

# *In Situ* Synthesis of Inorganic Filler-Filled Polyethylene Using Polyethersulfone-Supported TiCl<sub>4</sub> Catalyst System

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**ABSTRACT:** *In situ* ethylene polymerizations with inorganic fillers were performed using catalyst based on titanium tetrachloride supported on polyethersulfone. The inorganic fillers used were MgO, TiO<sub>2</sub>, and CaCO<sub>3</sub>, which were pretreated with cocatalyst (methylaluminoxine) for better dispersion onto the polymer matrix. The formation of polyethylene (PE) within the whole matrix was confirmed by Fourier transform infrared studies. The wide-angle X-ray diffraction profile of the synthesized PEs indicated the presence of crystalline region. It was found that the nature of inorganic filler did not have any remarkable effect on the melting characteristics of the polymer, but the degree of crystallinity of PE was found to be higher

for TiO<sub>2</sub>-filled PE. The amount of filler incorporated into the matrix was also evaluated through thermogravimetric analysis, where TiO<sub>2</sub>-filled PE showed ~ 49% of filler material, which was also reflected in the higher productivity obtained by this system. The morphology of the filler-filled PEs was different, whereas the elemental dispersion was found to be uniform on the surface as elucidated through energy-dispersive X-ray spectroscopy. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2611–2619, 2011

**Key words:** polymeric support; Ziegler-Natta polymerization; polyethylene; polyethersulfone; inorganic filler

## INTRODUCTION

The addition of fillers to polymer mixtures is an empirical procedure. Most of the polymers that are used in engineering applications are highly loaded with filler particles. These particles serve to control many critical physical properties, such as strength, modulus, thermal expansion, thermal conductivity, and density. The introduction of fillers into polyolefins exerts a strengthening influence on the materials. This is one of the ways to improve certain mechanical properties of polyolefins. The use of fillers is an established method of modifying the properties of plastics.<sup>1–3</sup> The recent increase in prices of plastic raw materials and the new developments in compounding technology increased the interest of the plastic industry in compounds of fillers and polyethylene (PE).<sup>2–5</sup>

PE is one of the most widely exploited polymers and is often compounded with natural minerals to enhance its stiffness, toughness, dimensional stability, or electric insulation properties.<sup>6,7</sup> Like most of

the natural minerals, CaCO<sub>3</sub>, MgO, and TiO<sub>2</sub> have high energetic hydrophilic surfaces. However, the PE surface is of low energy and hydrophobic nature,<sup>6,8</sup> and this often leads to aggregation (hard clusters that need attrition to be disintegrated) and agglomeration (soft flocks) of the filler particles to clusters in the polymer matrix. The number and strength of the clusters depend on the particles size, specific surface area, production method, and compounding conditions.

In addition to the component properties, the composite mechanical characteristics are influenced by the adhesion forces at the filler–matrix interface and by the thickness and properties of the interphase, for example, crystallite orientation and chain dynamics.<sup>9</sup> Moreover, the particulates can influence the polymer crystallization, thereby increasing or decreasing the crystallinity and thickness of the crystallites.<sup>10</sup>

Various methodologies of filler-filled synthesis are available globally, and one of the ways is the usage of coating agents. The application of coating agents favors a more homogeneous distribution of filler particles in the polymer matrix and the improvement of their adhesive interaction.<sup>11–15</sup> The coating agent really forms the transitional layer at the polymer–filler interface.<sup>16</sup> Another methodology is the method of polymerization filling, where filler is introduced into polyolefins during the synthesis of

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the polymer matrix, which gives the possibility to trace how the interlayer affects the properties of the filled polymer.<sup>17–20</sup> According to the method of polymerization filling, the polymer matrix is formed directly as a coating of regulated thickness at filler particles by the polymerization of a monomer or mixture of monomers on the filler surface activated by a suitable catalyst.<sup>21–24</sup> This is a way to incorporate, between the filler surface and the polymer matrix, an intermediate polymer layer of a desired nature and properties, and to affect the properties of the composition as a whole.<sup>25,26</sup>

In this study, we have used MgO, TiO<sub>2</sub>, and CaCO<sub>3</sub> as inorganic fillers using polymerization filling methodology for PE synthesis. The catalyst system used for producing the PEs was titanium tetrachloride (TiCl<sub>4</sub>), which was immobilized on polyethersulfone (PES). Fillers pretreated with cocatalyst (methylaluminoxane) were added to the catalyst system for synthesis of filler-filled PE. The PEs synthesized were characterized using Fourier transform infrared (FTIR), wide-angle X-ray diffraction (WAXD), and thermal properties to elucidate the fillers effect.

## EXPERIMENTAL

### Materials

Poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene), also known as PES, *n*-hexane (99.9%), and toluene (99.9%) were used as received from Aldrich. High-purity polymerization-grade ethylene gas of 99.9% purity was taken from commercial plant and used without further purification. Titanium tetrachloride and triethylaluminum were commercial products and used as such. Methylaluminoxane (MAO; 10% v/v in toluene) was used as obtained from Crompton, GmbH. MgO (99.9%), CaCO<sub>3</sub> (99.9%), and TiO<sub>2</sub> (99.9%) were used as received from Aldrich.

### Synthesis of PES-supported TiCl<sub>4</sub> catalyst

For synthesizing the polymeric-supported TiCl<sub>4</sub> catalyst, commercially available PES (having  $M_n = 38,000 \text{ g mol}^{-1}$ ; melt flow index = 16 g/10 min) was taken as the support. A known amount of PES was dissolved in the dry dichloromethane by stirring for 45 min (Table I). To this solution, the required amount of TiCl<sub>4</sub> was added dropwise with continuous stirring. The reaction mixture, which showed immediate formation of yellow precipitate, was allowed to stir at ambient temperature for 2 h, washed with dry hexane (100 mL × 5) to remove the excess TiCl<sub>4</sub>, and dried under vacuum. The dried catalyst was subjected to titanium estimation by calorimetric method using UV–vis spectroscopy.<sup>27,28</sup>

**TABLE I**  
Experimental Conditions<sup>a</sup> and Results for Synthesis of PES-Supported Catalysts

Entry	Cat-1	Cat-2	Cat-3
PES (g)	2.0	2.0	2.0
TiCl <sub>4</sub> (g)	0.6	0.6	0.6
TiCl <sub>4</sub> /PES weight ratio	0.3	0.3	0.3
Physical nature	Yellow	Yellow	Yellow
Ti (wt %)	2.3	2.5	2.4

<sup>a</sup> Dry dichloromethane.

### Polymerization of ethylene using PES-supported TiCl<sub>4</sub> catalyst

All the polymerizations were carried out in 1-L double jacketed glass reactor equipped with a top mounted mechanical stirrer under nitrogen atmosphere. After the addition of toluene (100 mL), it was saturated with ethylene followed by the addition of MAO (3 mL; 10% v/v; Al/Ti mole ratio = 200). Finally, the catalyst (100 mg) was added to start the polymerization at ambient temperature and a pressure of 1 bar. The addition of ethylene was continued during the 60-min polymerization. The polymerization was stopped by the addition of sufficient amount of the acidified methanol,<sup>29–32</sup> and the precipitated polymer was filtered, washed with methanol, and dried under vacuum.

### Synthesis of *in situ* filler-filled PE using PES-supported catalyst

The polymerizations were carried out in 1-L double jacketed glass reactor equipped with a top mounted mechanical stirrer under nitrogen atmosphere. In 100-mL toluene, MAO (2.6 mL 10% v/v; Al/Ti mole ratio = 200) was added followed by the filler (1 g; MgO/CaCO<sub>3</sub>/TiO<sub>2</sub>) and stirred for 30 min. Then, 200-mL toluene was added followed by MAO (3 mL, 10% v/v; Al/Ti mole ratio = 200). Finally, the catalyst (100 mg) was added to start the polymerization at ambient temperature and 1-bar pressure. The addition of ethylene was continued during the 60-min polymerization. The polymerization was stopped by the addition of sufficient amount of acidified methanol.<sup>33–36</sup> The precipitated polymer was filtered, washed with methanol, and dried under vacuum.

### Characterization of PES-supported TiCl<sub>4</sub> catalyst

For the determination of titanium content in the catalyst, the catalyst was dissolved in an acidic media. The titanium contained in the catalysts was converted into Ti<sup>4+</sup> by the addition of H<sub>2</sub>O<sub>2</sub>. UV–vis spectra of the resultant solution of peroxotitanium complexes were recorded on a Perkin-Elmer UV

**TABLE II**  
Experimental Conditions and Results for Synthesis of *In Situ* Filler-Filled PEs Using PES-Supported Catalyst (Cat-2)

	PE	PE-MgO	PE-CaCO <sub>3</sub>	PE-TiO <sub>2</sub>
Cat-2 (mg)	100	100	100	100
MAO-treated filler (g)	0	1	1	1
MAO (mL)	3	3	3	3
[Al]/[Ti]	200	200	200	200
Activity (kg PE mol Ti <sup>-1</sup> h <sup>-1</sup> )	38	31	42	56

Lambda12 spectrometer. The intensity of a peak at 410 nm ( $\epsilon = 782.7 \text{ L}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$ ) was used to quantify the titanium content. FTIR studies were performed on Perkin-Elmer spectrum GX instrument with  $4 \text{ cm}^{-1}$  resolution and 32 scans with KBr pellet for determining the characteristic vibrational modes of the catalyst.<sup>37-40</sup>

#### Characterization of *in situ* filler-filled PEs

FTIR studies were performed on Perkin-Elmer spectrum GX instrument with  $4 \text{ cm}^{-1}$  resolution and 32 scans with KBr pellet in transmittance mode. The melting points of PEs were measured by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 at a heating rate of  $10^\circ\text{C min}^{-1}$  from 50 to  $300^\circ\text{C}$  (with held for 3 min at  $300^\circ\text{C}$ ), cooling rate of  $10^\circ\text{C min}^{-1}$  from 300 to  $50^\circ\text{C}$  and again heating from 50 to  $300^\circ\text{C}$ . Thermal stability studies were performed using thermogravimetric analysis (TGA) with a TGA V 50 1A Perkin Elmer thermogravimetric analyzer in the presence of nitrogen in the temperature range of  $50\text{--}650^\circ\text{C}$  and at a heating rate of  $10^\circ\text{C min}^{-1}$ . The polymer morphology and energy-dispersive X-ray (EDX) spectroscopy were examined by FEI Inspect scanning electron microscope equipped with EDX analyzer (Oxford instruments; INCAx-Sight). The voltage and working distance were varied during the measurements.  $^{13}\text{C}\{^1\text{H}\}$ -NMR experiments were performed in 50%(v/v) 1,2,4-trichlorobenzene and d2-tetrachloroethane solution at  $130^\circ\text{C}$  with  $30^\circ$  pulse, 10,000 transients, 2-s delay time, and broadband proton decoupling.

### RESULTS AND DISCUSSION

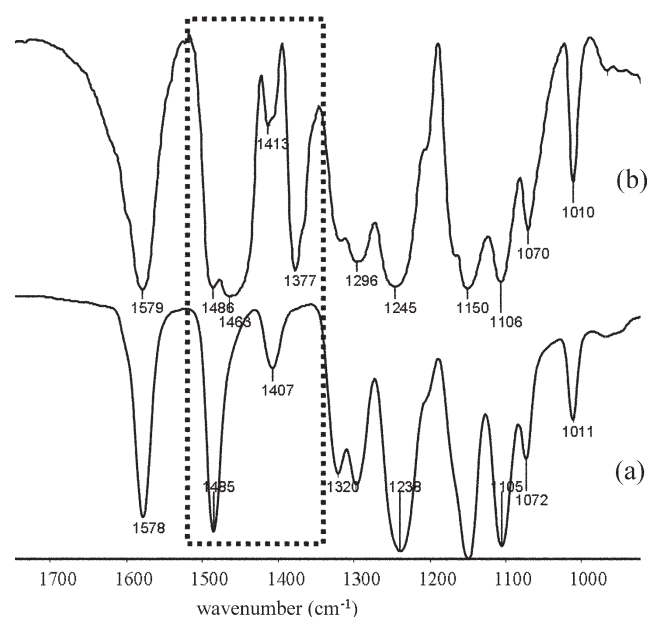
The synthesized supported catalyst system (Table I) has  $\text{TiCl}_4$  immobilized on PES, as PES has potential Lewis base sites in the form of oxygen of sulfonyl group where the coordination of titanium can be expected. For the evaluation of the performance of this catalyst, room temperature atmospheric polymerization of ethylene was carried out.<sup>41-44</sup> The catalyst system showed activity of  $38 \text{ kg PE mol}$

$\text{Ti}^{-1} \text{ h}^{-1}$ , indicating its potential for polymerization. After ensuring the reproducibility of titanium loading on to the PES, Cat-2 was further used for preparing *in situ* filler-filled PE. The inorganic fillers used for this study were anhydrous MgO,  $\text{CaCO}_3$ , and  $\text{TiO}_2$ . For this purpose, to ensure a homogenous dispersion of fillers in the PE matrix produced, it was necessary to activate the fillers in advance, which is unmasking the active centers for ethylene polymerization formed on the surface of the filler. Hence, the fillers were pretreated with MAO to minimize the deactivation effects of their surfaces on catalyst activity and to generate active centers for ethylene polymerization. If this is not done, then the polymerization yield of PE will be reduced substantially. Table II shows the activity for the filler-filled and non-filler-filled catalyst system (Cat-2). The maximum activity was obtained when  $\text{TiO}_2$  was used as filler, indicating the high reactivity of Ti-O for ethylene polymerization.

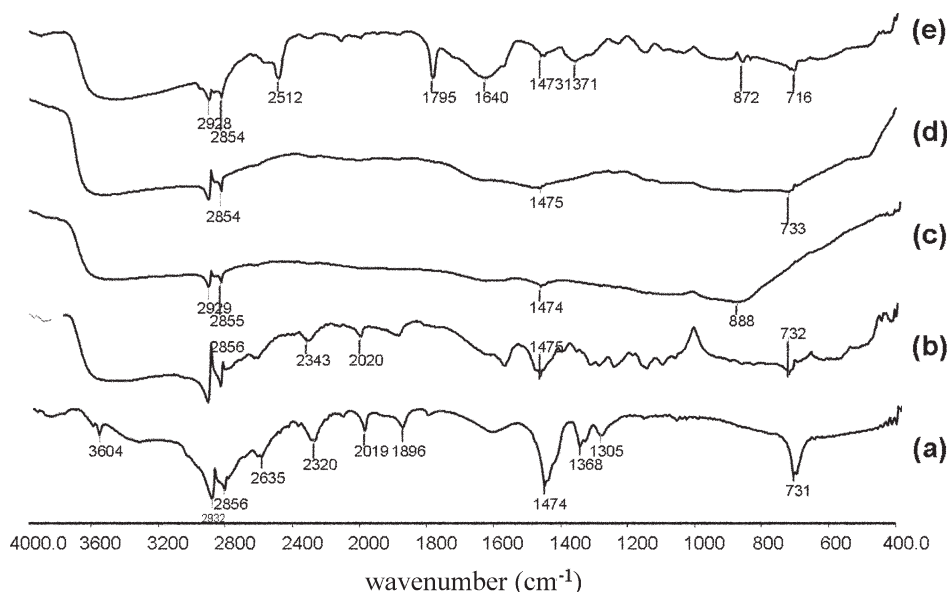
#### PES-supported $\text{TiCl}_4$ catalyst

##### Fourier transform infrared study

Figure 1 shows the FTIR spectra of pure PES and the PES-supported catalyst system. The pure PES shows a strong absorption band at  $1486 \text{ cm}^{-1}$  [Fig. 1(a)] attributed to the stretching vibration of the S=O groups belonging to the sulfone groups.<sup>45,46</sup> There is a band elongation at  $1407 \text{ cm}^{-1}$  [Fig. 1(a)] and absence of the strong band at  $1377 \text{ cm}^{-1}$  [Fig. 1(a)], which may be associated with vibration of the sulfur oxygen bonding, belong to the sulfone group. After the incorporation of titanium onto the



**Figure 1** FTIR spectra: (a) pure PES and (b) PES-supported  $\text{TiCl}_4$  catalyst.



**Figure 2** FTIR spectra: (a) pure PE; (b) PE synthesized from PES-supported  $\text{TiCl}_4$  catalyst; (c)  $\text{TiO}_2$ -filled PE; (d)  $\text{MgO}$ -filled PE; and (e)  $\text{CaCO}_3$ -filled PE.

polymer, a new absorption band at  $1463\text{ cm}^{-1}$  [Fig. 1(b)] appeared along with  $\text{S}=\text{O}$  band, which may be attributed to the complexation of titanium with the sulfone group of the polymer.

### *In situ* filler-filled PEs

#### Fourier transform infrared study

The FTIR spectra of pure PE, PE synthesized by PES-supported  $\text{TiCl}_4$  catalyst, and *in situ* filler-filled PE are shown in Figure 2. In Figure 2(a,b), strong absorption bands at  $2929$  and  $2856\text{ cm}^{-1}$  corresponding to  $\nu(\text{C}-\text{H})$  stretching are observed. These bands are also present in filler-filled PEs [Fig. 2(c-e)]. The occurrence of all these IR bands indicates that PE has been formed in the presence of organic support and inorganic fillers during the polymerization. A strong band at  $1474\text{ cm}^{-1}$  (Fig. 2) corresponding to  $\nu(\text{C}-\text{H})$  deformation of tertiary carbon is also present. The absorption band at  $731\text{ cm}^{-1}$ , corresponding to crystalline components of PE, shows strongly in Figure 2(a,b), but the intensity of this band decreases in  $\text{CaCO}_3$ -filled PE [Fig. 2(e)], whereas in  $\text{TiO}_2$ - and  $\text{MgO}$ -filled PE, it is marginally seen as in Figure 2(c,d).

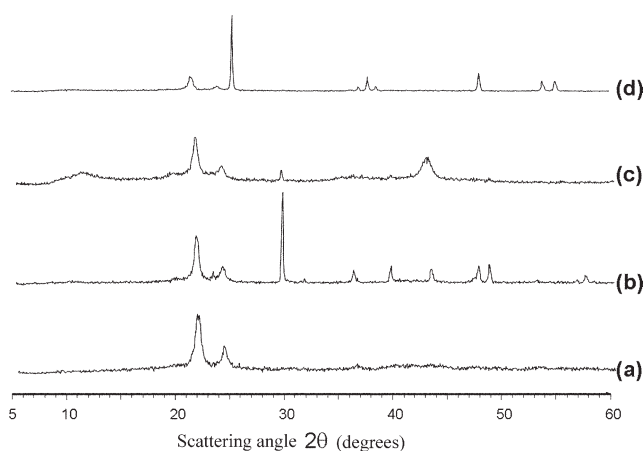
#### Wide-angle X-ray diffraction study

The X-ray diffractograms of the PEs synthesized using PES-supported  $\text{TiCl}_4$  catalyst and filler-filled PE are shown in Figure 3. The sharp and intense crystalline peaks observed at  $2\theta = 22.9^\circ$  and  $24.5^\circ$  correspond to the (110) and (200) crystallographic planes of the PE, suggesting that PE has been

formed.<sup>47,48</sup> The filler-filled PEs showing crystalline peaks at  $2\theta = 22.9^\circ$  and  $24.05^\circ$  correspond to the (110) and (200) crystallographic planes of orthorhombic unit cell of PE as depicted in Figure 3(b-d). This indicates that crystalline phase of PE is formed in the presence of MAO-treated filler particles.

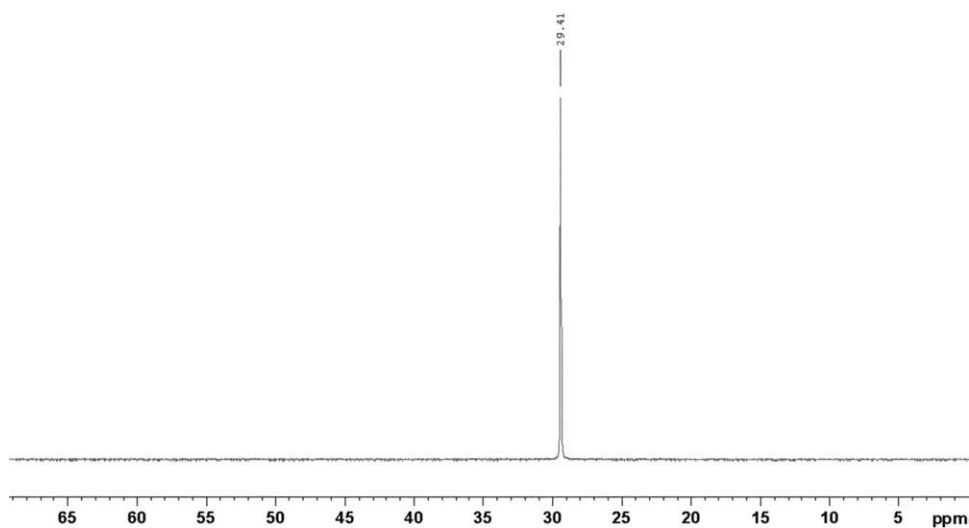
#### $^{13}\text{C}\{^1\text{H}\}$ -NMR study

Figure 4 shows the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PE synthesized by PES-supported  $\text{TiCl}_4$  catalyst, where only one strong resonance peak was observed at  $29.41\text{ ppm}$ , which is attributed to the main-chain methylene carbon.<sup>49,50</sup> Nonexistence of other resonance peaks indicates the absence of branching in the homopolymer synthesized using the polymeric-supported catalyst.



**Figure 3** WAXD profiles: (a) PE synthesized from PES-supported  $\text{TiCl}_4$  catalyst; (b)  $\text{TiO}_2$ -filled PE; (c)  $\text{MgO}$ -filled PE; and (d)  $\text{CaCO}_3$ -filled PE.



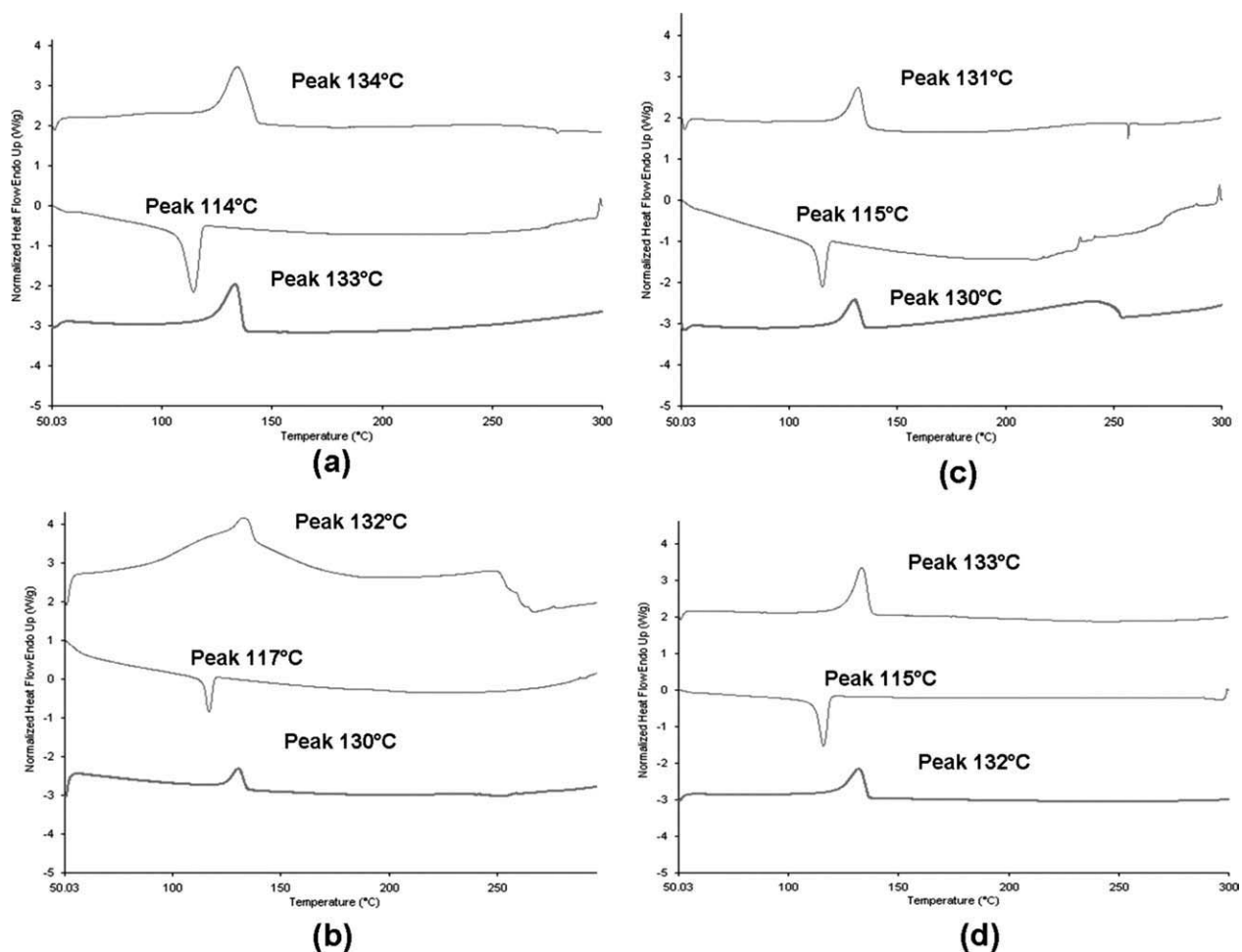


**Figure 4**  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of PES-supported PE synthesized from PES-supported  $\text{TiCl}_4$  catalyst.

Differential scanning calorimetry and thermogravimetry studies

The DSC analysis (Fig. 5) shows the melting and crystallization temperatures of the filler-filled PE

and nonfiller-filled PE. The melting as well as crystallization temperatures show no remarkable effect by the addition of inorganic fillers. There is no change in the crystallization onset temperature,



**Figure 5** DSC plots: (a) PE synthesized from PES-supported  $\text{TiCl}_4$  catalyst; (b) MgO-filled PE; (c)  $\text{CaCO}_3$ -filled PE; and (d)  $\text{TiO}_2$ -filled PE.

**TABLE III**  
Melting and Crystallization Temperatures of *In Situ* Filler-Filled PEs  
Using PES-Supported Catalysts

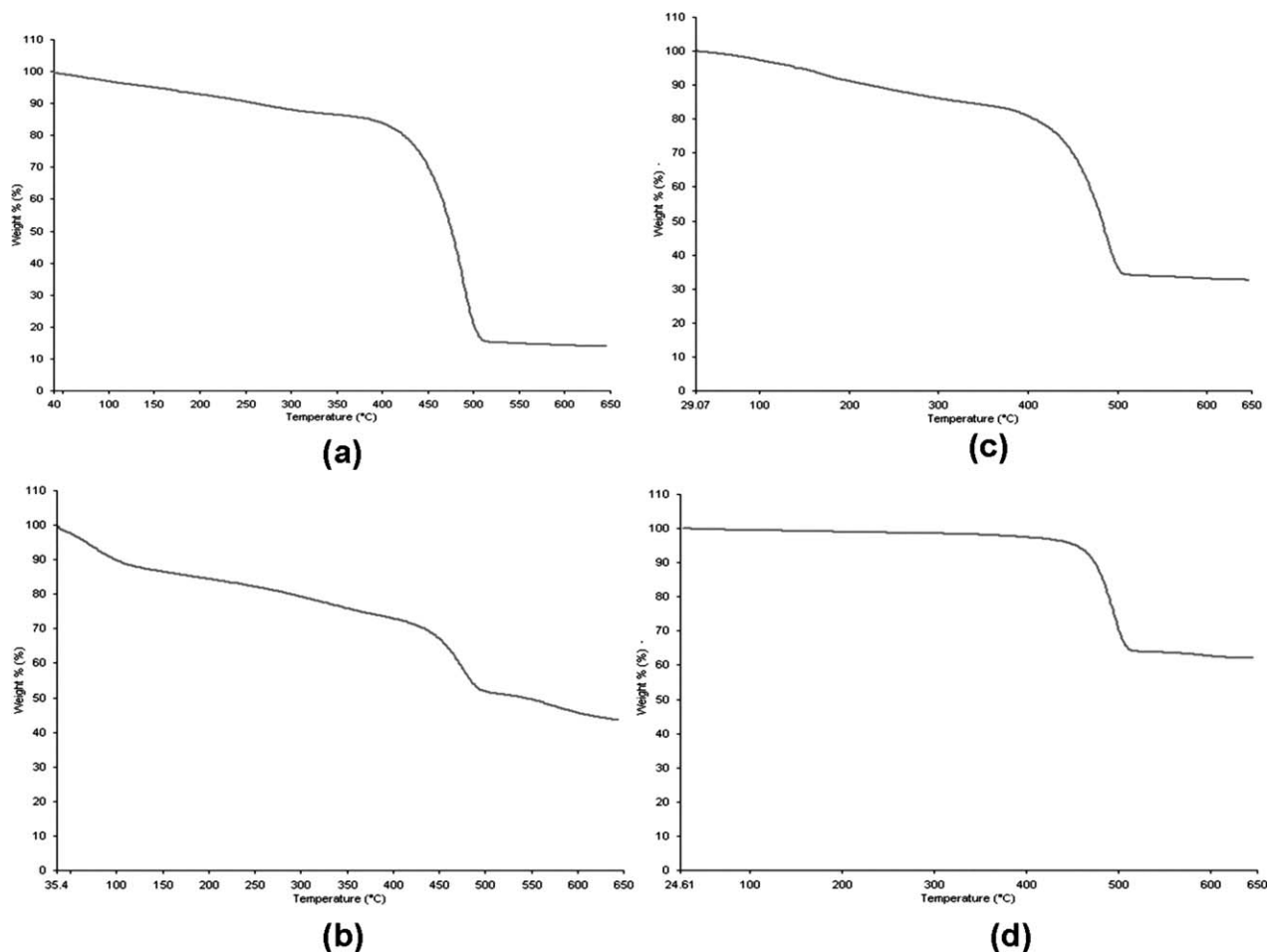
Filler	$T_{m, \text{onset}}$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$T_{c, \text{onset}}$ (°C)	$T_c$ (°C)	Crystallinity (%)
PES-PE	124	134	97	118	114	55.2
CaCO <sub>3</sub>	119	132	107	119	116	54.77
MgO	124	132	44	118	115	25.2
TiO <sub>2</sub>	126	133	62	118	116	31.58

$\Delta H_m$ , melting enthalpy (J g<sup>-1</sup>) of the filler-filled PE;  $T_{m, \text{onset}}$ , melting onset temperature;  $T_m$ , peak melting temperature;  $T_{c, \text{onset}}$ , onset crystallization temperature;  $T_c$ , peak crystallization temperature.

indicating that the inclusions induce heterogeneous nucleation. The high melt enthalpy observed for CaCO<sub>3</sub>-filled PE can be attributed to the difference in crystallites size as well as molecular weight of PE chain. Despite of little influence on the crystallization kinetics, presence of filler shows major influence on the degree of crystallinity of PE as shown in Table III. The degree of crystallinity of the filler-filled PEs was measured using the following formula,<sup>51,52</sup>

$$X = \frac{\Delta H_m}{\Delta H_o \left( \frac{m_p}{m_c} \right)} \times 100,$$

where  $X$  is the percent crystallinity of the composites;  $\Delta H_m$  the melting enthalpy (J g<sup>-1</sup>) of the filler-filled PE;  $\Delta H_o$  the melting enthalpy (293 J g<sup>-1</sup>) of 100% crystalline PE<sup>53,54</sup>;  $m_p$  the mass (g) of PE in the filler-filled PE; and  $m_c$  is the mass (g) of the filler-



**Figure 6** TGA plots: (a) PE synthesized from PES-supported TiCl<sub>4</sub> catalyst; (b) MgO-filled PE; (c) CaCO<sub>3</sub>-filled PE; and (d) TiO<sub>2</sub>-filled PE.

**TABLE IV**  
TGA and Theoretical Values of *In Situ* Filler-Filled PEs Using PES-Supported Catalysts

Filler	TGA (g)	Theoretical (g)
MgO-PE	32.9	33.3
TiO <sub>2</sub> -PE	62.6	64.5
CaCO <sub>3</sub> -PE	28.7	29.4

filled PE. CaCO<sub>3</sub>-filled PE possesses a higher degree of crystallinity and higher melting temperature than MgO- and TiO<sub>2</sub>-filled PEs. The high melting point of all the polymers indicates the branchless structure of the homopolymer.

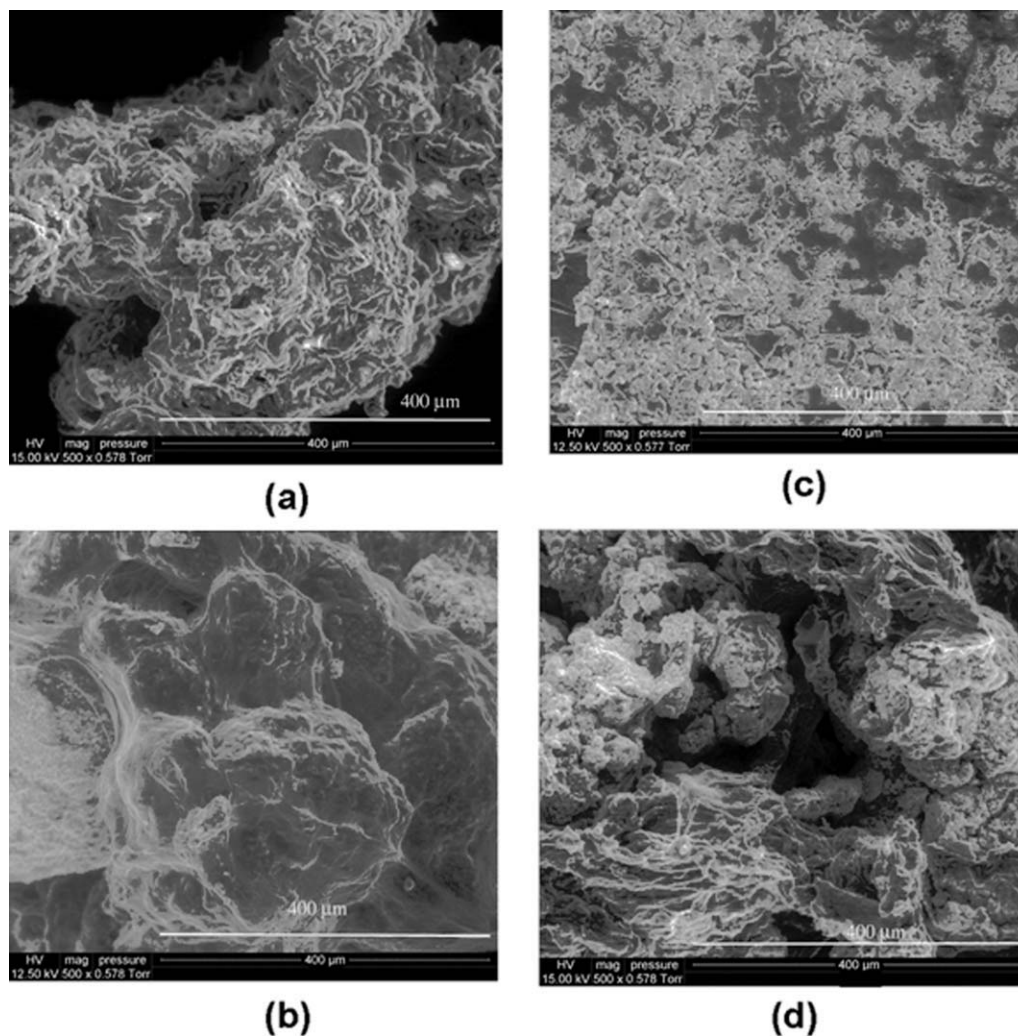
To understand the weight percentage of the filler material into the polymer, TGAs were conducted (see Fig. 6). The results obtained clearly indicate that when PES-supported catalyst-based PE was heated from 40 to 400°C [Fig. 6(a)], there was a gradual reduction in weight percentage. The weight loss of ~ 79% was observed from 400 to 500°C, which

remains constant after 500°C temperature. At 600°C, 14 wt % of material was obtained.

For MgO-filled PE, the weight loss was observed [Fig. 6(b)] to be ~ 20% on reaching 400°C, followed by drastic reduction in weight (~ 64%) from 400 to 500°C. At temperature above 550°C, no significant weight loss was observed, indicating that ~ 19 wt % MgO has been associated with PE.

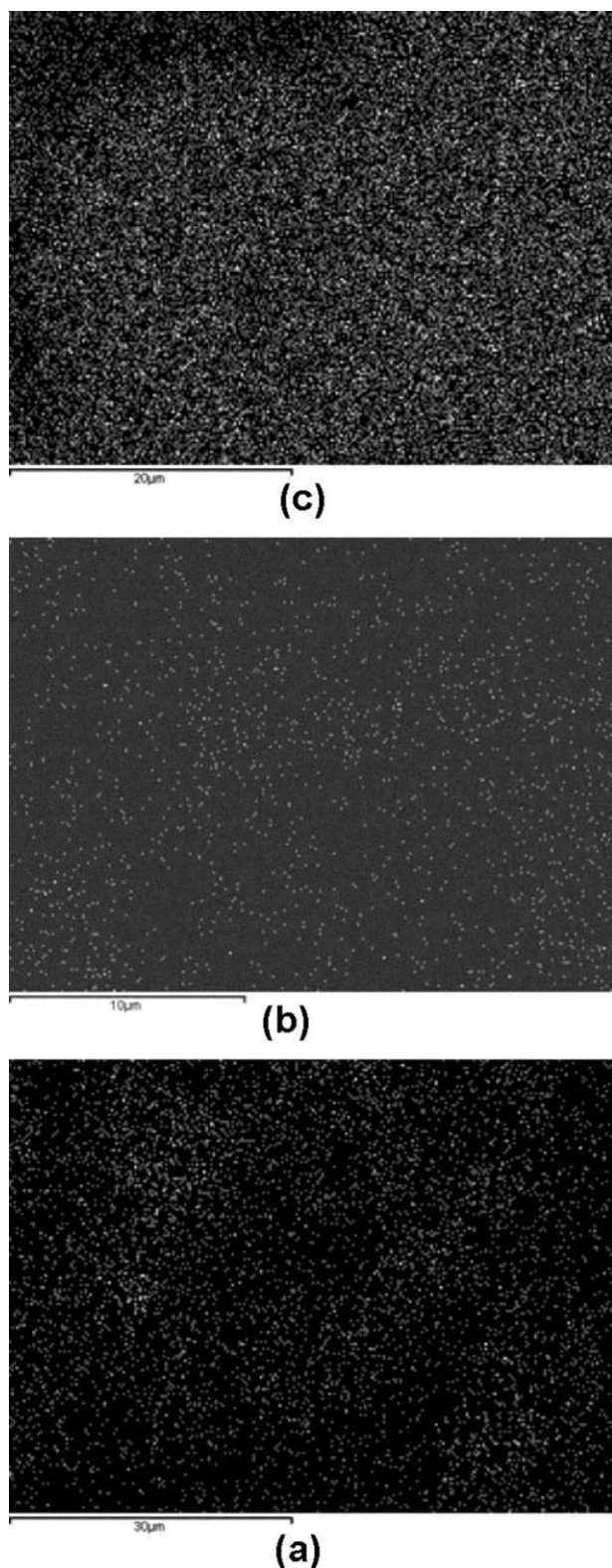
In case of CaCO<sub>3</sub>-filled PE [Fig. 6(c)], ~ 29% weight loss was observed on reaching 400°C, which increased to ~ 50% when temperature reached to 500°C. After 550°C, no weight loss was observed, which indicates ~ 35% association of filler with PE. Similarly, for TiO<sub>2</sub>-filled PE [Fig. 6(d)], only 4% weight loss was observed till 400°C followed by drastic weight loss of 37% from 400 to 500°C. After 550°C, no significant change in polymer weight was seen, indicating ~ 49% weight filler has been incorporated in PE.

The weight percentage of the fillers as elucidated by TGA and also in close agreement with theoretical



**Figure 7** SEM images: (a) PE synthesized from PES-supported TiCl<sub>4</sub> catalyst; (b) MgO-filled PE; (c) CaCO<sub>3</sub>-filled PE; and (d) TiO<sub>2</sub>-filled PE.





**Figure 8** EDX images: (a)  $\text{TiO}_2$ -filled PE; (b) MgO-filled PE; and (c)  $\text{CaCO}_3$ -filled PE.

as shown in Table IV. These data indicate that highest residual weight percent is for  $\text{TiO}_2$ -filled PE, which is also supported by the high activity observed for this system for polymerizing ethylene.

#### Scanning electron microscopy and energy-dispersive X-ray spectroscopy

For understanding the morphological aspects of filler-filled PE, scanning electron microscopy (SEM) micrographs were studied (Fig. 7). The morphology of the synthesized PE seems to be completely dependent on the filler. The nonfiller-filled PE seems to be a large globule [Fig. 7(a)], and comparing this with MgO-filled PE image [Fig. 7(b)], it seems that polymer has grown on to the filler and covered the filler surface completely.<sup>55–57</sup> Connecting thread-like polymer was also observed. For  $\text{CaCO}_3$ -filled PE, the morphology is completely different as clearly seen in Figure 7(c), whereas for  $\text{TiO}_2$ -filled PE, micrograph shows [Fig. 7(d)] thick thread-like polymer formation, which seems to be wrapped around and covered by polymer threads.

For evaluating the dispersion of inorganic fillers on the polymer surface, EDX was performed whose results are shown in Figure 8. The dispersion of Mg, Ca, and Ti is quite uniform in density with no large voids.

#### CONCLUSIONS

*In situ* polymerization of ethylene in the presence of MAO-treated inorganic fillers using PES-supported  $\text{TiCl}_4$  catalyst has been successfully carried out to formulate filler-filled PE. FTIR studies confirmed the formation of PE. DSC study shows that  $\text{CaCO}_3$ -filled PE is having high melting enthalpy than MgO- and  $\text{TiO}_2$ -filled PEs. TGA study indicates that  $\text{CaCO}_3$ -filled PE has higher thermal stability than MgO- and  $\text{TiO}_2$ -filled PEs. SEM micrographs confirm the formation of PE on the filler surfaces with homogenous dispersion of the inorganic filler particles in the PE matrix. We hope the results of this study may open a new field of research area where organic polymeric support can be used for catalyst preparation, which may be effectively and efficiently used for *in situ* polymerization.

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