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Preparation of Polyethylene/Layered Silicate Nanocomposites Using In Situ Polymerization Approach

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Summary: In this paper, preparation of polyethylene/clay nanocomposites (PECNC) by in situ Ziegler-Natta catalyst polymerization was investigated. A Ziegler-Natta catalyst was first supported on montmorillonite (MMT) type clay and subsequently used for polymerizing ethylene. Clay and clay supported catalyst were characterized by Fourier transmission infrared and ICP method. X-ray diffraction (XRD) and transmission electron microscopy results show that silicate layers of the mineral clay in prepared nanocomposites were intercalated and exfoliated in the polymeric matrix. Differential scanning calorimetry results show that the prepared nanocomposites have higher crystallization temperature than pure polyethylene.

Keywords: clay; in situ polymerisation; nanocomposites; polyethylene (PE)

Introduction

Polymer nanocomposites are a class of hybrid materials composed of an organic matrix with dispersed inorganic fillers that have at least one dimension in the nanometric range.[1] Over the last decade, the utility of inorganic nanoparticles as additive to enhance polymer performance has been established. Among the polymer/inorganic nanocomposites, polymer-layered silicate nanocomposites due to their enhanced physical and mechanical properties including barrier, flammability resistance, ablation performance, environmental stability, and solvent resistance have received so much interaction. [2,3]On the other hand, all these improvements can be obtained at very low filler content (e.g. 5% compared to 30% in typical conventional composites).[3] Generally speaking, melt blending, solution blending and in situ polymerization have been used to prepare polyolefin/clay nanocomposites.[4] Melt intercalation is a common method to prepare polymer/clay nanocomposite. However, this promising approach is not suitable for the preparation of polyolefin nanocomposites.[5,6] Polyolefins are nanopolar organic materials which cannot be easily intercalated between the clay layers.[5,7,8] In order to improve compatibility of the clay and polyolefin, alkyl-ammonium surfactants have been used to modify smectite type clay as montmorillonite (MMT). However, it was found that the thermal degradation of ammonium alkyl surfactants at high process temperature (200 ± 10 °C) not only accelerate the aging and decomposition of polyolefin, but also lead to the restacking of the silicate layers.[4,9]

Some attempts have been made to improve dispersion and exfoliation of clay in polyolefin/clay nanocomposites using polar group containing polymer such as MA-g-PP or MA-g-PE which have not given completely satisfactory results. So, in situ polymerization has been recently considered as alternative method for exfoliation of clay in clay containing polyolefin nanocomposites.[4] This method have been already used for production of many polymer/clay nonocomposites from polymers with polar group monomers such as nylons and epoxy resins with long chain

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amine modified clay called organoclay.[2] Many works also devoted to production of polyethylene clay nanocomposites using metalllocene catalyst supported on virgin and organo-modified clay.[1,10,11] Some researchers also used Ziegler-Natta catalyst with modified clay to produce polyethylene clay nanocomposites[12–14] and few papers reported production of PECNC using conventional Ziegler-Natta catalyst with unmodified clay.[5,6,14] Rong et al.[5,6] supported Ziegler-Natta catalyst on palygorskite, i.e. mineral clay with chainlike structure, to produce PE/palygorskite nanocomposite.

Smectite type clays such as montmorillonite (MMT) are the most commonly layered silicate used for production of polymer-layered silicate nanocomposites due to their good effects on the physical and mechanical properties of polymer/inorganic nanocomposites as mentioned above. The crystal structure of montmorillonite is characterized by a 0.96 nm thick silicate layer consisting of two silica tetrahedral sheet fused to an edge-shared octahedral sheet of nominally alumina or magnesia along with interlayer cations such as Li^+, Na^+, Rb^+, Mg^{2+}, ...[2] The lattice has an unbalanced charge because of substitution of alumina for silica in tetrahedral sheet and iron and magnesium for alumina in octahedral sheet. Due to this anomaly and because layers are adjacent when these unit layers are stacked, the attraction holding these layers together is weak, and cations and polar molecules can enter between the layers and cause explanation. These cations and water molecules are the interlayer material in this type of clay. Figure 1 shows the crystal structure of the montmorillonite.

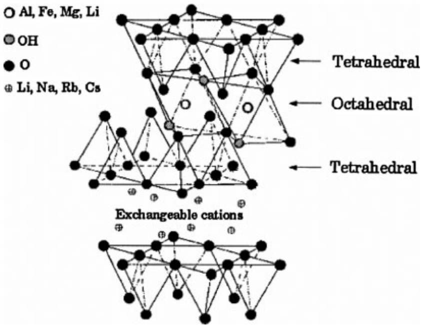


Figure 1.
Lattice structure of montmorillonite[2].

In this research work, direct production of polyolefin/clay nanocomposite with in situ polymerization of olefin monomers by Ziegler-Natta clay supported catalyst have been considered. To prepare active catalyst, titanium tetrachloride which is known as Ziegler-Natta catalysts was supported on the surface of montmorillonite smectite type clay and then the produced clay-catalyst complex was used for ethylene polymerization and production of polyethylene/clay nanocomposites in slurry phase. Characterizations of prepared catalysts and nanocomposites have been obtained and the results have been compared with those presented in literature by Rong et al.[5,6] for PE/palygorskite nanocomposites.

Materials and Methods

Materials

Montmorillonite type clay that has been used in this research was supplied from Tabriz mine in Iran. Ethylene (polymerization grade), titanium tetrachloride ($TiCl_4 > 99\%$ purity, Riedel), triethyl aluminum (TEA) ($AlEt_3 \sim 15\%$ in hexane, Fluka), triisobutyl aluminum (TIBA) ($Al(iBu)_3 > 96\%$ purity, Merck) were used after diluting in hexane. Hexane and toluene were used after refluxing over sodium wire for 24 h under argon for drying.

Characterization

Fourier transmission infrared (FTIR) measurements of the clay samples were conducted on a Shimadzu instrument. X-ray diffraction (XRD) analysis was performed on a Philips PW 1800 with Cu K_α radiation ($\lambda = 0.1504$ nm) at a generator voltage of 40kV and generator current of 100 mA. The interlayer spacing (d_{001}) of the samples (clay and produced polyethylene/clay nanocomposites) was calculated in accordance with Bragg's equation: 2d sin $\theta = \lambda$. Differential scanning calorimetry (DSC) analysis was conducted using a Perkin Elmer Pyris IDSC thermal analyzer under nitrogen atmosphere with heating rate of 10 °C/min in a temperature range of 50–200 °C for dynamic scanning, and T_m was determined in second scan. Transmission electron microscopy (TEM) tests were carried out on a PHLIPS-CM200-FEG transmission electron microscope using an acceleration voltage of 80kV. The titanium contents of the catalysts were measured using ICP/AES standard method.

Clay Calcinations

Existing water in clay can react with catalyst and so it can disturb supporting of catalyst on the clay. Therefore water should be removed from clay by suitable heat treatment. Smectite clay has three types of water or hydroxide groups in or on their crystallites structure. Physically absorbed water is held by less strong attractions and is found on the surface of the clay in defect sites or at sites of broken bond of silicate structure and eliminate at 80–90 °C. Bound water associated in a geometric structure around a cation, is found between the sheet layers of smectites is the second type of hydroxide groups. This water normally leaves clay structure at 100–200 °C. Crystalline water which is the last type of hydroxide source is found within the sheet layers as OH unites. This water is more firmly bound to the structure, and temperature of 500 °C or more are necessary to remove it. To be sure about removing all kind of hydroxide groups from considered clay, samples of clay were calcinated at 600 °C for about 6 h and subsequently stored under inert gas. Figure 2 shows the FTIR spectra of MMT Samples. The absorption peaks of OH for different types of bound water appear at different wavelengths. The peaks between 3600 and 3700 cm^{-1} stand for surface water. The three peaks between 3413 and 3524 cm^{-1} are the reflection of crystalline water. The peak at 1649 cm^{-1} stand for surface adsorbed water and the peak at 1626 cm^{-1} is due to coordinated water. Figure 2 shows that increasing clay heat treatment temperature from 200 °C to 600 °C changes the relative size of hydroxyl peaks.

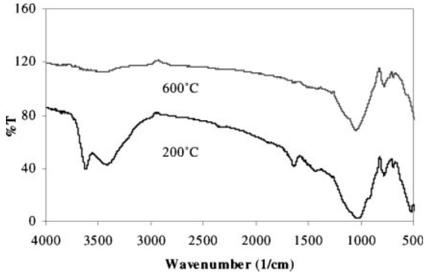
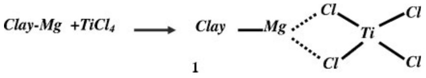


Figure 2.
FTIR spectra of MMT samples calcinated at given temperatures.

Activation of Clay

Activation of MMT to be able to polymerize olefin monomers in the presence of cocatalyst is an important step. In this step, titanium tetrachloride which is known as Ziegler-Natta catalyst was supported on the surface of montmorillonite smectite type clay in toluene under argon atmosphere. The product was washed with hexane at 50 °C at least three times to remove all unreacted titanium and subsequently used for polymerization in slurry phase. In absence of any other active group, titanium tetrachloride approachs interlayer magnesium according to the following reaction and produces suitable complex capable of polymerizing ethylene monomers in the presence of triethyl aluminum or triisobutyl aluminum cocatalyst.



In Situ Coordinated Polymerization

Polymerization experiments were done in a Buchi reactor in slurry phase. Hexane was used as a diluent in all experiments. Reactor was degassed and purified with argon at 90 °C before any polymerization experiments. Then, hexane, cocatalyst, slurry of the prepared clay supported catalyst, and ethylene monomer were added consecutively to reactor. It is evidence that polymerization should be done by produced complexes in clay interlayer spaces. After predetermind reaction time, polymerization was terminated with acidic ethanol. The composite dried in a vacuum oven at 60 °C for 5 h. The titanium content of the clay increases from 0.11 in original clay to 0.26% after supporting of catalyst. The prepared catalyst has been used for polymerization of ethylene monomers.

The pure PE was also prepared using the Ziegler-Natta catalysts in conventional form under the same polymerization condition, as a counterpart reference of the nanocomposites.

Results and Discussion

Effect of the Polymerization Temperature

The rate of polymerization initiated by Ziegler-Natta catalysts vary with temperature and monomer concentration. Normally, higher polymerization temperature results in higher activity of catalyst but lower monomer concentration due to decreasing monomer solubility in the reaction medium.[5,15] Consequently, the overall activity of catalyst exhibits a maximum. In ethylene polymerization by this catalyst, polymerization temperature has been varied from 45 °C to 70 °C, limited by the boiling point of the solvent. Figure 3 shows polymerization temperature effects on the activity of the catalyst. This figure shows that at 60 °C activity of catalyst attains to its maximum values. Decreasing activity of catalyst at above 60 °C could be attributed to increasing transfer and termination side reactions and also reduction of monomer solubility in the hexane diluent. So 60 °C could be considered as the best temperature for polymerization of ethylene monomer.

Effect of the Monomer Pressure

Effects of the monomer pressure, changed from 1 to 10 bars, on polymerization activity are presented in Figure 4. This figure shows that increasing the monomer pressure sharply increase the activity of the catalyst when pressure increase up to about 7 bars, but more increasing in monomer pressure does not show considerable effect on the catalyst activity. This could be due to increasing of monomer concentration on the catalyst surface with increasing polymerization pressure up to 7 bars and monomer saturation of catalyst surface at higher pressure. In the other world at pressure less than 7 bars reaction rate must be controlled by monomer diffusion rate when at higher pressure the polymerization rate should be controlled by catalyst activity.

Effect of the Cocatalyst

Cocatalyst could have important effects on the polymerization behavior. Effects of the Al/Ti weight ratio by TIBA and TEA cocatalyst on the polymerization activity are presented in Table 1. It can be seen that as the Al/Ti molar ratio increases up to 178, the activity increases and more increasing

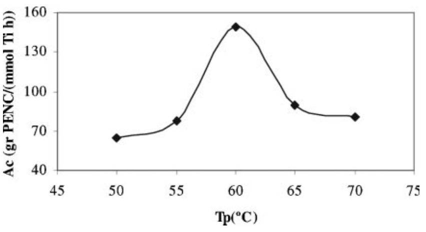


Figure 3.
Effect of polymerization temperature on the activity of the catalyst.

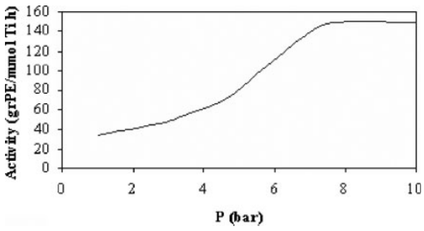


Figure 4.
Effect of monomer pressure on the catalyst activity.

Table 1.
The effects of Al/Ti molar ratio on polymerization activity by TIBA, T = 60 °C, P = 7 bars.

Sample	Al/Ti (mol mol^{-1})	Activity (TEA) (gPE (mmol Ti h)$^{-1}$)	Activity (TIBA) (gPE (mmol Ti h)$^{-1}$)
1	97	62	70
2	130	65	73
3	178	140	193
4	190	125	149
5	285	120	141

in this molar ratio resultes in decreasing of the activity. This behavior can be normally observed for Ziegler-Natta catalyst. Such, decreasing in activity at high Al/Ti weight ratios can be attributed to the overall reduction of active sites.[5] These results also show that TIBA has more activity than TEA, which may attribute to the low reduction capability of TIBA. Table 1 represents the effects of Al/Ti molar ratio on polymerization activity using TIBA as cocatalyst.

Comparing these results with those reported by Rong et al.[5,6] for preparation of PE/palygorskite nanocomposite shows that the maximum activity obtained by this catalyst is more than twice of the maximum activity that achieved by supported catalyst on the palygorskite clay. So it could be concluded that the montmorillonite smectite type clay has more efficiency in production of PE/clay nanocomposites compared to palygorskite chainlike clay.

XRD and TEM of PE/clay Nanocomposites

Figure 5 shows XRD patterns of the original clay, calcinated clay, and a PECNC that obtained from in situ polymerization of ethylene by clay supported catalyst. For XRD observation of nanocomposites, dried powdery obtained product from reaction were directly used without any further processing. XRD pattern of the clay shows a characteristic peak at $2\theta = 5.96°$. After calcinations this peak shift to $2\theta = 9.08°$.

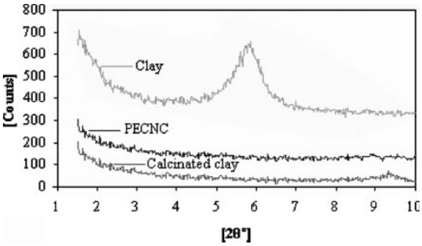


Figure 5.
X-ray diffraction pattern clay, supported clay, and PECNC.

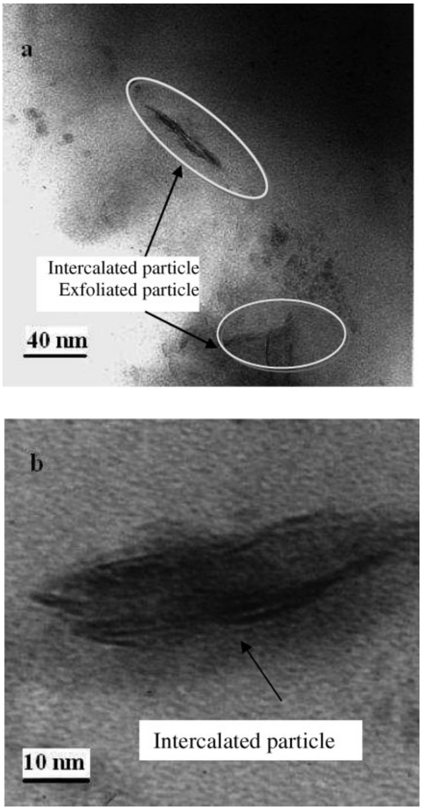


Figure 6.
TEM micrographs of a thin section of PECNC having 8 wt% of clay with magnifications of 40 and 10 nm.

Table 2.
Thermal properties of PE/clay nanocomposites formed from polymerization of ethylene with magnesium supported catalyst and clay supported one.

Clay content (wt %)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	X%
0	114.336	205.1	133	118.9	70
8	116.178	188.2	131.7	78.236	64
15	119.896	141.11	129.81	59.436	48

The diffraction pattern of a PECNC sample presented in Figure 5 shows that the characteristic peak of the clay is disappeared. These results show that the clay layers intercalated and exfoliated in the polymeric matrix after polymerization of monomers between the silicate layers.

To define the overall structure one must rely on TEM observation. Figure 6 displays the TEM micrographs of a thin section of PECNC having 8 wt% of clay; the dark lines denote the silicate layers. One can observe from this image that silicate layers are dispersed in polyethylene matrix as intercalated particles or exfoliated one. So, polymerization of the small molecule of ethylene between the clay layers and growing the polyethylene macromolecular chains can intercalate and exfoliate the clay layers in the polyethylene matrix.

DSC Analysis

In Table 2 the products crystallization and melting temperatures and their enthalpies obtaining from sample DSC spectrums are presented. Refereeing to this table, one can determine that these polyethylene clay nanocomposites have melting temperature close to pure PE, but have substantially higher crystallization temperature and less crystallization enthalpy or degree of crystallinity. These results are consistent with other reported data in the literatures.[13,16] Nanoscale MMT layers affect the crystallization in two opposite ways. On the one hand, the interaction between the MMT layers and PE chains decrease the number of crystalline PE chains. On the other hand, the nucleation of MMT results in more perfect crystallization structure.[6] The nucleation of MMT could relatively increase the number of crystallite whereas crystallization degree could slightly decrease due to movement hindering of polymer chains by MMT layers. The restricted chains might not crystallize. Therefore, the relative crystallization degree decreases with increasing MMT content in the PECNC.[6,17] The degree of the crystallinity of the samples was calculated using the equation $X\% = (\Delta H_f / \Delta H_f^\circ) \times 100\%$, where ΔH_f is the heat of the fusion determined by DSC, and ΔH°_f is the heat of fusion of pure PE, which has the value 293 J/g.[17]

Conclusion

In this work polyethylene-clay nanocomposite was successfully prepared by polymerization of ethylene monomers by Ziegler-Natta supported catalyst on the montmorillonite type clay. TEM micrographs and X-ray diffraction patterns show that the clay layers must be intercalated and exfoliated in the polymeric matrix.

Optimum temperature and pressure for in-situ polymerization regarding activity of catalyst were about 60 °C and 7 bars, respectively. The cocatalyst, alkyl aluminum, quantity plays an important role in polymerization activity and could be used as an adjusting agent for controlling concentration of clay in produced polyethylene/nanoclay. Presented results show that activity of catalyst prepared in this work is significantly more than that of achieved by catalyst supported on the palygorskite clay. So it could be concluded that the montmorillonite smectite type clay has more efficiency in production of PE/clay nanocomposites comparing to palygorskite chainlike clay.

Comparison of DSC curves of samples obtained from polymerization of ethylene with magnesium supported catalyst and clay supported one show that melting temperature of prepared nanocomposites has an infinitesimal change but the crystallization temperatures increase considerably.

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