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Impact of Spherical Anatase TiO_2 Nanoparticles on Thermal Properties Of Polypropylene Resin

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Abstract

Ceramics Nano metric reinforced polymer composite is a significant material for catalysis, solar cells, production of hydrogen and energy applications, etc. In order to take benefit from the interesting mechanical properties and thermal stability of TiO_2, this ceramic nanomaterial's was synthesized by the Sol-Gel process in attempt to study the thermal stability, structure, and morphology of the resulting nanoparticles powders. The obtained results revealed that, the sphere is composed of 20-30 nm nanoparticles with excellent thermal stability of nano-TiO_2, This work focused on the thermal characterization and the study of Nano composite xWt% TiO_2/PP (x=0, 2.5, 5, 7.5 mol%). In this study, the obtained results revealed that the molar ratio of TiO_2 influences the final thermal stability and degree of crystallinity of the composite. It was found that the use of TiO2 seems to be an effective and very promising way to increase the thermal properties of the resulting composite. The greatest degree of crystallinity (54.80%) and thermal degradation stability are obtained for composite reinforced by 7.5 Wt% TiO_2.

Keywords

Aerogel • Polymer • Sol-Gel • Thermal stability • Nano-TiO_2

Abbreviation

DTA: Differential Thermal Analysis; TG: Thermo Gravimetric; SEM: Scanning Electron Microscopy; TEM: Transmission Electron Microscopy; XRD: X-Ray Diffraction • MEB: Minimum Expenditure Basket; DSC: Differential Scanning Calorimetry; DTG: Derivative Thermo Gravimetry; MPD: Multipurpose X-ray Diffraction System

Introduction

Polymer composite materials are attractive for several technological applications because of their enhanced specific properties [1]. Thermal degradation, in combinations with their degree of crystallinity influences the physical and thermal behavior of polymer materials [2]. The correlation between structural and mechanical properties is one of the approaches to develop new Nano-materials for various applications. Recent overwhelming use of composites has motivated the reinforcement by nanoparticles for improving the interfacial bonding strength and thermal performances. According to several researchers, polypropylene has been used in several fields of application because of its excellent chemical stability [3,4]. It is widely used in advanced technologies due to its low density, low processing temperature and high stiffness [5].

In the present work, synthesis revealed the impact spherical anatase TiO_2 nanoparticles on the thermal performances of polypropylene resin. DTA/TG, SEM, TEM and XRD analysis determined the thermal, structural and morphology behavior of the TiO_2 nanoparticles. In this research study, details of Nano-composites synthesis were presented. MEB analysis revealed the nanoparticle dispersion in the Nano composites. Thermal degradation stability and degree of crystallinity were observed using DSC and TG/DTG.

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Materials and Methods

Elaboration of TiO_2 Nano powder

In order to synthesize TiO_2 Nano powder, methanol and acetic acid (CH_3COOH) used as catalysts and Titanium Tetra Iso-Propoxide (TTIP) precursor were mixed in the order shown. The mixture was stirred for 30 minutes at a constant speed to obtain the TiO_2 sol. Then, the resulting sols were introduced into autoclave heated up to 243°C and pressurized to overcome the critical point of ethanol (T_c=243°C, P_c=63 bar). After maintaining temperature at 243°C for 1 hour, the sol gelation occurred. To evacuate the interstitial solvent, depressurization for 1 hour down to room temperature was conducted with nitrogen gas. To avoid cracking of the sample due to thermal strain, the autoclave was opened after 24 hour to slowly achieve thermal equilibrium. Finally, TiO_2 aerogels was obtained and then annealed in air at 500°C for 1 hour.

Nano composites preparation

A For TiO_2/PP Nano composite preparation, commercially available isotactic PP (density=0.9 $g.cm^{-3}$) was purchased from National Industrialization Company JSC (TASNEE). Then, Nano composites were prepared with different nano-TiO_2 contents (0 wt%, 2.5 wt%, 5 wt% and 7.5% wt% TiO_2). To do so, TiO_2 Nano powder was added to PP resin and dispersed by using a mixer (30 min at room temperature). Then, the different Nano composites were prepared using a twin screws extruder MEG DS32-1A (screw diameter of 35/80 mm and T°=210°C). Then, the solidified Nano composites were pelletized with a crusher, and traction specimen were obtained by injection molding (SM-120 TSCE, T°=30°C).

Materials characterization

TiO_2 Nano powder characterization: For morphological characterization, the prepared aerogel was examined by Scanning Electron Microscopy (SEM) (FE-SEM, PhilipsXL30) using an accelerating voltage of 20 keV, a working distance of 11.3 mm and a transmission electron microscope (TEM, JEOL 2011) operating at 200 KV.

In order to study the structural properties and phase identification, TiO_2 Nano powder was analyzed using PANalyticalX'Pert Pro MPD diffractometer with Cu Kα radiation (λ=1.5418 Å) for X-Ray Diffraction (XRD) measurements recorded in the 20°-85° 2θ range at room temperature with an incidence angle of 0.05. From XRD patterns, average crystal sizes were calculated using Scherrer's formula.

The thermal stability of the nano-TiO_2 was studied by DTA and TG analysis. The DTA and TG analyzes were performed in an atmosphere from temperature to 800°C with a heating rate of 20°C/min. For the analysis, it was used approximately 10 mg of sample.

Nano composites characterization: Differential Scanning Calorimetry (DSC, TA Instruments model Q200) was used to measure the effect of Nano filler on thermal properties of PP such as melting temperature and melt crystallization. The DSC analysis were performed in a temperature range from -60°C to 180°C in two cycles (heating rate of 10°C/min and a cooling rate of 20°C/min). The thermal analyses of the different Nano composites are submitted to Thermo Gravimetric Analysis (TGA, TA Instruments Model TGA 500). The TGA analyses were performed from ambient temperature to 650°C with a heating rate of 10°C/min.

The morphological observation of the samples (surface and cross section) was conducted according to SEM with accelerating voltage of 15 KV.

Results and Discussion

TiO_2 Nano powder study

The thermal analyses (DTA/TG) of TiO_2 nanoparticle are given in Figure 1. The endothermic peaks observed near 224°C related of the evaporation and the release of free water is the phenomenon of dehydration of the sample so it also reflects to the removal of hydroxyl groups it is the phenomenon of dehydroxylation. The second exothermic peak, located at 288°C, corresponds to the partial decomposition and departure of organic matter (carbon dioxide...), and it can be attributed to the oxidation elimination of the Ti precursor (alcoxide). The corresponding mass losses are localized at 138°C of the order of 3.84%. This loss is characterized by the endothermic peak, which reflects the phenomenon of dehydration and the phenomenon of dehydroxylation. The second mass loss characterizes an exothermic accident. It is fast and important located between 138°C and 450°C is of the order of 5.7%. It corresponds to the partial decomposition of titanium dioxide. The recorded mass loss could be related by the evaporation of absorbed water which corresponds to a significant endothermic effect [6]. It is worth ion to mention that the excellent stability of TiO_2 anatase phase from 288°C to 800°C.

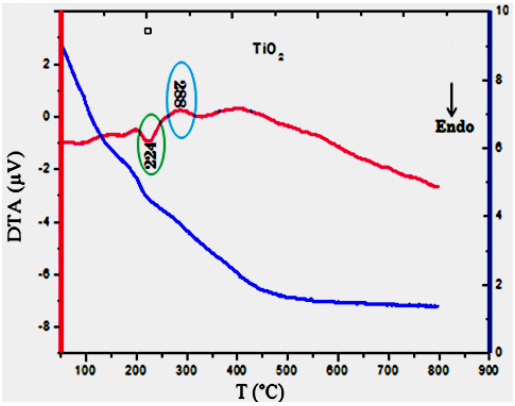

Figure 1. DTA and TG curves of TiO_2 nanoparticles.

The morphology study of nano-TiO_2 with the SEM shows that the prepared nanoparticle composed of fine particles with heterogeneous size and shape before the treatment (Figure 2). In addition to the presence of the agglomerates (is formed by primary crystallites connected together) that they are consolidated by the formation of a crystalline neck.

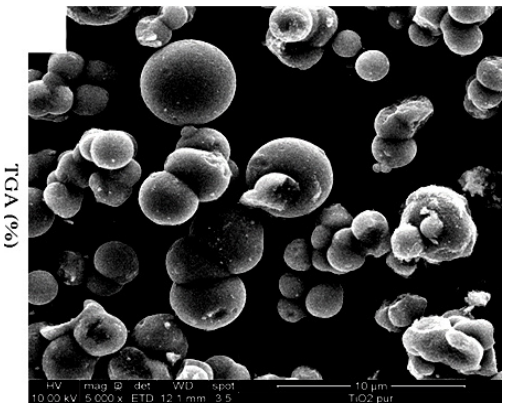

Figure 2. SEM micrographs.

To determine the size and morphology of the TiO_2 Nano powder TEM analyses have been performed (Figure 3). Furthermore, the TEM images of the Nano powders TiO_2 with diameters of about 10 nm and 20 nm. As a conclusion, the TiO_2 nanoparticles were prepared by sol gel method (10-20 nm) with spherical morphology through hydrothermal assisted sol-gel method.

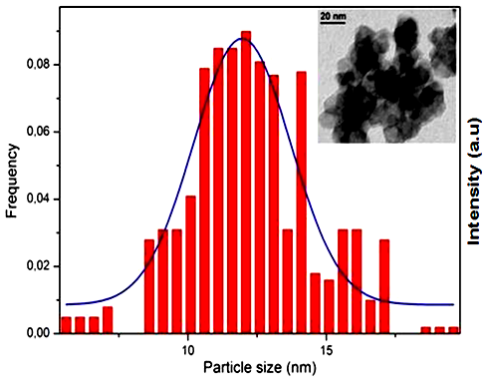

Figure 3. Size distribution from TEM observations.

Figure 4 illustrates the XRD patterns of TiO_2, anatase structure is identified (JCPDS files NO. 00-004-0477). The crystallite average size was calculated from the full width at half maximum of the diffraction peaks using the Scherrer formula: (D=0, 9 λ)βcosθ (1)

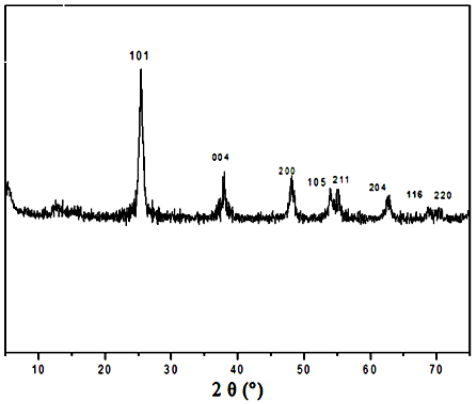

Figure 4. XRD pattern.

Where D is the crystallite size in nm, λ is the X-ray wavelength of Cu-Kα radiation in nm, K is the shape constant (0.9), θ is the Bragg's angle in degrees and β is the line broadening at half the maximum intensity (FWHM) in radians. It can be estimated the crystallite size of TiO_2 is 12 nm.

Polypropylene nano-composites study

Morphology analysis of surface and fracture for nano-composites: The micrograph of polypropylene (Figure 5a) surfaces presents a matrix micro-cracking and pot holes. The morphology study shows that, for 2.5 Wt%

TiO_2/PP Nano composite, the SEM images of surface reveals the Nano fillers dispersed into the matrix (Figure 5b). The fracture surfaces indicated the presence of porous material resulting from agglomerated particles. In addition, the homogeneous mixture between nano TiO_2 and polypropylene observed at 5 Wt% TiO_2 (Figure 5c). After comparison with the morphology of pure TiO_2, we observe a considerable modification of the size of grains as well as distribution. The sizes of the crystallites are of in the Nano metric order. The figure represents the microstructure of composite 7.5% TiO_2/PP consisting of agglomeration of spheres. The spherical Nano crystallite aggregates are formed of fine nanoparticles (similar to pure 2.5 TiO_2) (Figure 5d).

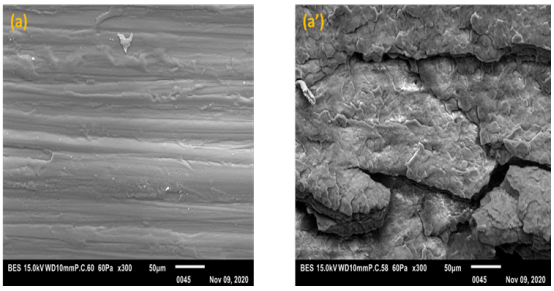

Figure 5a. SEM images of the PP Nano composites of Polypropylene.

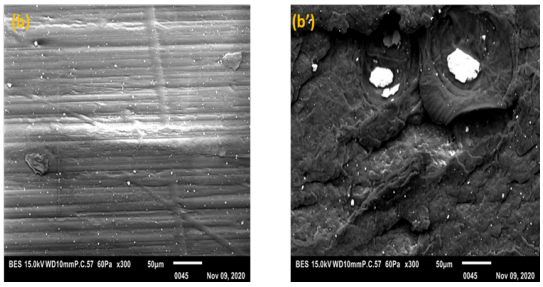

Figure 5b. SEM images of the PP Nano composites of 2.5Wt% TiO_2.

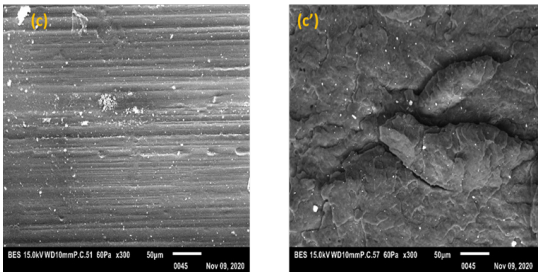

Figure 5c. SEM images of the PP Nano composites of 5Wt% TiO_2

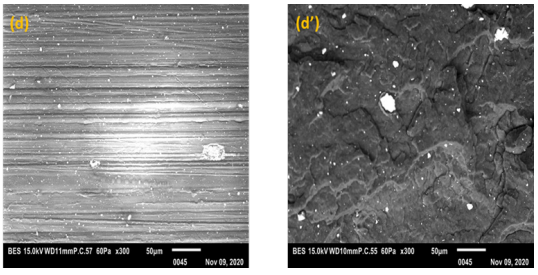

Figure 5d. SEM images of the PP Nano composites of 7.5Wt% TiO_2.

Thermal properties

Differential scanning calorimetry (DSC): The degree of crystallinity and the presence of polymorphisms into Nano composites were investigated by DSC analysis. The temperatures and enthalpy of fusion of the virgin PP and Nano composites were determined. The phase-change latent heat for calculation ranges from 81°C to 122°C. During the melting and solidification process, DSC thermo grams curve for PP reveals the presence of the phase-change peak (Tp) at 169.26°C and 111.22°C. As a result, the onset temperature (T_0) be 154.96°C and 116.63°C, and the latent heat of phase change was 90.28 and 107.1 kJ/kg for polypropylene, respectively (Figure 6a). The addition of varying content of nano-TiO_2 alters the endothermic and exothermic curve of PP. The degree of crystallinity of PP increases by the addition of nano-TiO_2 as reported in literature [7]. The degree of crystallinity first increased with the addition of 2.5 Wt%TiO_2 (Figure 6b), and then reached a maxima of 53.23%. At these conditions, the nanoparticles are acting as nucleating agents for PP and consequently increased the crystallization rate. Thus, the polymer crystals switched from homogeneous nucleation to heterogeneous nucleation, which facilitated crystallization. The addition of 5% Wt. nano-TiO_2 was found to increase the endothermic and exothermic peaks and delayed the end of the melting point during the phase change. Table 1 summarizes the DSC experimental results of the polypropylene and the different Nano composites for the melting and solidification processes with different concentrations of the nano-TiO_2. (Figure 6c) For the 5 Wt% TiO_2/PP Nano composite, the increase of crystallinity may be attributed to the accelerating effect of nano-TiO_2 on the PP crystals and the physical hindrance of nano-TiO_2 particles to the motion of the polymer's molecular chains [8,9]. As a result, incorporation of 7.5 Wt% nano-TiO_2 into the polypropylene matrix increases the degree of crystallinity (Figure 6d).

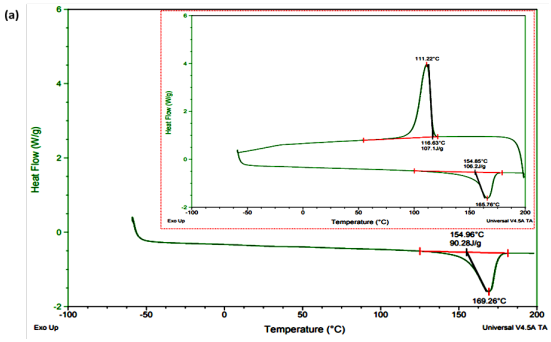

Figure 6a. DSC curves of the PP and Nano composites during the heating process of Polypropylene.

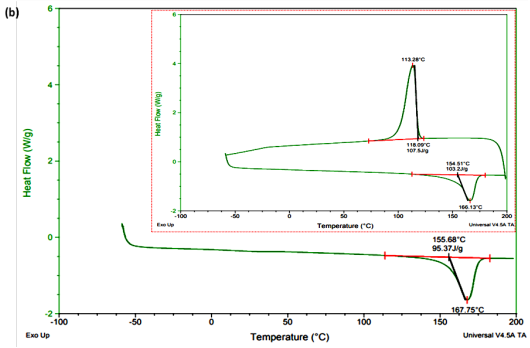

Figure 6b. DSC curves of the PP and Nano composites during the heating process of 2.5Wt%TiO_2.

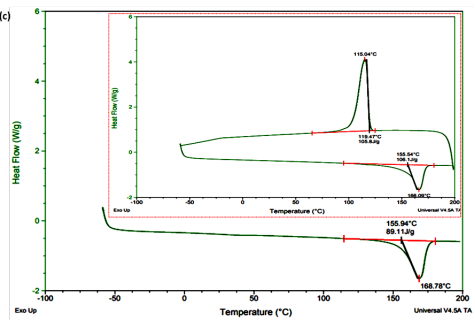

Figure 6c. DSC curves of the PP and Nano composites during the heating process of 5Wt%TiO_2.

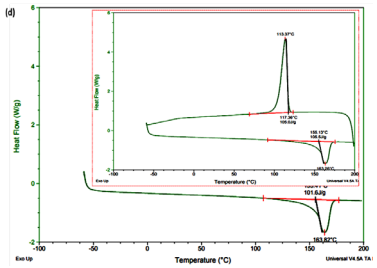

Figure 6d. DSC curves of the PP and Nano composites during the heating process of 7.5Wt% TiO_2.

The crystallization temperature (T_p), the melting peak temperature (Tmp) and the degree of crystallinity (X_c) of PP and derived Nano composites are indicated in Table 1. The results suggest that the incorporation of Nano fillers TiO_2 accelerates the crystallinity of polypropylene. The TiO_2 was considered to be important in increasing the thermal properties because it's a heterogeneous nucleation agent. In order to calculate the degree of crystallinity (X_c) of the samples the enthalpy area of the melting peak (ΔH_m) was divided by the literature value (ΔH_L) (equation 2). These results are consistent with previous findings [9].

Table 1. DSC (Differential Scanning Calorimetry) data of the tested nano-composites.

Nano composites	Tp,°C	Tmp,°C	ΔHm, J/g	ΔHc, J/g	Xc, %
PP/0 Wt% TiO_2	111.22	169.26	107.1	90.28	51.71
PP/2.5 Wt% TiO_2	113.28	167.75	110.25	97.81	53.23
PP/5 Wt% TiO_2	115.04	168.78	111.36	93.8	53.77
PP/7.5 Wt% TiO_2	113.37	163.82	113.5	109.83	54.80

$$\%Crystallinity=(\Delta H_m/\Delta H_L) \times 100\%;\ \Delta H_L=207.1\ J/g \quad (2)$$

Thermo Gravimetric Analysis (TGA): The thermal degradation stability and mechanisms of the Nano composites are an important property for various application areas due to the changes in the viscoelastic behavior and viscosity [8]. In this study, the thermal properties of the Nano composites have been investigated using TGA. (Figure 7a) shows the TGA curves of TiO_2/PP Nano composites. According to the obtained results, the addition of nano-TiO_2 slightly improved thermal stability of the neat PP, when TiO_2 Nano charges were added up to 5 Wt% (Figure 7b). The DTG curve of Nano composite suggested the presence of peaks located between 325°C and 475°C. This peak is attributed to the rupture of the C-C chain's bonds along with H-abstraction at the site of rupture [8].

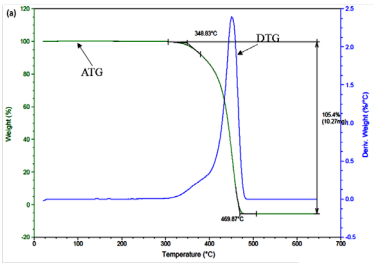

Figure 7a. Thermo gravimetric (TG) and first-order derivative (DTG) curves of Polypropylene.

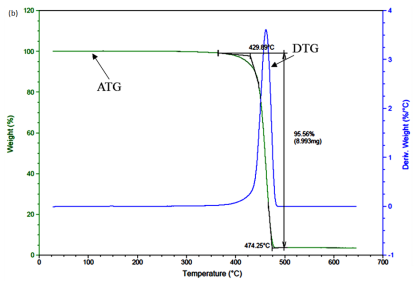

Figure 7b. Thermo gravimetric (TG) and first-order derivative (DTG) curves of 5Wt%TiO_2.

Incorporation of 2.5 Wt% nano TiO_2 into the polypropylene matrix increases the thermal stability with the decomposition temperature was found to be 433.42°C. The decomposition temperature was decreasing with nano-TiO_2 content increasing (Figure 7c). At 7.5 Wt% TiO_2, (Figure 7d) the result indicates that the decomposition temperature for the Nano composites is around 429°C (Table 2). It was reported that the incorporation of Nano TiO_2 with molar ratio in the range of 1%–3%, the degradation temperature for Nano composites shifts to high temperature (above 54°C) [10,11]. It should be noted that interaction degree between polymer matrix and Nano fillers is connected to the concentration of base phase, crystallite sizes of Nano fillers and acquisition condition of Nano composites. This confirms the presence of an interphase or border layer between Nano fillers and matrix with properties that differ from matrix properties in the bulk [11]. The crystalline structure in the transition regions of the polymer boundary layer are form in the Nano composites, at this time is formed the structural activity of nanoparticles and whereby the thermodynamic conditions of the crystallization of molecular chains in the boundary layer are likely to improve [10].

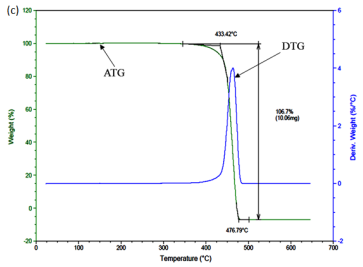

Figure 7c. Thermo gravimetric (TG) and first-order derivative (DTG) curves of 2.5Wt%TiO_2.

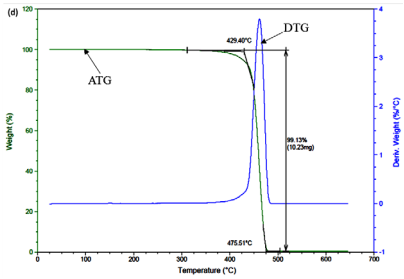

Figure 7d. Thermo gravimetric (TG) and first-order derivative (DTG) curves of 7.5Wt% TiO_2.

Table 2. Decomposition temperature of the tested nano-composites.

	T (°C)
Polypropylene	348.83
2.5 Wt% TiO_2	433.42
5 Wt% TiO_2	429.89
7.5 Wt% TiO_2	429.40

Conclusion

In this study, the nano-TiO_2 with spherical morphology and Nano metric crystallite size has been synthesized using hydrothermal-assisted sol-gel technique. Diffraction peaks reveal the anatase TiO_2 phase. From the TEM images, the sphere is composed of 20-30 nm nanoparticles. This article aimed at presenting the impact of the nano-TiO_2 powders in the morphology and thermal performances of the polypropylene resin. The thermal degradation stability of the polypropylene increased with the addition of Nano TiO_2. The results obtained show that the incorporation of Nano TiO_2 into the polypropylene matrix, the degree of crystallinity was relatively increased. Therefore, the interfacial interactions increased with the presence of anatase Nano fillers in polyester matrix.

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