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Research Article

Thermal and Mechanical Properties of Polyethylene/Doped-TiO₂ Nanocomposites Synthesized Using In Situ Polymerization

S. H. Abdul Kaleel,¹ Bijal Kottukkal Bahuleyan,¹ J. Masihullah,¹ and Mamdouh Al-Harthy^{1,2}

¹Department of Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

²Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Correspondence should be addressed to Mamdouh Al-Harthy, mamdouh94@yahoo.com

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Ethylene polymerization was carried out using highly active metallocene catalysts (Cp₂ZrCl₂ and Cp₂TiCl₂) in combination with methylaluminoxane. Titanium (IV) oxide containing 1% Mn as dopant was used as nanofillers. The effects of filler concentration, reaction temperature, and pressure on the thermal and mechanical properties of polymer were analyzed. The improvement of nanoparticles dispersion in the polyethylene matrix was checked by WAXD. The thermal properties were analyzed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The filler impact on the melting temperature of polyethylene synthesized using Cp₂ZrCl₂ was very minimal which is due to the degree of short-chain branching. The ash content was also analyzed for each nanocomposite and found to be in line with the activity of the catalyst. There was a significant increase in the mechanical properties of the polyethylene by addition of filler.

1. Introduction

The inorganic mineral fillers help in fulfilling polymer performance properties, such as increasing the stiffness, heat distortion temperature, dimensional stability, hardness, and toughening of the products [1–4]. The properties of polymer composites depend on the particles shape, size, loading, interfacial bonding, and dispersion of the fillers [5–8]. Polymer nanocomposites are a new class of materials incorporating an ultrafine dispersion of nanomaterials in a polymeric matrix. Inorganic nanoparticles such as silicon dioxide (SiO₂) [9–12], titanium dioxide (TiO₂) [13–16], Aluminium trioxide (Al₂O₃) [17, 18], and Zirconium dioxide (ZrO₂) [19, 20] have been used to improve polymer properties.

TiO₂ primarily served as a pigment than as filler for improving mechanical strength. TiO₂ was found to be well dispersed in polyvinyl alcohol using solution-mixing technique and these samples acted as efficient optically transparent UV filters due to the photo-responsive properties of TiO₂ [13]. In the recent past, TiO₂-filled polymers prepared by melt compounding have been reported to exhibit markedly improved properties over neat polymers and

micron-sized particle-filled polymer composites [21, 22]. Different kinds of polymer-based TiO₂ composites have been reported in the literature, such as high-impact polystyrene (HIPS)/nano-TiO₂ [23] and polyamide/nano-TiO₂ composite [24]. Polyethylene/TiO₂ composites were prepared, and it was found that the introduction of TiO₂ increased the viscosity of composites and produced a better dispersion of TiO₂ in the melt compounding with significant improvement in the impact strength and tensile strength of the polyethylene as well [25]. Various phases of TiO₂ were used for the synthesis of polyethylene/TiO₂ nanocomposites using direct mixing and masterbatch dilution, and it was found that no important differences in mechanical and morphological characteristics of anatase- and rutile-containing polyethylene composites were observed, except a higher increase of the elastic modulus in case of anatase-containing composites [26].

In general, polymer nanocomposites can be prepared by three methods, namely, (i) a melt mixing [27, 28], (ii) a solution blending [29], and (iii) in situ polymerization [30, 31]. Due to the direct synthesis via polymerization along with the presence of fillers, the in situ polymerization is perhaps considered the most promising technique to produce

polymer nanocomposites with homogeneous distribution of the nanoparticles inside the polymer matrix. Some research showed that the treatment of filler surfaces with metallocene-based catalysts can be used in the production of polyolefin nanocomposites [32].

Poly (ethylene terephthalate) (PET)/TiO₂ nanocomposites were synthesized using in situ polymerization and the homogeneous dispersion in nanoscale was found for nanocomposites when the content of TiO₂ is less than 2 wt%. Tensile performance shows that the nanoparticles can simultaneously provide PET improvement in modulus, strength, and elongation at break at rather low filler content. The addition of nano-TiO₂ to PET matrix also produces a broader UV absorption [33]. The high-energy density isotactic polypropylene-BaTiO₃ and TiO₂ nanocomposites were prepared via in situ metallocene polymerization, and it was found that there was effective dispersion of nanoparticles [34]. Recently, Owpradit et al. synthesized linear low-density polyethylene TiO₂ nanocomposite using in situ polymerization with zirconocene/MMAO catalyst, and it was found that the TiO₂ (Rutile) showed less deactivation upon increased [Al]/[Zr] ratio which was concluded by TGA measurements [35].

Progress made in the development of nanotechnology has rendered it possible to intensify TiO₂ effectiveness by modifying its surface with noble metal deposition. The purpose of doping TiO₂ nanoparticles with metals is to create a heterojunction [36]. The applications for doped TiO₂ nanocomposites range from antimicrobial coatings on textiles, the inactivation of endospores, solid-surface antimicrobial coatings, and aqueous system-based biocides [37–39]. To our knowledge, Mn-doped titania was never used in in situ polymerization which in turn motivated us to study its effect on the thermal and mechanical properties of the nanocomposites.

2. Experimental Methods

2.1. Materials. All manipulations were carried out under N₂ using standard polymerization reactor and glove box techniques. Titanium (IV) oxide containing 1% Mn as dopant, nanopowder (TiO₂/Mn), Cp₂ZrCl₂, Cp₂TiCl₂, and all other chemicals were purchased from Aldrich Chemicals and used without further purification. TiO₂/Mn nanofiller has a particle size of <100 nm with a surface area >14.0 m²/g. The TiO₂ used has an anatase phase composition. Solvents were purified by standard techniques.

2.2. Polymerization. The polymerization was carried out in a 1-liter autoclave reactor operated in a semibatch mode. The reactor was carefully cleaned and dried under vacuum at 150°C for 3 hours, and allowed to cool under nitrogen. Purified toluene was transferred to the reactor under nitrogen pressure through a transfer needle. The mixture was kept under stirring while the reactor was heated up to the desired polymerization temperature (30°C). Once the desired temperature was established, a prescribed amount of catalyst, cocatalyst, and filler solution or slurry was added

to the reactor under pure nitrogen atmosphere using gas-tight syringes. To start polymerization, the reactor was pressurized by ethylene to the desired pressure. The reactor was kept at constant pressure by continuous feeding of gaseous ethylene to the reactor. The reaction was stopped by rapid depressurization of the reactor followed by quenching with methanol. The polymer was washed with an excess amount of methanol and dried in vacuum at 50°C. To make a worthy comparison all data were collected under similar conditions.

2.3. Characterization. Wide-angle X-ray diffraction (WAXD) measurements were carried out on a Shimadzu X-ray diffractometer (40 kV, 40 mA) using Ni-filtered Cu K α radiation from 10 to 80 (in 2 θ) with 15 s standing per step.

The thermal transition of the composites was evaluated using nonisothermal DSC analysis. The analysis was performed by using TA Q1000 instrument equipped with liquid nitrogen cooling system and autosampler. The samples (sample size was around 6 mg) in nonhermetic pan were heated at 10°C/min and cooled at the rate 5°C/min and the temperature range of 20–170°C. The measurement process was as follows: first the sample was heated to 170°C, to eliminate the thermal history and then was cooled to observe the crystallinity behavior.

The thermal stability of the nanocomposites was studied using thermogravimetric analysis (TGA). TGA measurements were carried out using TA Instrument Hi-Res SDT Q600 thermogravimetric analyzer from 25 to 800°C with the heating rate of 10°C/min and a nitrogen gas flow rate of 50 cm³/min.

Tensile properties of the molded dog bone specimens were tested according to the ASTM-D638 standard, using an Instron machine (Model 5567) at room temperature and a crosshead speed of 50 mm/min. The average test specimen dimensions were 15 mm \times 3 mm \times 1 mm.

3. Results and Discussions

3.1. WAXD Analysis. The dispersion of filler in the polymer matrix is very important in enhancing the properties of the polymer nanocomposites. The improvement of doped-TiO₂ dispersion in PE matrix can be visibly checked by WAXD. Figure 1 shows the WAXD patterns of doped-TiO₂, control, and PE/doped-TiO₂ nanocomposites. The doped-TiO₂ has a sharp Bragg reflection at about 2 θ = 27°. WAXD curves of PE/doped-TiO₂ nanocomposites show disappearance of the basal peak, indicating that doped-TiO₂ is well dispersed in PE matrix during polymerization [40]. The strong reflections observed for the control were also present for comparison. This figure shows that the addition of doped-TiO₂ does not change the original crystal structure.

3.2. Thermal Properties of Polyethylene/Doped-TiO₂ Nanocomposites. Thermal properties of Polyethylene/doped-TiO₂ nanocomposites are reported in Table 1. A strong correlation was observed between filler loading and the degree of branching in polymer produced as evident in the DSC thermal analysis. The DSC thermal analyses are reported in

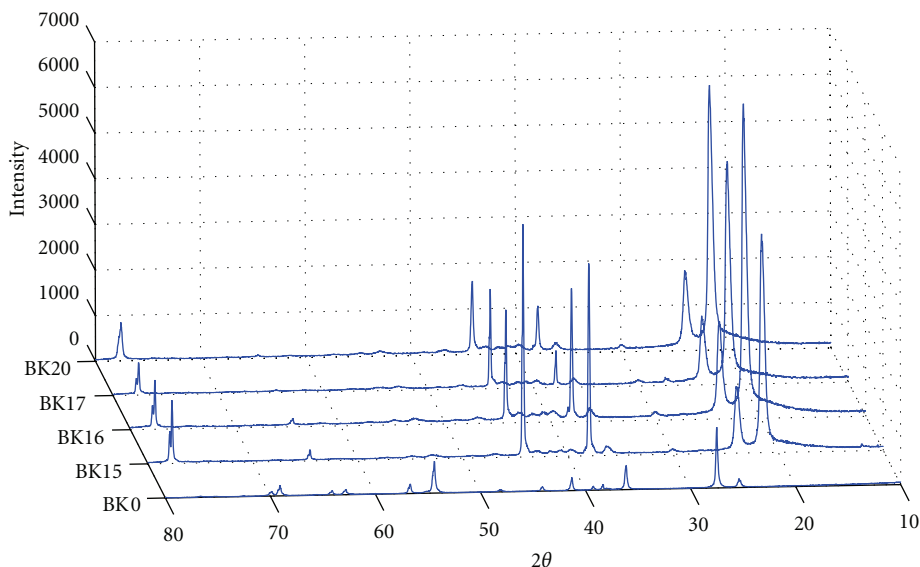


FIGURE 1: WAXD patterns of doped-TiO₂ (BK 0), control (BK 20, Entry 1 Table 1), and PE/doped-TiO₂ nanocomposites BK 16 (Entry 2 Table 1), BK 17 (Entry 4 Table 1) & BK 5 (Entry 3 Table 1).

TABLE 1: Results of ethylene polymerization^a.

Entry no.	Filler (in mg)	T_m^f (°C)	X_c^f	$T_{degradation}^g$ (°C)
1	0 ^b	136	67	452
2	15	137	62	475
3	15 ^c	137	64	478
4	15 ^d	135	71	468
5	15 ^e	130	71	469

^a Polymerization conditions: solvent toluene = 100 mL, temp = 30°C, catalyst (Cp₂ZrCl₂) amount = 20.5 μmol, filler is Mn (1%) doped TiO₂, [Al]/[M] = 700, ethylene Pressure = 5 bar, reaction time = 30 mins, ^bControl, ^cReaction Time = 60 mins, ^dReaction Time = 120 mins, ^eEthylene Pressure = 2 bar, ^fDetermined by DSC measurements, ^gDetermined by TGA analysis.

terms of melting temperature (T_m) and degree of crystallinity (X_c). The melting behavior of polyethylene is mainly related to the short-chain branching density.

Increasing short-chain branching density decreases lamellar thickness of the crystal structure and thus lowers melting temperature of the polymer. The short-chain branching also affects the degree of crystallinity which is proportional to the fractional amount of crystalline phase in polymer sample [41].

Table 1 illustrates the various crystallization behaviors of the polyethylene nanocomposites in reference to the effect of pressure. The crystallinity reduces by incorporation of the filler at the ethylene pressure of 5 bar (Entry 2 Table 1), which is due to the fact that this filler hinders the crystalline alignment of polymer chain. But with respect to time, the degree of crystallinity increases due to the decrease in filler to polymer ratio. As far as the melting temperature there is not much variation either by incorporation of filler or by increasing the reaction time at a constant ethylene pressure of 5 bar. At low pressure (Entry 5 Table 1) there is a decrease

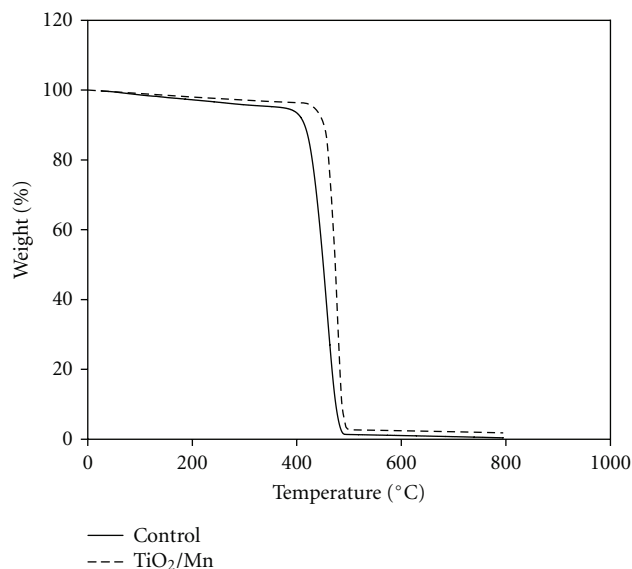


FIGURE 2: TGA curves of neat polyethylene (Entry 1 Table 2) and polyethylene with doped titania (Entry 2 Table 2) synthesized at high pressure (5 bar) using Zirconocene catalyst.

in the melting temperature of the nanocomposite which is due to increase in degree of short-chain branching.

Figure 2 shows that the thermal stability of polyethylene increases by the addition of doped titania to the polymer matrix. This variation in the thermal stability alludes to the fact that there is an increase in the molecular weight of the polyethylene by addition of filler. With respect to the ash content, the ash content for neat polyethylene (Entry 1 Table 1) is almost ground to zero, but in the case of nanocomposite (Entry 2 Table 1) small weight percentage of ash is left out which is due to the filler content in this sample.

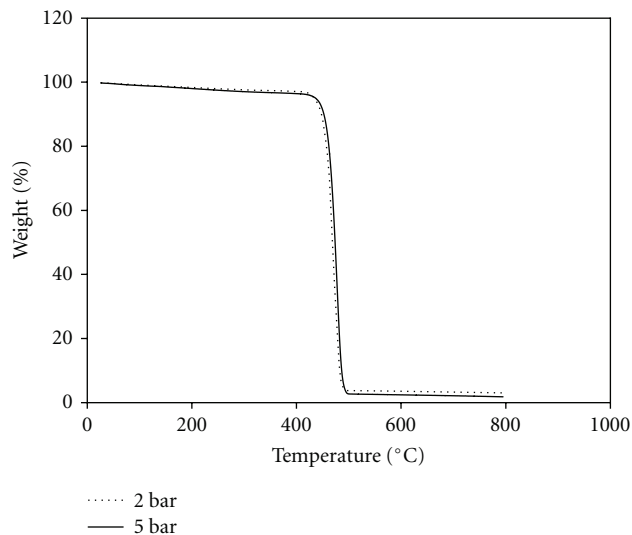


FIGURE 3: TGA curves of neat polyethylene synthesized at 5 bar (Entry 1 Table 1) and polyethylene with doped titania synthesized at 2 bar (Entry 5 Table 1) using Zirconocene catalyst.

TABLE 2: Results of ethylene polymerization^a.

Entry no.	Filler (in mg)	Pressure (Bar)	Time (minutes)	Ultimate strength (MPa)	Young's modulus (MPa)	Strain at Fracture (%)
1	0 ^b	5	30	17	325	7
2	15	5	30	17	338	454
3	15 ^c	5	60	33	342	1040

^aPolymerization conditions: solvent toluene = 100 mL, temp = 30°C, catalyst (Cp₂ZrCl₂) amount = 20.5 μmol, filler is Mn (1%)-doped TiO₂, [Al]/[M] = 700, reaction time = 30 mins, Ethylene Pressure = 5 bar, ^bControl, ^cReaction Time = 60 mins.

From Table 1 it can be concluded that there is an increase in the molecular weight of the synthesized polyethylene nanocomposites with respect to pressure. Figure 3 illustrates that the thermal stability of nanocomposite synthesized at ethylene pressure of 2 bar (Entry 5 Table 1) is less when compared to the nanocomposite synthesized at 5 bar (Entry 2 Table 1) ethylene pressure.

It is usually assumed that upon completion of TGA, all carbon has been removed in the forms of CO and CO₂ and that all remaining material consists of metal oxides. In the case of polyethylene/doped-titania nanocomposite less ash is found which is due to the polymer to filler ratio, since the activity in the presence of doped titania is very high [42], the filler weight percentage is very low which corresponds to less ash content in the TGA curves.

3.3. Mechanical Properties of Polyethylene/Doped-Titania Nanocomposites. Table 2 gives the overall view of mechanical properties of polyethylene/doped-titania nanocomposites, that is, elastic modulus, ultimate strength, strain at fracture with respect to reaction time. In each case, minimum of five samples were tested, and the tabulated values are the average of these results. It can be observed that the elastic

modulus and ultimate strength show good enhancement with the addition of filler, and this enhancement is further seen with respect to reaction time as well, which is believed to be due to good interface between polymer and TiO₂/Mn, thus transferring load from polymer to the nanofiller. It is evident from Table 2 that the filler enhances the mechanical properties of the polyethylene to a great extent as the percentage of strain at fracture increases in multitudes by addition of filler which further increases by the reaction time. This conclusion is very important as this filler not only enhances the activity of the polyethylene [42] but it even enhances the thermal and mechanical properties which widens the application of this filler.

4. Conclusion


The improvement of nanoparticles dispersion in the polyethylene matrix was checked by WAXD. The thermal properties were analyzed using differential scanning calorimetry and thermogravimetric analysis. The melting temperature varied in accordance to the degree of short-chain branching as increasing short-chain branching density decreases lamellar thickness of the crystal structure and thus lowers melting temperature of the polymer. The thermal stability of the polymer nanocomposites was found to vary in accordance with the molecular weight, and the ash content was analyzed in prospect of filler weight percentage in the nanocomposites. There was an increase in the mechanical properties of the polyethylene by addition of filler and with respect to reaction time as well.

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