Impact of Spherical Anatase TiO₂ Nanoparticles on Thermal Properties of Polypropylene Resin

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Abstract

Ceramics nanometric 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 , these ceramic nanomaterials 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 nanocomposite 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 TiO_2 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 7.5Wt. % TiO_2 .

1. Introduction

Polymer composite materials are attractive for several technological applications because of their enhanced specific properties (Harizi et al., 2015). Thermal degradation, in combinations with their degree of crystallinity influence the physical and thermal behavior of polymer materials (Zhang and Kraus, 2017). 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 (Hansen et al., 2019; Khaskhoussi et al., 2017). It is widely used in advanced technologies due to its low density, low processing temperature and high stiffness (Kumar et al., 2017).

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 nanocomposites synthesis were presented. MEB analysis revealed the nanoparticle dispersion in the nanocomposites. Thermal degradation stability and degree of crystallinity were observed using DSC and TG/DTG.

2. Materials And Methods

2.1. Elaboration of TiO_2 nanopowder

In order to synthesize TiO_2 nanopowder, methanol and acetic acid (CH_3COOH) used as catalysts and titanium tetra isopropoxide (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 ($T_c = 243^\circ\text{C}$, $P_c = 63\text{bar}$). After maintaining temperature at 243°C for 1h, the sol gelation occurred. To evacuate the interstitial solvent, depressurization for 1 h 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 h to slowly achieve thermal equilibrium. Finally, TiO_2 , Al_2O_3 and SiO_2 aerogels was obtained and then annealed in air at 500°C for 1 h

2.2. Nanocomposites preparation

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

2.3. Materials characterization

2.3.1. TiO_2 nanopowder 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 nanopowder was analyzed using PANalyticalX'Pert Pro MPD diffractometer with Cu K α radiation ($\lambda = 1.5418\text{\AA}$) for X-Ray Diffraction (XRD) measurements recorded in the $20-85^\circ 2\theta$ 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 a atmosphere from tempeture to 800°C with a heating rate of $20^\circ\text{C}/\text{min}$. For the analysis, it was used approximately 10mg of sample.

2.3.2. Nanocomposites characterization

Differential scanning calorimetry (DSC, TA Instruments model Q200) was used to measure the effect of nanofiller 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 nanocomposites are submitted to thermogravimetric 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) were conducted according to scanning electron microscope (SEM) with accelerating voltage of 15KV.

3. Results And Discussion

3.1. TiO₂ nanopowder study

The thermal analyses (DTA/TG) of TiO₂ nanoparticle are given in figure.1 (a). The endothermic peaks observed near 224°C are 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 deshydroxylation. 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 loss 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 (Salhi and Deschanvres, 2016). It is worth ion to mention that the excellent stability of TiO₂ anatase phase from 288°C to 800°C.

The morphology study of nano-TiO₂ with the SEM shows that the prepared nanoparticle composed of fine particles with heterogeneous size and shape before the treatment (Fig.1-b). 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.

To determine the size and morphology of the TiO₂ nanopowder TEM analyses have been performed (Fig.1-c). Furthermore, the TEM images of the nanopowders TiO₂ with diameters of about 10 nm and 20 nm. As a conclusion, the TiO₂ nanoparticles were prepared by sol gel method (10–20 nm) with spherical morphology through hydrothermal assisted sol-gel method.

Fig.1-d illustrates the XRD patterns of TiO₂, 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:

$$D = 0,9 \lambda / \beta \cos \theta \quad (1)$$

Where D is the crystallite size in nm, λ is the X-ray wavelength of Cu-K α 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 TiO₂ is 12 nm.

3.2. Polypropylene nanocomposites study

3.2.1. Morphology analysis of surface and fracture for nanocomposites

The micrograph of polypropylene surfaces (Fig.2-a) presents a matrix micro-cracking and pot holes. The morphology study shows that, for 2.5Wt. % TiO₂/PP nanocomposite, the SEM images of surface reveals the nanofillers dispersed into the matrix. The fracture surfaces indicated the presence of porous material resulting from agglomerated particles. In addition, the homogeneous mixture between nano-TiO₂ and polypropylene observed at 5Wt. % TiO₂. After comparison with the morphology of pure TiO₂, we observe a considerable modification of the size of grains as well as distribution. The size of the crystallites are of in the nanometric order. The figure Fig.2-d represents the microstructure of composite 7.5%TiO₂/PP consisting of agglomeration of spheres. The spherical nanocrystallite aggregates are formed of fine nanoparticles (similar to pure 2.5TiO₂).

3.2.2. Thermal properties

a. Differential scanning calorimetry (DSC)

The degree of crystallinity and the presence of polymorphisms into nanocomposites were investigated by DSC analysis. The temperatures and enthalpy of fusion of the virgin PP and nanocomposites were determined. The phase-change latent heat for calculation ranges from 81°C to 122°C. During the melting and solidification process, DSC thermograms 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 (To) was 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. The addition of varying content of nano-TiO₂ alters the endothermic and exothermic curve of PP. The degree of crystallinity of PP increases by the addition of nano-TiO₂ as reported in literature (Esthappan et al., 2012). The degree of crystallinity first increased with the addition of 2.5 Wt%TiO₂, 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-TiO₂ 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 nanocomposites for the melting and solidification processes with different concentrations of the nano-TiO₂. For the 5 Wt% TiO₂/PP nanocomposite, the increase of crystallinity may be attributed to the accelerating effect of nano-TiO₂ on the PP crystals and the physical hindrance of nano-TiO₂ particles to the motion of the polymer's molecular chains (Aydemir et al., 2016; Sun et al., 2019). As a result, incorporation of 7.5Wt% nano-TiO₂ into the polypropylene matrix increases the degree of crystallinity.

The crystallization temperature (T_p), the melting peak temperature (T_{mp}) and the degree of crystallinity (X_c) of PP and derived nanocomposites are indicated in Table 1. The results suggest that the incorporation of nanofillers 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 (Sun et al., 2019).

$$\% \text{ Crystallinity} = \left(\frac{\Delta H_m}{\Delta H_L} \right) \times 100\% ; \Delta H_L = 207.1 \text{ J/g} \quad (2)$$

Table 1. DSC data of the tested nanocomposites

Nanocomposites	$T_p, ^\circ\text{C}$	$T_{mp}, ^\circ\text{C}$	$\Delta H_m, \text{J/g}$	$\Delta H_c, \text{J/g}$	$X_c, \%$
PP/0Wt% TiO_2	111.22	169.26	107.1	90.28	51.71
PP/2.5Wt% TiO_2	113.28	167.75	110.25	97.81	53.23
PP/5Wt% TiO_2	115.04	168.78	111.36	93.8	53.77
PP/7.5Wt% TiO_2	113.37	163.82	113.5	109.83	54.80

b. Thermogravimetric analysis (TGA)

The thermal degradation stability and mechanisms of the nanocomposites are an important property for various application areas due to the changes in the viscoelastic behaviour and viscosity (Aydemir et al., 2016). In this study, the thermal properties of the nanocomposites have been investigated using TGA. Fig.4 shows the TGA curves of TiO_2 /PP nanocomposites. According to the obtained results, the addition of nano- TiO_2 slightly improved thermal stability of the neat PP, when TiO_2 nanocharges were added up to 5 Wt%. The DTG curve of nanocomposite suggested the presence of peaks located between 325 and 475 $^\circ\text{C}$. This peak is attributed to the rupture of the C-C chain's bonds along with H-abstraction at the site of rupture (Aydemir et al., 2016).

Incorporation of 2.5Wt% nano- TiO_2 into the polypropylene matrix increases the thermal stability with the decomposition temperature was found to be 433.42 $^\circ\text{C}$. The decomposition temperature was decreasing with nano- TiO_2 content increasing. At 7.5Wt% TiO_2 , the result indicates that the decomposition temperature for the nanocomposites is around 429 $^\circ\text{C}$ (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 nanocomposites shifts to high temperature (above 54 $^\circ\text{C}$) (Maharramov et al., n.d.; Ramazanov et al., 2018). It should be noted that interaction degree between polymer matrix and nanofillers is connected to the concentration of base phase, crystallite sizes of nanofillers and acquisition condition of nanocomposites. This confirms the presence of an interphase or border layer between nanofillers and matrix with properties that differ

from matrix properties in the bulk (Maharramov et al., n.d.). The crystalline structure in the transition regions of the polymer boundary layer are form in the nanocomposites, 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 (Ramazanov et al., 2018).

Table 2. Decomposition temperature of the tested nanocomposites

	T (°C)
Polypropylene	348.83
2.5Wt%TiO₂	433.42
5Wt%TiO₂	429.89
7.5Wt%TiO₂	429.40

4. Conclusion

In this study, the nano-TiO₂ with spherical morphology and nanometric crystallite size has been synthesized using hydrothermal-assisted sol-gel technique. Diffraction peaks reveal the anatase TiO₂ phase. From the TEM images, the sphere is composed of 20–30 nm nanoparticles. This article aimed at presenting the impact of the nano-TiO₂ powders in the morphology and thermal performances of the polypropylene resin. The thermal degradation stability of the polypropylene increased with the addition of nano-TiO₂. The results obtained show that the incorporation of nano-TiO₂ into the polypropylene matrix, the degree of crystallinity were relatively increased. Therefore, the interfacial interactions increased with the presence of anatase nanofillers in polyester matrix.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

DTA and TG curves of TiO_2 nanoparticles, (b) SEM micrographs (c) size distribution from TEM observations and (d) XRD pattern

Figure 2

SEM images of the PP nanocomposites: (a) Polypropylene; (b) 2.5Wt% TiO₂; (c) 5Wt% TiO₂; (d) 7.5Wt% TiO₂

Figure 3

DSC curves of the PP and nanocomposites during the heating process: (a) Polypropylene; (b) 2.5Wt%TiO₂; (c) 5Wt%TiO₂; (d) 7.5Wt% TiO₂

Figure 4

Thermogravimetric (TG) and first-order derivative (DTG) curves of/ (a) Polypropylene; (b) 2.5Wt%TiO₂; (c) 5Wt%TiO₂; (d) 7.5Wt% TiO₂