Chapter 2

Poly(styrene-co-methyl methacrylate) supported Ziegler-Natta catalyst for ethylene polymerization in slurry process
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2.1. Introduction

In this chapter we have explored poly(styrene-co-methyl methacrylate) as a support for Ziegler-Natta catalyst. Although various cross-linked polystyrene beads have been used as support in Ziegler-Natta catalyst.\textsuperscript{1-4} To the best our knowledge there appears no report of using poly(styrene-co-methyl methacrylate) as a support in Ziegler-Natta catalyst. As like the other cross-linked polystyrene, poly(styrene-co-methyl methacrylate) possess several amenable features viz. unreactive towards the catalyst during polymerization process and prevents the Lewis acid (TiCl\textsubscript{4}) from contamination by the atmospheric moisture. Thus it is worthwhile to study the use of poly(styrene-co-methyl methacrylate) as a support in Ziegler-Natta catalysis. Poly(styrene-co-methyl methacrylate) was synthesised by mini emulsion polymerization under ultrasonication. Supported catalyst was used for ethylene polymerization at 50 °C under atmospheric pressure. The catalytic activity was co-related with the Ti content of the supports. The stability and storability of the supported catalysts were also evaluated.

2.2. Experimental

All air sensitive compounds were manipulated inside an inert atmosphere of glove box in which dry nitrogen was purged continuously.

2.2.1. Materials

Titanium tetrachloride (TiCl\textsubscript{4}) and triethylaluminium (TEA) were received from Aldrich and were used as such. The monomers styrene (Sty) and methyl methacrylate (MMA) were purchased from Aldrich and washed with 5% NaOH followed by distilled water to remove the inhibitor. Ethylene (>99.99 % purity) was taken from Chemtron Science Lab. Pvt Ltd. (Mumbai). The surfactant sodium dodecylbenzenesulfonate (SDBS), Octadecanoic acid [4-dihydroxy-2-tetrahydrofuranyl]-2-hydroxyethyl] ester (Span-60) and the co-surfactant hexadecane were used as received from Merck chemical. Solvents (hexane, heptanes, ethanol, methanol and toluene) were distilled and kept over molecular sieves for at least 8 days before use. For all purposes double distilled water was used.

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2.2.1.1. Gas (ethylene and nitrogen) purification

Ethylene and nitrogen used were of “polymer grade”. Ziegler-Natta catalyst is highly sensitive to some impurities eg. moisture, oxygen, CO, water, CO₂, H₂S and COS etc. which has a dramatic poison influence on catalytic activity and the reaction rate. So it is essential to remove the impurities before carrying out the polymerization with Ziegler-Natta catalyst. Thereby ethylene and nitrogen were purified in a series of purification column before used.

Ethylene used in this study is further purified by passing through four purification columns (3.5 x 42 cm). These columns consist of different catalysts, molecular sieves and CaCl₂ as shown in Figure 2.1. Their significant functions are as follows:

- oxidized BTS (BASF R3-16) catalyst for oxidizing CO to CO₂
- Reduced BTS (BASF R3-16) catalyst for chemically absorb oxygen
- molecular sieves (3Å, 4Å, 10Å, 13X, taken from Sigma-Aldrich) to physically absorb CO₂, H₂O and other impurities
- Selexsorb COS (Alcoa) for removing COS, H₂S, PH₃, and Selexsorb CD (Alcoa) for removing oxygenates (eg. ethers, alcohols, aldehydes, carbonyls, ketones, peroxides).
- CaCl₂ for removing moisture

Figure 2.1: Purification scheme for ethylene
Likewise, nitrogen (purity >99.99%, Rass Cryogenics) was also purified through the separate purified columns and conc. H₂SO₄. Those included two columns, one filled with reduced BASF 3R-11 catalysts to chemically absorb oxygen and the other one with molecular sieves (3Å, 4Å, 13X, Sigma-Aldrich) to physically absorb CO₂, H₂O and other impurities, respectively (Figure 2.2).

![Figure 2.2: Purification scheme for nitrogen](image)

2.2.2. Equipment

The ethylene polymerization was conducted in a 150 ml, high pressure autoclave (Amar Equipment, Mumbai). The schematic diagram of the experimental set up is shown in Figure 2.3. The reactor was equipped with a magnetic stirrer, a septum inlet, an electrical heater, high pressure metering pump, high efficient cooler and a regulated supply of dry nitrogen and ethylene. The pressure inside the reactor can be raised upto 100 kg/cm² (advised to perform bellow 70 kg/cm²), which is measured with a pressure transducer attached with a digital display. With an industrial mineral isolated thermocouple the internal temperature of the reactor is measured. The temperature controlling is done manually in the equipment.
2.2.3. Procedure

2.2.3.1. Preparation of poly(styrene-co-methyl methacrylate) (PS-PMMA)

The poly (styrene-co-methyl methacrylate) particles were obtained through emulsion polymerization of styrene (Sty) and methyl methacrylate (MMA). In a typical reaction, Sty (10g, 0.09 mol) and MMA (5g, 0.04 mol) were taken in a 100 ml beaker and stirred magnetically for 1 h at room temperature. The resulting mixture was kept in a refrigerator for 10 min and then sonicated for another 10 min (phase I). Meanwhile, the aqueous solution (phase II) was prepared by mixing water (70 ml), span-60 (0.20g, 0.46 mmol), hexadecane (0.15g, 0.66 mmol) and NaHCO$_3$ buffer under simple stirring at room temperature and then kept in the refrigerator for 10 min.

Phase I and phase II were mixed together under vigorous stirring for 15 min and then SDBS (0.15g, 0.43 mmol) was added to the mixture. This mini-emulsion was transferred to a four-necked round bottom glass reactor equipped with a refluxing condenser, a mechanical stirrer, a nitrogen inlet and a thermometer pocket for polymerization. Subsequently, the system was degassed by nitrogen for 30 minutes at room temperature. When temperature of the mixture reaches 70 °C, benzoyl peroxide (0.14g, 0.57 mmol)
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(1% of the monomer, dispersed in 20ml distilled water) was added to the mixture to initiate the polymerization under continuous mechanical stirring. Polymerization was carried out at 70 °C for 7 h. Polymerization was terminated by adding 1% aqueous solution of hydroquinone and heating was stopped subsequently. As soon as the temperature of the reactor reaches room temperature, the latex was filtered, washed with water and dried at 40 °C under vacuum oven and pulverized to get PS-PMMA particles.

2.2.3.2. Preparation of PS-PMMA supported-TiCl₄ catalysts (SMT1-3)

To investigate the effect of Ti on catalytic activity regarding ethylene polymerization, three catalysts (SMT1, SMT2 and SMT3) with different proportion of PS-PMMA and TiCl₄ were prepared (Table 2.1). The supported catalysts were prepared by loading TiCl₄ solution directly onto the polymer matrix. In a three necked round bottom flask PS-PMMA powders (2g) having number average molecular weight ($M_n$) ~ 59,083 g/mol and polydispersity index (PDI) = 1.51 were suspended in 50 ml hexane at -5 °C and the dry nitrogen atmosphere was maintained in the flask. After 30 minutes, calculated amount of TiCl₄ was added dropwise with constant stirring at that temperature to the dispersion of PS-PMMA. The solution was stirred for 6 h at -5 °C and subsequently for 8 h at 50 °C. The generated solid product was filtered out, washed with ample amounts of dry toluene for several times to remove the unreacted TiCl₄, and dried under reduced pressure at 50 °C for 24 h. The dried catalysts were subjected to titanium estimation following colorimetric method using UV-visible spectroscopy.³

Table 2.1: Experimental conditions for PS-PMMA-Ti catalysts synthesis

<table>
<thead>
<tr>
<th>Entry</th>
<th>SMT1</th>
<th>SMT2</th>
<th>SMT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-PMMA (g)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>TiCl₄ (g)</td>
<td>0.674</td>
<td>2.022</td>
<td>4.044</td>
</tr>
<tr>
<td>TiCl₄/PS-PMMA wt ratio</td>
<td>0.224</td>
<td>0.674</td>
<td>1.348</td>
</tr>
<tr>
<td>Physical appearance</td>
<td>Yellow powder</td>
<td>Yellow powder</td>
<td>Yellow powder</td>
</tr>
<tr>
<td>*Weight ratio of Ti/ doped catalyst</td>
<td>0.006</td>
<td>0.011</td>
<td>0.025</td>
</tr>
</tbody>
</table>

*Weight ratio of Ti/doped catalyst used for ethylene polymerization
2.2.3.3. Polymerization of ethylene using polymer supported titanium based catalyst

All polymerization experiments were performed in a water-cooled jacketed 100 ml stainless steel high pressure autoclave reactor in the slurry phase. Before carrying out the reaction, the autoclave was heated at approximately 115 ºC for 2 h, purged with dry nitrogen (80 ºC, 1 h) followed by repeated filling (3 times) and venting with ethylene at 80 ºC. Then the reactor was cooled to room temperature before catalysts and ethylene was introduced. All glassware were also heated to 120 ºC for 3h at oven and subsequently allowed to cool under nitrogen to avoid any unwanted inhibition during polymerization reaction.

The polymerization of ethylene was typically performed with three supported catalysts (SMT1, SMT2 and SMT3) in the presence of triethylaluminium (TEA) as a co-catalyst (Table 2.5). After depletion of all moisture and oxygen in the reactor, catalyst (0.05 g) was loaded in 100 ml dry heptane as diluents under nitrogen atmosphere. The desired amount of TEA (10%, v/v; Al/Ti mole ratio = 300) was added to the ethylene saturated heptane containing catalyst. Polymerization reaction was run at 50 ºC and 1 atm. for an hour. The flow of ethylene was maintained during the initial 60 minutes of polymerization to maintain the saturated ethylene concentration at atmospheric pressure. After one hour, the reaction was quenched with ethanol containing 20 vol% of conc. HCl and subsequently the untreated gases were slowly released. The reaction mixture was precipitated into a large amount of ethanol, filtered and washed for several times with ethanol. The resulting polymer was usually subjected to Soxhlet extraction with THF for 24 h, to remove the support. The THF-insoluble fraction was washed with methanol and dried in vacuum at 70 ºC for 4 h before any characterization.

2.2.4. Characterization

2.2.4.1. X-ray photoelectron Spectroscopy (XPS)

XPS is a well-known surface technique to analyze the elemental composition of material, the chemical bonding and the oxidation state of the species. The XP spectra of all the samples were recorded on Shimadzu (ESCA 3400) spectrometer using monochromatic Al Kα (1486.6 eV) X-ray radiation as the excitation source. All the
binding energy of the samples was corrected by setting the binding energy of the adventitious carbon (C1s) at 284.6 eV. The XPS analysis was performed at ambient temperature and pressure typically in the order of less than $10^{-6}$ Pa.

2.2.4.2. NMR spectrum

$^1$H NMR spectrum of the polymer was recorded on a JEOL JSM ESS-400 spectrometer operated at 400 MHz in the pulse Fourier transform (FT) mode. In $^1$H NMR measurements, the pulse angle was $45^\circ$ and 8-10 scans were accumulated in 5 s of pulse repetition. The spectra were recorded at 25°C in deuterated chloroform for 10% (w/v) polymer solutions.

2.2.4.3. Determination of titanium content of catalysts

The titanium content of the synthesized catalysts was determined by colorimetric method. For determination of titanium content, the polymer supported catalysts were dissolved in an acidic media followed by dilution with double distilled water to 100 ml. The diluted solution was reacted with H$_2$O$_2$ to form the peroxo compex. UV-visible spectra of the resultant solution of peroxotitanium complexes were recorded on a Hitachi U-2001 UV–visible spectrophotometer. The peak intensity at 410 nm was used to quantify the titanium content.

2.2.4.4. Determination of the Acidity of the Polymer supported TiCl$_4$ Complex

The catalyst was hydrolyzed in 60% acetone solution in water at room temperature. The pH of the resultant solution was measured by a standard pH meter (Orion).

2.2.4.5. Fourier Transformed-Infrared (FT-IR) spectra

The FT-IR spectra of the catalysts and PE were recorded in Nicolet Impact-410 IR spectrometer in KBr medium at room temperature in the region 4000–450 cm$^{-1}$. 

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2.2.4.6. Scanning electron microscopy and energy dispersive X-ray detector (SEM-EDX)

The morphology of the powdered polymer particles and energy dispersion spectroscopic analysis of catalysts were examined by using the JEOL-JSM-6390LV scanning electron microscope coupled with energy dispersive X-ray detector. Samples were coated with platinum to a thickness of 200 Å. The voltage and working distance was varied during the measurements. To obtain semi quantitative compositional information, EDX spectra were recorded.

2.2.4.7. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of pure polymer and polymer supported-TiCl$_4$ catalysts was studied in a Shimadzu TGA-50 Thermal analyzer over a temperature range of 30 °C to 600 °C with the heating rate 5°C/min under N$_2$ atmosphere.

2.2.4.8. Gel permeation chromatography (GPC)

Molecular weight of the PS-PMMA and polyethylene was determined by gel permeation chromatography (GPC, Waters, USA) using 1, 2, 4-trichlorobenzene as a mobile phase.

2.2.4.9. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is one of the main techniques used to study the melting behaviour of polymers.$^{7,8}$ The melting point of polymers was measured by Differential Scanning Calorimetry (DSC, Model DSC-60, Shimadzu) at a heating rate of 5 °C/min under the nitrogen flow rate of 30 ml/min from 25- 400 °C.

2.2.4.10. X-Ray diffraction analysis (XRD)

Powder X-ray diffraction (XRD) data were collected on a Rigaku Miniflex X-ray diffractometer with Cu $K_a$ radiation ($\lambda= 0.15418$ nm) at 30 kV and 15 mA using a scanning rate of 0.05°/s in 2θ ranges from 10° to 70°.
2.2.4.11. Computational work

All the density functional calculation (DFT) are carried out using the DMol³ program with VWN correlation functional and double numeric (DN) basis set.⁹ We performed all electron calculations on the neat polymer (PS-PMMA), TiCl₄ and TiCl₄ incorporated PS-PMMA. For the simplicity of our calculation in case of TiCl₄ modified polymer we consider only a unit of PS-PMMA considering of 13 no of carbons.

2.3. Results and Discussion

2.3.1. Spectroscopic characterization of the PS-PMMA and PS-PMMA-Ti catalysts

The poly (styrene-co-methyl methacrylate) copolymer synthesized via mini-emulsion polymerization was primarily characterized by ¹H-NMR technique. Figure 2.4 shows the ¹H-NMR spectrum of the PS-PMMA copolymer which corresponds to the statistical distribution of the monomeric units along the polymeric chains and the ¹H-NMR spectral values are listed in Table 2.2. The resonance peaks observed at 0.5-1.0 ppm correspond to methylic proton while those observed at 1.5-1.9 ppm correspond to methylene protons. The peaks observed in the region 2.7-3.9 ppm correspond to ester protons while those observed near 7.00 ppm correspond to aromatic protons of the polystyrene. This confirms the expected structure of PS-PMMA.¹⁰

![Figure 2.4: ¹H-NMR spectrum of PS-PMMA](image)

Figure 2.4: ¹H-NMR spectrum of PS-PMMA
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An XPS survey scan is performed on PS-PMMA and the polymer supported catalyst (SMT2) to study the state and chemical environment of the atom. The oxygen co-ordination is also confirmed in the XPS of PS-PMMA and PS-PMMA-Ti catalyst. As shown in [Figure 2.5 (a) and (b)], the O1s binding energy for PS-PMMA is 531.9 eV, attributed to oxygen doubly bound to carbon; while that for PS-PMMA-Ti catalyst, a shift to higher binding energy region 533.7 eV is observed. It indicates that the carbonyl group of the PS-PMMA provides some electrons to Ti species and makes the binding energy of O$_{1s}$ to higher region. On the other hand, the titanium spin orbit doublet, 2p$_{3/2}$ and 2p$_{1/2}$

**Table 2.2:** $^1$H-NMR chemical shifts and the signal assignations of PS-PMMA

<table>
<thead>
<tr>
<th>Chemical Shifts(δ)</th>
<th>Assignation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.9-7.2</td>
<td>Aromatic protons</td>
</tr>
<tr>
<td>6.5-6.9</td>
<td>3 (meta and para) protons and 2 ortho protons of the benzene moiety</td>
</tr>
<tr>
<td>3.4-3.9</td>
<td>-COOCH$_3$ protons</td>
</tr>
<tr>
<td>2.7-3.1</td>
<td>-COOCH$_3$ protons</td>
</tr>
<tr>
<td>1.5-1.9</td>
<td>-CH$_2$ methylene protons</td>
</tr>
<tr>
<td>0.5-1.0</td>
<td>-CH$_3$ methylic protons</td>
</tr>
</tbody>
</table>

appears at 458.7 and 464.9 eV whose binding energy is higher than TiCl$_3$ and lower than TiCl$_4$ in its molecular states [Figure 2.5 (c)]. It is expected that electron donation to Ti atom makes the Ti 2p peak shift to lower binding energy region. Thus it is reasonable to consider that the carbonyl group of PS-PMMA co-ordinate with Ti $^{4+}$ through oxygen atom which further reveals that titanium incorporation into the polymer matrix is successful.
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Figure 2.5: XPS spectra of O1s binding energy in (a) PS-PMMA, (b) SMT2 and (c) Ti2p level of SMT2

FT-IR analysis of the pristine PS-PMMA and PS-PMMA supported catalysts was performed to confirm the formation of PS-PMMA and understanding the variation of chemical environment of the various species of the synthesized catalysts. Figure 2.6 (a) shows the FT-IR spectrum of the virgin PS-PMMA polymer. The characteristic absorption band appearing at around 3023 cm\(^{-1}\) indicates the –CH- stretching from the benzene ring of PS while those at 2923 and 2852 cm\(^{-1}\) are assigned to the C-H stretching modes for the –CH- and –CH\(_2\)- groups on the alkyl chain of the polymer. The sharp peak centred at 1727 cm\(^{-1}\) is related to the C=O stretching vibration of the ester group of PMMA. The absorption peak at 1197 cm\(^{-1}\) represents the C-O stretching of the ester group. The absorption band at 1374 cm\(^{-1}\) is attributed to the stretching vibration of CH\(_3\) groups of PMMA. The peaks at 1448 and 1598 cm\(^{-1}\) are assigned to aromatic C=C stretching. The other typical absorption bands observed at 695 and 757 cm\(^{-1}\) is related to the phenyl C-H out-of-plane bending and benzene out of plane ring bending. The existence of the PS and PMMA characteristic absorption peaks in the spectrum of the virgin polymer implies the formation of PS-PMMA copolymer.

It is well known that PS-PMMA has a nucleophilic site in the form of carbonyl of the ester group which has tendency to co-ordinate with TiCl\(_4\). Since TiCl\(_4\) (d\(^0\)) has vacant d-orbital so it has the ability to accept electron density donated from the electron rich C=O

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moiety (electronic effect) of PS-PMMA leading to a PS-PMMA-TiCl₄ complex. After incorporation of TiCl₄ into polymer matrix, the colour of the neat polymer changes from white to yellow which gives physical evidence of complex formation taking place between TiCl₄ and PS-PMMA. Incorporation of TiCl₄ on to the polymer matrix is confirmed by FT-IR study (Figure 2.6). It is observed that after incorporation of TiCl₄ on to the polymer matrix the typical absorption peak intensity of 1727 cm⁻¹ interestingly decreases where as a smaller new absorption band at around 1630 cm⁻¹ appeared along with C=O. This indicates the formation of complex between TiCl₄ and PS-PMMA. On

Figure 2.6: FT-IR spectra of (a) PS-PMMA, (b) SMT1, (c) SMT2 and (d) SMT3
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comparing the relative intensity \( \frac{A_{1727}}{A_{1630}} \sim 0.6-1.9 \) of these two characteristic bands (Table 2.3) it is observed that the lowering of C=O stretching frequency continued to become more dramatic with increase in TiCl\(_4\) content (SMT1- SMT3). This gives a strong evidence towards the chemical interaction between >C=O of PS-PMMA with TiCl\(_4\) in the catalyst.

2.3.2. UV-visible Spectroscopy

Figure 2.7 shows the UV-visible spectra for the pure PS-PMMA and PS-PMMA supported TiCl\(_4\) catalysts. It is believed that Ziegler-Natta catalyst does not show any absorption band in the UV-visible region.\(^{11}\) Moreover, to determine the existence and extent of Ti in the synthesized catalysts we use a simple approach; first we have digested the catalyst in 20% conc. H\(_2\)SO\(_4\) and the solution turns yellow. On addition of 30% (w/v) H\(_2\)O\(_2\) solution the yellow solution turned into orange which might be due to the formation of peroxotitanium complex [TiO\(_2\) (H\(_2\)O\(_2\))] as visualized from Figure 2.7.\(^{12}\)

Figure 2.7: UV-visible spectra of (a) PS-PMMA, (b) SMT1, (c) SMT2, (d) SMT3 and the solution of peroxotitanium complexes (e) SMT1, (f) SMT2 and (g) SMT3
The broad peak observed at 410 nm [Figure 2.7(b)] is attributed to $p_{\pi} \rightarrow d_{\pi}$ transition that arises due to the transition of lone pair of electrons on oxygen to the vacant d-orbital of Ti$^{4+}$. The occurrence of this broad spectrum confirms the formation of peroxotitanium complex which indicates the presence of Ti in the catalyst. Interestingly, on increasing the amount of TiCl$_4$, the absorption peak intensity also increases gradually indicating the successful incorporation of TiCl$_4$ into the polymer matrix. The peak intensity at 410 nm is used to quantify the titanium content immobilized in polymer chain. The wt% titanium of the supported catalysts (SMT1- SMT3) is found to be in the range of 0.6 – 2.5 wt% of Ti in the polymer support (Table 2.5). This illustrates that by adjusting the relative amount of TiCl$_4$ and PS-PMMA, the amount of Ti incorporation into the polymer matrix can be easily controlled.

On the other hand, only one broad peak is observed at around 240 nm in case of pristine polymer [Figure 2.7 (a)] due to the $n-\pi^*$ transition of the C=O group of the ester moiety of PS-PMMA.

2.3.3. Acidity of the solution obtained on Hydrolysis of PS-PMMA-Ti catalysts

pH of PS-PMMA supported TiCl$_4$ catalysts dispersed in 60% acetone-water solutions is shown in Figure 2.8. It is noticed from Figure 2.8 (a) that the acidity of solution containing catalyst SMT1 gradually increases with time. This is due to the liberation of HCl into the acetone-water solution by the hybrid catalysts after hydrolysis with water. This reveals that there must be a Lewis acid (TiCl$_4$) in the complex. The most probable reaction is presented in Scheme 2.1. A slightly higher acidity is seen for the other two catalysts (SMT2 and SMT3), probably due to the incorporation of higher amount of TiCl$_4$ into the polymer. The same experiment was also performed with the neat polymer which shows pH = 8.2.
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**Figure 2.8:** Change of pH of the catalysts (1g) in acetone water solution with time (a) SMT1, (b) SMT2 and (c) SMT3

**Scheme 2.1:** Probable pathway of hydrolysis of PS-PMMA-Ti catalysts
2.3.4. SEM-EDX studies

SEM studies were performed to study the surface morphological information of the polymer as well as hybrid catalysts. Whereas EDX analyses were conducted to evaluate the distribution of the Ti species on the polymer support. The representative micrographs of the pristine polymer and the synthesized hybrid PS-PMMA-TiCl$_4$ catalysts are displayed in Figure 2.9. After immobilization of TiCl$_4$ into the polymer matrix a significant morphological change is observed for the pure polymer and the prepared PS-PMMA-TiCl$_4$ catalysts. SEM illustrates the typical randomly aggregated uneven shape and size non globular particles of neat polymer with an average size of in the range of 2-6 µm. However the supported catalysts (SMT1- SMT3) become large in size. The TiCl$_4$ present on the surface of one polymer particle may co-ordinate the $>$CO group of other polymer particle resulting in increase of size.

To confirm the occurrence of titanium in PS-PMMA-Ti catalysts, EDX analysis is performed at room temperature. Figure 2.10 represents the EDX mapping of the catalysts (SMT1- SMT3). The existence of titanium and chlorine into the polymer supported hybrid catalysts reveals that TiCl$_4$ is undoubtedly immobilized into the polymer matrix. Furthermore, on addition of larger amount TiCl$_4$ into the PS-PMMA polymer, Ti content also systematically increases as listed on Table 2.3. Since EDX measures the % of elements present on the outermost surface, this reveals the presence of the catalytic groups on the surface to be exploited on ethylene polymerization.$^{12}$ Elemental distribution on the surface of PS-PMMA of the catalyst is shown in Figure 2.11. It is observed that, Ti and Cl are evenly distributed throughout the surface without leaving any void space. Similar fashion is also noted for the other two catalysts (SMT1 and SMT3) suggesting the homogeneous surface composition of the three catalysts following the aforementioned preparation methods.
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**Figure 2.9:** SEM images of the (a) PS-PMMA, (b) SMT1, (c) SMT2 and (d) SMT3

**Table 2.3:** Surface composition and comparison of the relative intensities of the characteristic vibration stretching bands of the PS-PMMA-Ti catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ti (wt %)</th>
<th>Cl (wt %)</th>
<th>(^{1727}/A_{1630})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMT1</td>
<td>63.2</td>
<td>36.8</td>
<td>1.9</td>
</tr>
<tr>
<td>SMT2</td>
<td>71.6</td>
<td>28.4</td>
<td>1.5</td>
</tr>
<tr>
<td>SMT3</td>
<td>81.1</td>
<td>18.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Figure 2.10: EDX Patterns of (a) SMT1, (b) SMT2 and (c) SMT3

Figure 2.11: Elemental distribution on the surface of PS-PMMA of the catalyst (SMT2): (a) Ti and (b) Cl

2.3.5. XRD analysis

XRD patterns of the neat PS-PMMA and the hybrid catalysts (SMT1- SMT3) are shown in Figure 2.12. It is observed that the virgin polymer (PS-PMMA) exhibited a broad XRD peak at \(2\theta = 18^\circ-22^\circ\) assigning to crystalline nature of the polymer. After incorporation of TiCl\(_4\) into polymer matrix (SMT1), the characteristic reflection peak at \(2\theta = 18^\circ-22^\circ\) has been considerably reduced suggesting the loss of crystallinity due to the lattice disorder of the pure polymer chains [Figure 2.12 (b)]. The phenomenon becomes more pronounced with increasing amount of TiCl\(_4\) into the polymer matrix (SMT2 and SMT3). Eventually, polymer becomes complete amorphous in nature at higher % of
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TiCl₄. This reveals that TiCl₄ is immobilized into the polymer chains which combines with the functional >C=O group of polymer matrix.

![Figure 2.12: Powder XRD patterns of (a) PS-PMMA, (b) SMT1, (c) SMT2 and (d) SMT3](image)

2.3.6. TG analysis

Thermogravimetric analysis is used to estimate the percentage weight loss of pure polymer and the prepared polymer supported hybrid catalysts against increase in temperature. The TGA curves of PS-PMMA and the representative PS-PMMA supported TiCl₄ catalysts are shown in Figure 2.13. The degradation temperature of the pure polymer and the hybrid catalysts are listed in Table 2.4. The initial weight loss of the pure PS-PMMA polymer occurred at temperature 190°C corresponding to 5% weight loss due to the volatilization of the residual solvent. The major weight loss of the polymer obtained over the range of 320-420 °C which is related to the structural decomposition of the main chain of PS-PMMA. On the other hand, the polymer supported catalysts showed initial weight loss in the temperature range of 100-150 °C (150 °C for SMT1, 110 °C for SMT2 and 100 °C for SMT3) with a slight digression temperature than the parent PS-PMMA polymer. This is possibly due to the release of TiCl₄ from the polymer matrix.
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is also noticed that the major degradation temperature of all catalysts gradually decreases with the increasing amounts of TiCl4 into the polymer matrix which is reflected as a loss of crystallinity in the XRD data. Moreover, the residual weight percentage of the catalysts is found to be more than the pure polymer. This might be due to the gradual increase of Ti in the catalyst (SMT3 > SMT2 > SMT1 > PS-PMMA), allowing formation of stable compounds with degraded polymer matrix.

![Figure 2.13: TGA plots of (a) PS-PMMA, (b) SMT1, (c) SMT2 and (d) SMT3](image)

**Table 2.4: TGA data of PS-PMMA and PS-PMMA-Ti catalysts**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Degradation temperature (°C)</th>
<th>Wt% of ash at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; degradation</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; degradation</td>
</tr>
<tr>
<td>PS-PMMA</td>
<td>190</td>
<td>320</td>
</tr>
<tr>
<td>SMT1</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>SMT2</td>
<td>110</td>
<td>290</td>
</tr>
<tr>
<td>SMT3</td>
<td>100</td>
<td>280</td>
</tr>
</tbody>
</table>
Poly(styrene-co-methyl methacrylate) supported Ziegler-Natta catalyst for ethylene polymerization in slurry process

All the TG analyses results suggest that TiCl₄ incorporated PS-PMMA supported catalysts are stable upto 100-150 ºC (depending on the amount of TiCl₄ into the polymer matrix). This indicates that PS-PMMA does not slaughter its molecular configuration during catalysts preparation. Usually ethylene polymerization is conducted with Ziegler-Natta catalyst in slurry process at 60-70 ºC. Therefore, the newly prepared PS-PMMA supported TiCl₄ catalysts are adequately thermally stable for examining as a catalyst for ethylene polymerization.

2.3.7. Theoretical calculation

Further, to investigate the nature of interaction between TiCl₄ and the polymer matrix, density functional calculations were carried out. A system comprising of a monomer unit of poly(styrene-co-methyl methacrylate) polymer and TiCl₄ [Figure 2.14 (a)] is subjected to geometry optimization using double numerical (DN) basis set in combination with the Vosko-Wilk-Nusair (VWN) co-relation functional as provided in the DMol³ program. In the optimized geometry, the C-C, C-H, C=C, >C=O, >C=O and Ti-Cl bond lengths are found to be 1.521, 1.104, 1.403, 1.385, 1.266 and 2.237 Å respectively, and are within considerable range. The distance between Ti and O atom of carbonyl group of polymer moiety is found to be 1.984Å which is found to be 12% shorter than the sum of the covalent radii of Ti and O (2.260 Å) [Figure 2.14 (b)]. Thus, the incorporation of TiCl₄ into the polymer matrix takes place via an interaction between the O atom of the carbonyl group of the polymer matrix and Ti atom of TiCl₄. Further, the hybrid material is found to be stabilized by 43.3 kcal mol⁻¹ than the individual moieties. This interaction between the Ti and O atom of the >C=O group of polymer lengthens the >C=O bond length by 0.02 Å than in the free monomer which has been further confirmed from the FTIR analysis where we found a decrease in the stretching frequencies of >C=O group. Thus, this experimental and theoretical prediction further clears the fact that treatment of the TiCl₄ with the polymer moiety reduces carbonyl stretching frequency via the formation of O···Ti dative bond.
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Figure 2.14: (a) Probable complex of PS-PMMA-Ti and (b) Selected bond length of the optimized geometry

2.3.8. Catalytic activity of PS-PMMA-Ti catalysts on ethylene polymerization

This study is aimed at ethylene polymerization with the newly synthesized PS-PMMA supported titanium based Ziegler-Natta catalyst (SMT1- SMT3) with TEA as a cocatalyst in slurry process in heptane medium in mild condition (50 °C and atmospheric pressure). Catalysts are insoluble in the medium (heptane). So it is a heterogeneous catalytic system. As the reaction is heterogeneous in nature so polymerization of ethylene proceeds at the surface of the PS-PMMA-Ti catalysts. This implies that productivity mainly depends on the effective catalytic sites (Ti-O) on the surface. Catalytic sites are active for ethylene polymerization after addition of proper amount of TEA as a co-catalyst which is responsible for reduction of Ti$^{4+}$ to Ti$^{3+}$ in TiCl$_4$ and forms Ti-C bond. Ti-C bond is significantly active for ethylene polymerization.$^{1, 2, 16-18}$

The overall productivity of the catalysts is found to be in the range of 0.6-1.01 kg of PE/ g of Ti/ h as displayed in Table 2.5. Amongst three catalysts, SMT2 shows the highest productivity since; SMT2 contains higher Ti which is responsible for enhancing the active sites for ethylene polymerization after alkylation. Interestingly, increasing concentration of Ti into the polymer matrix leads to lower productivity in SMT3. This is possibly due to the formation of agglomerate between TiCl$_4$ which leads to lowering of
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effective sites. This is an indication that the persistency of the optimum amount of Ti into the polymer matrix is essential for high productivity.

Table 2.5: Polymerization condition and activity of three catalysts in ethylene polymerization

<table>
<thead>
<tr>
<th>Entry</th>
<th>SMT1</th>
<th>SMT2</th>
<th>SMT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti wt % (UV-visible)</td>
<td>0.6</td>
<td>1.1</td>
<td>2.5</td>
</tr>
<tr>
<td>Catalyst amount (g)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Al/Ti mole ratio</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Ethylene pressure (atm.)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Solvent (ml)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Polymerization time (h)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Productivity (kg of PE/ g of Ti/ h)</td>
<td>0.6</td>
<td>1.01</td>
<td>0.8</td>
</tr>
</tbody>
</table>

2.3.9. Stability of the supported catalysts

We have seen that supported catalysts are effective in ethylene polymerization. In the catalysts TiCl₄ is anchored on the support through co-ordination bond formation between >CO with Ti. There is a chance of leaching of TiCl₄ from the support during polymerization. Therefore, stability of the supported catalysts is an important factor to assess the suitability of the catalysts. UV-visible spectroscopy is a very usefull method to evaluate the leaching property of the catalysts. For this purpose the following experiment was conducted. In a 250 ml three necked round bottom flask, 0.05 g SMT2 was dispersed in dry heptane in an inert nitrogen atmosphere. Calculated amount of TEA (Al/Ti = 300) was injected into the solution with a gas tight syringe. After vigorously stirring at 50 °C for about 2 h, the mixture was filtered in dry nitrogen atmosphere. The titanium content of the filtrate was estimated using UV-visible spectroscopy as mentioned above. Furthermore, similar experiment was also carried out without alkylation with the SMT2 catalyst. Interestingly, no absorption peak was found in the 350-410 nm characteristic ranges for both experiments. The absence of trace amount of titanium reveals no leaching of TiCl₄ from the polymer matrix during alkylation and without alkylation. The same
experiment was performed for the other two catalysts (SMT1 and SMT3) and no leaching of Ti was found. It is confirmed that Ti complex is anchored firmly on PS-PMMA matrix.

2.3.10. Catalytic activity Vs storability of the catalysts

Polymer supported TiCl₄ based Ziegler-Natta catalysts are easy for handling and storing. To evaluate the storability of the catalysts, the synthesized PS-PMMA-Ti catalysts are kept in a stopper vessel under dry nitrogen environment upto 80 days. Time to time catalytic activity is checked. Interestingly, it is found that the newly prepared PS-PMMA-Ti catalysts (SMT1- SMT3) are stable upto 80 days without losing its catalytic activity as presented in Figure 2.15. Although the catalytic activity of the synthesized catalysts is lower than MgCl₂ supported Ziegler-Natta catalyst. However, PS-PMMA-Ti hybrid catalysts has an advantage over the conventional Ziegler-Natta catalyst due to its high storability.

Figure 2.15: Catalyst activity with storage time (a) SMT1, (b) SMT2 and (c) SMT3

2.3.11. Characterization of PEs synthesized by PS-PMMA-Ti catalysts

FT-IR spectra of the PE synthesized by the polymer supported catalysts (SMT1, SMT2 and SMT3) are shown in Figure 2.16. Likewise for pure PE, strong characteristic absorption band at 2929 and 2856 cm⁻¹ corresponding to C-H stretching mode is noticed. In addition, two strong peak at 1470 and 719 cm⁻¹ is also found for the deformations of
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methylene group. The presences of all these significant bands imply the formation of PE. The broad band at about 3460 cm\(^{-1}\) is due to O-H of the moisture adsorbed in PE.\(^{21}\)

**Table 2.6:** Characterization of PE synthesized by PS-PMMA supported titanium catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>(\bar{M}<em>n)(</em>{\text{GPC}}) g/mol</th>
<th>(\bar{M}<em>w)(</em>{\text{GPC}}) g/mol</th>
<th>PDI</th>
<th>(T_m)(^{\circ}\text{C})</th>
<th>MFI (g/ 10 min)</th>
<th>Bulk density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMT1</td>
<td>26,662</td>
<td>237,300</td>
<td>8.9</td>
<td>129.5</td>
<td>1.89</td>
<td>0.17</td>
</tr>
<tr>
<td>SMT2</td>
<td>35,333</td>
<td>275,600</td>
<td>7.8</td>
<td>133.4</td>
<td>1.38</td>
<td>0.25</td>
</tr>
<tr>
<td>SMT3</td>
<td>22,652</td>
<td>260,500</td>
<td>11.5</td>
<td>131.7</td>
<td>1.63</td>
<td>0.23</td>
</tr>
</tbody>
</table>

MFI (230\(^\circ\text{C}/2.16\ Kg)

**Figure 2.16:** FT-IR spectra of the PE synthesized from (a) SMT1, (b) SMT2 and (c) SMT3
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These catalysts are found to produce PE with broad molecular weight distribution with moderate molecular weight. The molecular weight of the PE was determined by GPC and the results are displayed in Table 2.6. The resulting PE exhibited weight average molecular weight ($\bar{M}_w$) in the range of 237,300-275,600 g/mol with PDI in the range of 7.8-11.5. The broad molecular weight distribution indicates the presence of different population of active centres of the catalysts (SMT1- SMT3).

Differential scanning Calorimetry (DSC) of the polyethylene under nitrogen atmosphere is shown in Figure 2.17. The melting point of the produced PE is found in the range of 129.5-133.4 °C indicating less branching in the polymer chain (Table 2.6). The thermal properties of the polyethylene have been investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. The TGA curve of product polyethylene is shown in Figure 2.18. From the TGA curves, it is seen that the resulting polyethylene are relatively thermally stable until around 300 °C and after the onset degradation temperature of 350 °C, the degradation rate of polyethylene accelerates. Above 500 °C only 3% char residue is found for all the resulting polyethylene.
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The surface morphology of the resulting PE is examined with SEM and corresponding SEM micrographs are shown in Figure 2.19. The products beads are found to be granular like structure with millimetre dimension (0.2-0.4 mm) for each catalyst (SMT1-SMT3). At low magnification, the polymer beads seem to be granular like structure, but at higher magnification a cauliflower like morphology is seen with less number of pores. The SEM picture also implies that each PE particle originate from one catalyst beads since the size of PE beads are significantly larger than the catalysts template. Furthermore, the absence of reactor fouling and powder like particles give clear evidence that there is no leaching happening during polymerization which generally seen in homogeneous catalyst.

Figure 2.18: TGA plots of polyethylene synthesized from (a) SMT1, (b) SMT2 and (c) SMT3
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**Figure 2.19:** SEM images of PE synthesized using SMT2 catalyst collected at magnification of (a) 350, (b) 1000, (c) 2000 and (d) 5,500

The rheological properties of the resulting polyethylene were studied by melt flow index (MFI) and the data are provided in Table 2.6. It is observed that MFI of the PE decreases with increase in molecular weight of the resulting PE. The bulk density of the ensuing PE increases with increasing the polymerization activity (Table 2.6). However, the bulk density of the PE is relatively low (0.17-0.25 g/cm$^3$, runs SMT1, SMT2 and SMT3) which is due to the lower ethylene pressure.
2.4. Conclusions

The important conclusions drawn from the above study are compiled below:

- XPS analysis provides evidence for the successful incorporation of TiCl$_4$ into the polymer matrix through the co-ordination of the >CO group of PS-PMMA which has been further substantiated by FT-IR study and DFT calculations.

- SEM micrographs show the differences in microstructure between pure PS-PMMA and PS-PMMA supported catalysts. The particle size of pristine polymer is found to be 2-6 µm while, the supported catalysts becomes agglomerated with larger in size (10-50 µm).

- XRD analysis reveals that PS-PMMA supported catalysts become completely amorphous in nature after addition of TiCl$_4$ into the polymer.

- Polymer supported catalysts are found to be stable upto 100 °C (depending on TiCl$_4$ concentration).

- TiCl$_4$ supported PS-PMMA catalysts activated with TEA showed productivity in the range of (0.6-1.01 kg of PE/g of Ti/h) for ethylene polymerization at 50 °C under atmospheric pressure in slurry process.

- Catalyst SMT2 with 1.1 wt% of Ti gives the highest productivity, which gives a clear indication that optimum amount of Ti is needed for better performance.

- The supported catalysts showed good stability as there is no leaching of TiCl$_4$ after alkylation during polymerization and storability upto 80 days.

- Catalysts are found to produce polyethylene with broad molecular weight distribution (PDI~7.8-11.5) due to presence of different population of active centers of the catalysts and melting temperatures in the range of 129.5-133.4 °C.
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References