

## IN SITU SYNTHESIS OF NANOCLAY FILLED POLYETHYLENE USING POLYMER SUPPORTED METALLOCENE CATALYST SYSTEM

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*In situ* ethylene polymerizations were performed using bis(cyclopentadiene)titanium dichloride supported on polyethersulfone as catalyst. The bis(cyclopentadiene)titanium dichloride supported on polyethersulfone catalyst activity estimated by ethylene polymerization was 360 kgPE/molTi/h. During polymerization the fillers used were montmorillonite nanoclays having surface modifications with 35-45 wt% dimethyl dialkyl(14-18)amine (FA) and 25-30 wt% trimethyl stearyl ammonium (FB). These fillers were pretreated with methylaluminoxine (MAO; cocatalyst) for better dispersion onto the polymer matrix. The formation of polyethylene within the whole matrix was confirmed by FTIR studies. It was found that the nature of nanofiller did not have any remarkable effect on the melting characteristics of the polymer. TGA study indicates that nanoclay FB filled polyethylene has higher thermal stability than nanoclay FA filled polyethylene. The melting temperature of the obtained polyethylenes was 142 °C, which corresponds to that synthesized by the polyether sulfone supported catalyst.

Keywords: nanoclay; polymeric support; bis(cyclopentadiene)titanium dichloride.

### INTRODUCTION

Polymer nanocomposites have attracted great interest, both in industry and in academy, because they exhibit remarkable improvement in material properties compared to virgin polymer or conventional micro- and macro-composites.<sup>1-3</sup> Preparation of desired products from polymer nanocomposites is a challenging area that requires considerable efforts. Polyethylene (PE) is one of the most widely used polyolefin but the use is restricted in certain applications because of its low melting point, non-degradability, and the tendency to crack when stressed. Research on reactions like grafting, cross-linking and blending of PE with inorganic fillers to mitigate these disadvantages has been extensively investigated for many years.<sup>4-6</sup> Introduction of nanofillers onto polyethylene matrix have a strong impact on the macroscopic properties of the polymer even though the filler content is hardly few weight percent. The properties such as heat distortion temperatures, flame resistance, modulus, barrier properties and electronic and optical properties are dramatically enhanced.<sup>7-9</sup>

Various methodologies of nanofiller filled PE synthesis are available globally which includes foremost ones like sol-gel reactions, intercalative polymerization, melt processing and polymerization filling technique (PFT). Originated by Howard *et al.*,<sup>10</sup> PFT in which onto the surface of filler, Ziegler-Natta-type catalyst is immobilized where further on olefin monomer is polymerized, has been further explored by Jerome *et al.*<sup>11-13</sup> and Das *et al.*<sup>14,15</sup> This methodology provides with such nanocomposites which have higher filler content but without sacrificing their enhanced mechanical properties.

The commodity polymers i.e. polyethylenes are synthesized using organometallic coordination catalysts such as heterogeneous Ziegler-Natta catalysts and homogeneous metallocene catalysts.<sup>16,17</sup>

Metallocene catalysts have created a new area in the polymerization of olefins by providing new polymer structures and resulting properties in comparison to the traditional Ziegler catalysts. These complexes exhibit high catalyst activities and only one type of active site (single site catalyst). Control of molar mass, narrow molecular weight distributions and structural uniformity related to comonomer content are achieved through precise selection of reaction conditions.<sup>18-22</sup>

In recent years, special attention has been devoted to the immobilization methodology of these catalyst systems either on organic or inorganic materials. Apart from using inorganic supports like magnesium chloride, silica, alumina, TiO<sub>2</sub> etc, polymeric support like pentaerythritol trimethacrylate, divinyl benzene, 2-hydroxyethyl methacrylate, styrene etc have been utilized for immobilization of metallocenes.<sup>23-29</sup> Beside performing the basic role of the support like exposure of active sites, stabilization of active sites, high activity of catalyst and precise control over polymer properties, polymeric support also eliminates the side effects of inorganic support like reduction in ash content etc.

In the present work, we have immobilized bis(cyclopentadiene) titanium dichloride onto polyethersulphone as the support. The resultant light red colored solid catalyst was added to the MAO pre-treated nanoclays having surface modification of 35-45 wt% dimethyl dialkyl(14-18)amine (FA) and 25-30 wt% trimethyl stearyl ammonium (FB). This mixture of nanofiller, cocatalyst and supported catalyst was used for atmospheric ethylene polymerization. The resultant *in situ* nanoclay filled polyethylenes were characterized by FTIR, DSC for melting temperature and crystallinity impact and TGA for filler weight percent. The ratio of catalyst to MAO treated nanoclay were also varied to understand the impact on the polymerization performance, melting properties, crystallinity and inclusion of filler onto PE matrix.

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## EXPERIMENTAL

### Materials

All the chemicals were procured from Sigma-Aldrich and used as such or otherwise stated. Poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene; PES), n-hexane (99.9%), toluene (99.9%), nanoclay based on montmorillonite, whose surface has been modified with 35-45 wt% dimethyl amine (FA) and nanoclay modified with 25-30 wt% trimethyl stearyl ammonium (FB) were used as received. Bis(cyclopentadiene)titanium dichloride ( $\text{Cp}_2\text{TiCl}_2$ ; Strem) was used as such. High purity polymerization grade ethylene gas of 99.9% purity was taken from commercial plant and used with out further purification. Methylaluminoxane (MAO; 10% v/v in toluene) was used as obtained from Crompton, GmbH.

### Synthesis of PES supported $\text{Cp}_2\text{TiCl}_2$ catalyst

For synthesizing the polymeric supported metallocene catalyst, commercially available PES (having  $M_n = 38000 \text{ g mol}^{-1}$ ; melt flow index = 16 g/10 min) was taken as the support. A 5.0 g of PES was dissolved in the dry dichloromethane by stirring for 45 min. To this solution, 0.2 g of bis(cyclopentadiene)titanium dichloride was added to keep the ratio 0.04 with continuous stirring. The reaction mixture was allowed to stir at ambient temperature for 24 h, washed with dry toluene (100 mL  $\times$  5) to remove the excess metallocene and dried under vacuum. The dried light red catalyst was subjected to titanium estimation, which was 0.80 wt% by calorimetric method using UV-Vis spectroscopy.

### Polymerization of ethylene using PES supported $\text{Cp}_2\text{TiCl}_2$ 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 = 2500). Finally the catalyst (0.25 g) was added to start the polymerization at ambient conditions. Addition of ethylene was continued during the 60 min polymerization. Polymerization was stopped by the addition of sufficient amount of acidified methanol and the precipitated polymer was filtered, washed with methanol and dried under vacuum.

### Synthesis of *in situ* nanoclay filled polyethylene using PES supported catalyst

In 100 mL toluene, MAO (2.6 mL; 10%, v/v; Al/Ti mole ratio = 2500) was added followed by the nanoclay (0.12, 0.25, 0.50 g) and stirred for 30 min. Then 200 mL toluene was added followed by MAO (3 mL, 10% v/v; Al/Ti mole ratio = 2500) and finally the catalyst (0.25 g) was added to start the polymerization, then ethylene addition was continued during the 60 min polymerization. The polymerization was stopped by the addition of sufficient amount of acidified methanol. The precipitated polymer was filtered, washed with methanol and dried under vacuum.

### Characterization of PES supported $\text{Cp}_2\text{TiCl}_2$ 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 in to  $\text{Ti}^{4+}$  by the addition of  $\text{H}_2\text{O}_2$ . UV-vis spectra of the resultant solution of peroxotitanium complexes

were recorded on a Perkin-Elmer UV Lambda12 spectrometer.<sup>30</sup> 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>31</sup>

### Characterization of *in situ* nanoclay filled polyethylene

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  $10 \text{ }^\circ\text{C}/\text{min}$  from 50 to  $300 \text{ }^\circ\text{C}$  (with held for 3 min at  $300 \text{ }^\circ\text{C}$ ), cooling rate of  $10 \text{ }^\circ\text{C}/\text{min}$  from 300 to  $50 \text{ }^\circ\text{C}$  and again heating from 50 to  $300 \text{ }^\circ\text{C}$ . Thermal stability studies were performed using thermogravimetric analysis (TGA) with a TGA V 50 1A Perkin Elmer thermo gravimetric analyzer in the presence of nitrogen in the temperature range of 50-650  $^\circ\text{C}$  and at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ .<sup>31</sup>

## RESULTS AND DISCUSSION

### Synthesis and characterization of PES supported $\text{Cp}_2\text{TiCl}_2$

Bis(cyclopentadiene)titanium dichloride ( $\text{Cp}_2\text{TiCl}_2$ ) was immobilized on PES, since PES has potential Lewis base sites in the form of oxygen of sulfonyl group where the coordination of titanium can be expected.<sup>32,33</sup> The resulting PES supported  $\text{Cp}_2\text{TiCl}_2$  catalyst had 0.8 wt% of titanium content. The FTIR spectra of pure PES, PES supported  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Cp}_2\text{TiCl}_2$  is shown in Figure 1. The pure PES shows a strong absorption band at  $1486 \text{ cm}^{-1}$  attributed to the stretching vibration of the S=O groups belonging to the sulfone groups.<sup>31</sup> After the incorporation of titanium onto the polymer a weak vibration centered at  $820 \text{ cm}^{-1}$  corresponding to the complexation of titanium with sulfur group of the polymer was observed.<sup>15,33</sup> The room temperature atmospheric polymerization of ethylene was carried out using PES supported  $\text{Cp}_2\text{TiCl}_2$  which showed activity of 670 kg PE/mol Ti/h indicating its potential for polymerization.

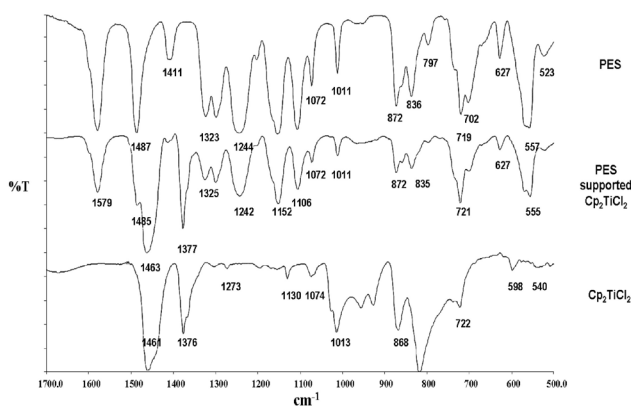
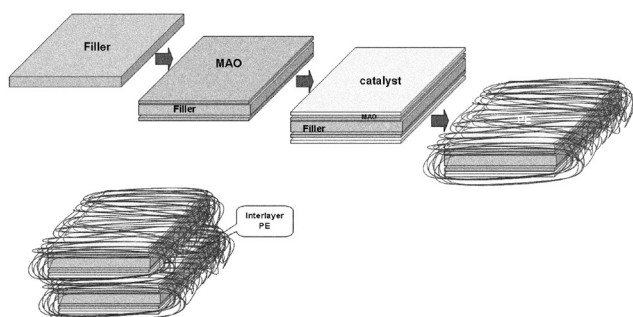


Figure 1. FTIR spectra of  $\text{Cp}_2\text{TiCl}_2$  catalyst; PES supported  $\text{Cp}_2\text{TiCl}_2$  catalyst; pure PES

### Synthesis of *in situ* nanoclay filled polyethylene

After ensuring the reproducibility of titanium loading on to the support (PES), this supported  $\text{Cp}_2\text{TiCl}_2$  was further utilized for preparing *in situ* nanoclay filled PE. The two fillers used for this study are nanoclay based on montmorillonite, whose surface has been modified with 35-45 wt% dimethyl dialkyl(14-18)amine (FA) and with 25-30

wt% trimethyl stearyl ammonium (FB). The whole methodology of synthesizing *in situ* nanoclay filled PE has been depicted in Scheme 1.



**Scheme 1.** Pictorial representation of methodology of synthesizing *in situ* nanoclay filled PE

For homogenous dispersion of fillers in the polyethylene matrix, the fillers were activated in advance with MAO. This pretreatment of fillers with MAO minimizes the deactivation effects of their surfaces on catalyst activity and generates active centres for ethylene polymerization.<sup>14</sup>

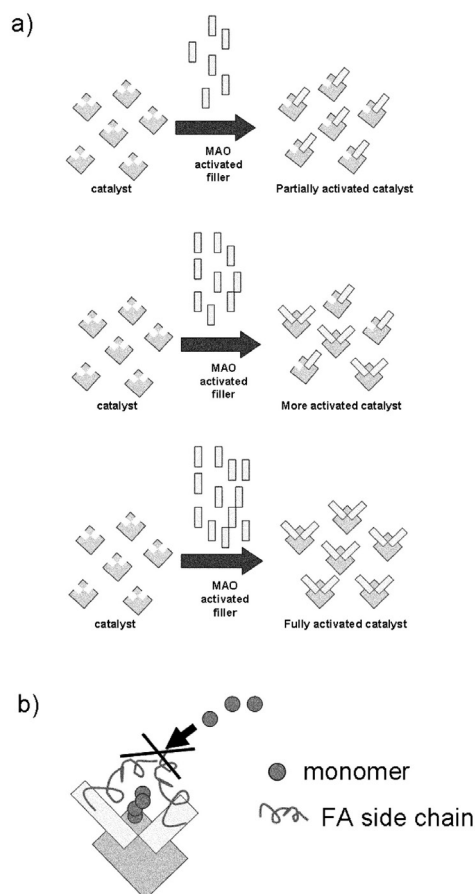
For *in situ* nanoclay filled PE synthesis, catalyst to MAO treated nanoclay ratio was varied in order to see how the activity of the PES supported  $Cp_2TiCl_2$  was affected. Table 1 shows the experimental data and the results of the variations carried out. For system where MAO treated FB filler was used, with the introduction of the FB filler, the activity (950 kg PE/mol Ti/h) of PES supported  $Cp_2TiCl_2$  increased. As the PES supported  $Cp_2TiCl_2$  catalyst to MAO treated FB filler ratio was increased to 2, activity showed decreasing trend, whereas, when the ratio was changed to 0.5, marked increase in activity was observed. The observed increase in activity with increase in MAO treated filler content may be due to the generation and stabilization of active centers which are formed when enough cocatalyst is present to reduce titanium as depicted in Scheme 2a. At lower supported catalyst to FB ratio, there is not enough cocatalyst to activate the sites for polymerizing ethylene but once the amount of cocatalyst is enough, all the sites are activated to get the polymer.

For system where MAO treated FA filler was used, with introduction of filler, activity was found to be unaffected. This may be due to the bulkiness in the chain length of FB filler. As the PES supported catalyst to MAO treated FA filler ratio was changed to 2, activity got decreased. Even when the ratio was changed to 0.5, one observed decrease in activity. Again this might be assumed that bulkiness of FA filler is decreasing the activity by resisting the chain growth of ethylene monomer as shown in Scheme 2b.

**Table 1.** Experimental conditions and results for synthesis of *in situ* filler filled PE using PES supported catalyst (Ti wt% ~ 0.8)

S No.	PES supported $Cp_2TiCl_2$ (g)	Nanoclay (FB) (g)	Nanoclay (FA) (g)	Supported cat:nanoclay ratio	Yield (PE) (g)	Activity (kg PE/mol Ti/h)
1 <sup>a</sup>	0.00*	0.00	0.00	-	1.5	360
2	0.25	0.12	0.00	2:1	3.6	860
3	0.26	0.25	0.00	1:1	3.9	950
4	0.25	0.50	0.00	1:2	5.4	1290
5 <sup>b</sup>	0.24	0.00	0.00	-	2.8	670
6	0.25	0.00	0.12	2:1	2.1	500
7	0.26	0.00	0.25	1:1	2.5	600
8	0.25	0.00	0.50	1:2	0.5	120

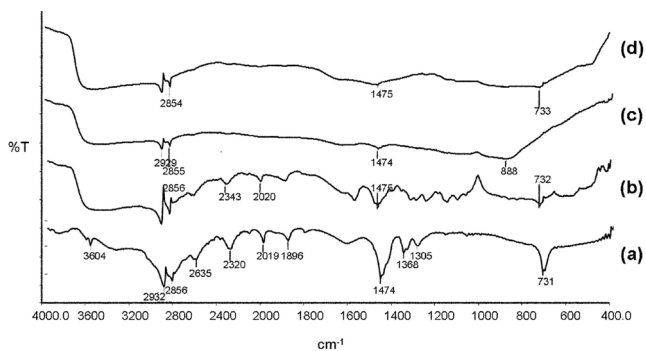
<sup>a,b</sup>MAO = 6.0 MI. Al/Ti mole ratio = 2500. \*  $Cp_2TiCl_2$  = 0.24 g



**Scheme 2.** Schematic representation: a) Generation of active sites when FB is used as filler; b) Spatial hindrance for monomer onto active site when FA is used as filler

### Characterization of *in situ* nanoclay filled polyethylene

A comparison of FTIR spectra of PE synthesized by  $Cp_2TiCl_2$ ; PES supported  $Cp_2TiCl_2$ ; *in situ* FB filled PE and *in situ* FA filled PE is shown in Figure 2. The strong absorption band at 2856  $cm^{-1}$  corresponding to  $\nu(C-H)$  stretching of PE is being observed in Figures 2a,b. This band is also present in nanoclay filled PE (Figures 2c,d). The occurrence of these IR bands indicates that PE has been formed in the presence of organic support and nanoclay during the polymerization. A strong band at 1474  $cm^{-1}$  corresponding to  $\nu(C-H)$  deformation of tertiary carbon is also present. The  $^{13}C\{^1H\}$  NMR spectrum of PE synthesized by PES supported  $Cp_2TiCl_4$  ca-



**Figure 2.** FTIR spectra: (a) pure PE; (b) PE using  $Cp_2TiCl_2$  catalyst; (c) PE synthesized from PES supported  $Cp_2TiCl_2$  catalyst with in situ FB; (d) PE synthesized from PES supported  $Cp_2TiCl_2$  catalyst with in situ FA

talyst where only one strong resonance peak was observed at 29.41 ppm, which is attributed to the main chain methylene carbon.<sup>14</sup> Non-existence of other resonance peaks indicates the absence of branching in the homopolymer synthesized using the polymeric supported catalyst.

The DSC analysis (Figure 3) shows the melting and crystallization temperatures of nanoclay filled PE. The melting as well as crystallization temperatures show no remarkable effect by the addition of nanoclays. There is insignificant change in the crystallization onset temperature indicating that the inclusions induce heterogeneous nucleation. The melt enthalpy observed for FB case increases as the supported catalyst to FB ratio decreases which can be attributed to the difference in molecular weight of PE chain as the productivity is different. The presence of nanoclay shows major influence on the degree of crystallinity of PE as shown in Table 2. The degree of crystallinity<sup>14, 31</sup> of nanoclay filled PEs were measured using the following formula

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

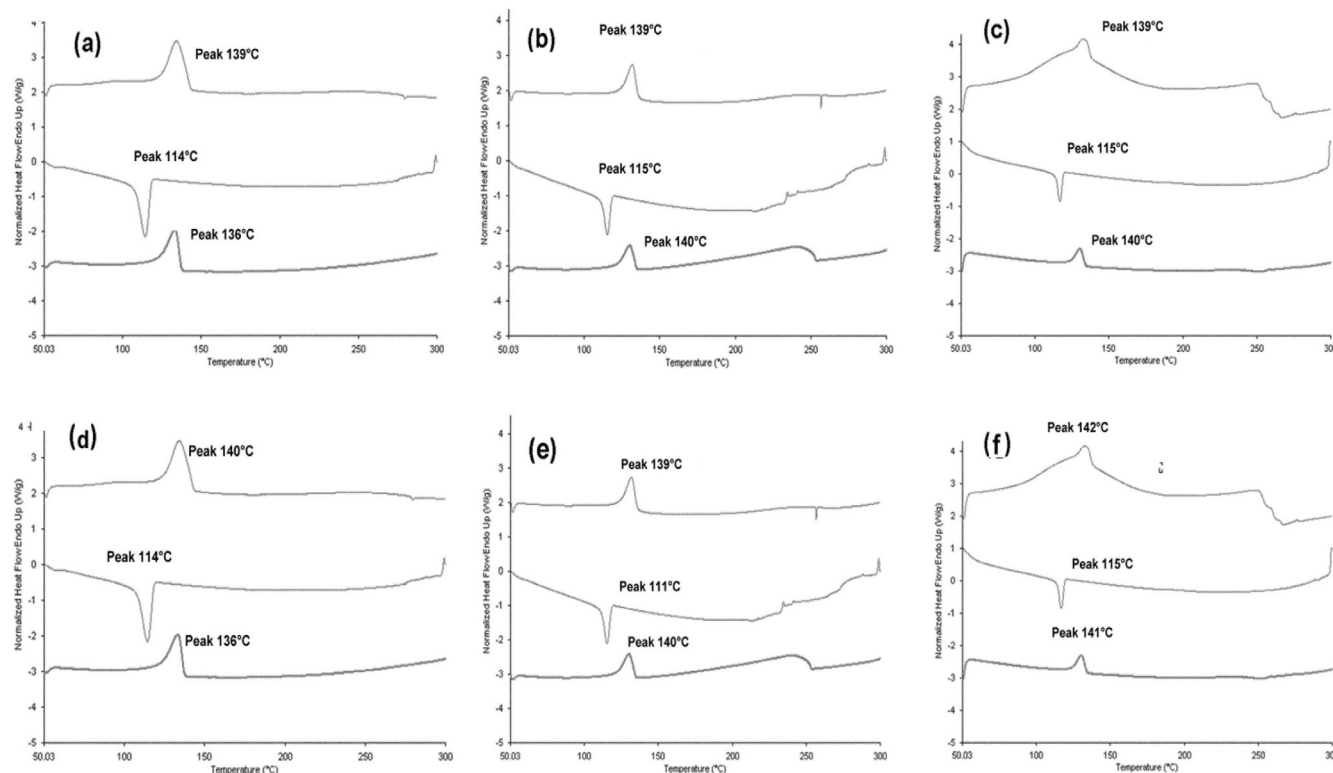
where  $X$  = percent crystallinity of the composites;  $\Delta H_m$  = melting enthalpy ( $J g^{-1}$ ) of the nanoclay filled PE;  $\Delta H_o$  = melting enthalpy ( $293 J g^{-1}$ ) of 100% crystalline PE;<sup>14</sup>  $m_p$  = mass (g) of PE in the nanoclay filled PE; and  $m_c$  = mass (g) of the nanoclay filled PE. The high melting point of the polymers ( $139^\circ C$ ) indicates the branchless structure of the homopolymer.

**Table 2.** Melting and crystallization temperatures of *in situ* filler filled PE using PES supported catalysts

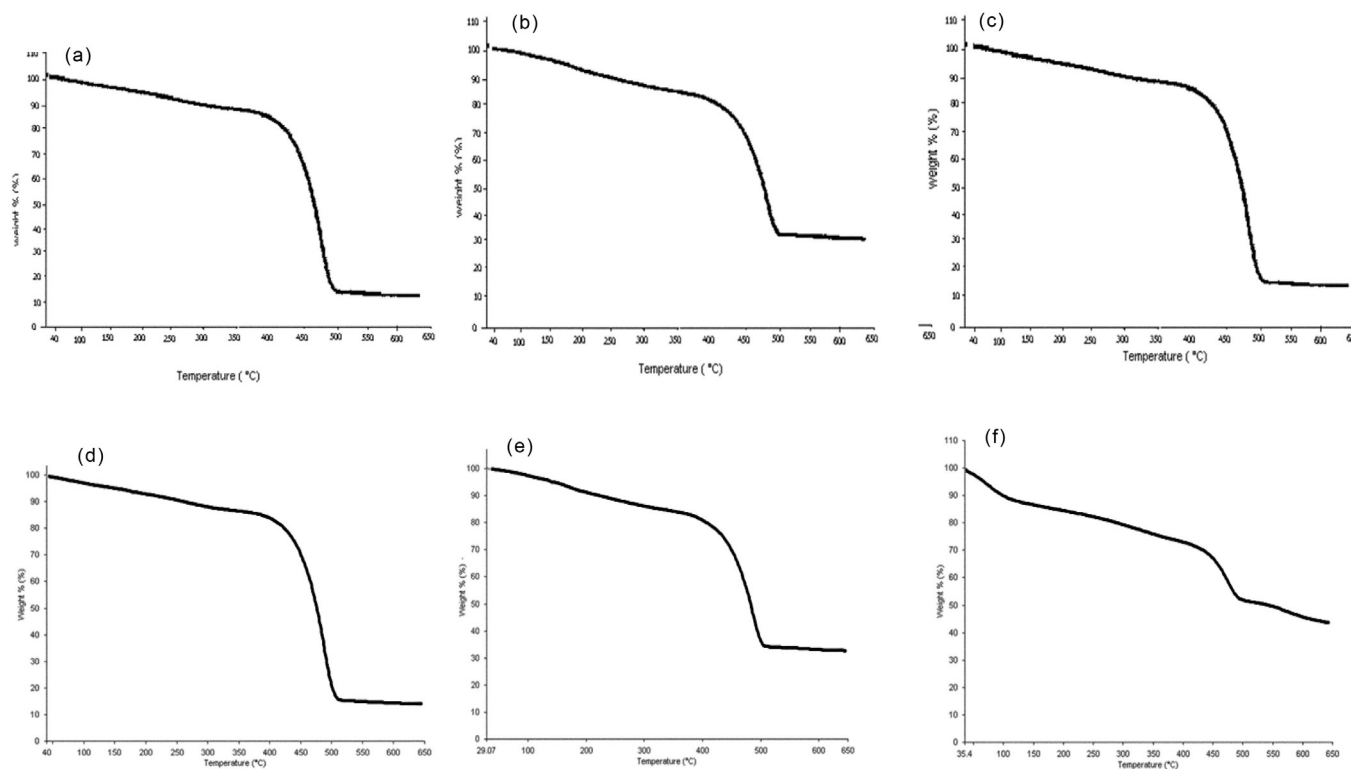
Nanoclay	Cat:nanoclay ratio	$T_m$ °C	$\Delta H_m$ ( $J g^{-1}$ )	$T_c$ °C	% Crystallinity
FB	2:1	139	145	114	55
	1:1	139	192	115	70
	1:2	139	231	115	82
FA	2:1	139	183	114	69
	1:1	140	209	112	76
	1:2	Low productivity			

$\Delta H_m$  = melting enthalpy ( $J g^{-1}$ ) of the filler filled polyethylene;  $T_m$  = melting temperature;  $T_c$  = crystallization temperature.

To understand the weight percentage of the nanoclay into the polymer, thermo gravimetric analyses were conducted (Figure 4). The results obtained clearly indicate that when PES supported catalyst with FB at 1:0.5 ratio based PE was heated from 40 to 400 °C (Figures 4a-c); there was a gradual reduction in weight percentage. The weight loss of ~68% was observed from 400 to 500 °C, which remains constant



**Figure 3.** DSC plots of PE synthesized from PES supported  $Cp_2TiCl_2$  catalyst with in situ FB having: (a) 1:0.5 ratio (b) 1:1 ratio (c) 1:2 ratio and PE synthesized from PES supported  $Cp_2TiCl_2$  catalyst with in situ FA having (d) 1:0.5 ratio; (e) 1:1 ratio; (f) 1:2 ratio



**Figure 4.** TGA plots of PE synthesized from PES supported  $Cp_2TiCl_2$  catalyst with in situ FB having: (a) 1:0.5 ratio (b) 1:1 ratio (c) 1:2 ratio and PE synthesized from PES supported  $Cp_2TiCl_2$  catalyst with in situ FA having (d) 1:0.5 ratio; (e) 1:1 ratio; (f) 1:2 ratio

after 500 °C temperature. At 600 °C, 12 wt% of material was obtained. Similar was the case when the catalyst-to-clay ratio was maintained as 1:1 and 1:2 and 1:3 indicating there is no much change in the weight reduction during heating due to the incorporation of clay to the PE.

For FA filled PE, the weight loss was observed to be ~20% on reaching 400 °C (Figures 4d-f), followed by reduction in weight (~64%) from 400 to 500 °C. At temperature above 550 °C no significant weight loss was observed, indicating that ~19 wt% clay has been associated with PE. The gradual weight loss was observed in all the cases where nanoclay-FA was incorporated with PE.

The weight percentages of the fillers, as elucidated by ash content, are also in close agreement as shown in Table 3. These data indicate that highest residual weight percent is for FB filled at a ratio of 1:2 PE which is also supported by the high activity observed for this system for polymerizing ethylene.

**Table 3.** Comparison of thermal gravimetric analysis and ash content with the theoretical values of *in situ* filler filled PE using PES supported catalysts

Nanoclay	Cat:nanoclay ratio	TGA(g)	Ash content (g)
FB	2:1	29	27
	1:1	33	34
	1:2	63	62
FA	2:1	25	23
	1:1	23	21
	1:2	-	-

## CONCLUSIONS

*In situ* polymerization of ethylene in the presence of MAO treated nanoclay using polyethersulfone supported  $Cp_2TiCl_2$  catalyst has been successfully carried out to formulate nanoclay filled polyethylene

with a polymer supported catalyst system. FTIR studies confirmed the formation of polyethylene. DSC study shows that both nanoclay FA and FB filled PE have high melting enthalpies with high crystallinity. The high melting point of the polymers indicates the branchless structure of the homopolymer. TGA study indicates that nanoclay FB filled polyethylene has higher thermal stability than nanoclay FA filled polyethylene. Use of  $Cp_2TiCl_2$  for the anchoring of titanium species on to the surface of polymeric support can be used for catalyst preparation, which may be effectively and efficiently used for *in situ* polymerization.

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