Thermal properties of Polypropylene/Strontium Carbonate (srco$_3$) Nanocomposites

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Abstract

The aim of the present study is to analyze the thermal behavior of thermoplastic polymer matrix of polypropylene (PP) incorporated with Strontium carbonate (SrCO$_3$) nanoparticles. SrCO$_3$ nanoparticles were synthesized and reinforced in polypropylene (PP) polymer matrix in order to prepare PP/SrCO$_3$ nanocomposites with filler loadings of 1%, 3%, 5% & 10% wt. of PP by melt-mixing method. Confirmation of nanocomposite formation was obtained by SEM micro graphs. In fact thermal studies play a vital role in various applications of nanocomposites. Thermogravimetric (TG) analysis showed an increase in the thermal stability of the resultant nanocomposite. However, differential scanning calorimetry (DSC) results indicated a decrease in degree of crystallinity of the nanocomposite following filler content. The studies have revealed that a considerable change in the degree of crystallinity and a good thermal stability was observed at SrCO$_3$ filler loading of 5% wt. of PP when compared to other filler loadings for enhanced properties and applications.

Keywords: Strontium Carbonate Nanoparticles, Polypropylene, Thermal properties, morphology.

1. Introduction

Researchers are struggling in designing light weight and high strength materials for decades. Toughening process involves Stress concentration and de-bonding of the polymer nanocomposites[1]. Nanocomposites containing MWNTs with low filler loadings exhibit the enhanced properties compared to the conventional materials [2][3][4][5]. The enhanced properties are possible with only nanocomposites containing uniform dispersion of the nanoparticles in the polymer matrix[6]. But same filler of macroscopic particles of same kind cannot produce such enhanced properties[7][8]. Recently over the other traditional polymers, polymer nanocomposites are attracting the attention of the researchers and industry[9]. In fact in nanocomposite the inorganic filler particle will act as stress concentrator [10]. TiO$_2$ nano-particles, silver nano-particles, gold nano-particles and zinc oxide nano-particles etc; are used as fillers in various nanocomposites for desired applications[11] [12]. Because of the highest growth rate PP is the most commonly used commodity plastic. CaCO$_3$ is the most commonly used inorganic fillers in thermoplastic polymer like PP Among several fillers. PP composites find wide range of applications like sewer pipes, garden furniture etc;[14]; Calcium carbonate nanoparticles could able to improve thermal and mechanical properties of polypropylene. According chan

et al, studies of mechanical and thermal properties of nano-$CaCO_3$ filled PP proved as one of the best inorganic filler in various thermo plastic polymers like polyethylene, PVC and polypropylene due to its most availability, low cost and providing more enhanced properties[15][16][17].

According to recent reports on PP nanocomposites. Marques 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. There is a report on 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]. 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 synthesiszed 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, $SrCO_3$ 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 an attempt has been initiated by incorporating strontium carbonate ($SrCO_3$) nanoparticles in polypropylene (PP) thermoplastic polymer matrix to investigate the thermal properties of PP nanocomposites with filler loadings 1%, 3%, 5% and 10% wt. of PP.

2. Materials and Methods

2.1 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 $SrCl_2$ and Na_2CO_3 of analytical grade are purchased from Akshay Scientifics Ltd., INDIA.

2.2 Preparations

2.2.1 Preparation of SrCO₃ Nanopowder

For the synthesis of $SrCO_3$ nanoparticle powder, $SrCl_2$ and sodium carbonate Na_2CO_3 were used as the starting materials. 100ml aqueous solution of $SrCl_2$ of 0.1M was mixed with 100 ml of sodium carbonate, later the mixture was stirred for 2 hours. To get purity the resulted reaction mixture was washed for four times. After that it was centrifuged and dried at 60^0C. As a result nanoparticle $SrCO_3$ was obtained in the form of a powder.

2.2.2 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 200^0C for 15 minutes and $SrCO_3$ nanopowder of 0.1 gm was mixed. The resulted mixture was stirred for 15 minutes. After that it was cooled for solidification. As a result a polymer nanocomposite of $PP/SrCO_3$ with filler loading of nanoparticle $SrCO_3$ of 1% wt. of PP was obtained. The same procedure was repeated in order to obtain $PP/SrCO_3$ nanocomposites with concentrations of filler 3%, 5% and 10% wt. of PP.

2.3 Methods

Morphology has been carried out by Scanning electron microscopy using the instrument Hitachi Model S4700. DSC thermograms have been recorded using Differential Scanning Calorimeter instrument DSC Q20 V 24.10 Build 122. Here the sample of about 3.5 mg was heated from 40 to 600^0C at a heating rate of 10^0C per minute in flushing nitrogen. TG Thermograms were recorded using thermo gravimetric analysis instrument TGAQ50, V20.13 Build 39. For such studies a sample of about 10mg was heated from 30 to 800^0C at a heating rate of 10^0C per minute in nitrogen atmosphere.

3 Results and Discussions

3.1 Morphological studies of PP/SrCO₃ Nanocomposites

The impact of fracture surfaces on the study of mechanical properties of nanocomposites are significantly affected due to dispersion of nanoparticles[23][24]. The distribution of nanoparticles in the composite morphology of nanocomposites has been evaluated by scanning electron microscopy. SEM images of $PP/SrCO_3$ nanocomposites are as shown in figure 1(a) to (d) 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% & 10% weight of PP.
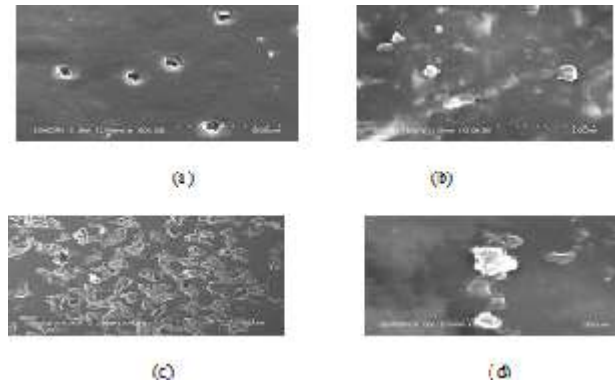
Figure 1: SEM images of (a) PP/1% SrCO3 (b) PP/3%SrCO3 (c) PP/5% SrCO3 & (d) PP/10% SrCO3.

A better dispersion is found for nanocomposite containing 5% w/w SrCO$_3$ 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.

3.2 Thermal and Crystallization Studies

3.2.1 Thermo gravimetric (TGA) analysis of PP/SrCO$_3$ Nanocomposites:

Thermo gravimetric analysis (TGA) has been used for the investigation of thermal stability of thermo plastic polypropylene polymer nanocomposites with an atmosphere of nitrogen with linear temperature ramp of 10^0c/min. TGA thermograms and corresponding derivatives of the PP/SrCO$_3$ nanocomposites with filler loadings of 1%, 3%, 5% & 10% wt. of PP are as shown in figure 2. It is observed that initial degradation temperature (T_i) is not effected with the incorporation of nanoparticles in the polymer matrix. A single phase degradation smooth curves are a sign of homogeneity of nanocomposites and it reveals a good formation of nanocomposites. Two ways to describe the oxidation temperature are (i) the weight loss onset temperature (T_{onset}) (ii) the temperature of the maximum weight loss rate (dm/dT_{max}). In fact T_{onset} is ambiguous but dm/dT_{max} is relatively straight forward. Oxidation temperature $T_o= dm/dT_{max}$ has been considered for the determination of thermal stability of the polymer nanocomposites in the present study. The oxidation values obtained from the derivative graphs for filler loadings of 1%, 3%, 5% & 10% wt. of PP are ranging from 400^0C to 500^0C. Oxidation temperature T_o, is an indication of thermal stability of nanocomposites in air. Higher

oxidation temperature is always associated with purer, the values of T_o for nanocomposites emphasizes the well dispersion of nanoparticles and de-bonding of the polymer matrix.
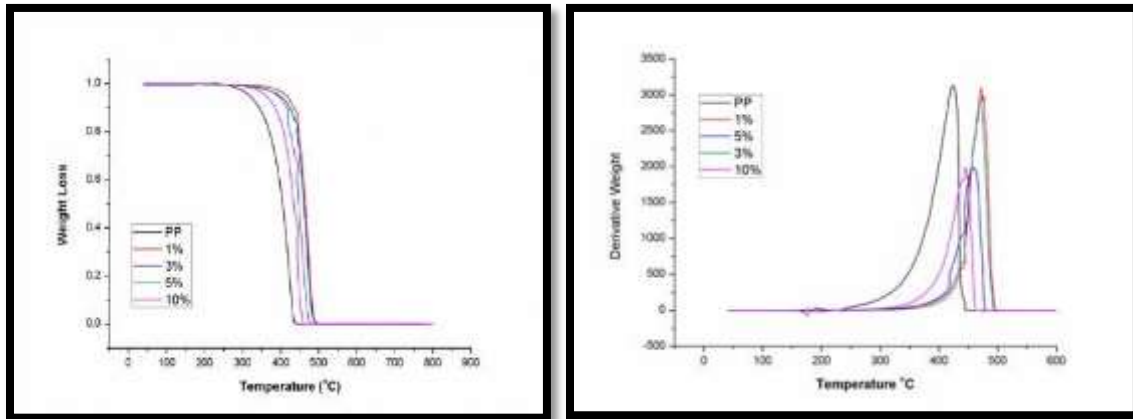

Figure 2: (a) TGA Thermograms & (b) their first derivatives of Pure PP, PP/1% SrCO3 , PP/3%SrCO3, PP/5% SrCO3 & PP/10% SrCO3.

3.2.2 Differential Scanning Calorimetry (DSC) Analysis of PP/SrCO$_3$ nanocomposites:

The morphology developed during the fabrication plays a vital role on the physico-mechanical properties of the polymeric nanocomposite. Hence it could be a successful way for the improvement of physico-mechanical properties of the composites by controlling the crystallization process. Hence nucleation, crystallization and structural development of the polymer incorporated with nanoparticles are of great interest[25]. This could help to have feasible manufacturing conditions to obtain good practical applications. The semi crystalline polypropylene polymer crystallization behavior influences mechanical properties a lot. Hence investigation of the thermal properties is significant both from theoretical as well as practical points of view. The data related to thermal properties of PP/SrCO$_3$ nanocomposites include melting temperature (T_m), enthalpy (ΔH), and degree of crystallinity (χ_c). Typical DSC thermograms for neat isotactic polypropylene and composites reinforced with SrCO$_3$ with 1%, 3%, 5% & 10% wt. of PP are shown in figure 3.
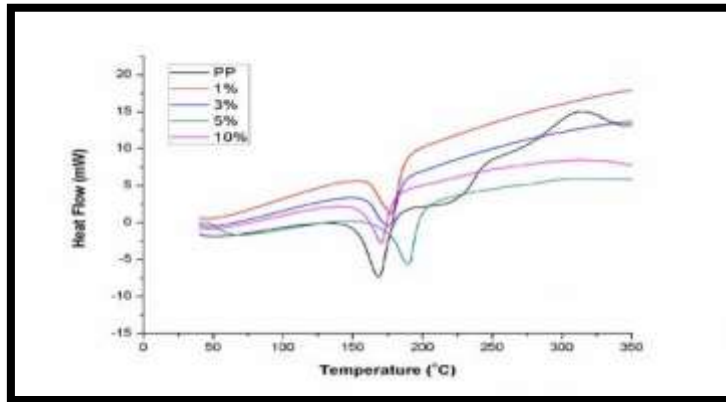
Figure 3: DSC Thermograms of PP, PP/1% SrCO3, PP/3%SrCO3, PP/5% SrCO3 & PP/10% SrCO3.

Differential Scanning Calorimetry (DSC) analysis has been carried out to the pure form of isotactic polypropylene (PP) and the composites of PP filled with nanoparticle strontium carbonate. Melting temperatures of the polymer PP are taken from the peak values of the thermograms. Whereas melting enthalpy was calculated from the peak area. According to the studies of A.Buasri at al; melting temperature of pure PP is 164.75^0C[26]. It is to be noted that melting enthalpy (ΔH) values shown are expressed in J/g. The degree of crystallinity of nanocomposites were calculated using enthalpy values, taken 207.1 J/g as the theoretical enthalpy value for a pure crystalline PP[31]. Chemical and mechanical properties are very much influenced by the degree of crystallinity (χ_c) in thermoplastic polymers. Stiffness and tensile strength could be improved by the crystalline phase while the amorphous phase is prominent in absorbing the impact energy. According to the studies of A.Akinci, the melting temperature of PP is 163.73^0C, ΔHm 66.43 J/g and χ_c 32% [27]. In the present study the obtained experimental values are presented in table-1 are almost good agreement with them. The parametric values of the composites of PP with 1%, 3%, 5% and 10% $SrCO_3$ viz; melting temperature (T_m); enthalpy (ΔHm) and percentage of crystallinity (χ_c) of polypropylene and $SrCO3$ are presented in table-2. The crystallization of the polymer and nucleation activity of the filler were calculated by using the relationship

$$\chi_c = \frac{\Delta Hm . (\frac{mc}{mp})}{\Delta H0} \times 100$$

Where ΔH_m: melting enthalpy measured in heating experiments;

ΔH_0: theoretical value of enthalpy of 100% crystalline PP (standard value of ΔH_0 = 207.1J/g),

m_c : mass of the sample and

m_p: mass of PP in the sample.

Table-1: Details of DSC thermal characteristics of PP/SrCO$_3$ nanocomposites

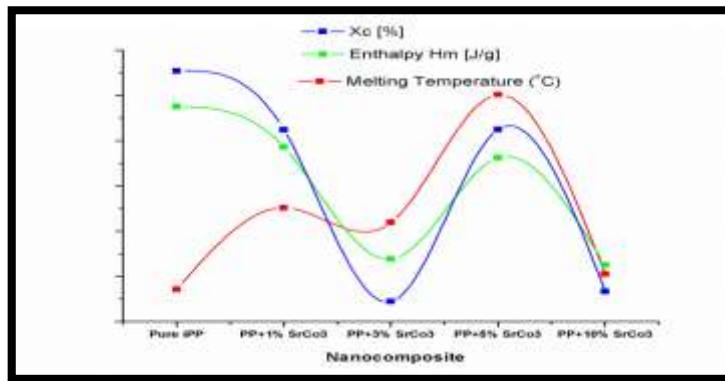| Composite (sample)	Polypropylene (PP)		
	Melting Temperature T_m [^{0}C]	Enthalpy ΔHm [J/g]	Percentage of Crystallinity X_c [%]
Pure iPP	168.59	63.6	30.70
PP/1% SrCO3	177.6	55.4	27.02
PP/3% SrCO3	175.98	32.7	16.27
PP/5% SrCO3	190.1	53.2	27.04
PP/10% SrCO3	170.28	31.5	16.90

Figure 4: Trend of melting temperature, enthalpy and percentage of crystallinity of various filler loadings.

4. Conclusion

Polymer nanocomposites of PP with various filler loadings of $SrCO_3$ 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 SEM and TGA studies. The results of DSC tests revealed that melting temperature of host polymer matrix is affected considerably by the filler loadings of nanoparticles and a significant change in enthalpy and degree of crystallinity were observed. It has been noted that melting temperature increased up to weight 5% $SrCO_3$ of PP and later followed decreasing trend; it reveals its thermal stability. Whereas the percentage of crystallinity of polymer matrix is reduced with the incorporation of the nanoparticles, it is a sign of the formation of the composites. But a raise during the reduction has also been found at filler loading of 5% $PP/SrCO_3$, it is an indication of good dispersion of the particles in the polymer matrix, the result obtained during the DSC studies has been supported by the observations in the SEM images of figure 1(e). 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 $SrCO_3$ 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 mechanical and electrical studies.

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