%, 3%, 5% and 10% weight of PP by melt-mixing method. The formed SrCO₃ nanoparticles size ranging from 6–9.8 nm was calculated by XRD analysis. The XRD findings are in good agreement with SEM results. Confirmation of nanocomposite formation was obtained by FTIR studies. The studies have revealed that a considerable change in the morphology was observed at SrCO₃ filler loading of 5% weight of PP when compared to other filler loadings for enhanced properties and applications.

Highlights

- First report on the synthesis of nanocomposites based on polyolefin's incorporated with SrCO₃ nanoparticles.
- Structural and morphological studies were carried out with XRD, SEM and FTIR.
- SEM studies were in agreement with XRD reports.
- PP/5% SrCO₃ was found to be the better composite, which has the potential to exhibit good enhanced properties.

Keywords: Strontium Carbonate Nanoparticles, Polypropylene, morphology, nanocomposites.

INTRODUCTION

Designing light weight and high strength materials has become a challenge for researchers for decades. Stress concentration and de-bonding are the key parameters involved during the toughening process of the polymer nanocomposites [1]. Nanocomposites containing low filler loadings like carbon nano tubes and MWNTs exhibit the desired properties compared to the conventional materials [2-5]. Such desired properties could be exhibited when there is a uniform dispersion of the

nanoparticles in the polymer matrix [6], whereas macroscopic particles of same kind of filler cannot provide such enhanced properties [7, 8]. Due to betterment of mechanical, thermal and electrical properties over the other traditional polymers, polymer nanocomposites are attracting the attention of the researchers and industry [9]. In fact the inorganic filler particle will act as stress concentrator in nanocomposite [10]. Nanocomposites have been synthesized by incorporating several inorganic fillers like TiO₂ nano-particles, silver nano-particles, gold nano-particles and zinc oxide nano-particles etc., [11-13]. PP is the most commonly used commodity plastic which has the highest growth rate. Among several fillers CaCO₃ is the most commonly used inorganic fillers in thermoplastic polymer like PP. PP composites find wide range of applications like sewer pipes, garden furniture etc.[14], it has been reported that addition of Calcium carbonate nanoparticles could able to improve thermal and mechanical properties of polypropylene. In early work of Chan *et al.*, studies of mechanical and thermal properties of nano-CaCO₃ filled PP were reported, CaCO₃has been proved as one of the best inorganic filler in various thermo plastic polymers like polyethylene, PVC and polypropylene because of its most availability, low cost and providing more enhanced properties [15-17].

There are several recent reports on PP nanocomposites. Margues et al., [18] have prepared polypropylene/ mica nanocomposites via in-situ polymerization and reported that the thermal stability of the prepared nanocomposite is better than pure polypropylene because of mica's barrier effect against heat. Graphene-modified polypropylene polymer was prepared using two techniques, surface coating and extrusion to improve the electrical and thermal conductivity of polypropylene [19]. Breakage of agglomerations and homogeneous graphene-coated polypropylene pellets were prepared from surface coating technique, where as graphene segregation was observed in latter technique [20]. In another report, polypropylene (PP) nanocomposites were synthesized by reinforcing halogen-free flame retardants with 30 wt% of PP by melt compounding in a twin-screw extruder followed by injection molding technique. Flame retardancy behavior was observed from thermal studies and it was concluded that the PP composite was improved with increasing mineral content, indicating a good compatibility between huntite/hydromagnesite and PP. Shokoufeh Hakim *et al.*, reported in their work thermal degradation of the PVB is improved by blending with PA, while incorporation of nanoclay didn't have any significant effect on thermal stability of the blends in the nanocomposites of PA/PVB blends and PA/PVB/ nanoclay [21]. Polypropylene (PP)/graphene nanoplatelet (GnPs) nanocomposites were synthesized by melt extrusion followed by injection molding. In their studies they have emphasized that the introduction of GnPs in PP provided the necessary crystallization of polymer matrix. Adding of large sized GnPs in small amounts is clearly beneficial for obtaining high electrical conductivity of nanocomposite with enhanced dispersion of fillers [22].

Despite of the global research interest in developing new polymer nanocomposites incorporated with inorganic metallic carbonates,SrCO₃ nanoparticles has not yet been reported. This study is of fundamental importance to create new possibilities to obtain nanocomposites composed of polyolefin's by melt mixing method.Here is an attempt that has been initiated by incorporating strontium carbonate (SrCO₃) nanoparticles in polypropylene (PP) thermoplastic polymer matrixto investigate the structural, morphological and thermal properties of PP nanocomposites with filler loadings 1%, 3%, 5% and 10% wt. of PP by melt mixing method.

MATERIALS AND METHODS

Materials: The polymer matrix used in the present study is a commercial grade isotactic polypropylene supplied by SIGMA-ALDRICH, USA with purity 99.99%. Other chemicals like SrCl₂ and Na₂CO₃ of analytical grade are purchased from Akshay Scientifics Ltd., India.

Preparation of SrCO₃ Nano powder: For the synthesis of SrCO₃ nanoparticle powder, SrCl₂ and sodium carbonate (Na₂CO₃) were used as the starting materials. 100 mL aqueous solution of SrCl₂ of 0.1M was mixed with 100 mL of sodium carbonate, later the mixture was stirred for 2 h. To get purity

the resulted reaction mixture was washed for four times. After that it was centrifuged and dried at 60° C. As a result nanoparticle SrCO₃ was obtained in the form of a powder.

Synthesis of PP/SrCO₃ Nanocomposites: For the synthesis of polypropylene Strontium carbonate nanoparticle composites melt mixing has been considered as the best technique. In the present melt mixing technique 10 gm of PP was heated at 200°C for 15 min and SrCO₃ nano powder of 0.1 gm was mixed. The resulted mixture was stirred for 15 min, after that it was cooled for solidification. As a result a polymer nanocomposite of PP/SrCO₃ with filler loading of nanoparticle SrCO₃ of 1% wt. of PP was obtained. The same procedure was repeated in order to obtain PP/SrCO₃ nanocomposites with concentrations of filler 3%, 5% and 10% wt. of PP.

Methods: Bruker's AXS Model D8 Advanced Powder X-ray Diffractometer was used for XRD measurements which was operated with copper (Cu) of K_{α} radiation as X-ray source with wavelength of λ =1.54056A⁰ for the determination of the phase of the samples. Morphology has been carried out by Scanning electron microscopy using the instrument Hitachi Model S4700.

RESULTS AND DISCUSSION

XRD Analysis: The X-ray diffractograms of pure Polypropylene, pure SrCO₃ and nanocomposites of PP filled with SrCO₃ nanoparticles with filler loadings of 1, 3, 5, 10% weight of PP are as shown in figures 1()a to (f) respectively. By observing diffractograms, diffraction peaks of the nanocomposites were identified. Using Scherrer formula the average crystallite size of the SrCO₃ was calculated. Due to drastic increase of temperature, there are strong peaks of orthorhombic structure of SrCO₃XRD pattern [23]. The Bragg's peaks of the crystallized powders correspond to each sample agree well with the reflections of pure orthorhombic SrCO₃ single phase [24]. XRD patterns of all the PP/SrCO₃ nanocomposites showed the intensities of basic peaks of the (111), (021), (221) and (131) planes were dominant than the other peaks [25]. The mean crystallite sizes were calculated by the Scherer's formula, which is given by

$$d_{\rm XRD} = \frac{k\lambda}{\beta Cos\theta}$$

Where' θ' is the of diffraction Bragg's angle; 'k' is the shape factor depends on shape of crystallite. By assuming the shape of crystallite to be spherical, it is taken as 0.94. ' λ' is the wavelength of X-rays ($\lambda = 1.54056 \text{ A}^0$ for K_a of 'Cu') and ' β ' is the full – width at half maximum (FWHM) [26]. From XRD patterns and calculations, it is concluded that the width of peak (221) has decreased with the increase of filler loadings up to 5% and later increased. Increase of degree of crystallinity was observed for nanocomposites up to 5% weight of the filler loadings and later decreased due to the agglomeration of SrCO₃ nanoparticles in the host polypropylene matrix. The details of XRD diffractograms like FWHM, mean crystallite size, Mean Lattice strain and d-values (Fig 2) of nanocomposites with filler percentages 1%, 3%, 5% and 10% wt. of PP are presented in table 1.

It is observed from the table that the average values of d are in nanometric orders. So it is confirmed that the composites are in the nanometric sizes by the values determined by Scherer's formula and XRD generated data. Hence there has been a confirmation of crystalline structure in the nanocomposites as the increase in average crystallite sizes with increase in the percentage of filler content. It is also observed that the lattice strain is very less at the filler loading of 5% weight of formed nanocomposite. It shows that there is a good crystalline formation and good nanoparticle dispersion in the nanocomposite of PP/SrCO₃at filler loading of 5% when compared to other loadings.



Figure 1. XRD diffractograms of (a) pure PP (b) pure SrCO3 (c) PP/1% SrCO3(d) PP/3%SrCO3 (e) PP/5% SrCO3 and (f) PP/10% SrCO3.

Morphological studies of PP/SrCO₃Nanocomposites: The impact of fracture surfaces on the study of mechanical properties of nanocomposites are significantly affected due to dispersion of nanoparticles [27, 28]. The distribution of nanoparticles in the composite morphology of nanocomposites has been evaluated by scanning electron microscopy. SEM images of PP/SrCO₃ nanocomposites are as shown in figure 3(a) to (e) which reveals the morphology of a fractured surface of the nanocomposites for different filler contents. The fractured surface of pure polypropylene is

smooth, where as good dispersion of nanoparticle is found in the micro graphs of PP with $SrCO_3$ filler loadings of 1%, 3%, 5% and 10% weight of PP.

A better dispersion is found for nanocomposite containing 5% w/w SrCO₃ nano particles. The composite containing the filler content of 10% w/w, aggregates of nanoparticles are observed. The SEM images of the nanocomposites were analyzed and the obtained crystallite sizes were compared with the values obtained from XRD using Scherrer formula. The mean values of crystallite sizes calculated from XRD ranges from 6-10 nm are in good agreement with the values as observed from SEM studies.

Sample (composite)	Miller Indices (hkl)	20	FWHM	d (nm)	Mean crystallite size <d> (nm)</d>	Lattice Strain	Mean Lattice strain
PP/1% SrCO3	(111)	25.149	0.8955	9.5		0.0175	
	(021)	27.985	1.492	5.729	6.0713	0.0261	0.02583
	(221)	42.089	2.985	2.985		0.0339	
PP/3% SrCO3	(111)	25.597	0.8955	9.51		0.0172	
	(130)	36.493	1.4925	5.86	6.78	0.0198	0.01906
	(221)	42.388	1.791	4.97		0.0202	
PP/5% SrCO3	(111)	25.597	0.8955	9.51		0.0172	
	(130)	36.791	0.8955	9.77	9.756	0.0117	0.0128
	(221)	44.402	0.897	9.99		0.0096	
PP/10% SrCO3	(111)	25.298	0.8953	9.5		0.0174	
	(130)	39.896	0.8955	9.86	8.95	0.0108	0.01373
	(221)	43.582	1.194	7.49		0.0130	

Table 1. Details of XRD patterns of PP/SrCO₃nanocomposites in different crystallography orientations with various filler loadings of PP.



Figure 2. Comparison of FWHM, mean lattice strain and mean crystallite size.



(a) SEM image of pure PP



(b) SEM Image of SrCO3 nano particles



(c) SEM image of PP/1% SrCO3



(d) SEM image of PP/3% SrCO3



(e) SEM image of PP/5% SrCO3



(f) SEM image of PP/10% SrCO3





Figure 4. FT-IR spectra of pure PP, PP/1% SrCO3 (d) PP/3%SrCO3 (e) PP/5% SrCO3 and (f) PP/10% SrCO3.

FT-IR Analysis of PP/SrCO₃ Nanocomposites: Figure 4 shows FTIR spectra of pure PP, polymer PP reinforced with SrCO₃ nanoparticles with filler loadings of 1%, 3%, 5% and 10%. The IR spectrum range 400-3500 cm⁻¹ show well pronounced broad intense peaks in both polypropylene and SrCO₃. The IR bands at 693.3–856 cm⁻¹ correspond to in plane and out plane bending of CO_3^{-2} . The IR bands at 1462 cm⁻¹ correspond to asymmetric C-O stretching vibrational mode [**29**]. The IR bands between 2960- 2850 cm⁻¹ correspond to C-H stretching mode, where as 1000- 675 cm⁻¹ correspond to C-H bending mode of the polymer; 1470-1350 cm⁻¹scissoring and bending mode [**30**].

APPLICATON

Despite of the global research interest in developing new polymer nanocomposites incorporated with inorganic metallic carbonates, SrCO₃ nanoparticles has not yet been reported. This study is of fundamental importance to create new possibilities to obtain nanocomposites composed of polyolefin's by melt mixing method. Here is an attempt that has been initiated by incorporating strontium carbonate (SrCO₃) nanoparticles in polypropylene (PP) thermoplastic polymer matrix to investigate the structural, morphological and thermal properties of PP nanocomposites with filler loadings 1%, 3%, 5% and 10% wt. of PP by melt mixing method.

Here PP with filler loading of nanoparticle SrCO3 with 5% wt. of PP has been considered as a good thermoplastic nanocomposite, which can exhibit good enhanced properties compared to other synthesized nanocomposites as well as the conventional thermo plastic polymers. They can be utilized in several thermoplastic applications by examining the composites with thermal, mechanical and electrical studies.

CONCLUSIONS

Polymer nanocomposites of PP with various filler loadings of SrCO₃ containing 1, 3, 5 and 10% weight of PP have been successfully synthesized by melt mixing method. The conformation of the formation of the nanocomposites was obtained from the XRD, SEM and FTIR studies. A considerable decrease in the lattice strain has been noted at the filler loadings of 5% weight of the filler in the polymer matrix, it has also been observed a good dispersion of nano particles at the same filler loadings by SEM micro graphs. In fact the well dispersed nanoparticles act as stress concentrators and load bearing centers, which supports the present obtained results. Hence PP with filler loading of nanoparticle SrCO₃ with 5% wt. of PP can be a good thermoplastic nanocomposite, which can exhibit good enhanced properties compared to other synthesized nanocomposites as well as the conventional thermo plastic polymers. They can be utilized in several thermoplastic applications by examining the composites with thermal, mechanical and electrical studies.

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