

## New Clay-Supported Ziegler–Natta Catalyst for Preparation of PE/Clay Nanocomposites via *In Situ* Polymerization

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**ABSTRACT:** Polyethylene/clay (PE/Clay) nanocomposites were prepared by the *in situ* polymerization of ethylene using the new Clay/butyl octyl magnesium (BOM)/Chloroform/EtOH/TiCl<sub>4</sub>/tri ethyl aluminum (TEA) catalyst system in heptane where BOM and TEA were the support for the clay modification and cocatalyst, respectively. The influence of the modified clay using BOM on the catalyst and polymerization was investigated. Also, the effect of temperature, pressure, hydrogen, and the molar ratios of TEA/Ti on the catalyst yield and ethylene consumption (polymerization rate) were studied. It was found that the above clay-supported catalyst was an efficient Ziegler–Natta type catalyst due to its suitable yield for the polymerization of ethylene toward the production of the PE/Clay nanocomposites. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** clay; catalysts; polyolefins

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### INTRODUCTION

Polyethylene (PE) is widely produced in the commercial scale and has a lot of applications because it is the most easily molded by many different processes and exhibits a wide variety of useful physical and mechanical properties. These properties of PE can be further improved by adding some inorganic agents such as calcium carbonate, talc, carbon black, and so on.<sup>1–4</sup>

Dramatic modification in the physical and mechanical properties of polymers can be performed by adding just a small fraction of nanoparticles including clay, nanotube, and CaCO<sub>3</sub> to a polymer matrix. Totally, the nanocomposite technology offers superior mechanical, thermal, and barrier properties which are not achievable in the conventional polymer composites.<sup>4–8</sup>

The synthesis of polymer/clay nanocomposites can be performed by three methods containing melt processing, solution, and *in situ* polymerization.<sup>4–6,9,10</sup> The melt processing of PE with nanoparticles is often led to insufficient filler dispersion, what leads to aggregation and intercalation, especially at high filler contents which in turn decreases the mechanical properties. The solution method suffers from some drawbacks including the low solubility of PE in the low boiling organic solvents. Another problem of the both of the above methods is the hydrophilic nature of most inorganic fillers and the hydrophobic nature of the PE. The diverseness results in weak interfacial

adhesion between the filler and the PE matrix and low mechanical properties. Therefore, fillers must be modified by surface active agents. These disadvantages can be solved by *in situ* polymerization.<sup>11,12</sup> The comparison of the silicate dispersions indicates that the *in situ* polymerization is more effective in nanocomposite formation than the melt processing method.<sup>12,13</sup>

Metallocene, Ziegler–Natta, and late transition metals catalysts supported on the clay have been mostly used for the *in situ* polymerization of ethylene.<sup>14–17</sup> Metallocene catalysts need an excessive amount of cocatalyst for activation which is the most critical limitation for using metallocene catalysts in this aspect. Ziegler–Natta catalysts supported on the clay for the preparation of PE/Clay nanocomposites suffer from some deficiencies including low yield which is the basic main restriction for the production of PE/Clay nanocomposites by *in situ* polymerization, especially from the industrial perspective.<sup>14,15</sup>

In this article, the new Clay/butyl octyl magnesium (BOM)/Chloroform/EtOH/TiCl<sub>4</sub>/tri ethyl aluminum (TEA) catalyst system was investigated for the ethylene polymerization toward the preparation of PE/Clay nanocomposites. This catalyst exhibited a reasonable yield in the ethylene polymerization which is the most required situation in the clay-based type catalysts. Also, the present article reports the effect of the amount of BOM and polymerization conditions on the prepared catalysts

**Table I.** Clay-BOM Supports, Catalysts, and Their Ti Content

Support and catalyst No.	1	2	3	4	5
Clay : BOM (g)	15 : 0	15 : 2	15 : 4	15 : 8	15 : 12
Ti (wt %)	1.01	1.12	1.23	2.05	3.01

and polymerization behavior. Such results propose a promising approach for producing PE/Clay nanocomposites via *in situ* polymerization using Ziegler–Natta type catalysts.

## EXPERIMENTAL

### Materials

Ethylene (polymer grade), nitrogen (>99.99%), and heptane ( $H_2O < 3\text{ppm}$ ) were purchased from Linde (Munich/Germany), Arkan gas (Tehran/Iran), and Pentane Chemistry Industries (Esfahan/Iran).  $TiCl_4$  and TEA were purchased from Fluka (Buchs/Switzerland). Chloroform and ethanol (extra pure grade) were purchased from Merck (Darmstadt/Germany). Butyl octyl magnesium and clay were prepared from Chemtura (Darmstadt/Germany) and Crystal Clay (Pune/India), respectively.

### Preparation of Support

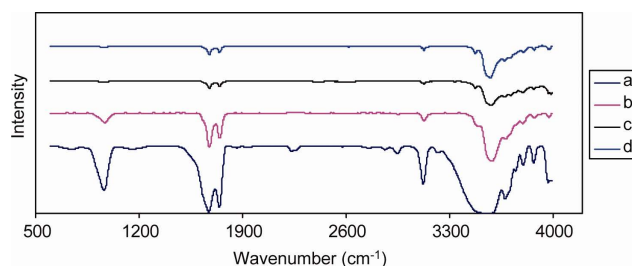
The clay used in the synthesis of the Clay-BOM supports was heated at  $80^\circ\text{C}$  *in vacuo* for 4 h.<sup>18</sup> Heptane (250 mL) and 15 g of clay were added to a 500 mL flat-bottom flask under  $N_2$  and vigorously mixed for 10 min. Then, the prescribed amount of BOM was added to the flask during 15 min (Table I). The mixture was heated to  $60^\circ\text{C}$  and further mixed for 10 h. The obtained product was washed eight times and used as the support for the catalyst preparation.

### Preparation of Catalyst

The preparation of the catalysts was carried out in a 1.0 L steel jacket Buchi autoclave reactor equipped with a mechanical seal stirrer. After running out of moisture and oxygen by nitrogen, 350 mL of heptane containing 15 g of the above support were added and then mixed for 10 min. The temperature was increased to  $70^\circ\text{C}$  and 2.2 mL of chloroform in 20 mL of heptane was added dropwise to the mixture during 90 min and further mixed at  $75\text{--}78^\circ\text{C}$  for 2 h. The temperature was increased to  $85^\circ\text{C}$  and 0.16 mL of ethanol in 10 mL of heptane was injected and mixed for 1 h.  $TiCl_4$  (3 mL) in 10 mL of heptane was introduced to the reactor over 25 min and further mixed at  $94^\circ\text{C}$  for 2 h. Finally, the produced catalyst was washed eight times with heptane until no traces of titanium were detected in the washing liquid.

**Table II.** BET Surface Area Analysis

Sample	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{mL/g}$ )	Average pore diameter ( $\text{\AA}$ )
Support No. 1	8.7	0.041	93
Support No. 2	11.9	0.076	129.2
Catalyst No. 1	19.6	0.091	76.4
Catalyst No. 2	25.1	0.096	92.6



**Figure 1.** FTIR spectra of (a) clay (b) support No. 2 (c) catalyst No. 1 (d) catalyst no. 2. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Polymerization

Polymerization was carried out in a 1.0 L steel jacket Buchi autoclave reactor equipped with a mechanical seal stirrer in the slurry phase.

After running out of moisture and oxygen by nitrogen, 500 mL of heptane was added and then mixed for 10 min. The prescribed amount of TEA was added to the reactor and then, the reactor was warmed up to the required temperature. After injection of 100 mg of the catalyst, ethylene was supplied continuously for 2 h. In the polymerization in which hydrogen was used, hydrogen was injected before ethylene was supplied. The ethylene consumption was measured by using MFC (Mass Flow Controller) (Brooks, Holland).

After the polymerization, the untreated gases were slowly released, and the polymer was then filtered and dried.

### Characterization

The titanium content of the synthesized catalysts was measured by the UV-visible method (at a wavelength of 410 nm) on Shimadzu, UV-1650 PC (Kyoto/Japan). IR spectra were carried out by Bruker, Vertex 80 (Ettlingen/Germany) for studying the functional groups on the clay, especially reacted with BOM. The surface area, pore volume and pore radius of the clay, Clay-BOM support, and catalyst were measured by using the BET (Brunauer Emmett Teller) method (NOVA2000 Quantachrome apparatus). The morphology of the clay, Clay-BOM support, and catalyst was depicted using SEM (Scanning Electron Microscope) (CamScan MV2300).

Catalyst yield was determined in terms of the produced PE (kg) per the used titanium (mol) in the polymerization.

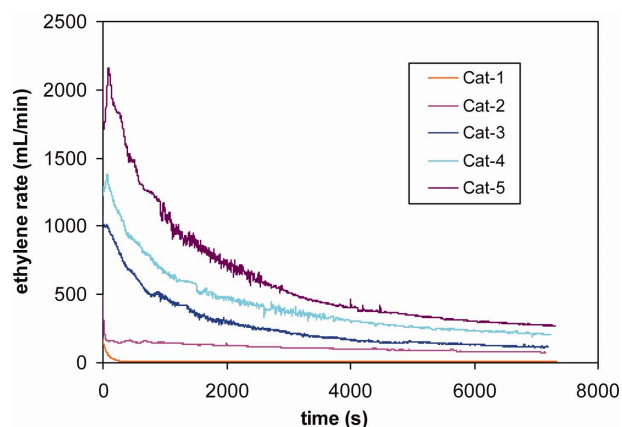
## RESULTS AND DISCUSSION

The clay was reacted to the different amounts of BOM to modify the clay toward achieving suitable supports for the preparation of the clay-based Ziegler–Natta catalysts for the ethylene

**Table III.** Yield of Produced Catalysts<sup>a</sup>

Catalyst No.	1	2	3	4	5
Yield (kgPE/molTi)	95.2	1217.4	2346.1	2209.3	2206.3

<sup>a</sup>Polymerization conditions:  $PC_2 = 8$  bar, Time = 2 h,  $PH_2 = 0$ , TEA/Ti = 20, Temp. =  $70^\circ\text{C}$ .



**Figure 2.** Polymerization rate of prepared catalysts. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

polymerization (Table I). The table shows that the content of Ti loaded on the catalysts rose with increasing the amount of BOM treated with the clay.

Table II shows the BET surface area of the supports (No. 1 and 2) and catalysts (No. 1 and 2). With regard to the table, the surface area of the clay enhanced under the reaction of the clay with BOM and also the catalyst preparation. Totally, an increase in the surface can lead to improvement in the behavior of the Ziegler–Natta type catalysts in the olefins polymerization.<sup>19</sup>

Fourier transform infrared (FTIR) spectroscopy was used for studying the changes in the functional groups of the clay due to the reaction between the clay and BOM. Figure 1 illustrates the FTIR spectra of the clay, Clay-BOM support, and catalysts No. 1 and 2. As observed in Figure 1(a), the clay showed the absorption bands at 3632 and 1046  $\text{cm}^{-1}$ , which can be contributed to N–C and N–H groups of the alkyl ammonium used for the clay modification. In addition, the alkyl group showed the absorption bands at 2924 and 2851  $\text{cm}^{-1}$  corresponding to C–H. Compared to Figure 1(b), the intensity of the absorption bands, especially at 3632  $\text{cm}^{-1}$ , remarkably decreased. This indi-

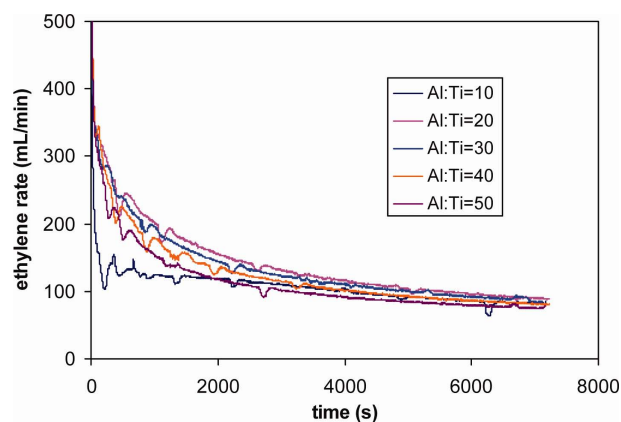
**Table IV.** Effect of Polymerization Conditions on Catalyst Yield

Al : Ti <sup>a</sup>	10	20	30	40	50
Yield (kgPE/molTi)	826.1	1217.4	1173.9	1043.5	869.6
Temperature (°C) <sup>b</sup>	50	60	70	80	90
Yield (kgPE/molTi)	1043.5	1730.4	1217.4	956.5	782.6
P (bar) <sup>c</sup>	2	4	6	8	10
Yield (kgPE/molTi)	347.8	652.2	869.0	1217.4	1434.8

<sup>a</sup>Polymerization conditions: catalyst No. = 2,  $\text{PC}_2 = 8$  bar, Time = 2 h,  $\text{PH}_2 = 0$ , Temp. = 70°C.

<sup>b</sup>Polymerization conditions: catalyst No. = 2,  $\text{PC}_2 = 8$  bar, Time = 2 h,  $\text{PH}_2 = 0$ , TEA/Ti = 20.

<sup>c</sup>Polymerization conditions: catalyst No. = 2, Temp. (°C) = 70, Time = 2 h,  $\text{PH}_2 = 0$ , TEA/Ti = 20.

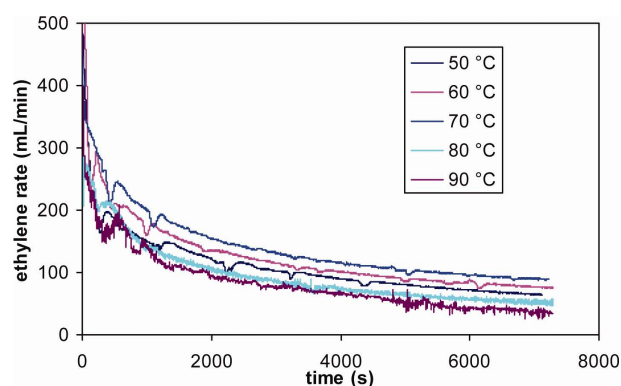


**Figure 3.** Dependence of polymerization rate on Al/Ti ratio. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

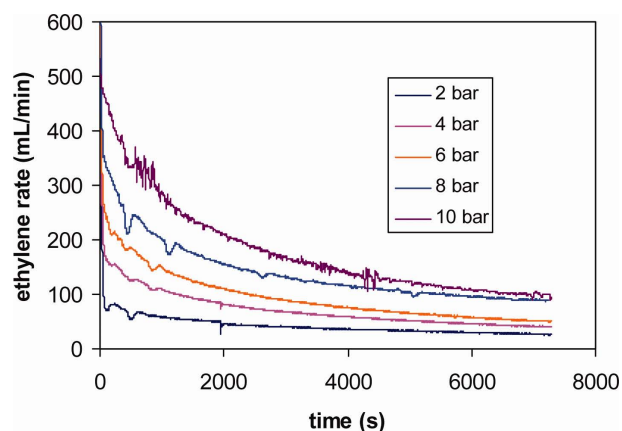
cates that a large portion of alkyl ammonium in the clay was removed by BOM. According to Figure 1(c), the untreated clay also lost its alkyl ammonium during the titaniation (catalyst preparation). In addition, catalyst No. 2 contained some alkyl ammonium [Figure 1(d)].

According to Table III, the yield of the catalysts increased with increasing the Clay/BOM ratio, rising from 95.2 kgPE/molTi in catalyst No. 1 to 2206.3 kgPE/molTi in catalyst No.5. This effect can be related to the increase of the amount of BOM and Ti loaded on the Clay-BOM support in which the Clay-BOM component acts as a suitable support in the preparation of the catalyst. Therefore, BOM offers the most loading sites and consequently, the titanium catalyst is avoided directly anchoring on the clay surface. In addition, as the presence of the nitrogen groups on the clay surface acts as poison for the Ziegler–Natta type catalysts, the removal of such groups through the clay treatment by using BOM reduces their adverse effects on the catalyst behavior. The obtained results indicate that the Clay–BOM-supported catalysts enjoyed an acceptable yield in the ethylene polymerization.

Figure 2 exhibits the polymerization rate of ethylene using the prepared catalysts. As expected, the polymerization rate of the catalysts rose by increasing their yield. Like the yield of catalyst



**Figure 4.** Effect of temperature on rate profile. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Influence of ethylene pressure on rate profile. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

No. 1, this catalyst showed the least polymerization rate; conversely, catalyst No. 5 had the highest yield. Although catalysts No. 1 and 2 showed low yield, they enjoyed a smooth polymerization rate; whereas, catalysts No. 3, 4, and 5 showed a rapid drop in their rate during the polymerization. However, the polymerization rate reached almost a stable state after about 1 h of the polymerization.

According to Table IV, the maximum yield of the catalyst was observed at the molar ratio TEA/Ti of 20–30. It means that the TEA/Ti ratio of 20–30 was required for obtaining the maximum activation of the catalyst, but further amounts of the cocatalyst had an adverse effect on the catalyst. Like the catalyst yield, the highest polymerization rate was obtained at the ratio TEA/Ti of 20–30 (Figure 3). The reduction of the catalyst activity and rate in the presence of the high concentration of the cocatalyst can be attributed to the overall reduction of active sites.<sup>20</sup>

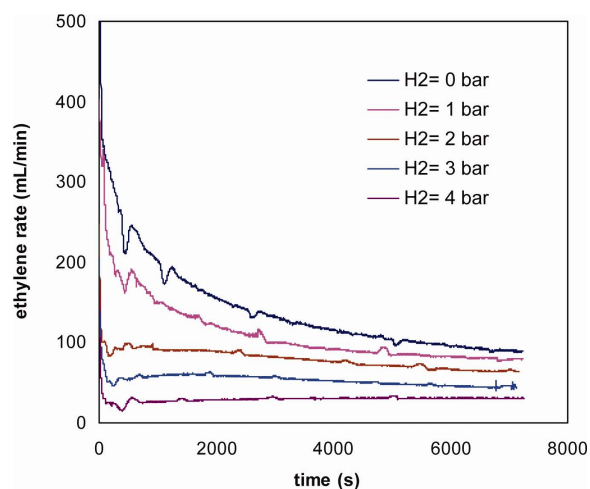
As Table IV shows, the yield of the catalyst gave a maximum at 60–70°C and then decreased with increasing temperature. That result might be ascribed to an irreversible destruction of active sites at the higher temperature in the polymerization condition.<sup>21,22</sup> The influence of the temperature on the polymerization rate is shown in Figure 4. Similar to the catalyst yield, the highest rate was obtained at 60–70°C. With regard to the figure, the catalyst showed a gentle polymerization rate at the range of 50–90°C, which is a usual range for the Ziegler–Natta type polymerization.

According to Table IV, the catalyst yield was roughly proportional to the monomer pressure, rising from 347.8 kgPE/molTi at 2 bars to 1434.8 kgPE/molTi at 10 bars. This can be contrib-

**Table V.** Effect of Hydrogen on Catalyst Yield<sup>a</sup>

H <sub>2</sub> (bar)	0	1	2	3	4
Yield (kgPE/molTi)	1217.4	739.1	521.7	347.8	130.43

<sup>a</sup>Polymerization conditions: catalyst No. = 2, Temp. (°C) = 70, Time = 2 h, PC<sub>2</sub> = 8 bar, TEA/Ti = 20.



**Figure 6.** Effect of hydrogen on rate profile. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

uted to the increase of the monomer concentration in the polymerization system at higher pressures.

Figure 5 illustrates the polymerization rate at various pressures. As expected, the rate of the polymerization enhanced by increasing the ethylene pressure. The profiles of the polymerization rate were smoother in lower pressures because of the reduction of the catalyst activity in these pressures.

Hydrogen is used as a chain transfer agent for controlling molecular weight in the Ziegler–Natta type polymerization.<sup>23–25</sup> Table V exhibits the effect of hydrogen on the yield of catalyst No.2. According to the table, the yield of the catalyst showed a decrease in the presence of hydrogen, reducing from 1217.4 kgPE/molTi in the absence of hydrogen to 130.4 kgPE/molTi in the presence of 4 bar of hydrogen. The main reason for such a decline in the catalyst yield was the reduction of the partial pressure of the monomer in the polymerization system by increasing the amount of hydrogen. Furthermore, the slow addition of the monomer to the catalyst-hydrogen bond formed in the step of the chain transfer to hydrogen causes an adverse effect on the catalyst yield.<sup>26</sup> Accordingly, hydrogen also had a negative effect on the polymerization rate, so that the polymerization rate fell from about 150 mL/min in the absence of hydrogen to about 29 mL/min in the presence of 4 bar of hydrogen (Figure 6).

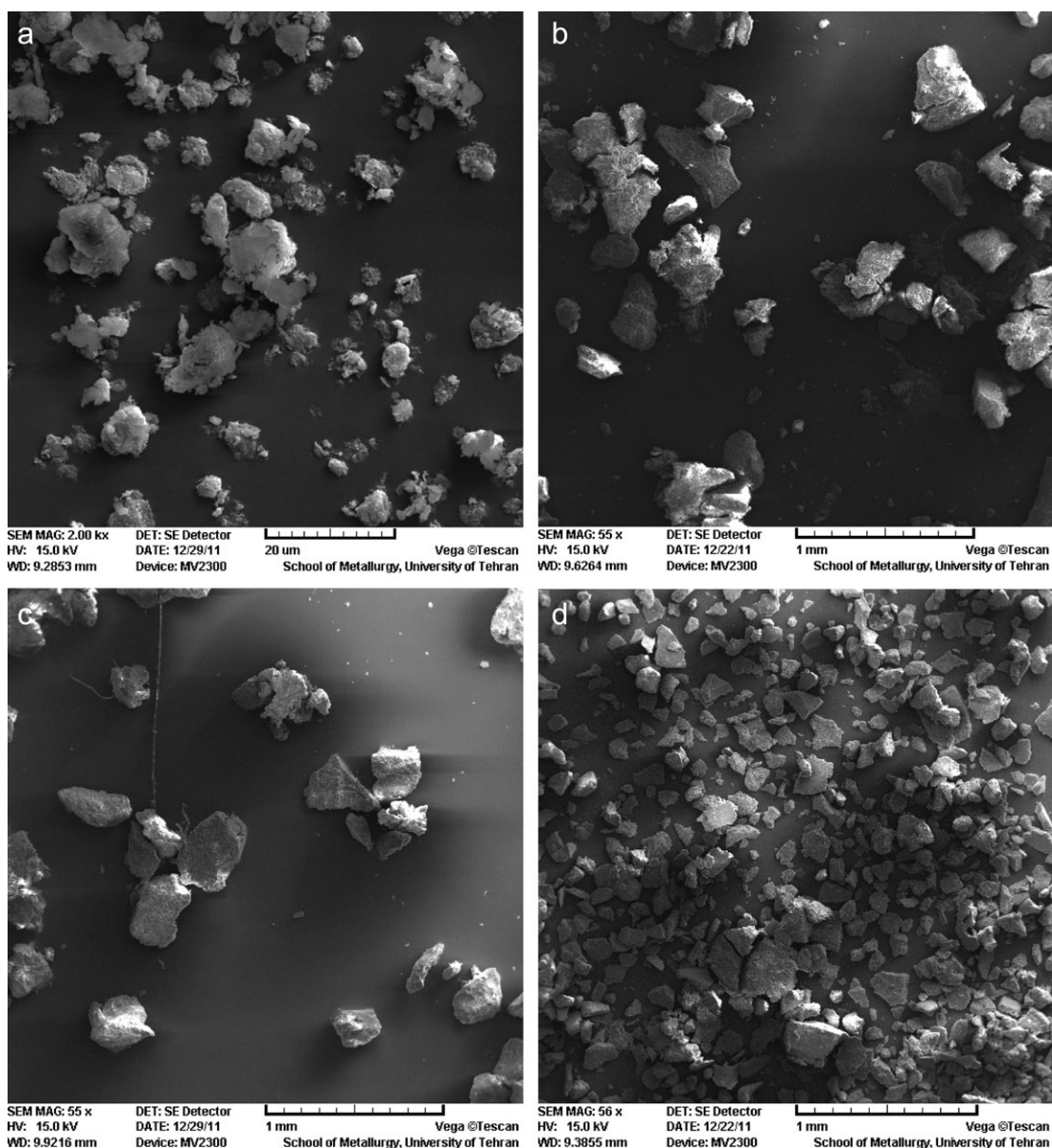
It has been found that the shape of the support outshines the catalyst shape. On the other hand, both yield and texture of the catalyst affect the polymer morphology, and the catalysts are also known to replicate their morphology into the polymer particles. In other words, the catalyst particle acts as a template for growth of the polymer particle.<sup>27–29</sup>

The morphology of the supports and catalysts was elucidated by SEM (Figure 7). According to the figure, the clay, supported Clay-BOM, and catalyst did not have a regular shape.

## CONCLUSIONS

The Clay/BOM/Chloroform/EtOH/TiCl<sub>4</sub>/TEA catalyst system showed a high yield in the ethylene polymerization. The clay





**Figure 7.** SEM micrographs of (a) clay, (b) support No. 2 (c) catalyst No. 1 (d) catalyst No. 2.

lost a lot of its alkyl ammonium groups under the reaction to BOM. Meanwhile, with increasing the amount of the reacted BOM to the clay, the loaded Ti on the catalysts and surface area of the catalysts were enhanced which led to an enhancement in the catalyst yield as well as polymerization rate. The studies on the polymerization conditions showed that the optimum yield and polymerization rate of the catalyst were obtained at around 60–70°C, a pressure of more than 6 bar, and a 20–30 molar ratio of TEA/Ti; whereas, the addition of hydrogen decreased the catalyst yield and polymerization rate. SEM studies showed that the clay, Clay-BOM support, and catalyst did not have an identified geometric shape. On the whole, the above catalyst system was an efficient clay-supported Ziegler–Natta type catalyst to prepare PE/Clay nanocomposites through *in situ* polymerization.

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## REFERENCES

1. Peacock, J. Handbook of Polyethylene: Structures, Properties and Applications, 1st ed.; Marcel Dekker: New York, 2000.
2. Piatti, G. Advances in Composite Materials, 1st ed.; Applied Science Publisher: London, 1978.

3. Sedlacek, B. *Polymer Composites*, 1st ed.; Walter de Gruyter: Berlin, **1986**.
4. Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.
5. Fuad, M. Y. A.; Hanim, H.; Zarina, R.; Isha, M. Z. A.; Hassan, A., *eXPRESS Polym. Lett.* **2010**, *4*, 611.
6. Ray, S. S.; Okamoto, M. *Macromol. Rapid Commun.* **2003**, *24*, 815.
7. Alexandre, M.; Dubois, P. *Mat. Sci. Eng.* **2000**, *28*, 1.
8. Bikiaris, D. *Materials* **2010**, *3*, 2884.
9. Kaminsky, W.; Funck, A. *Macromol. Symp.* **2007**, *260*, 1.
10. Raka, L.; Gaceva, G. B.; Lu, K.; Loos, J. *Polymer* **2009**, *50*, 3739.
11. Weirner, M. W.; Chen, H.; Giannelis, E. P.; Sogah, D. Y. *J. Am. Chem. Soc.* **1999**, *121*, 1615.
12. Scharlach, K.; Kaminsky, W. *Macromol. Symp.* **2008**, *261*, 10.
13. Jin, Y. H.; Park, H. J.; Im, S. S.; Kwak, S. Y.; Kwak, S. *Macromol. Rapid Commun.* **2003**, *23*, 135.
14. Oliveira, M.; Marques, M. F. *Chem. Chem. Tech.*, **2011**, *5*, 201.
15. Huang, Y.; Yang, K.; Dong, J. Y. *Macromol. Rapid Commun.* **2006**, *27*, 1278.
16. Mignoni, M. L.; Silva, J. V. M.; Souza, M. O.; Mauler, R. D. S.; Souza, R. F.; Gusmao, K. B. *J. Appl. Polym. Sci.* **2011**, *122*, 2159.
17. Marques, M. F.; Oliveira, M. *Polym. Bull.* **2010**, *64*, 221.
18. Ray, S. S.; Galgali, G.; Lele, A.; Sivaram, S. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 304.
19. Moore, E. P. *Polypropylene Handbook*, 1st ed.; Hanser: Munich, **1996**.
20. Rong, J.; Li, H.; Jing, Z.; Hong, X.; Sheng, M. *J. Appl. Polym. Sci.* **2001**, *82*, 1829.
21. Bohm, L. L. *Polymer* **1978**, *19*, 553.
22. Abedi, S.; Daftari-Besheli, M.; Shafiei, S. *J. Appl. Polym. Sci.* **2005**, *97*, 1744.
23. Abedi, S.; Hassanpour, N. *J. Appl. Polym. Sci.* **2006**, *101*, 1456.
24. Chien, J. C.; Nozaki, T. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 505.
25. Nikolaeva, M. I.; Mikenas, T. B.; Matsko, M. A.; Echevskaya, L. G.; Zakharov, V. A. *J. Appl. Polym. Sci.*, **2011**, *122*, 3092.
26. Chu, K. J.; Soares, J. B. P.; Penlidis, A.; Ihm, S. K. *Eur. Polym. J.* **2000**, *36*, 3.
27. Natta, G. *Adv. Catal.* **1959**, *11*, 1.
28. Hammawa, H.; Wanke, S. E., *J. Appl. Polym. Sci.* **2007**, *104*, 514.
29. Hutchinson, R. A.; Chen, C. M.; Ray, W. H. *J. Appl. Polym. Sci.* **1992**, *44*, 1389.