Novel Organic/Inorganic Nanocomposite of Polyethylene. I. Preparation via In Situ Polymerization Approach

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ABSTRACT: A novel methodology for the preparation of polyethylene/palygorskite, "in situ coordinated polymerization," was proposed. A Ziegler–Natta catalyst was first supported on the surface of nanoscale crystal fibers of palygorskite and subsequently used to initiate ethylene polymerization on the surface of the fibers. The palygorskite was encapsulated by polyethylene and became reinforcement fibers of the composite. The palygorskite fibers were heat-treated to remove water, to ensure that the supported titanium species possessed proper activity for the polymerization of ethylene. The effect of the conditions of heat-treating, titanium-supporting, and other factors such as temperature and type and amount of the cocatalyst on the initiation activity of the palygorskite fibers were investigated. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1829–1837, 2001

Key words: nanocomposite; polyethylene; clay; palygorskite; coordinated polymerization

INTRODUCTION

Organic/inorganic nanocomposites have opened a new horizon for composite materials. Intercalation is a novel method for the preparation of such composite materials; nylon/clay nanocomposites have been prepared via either the monomer intercalation/condensation approach[1–3] or melt intercalation.[4–6] Unfortunately, these promising approaches are not suitable for the preparation of polyolefin nanocomposites. Because polyolefins and olefin monomers are nonpolar, they cannot be easily intercalated between the lattice layers of clay, if not impossible.

In this article, a novel approach to the polyethylene/palygorskite nanocomposite was proposed, that is, "in situ coordinated polymerization." Ziegler–Natta catalysts were first supported on the surface of a nanoscale crystal fiber: palygorskite, and subsequently ethylene was supplied to the activated surface and polymerization was initiated on the surface of the fibers. As the polymerization proceeded, the surface of the fiber was gradually covered by the forming polymer, until the fiber was fully encapsulated by polyethylene. The role of palygorskite was twofold: It was a support of the catalyst for initiating the polymerization and reinforcement after the polymerization was stopped.

Palygorskite is a family of fibrous hydrous magnesium silicates. The structure of these kinds of fibrous minerals differs from that of other layer silicates used in nanocomposites in that they lack continuous octahedral sheets. The reason for choosing this kind of clay lies in the ease with which it can to be dispersed in a nanosize and support Ziegler–Natta catalysts.

In the preparation of a polyethylene/palygorskite nanocomposite, the most important step is the activation of the palygorskite fibers, that is, to support titanium onto the surface of the fibers.
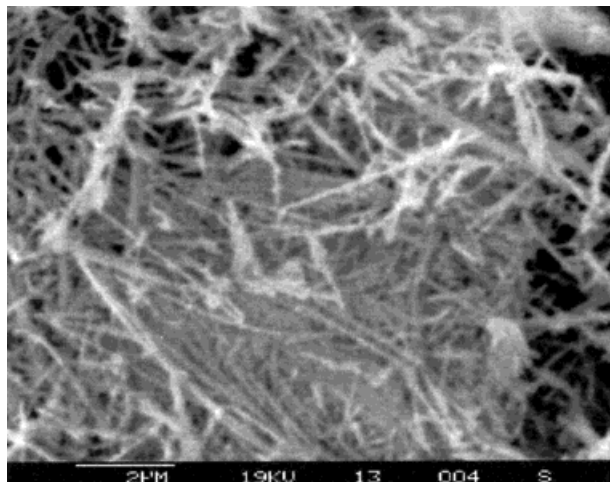
Figure 1 SEM photograph of palygorskite.

Before activation, the palygorskite fibers should be heat-treated, that is, calcined, to remove water from the surface and inside the fibers. The calcination ensures that the supported titanium species possesses proper activity for the polymerization of ethylene. The conditions of calcination, activation, as well as other parameters such as temperature, type, and amount of the cocatalyst all have effects on the rate of polymerization.

Palygorskite is characterized by a fibrous morphology, SEM photography of which shows it resolved as a randomly oriented network of densely packed fibers, as shown in Figure 1. The diameter of a single fiber is less than 100 nm, and the length of a fiber is between several hundreds of nanometers to several micrometers.

Palygorskite has a great surface area and strong absorptive capacity. The absorptive capacity of palygorskite is greater than that of any other natural mineral.[7] In addition, the mechanical strength and thermal stability of it are very good. These properties make palygorskite an ideal material for the supporting of a catalyst and for reinforcement.

The lattice structure of palygorskite is shown in Figure 2. It is seen that it contains some kinds of water in the form of molecular water, zeolitic water, coordinated water, hydroxyl groups, and surface-sorbed water. The presence of water is harmful for supporting the catalysts and therefore should be removed via calcining. However, at different temperatures, different kinds of water can be removed. Zeolite water is removed between 100 and 300°C together with about half of the coordinated water, and the removal of water

causes a partial collapse or folding of the structure[8]; at this stage, the structures are readily rehydrated if water vapor is readmitted. Further heating to 500°C drives off the remainder of the coordinated water and also initiates dehydroxylation. Rehydration after this stage can only be achieved by heating with water under pressure.

Figure 3 shows the FTIR spectra of palygorskite samples calcined at different temperatures. The absorption peaks of —OH for different types of bound water are located at different sites. The three peaks between 3614–3550 cm^{-1} are the reflection of hydroxyl groups of 2:1 layer silicates and coordinated water to the edge octahedral cations. The broad peak near 3375 cm^{-1} stands for molecular or zeolitic water within the lattices, the sharp peak at 1656 cm^{-1} stands for surface-sorbed water, and the peak next to it, at 1625cm^{-1}, is due to coordinated water.[9]

With increase of the treating temperature, palygorskite loses its water gradually. It is seen from the figure that, when the temperature is below 300°C, all kinds of water still exist, although the quantity of water decreases. At temperatures above 500°C, the strength of the absorption peaks, which stand for surface-sorbed water, coordinated water, zeolitic water, and hydroxyl groups, decrease greatly. This indicates that most of the water is removed. When heated to 800°C, no peak for water appears, indicating the complete removal of water.

With the loss of water, the crystal structure of the palygorskite changes: Calcining at temperatures higher than 500°C leads to collapse of the crystal structure. This kind of "folding" effect[7] leads to decrease of the surface area and pore volume
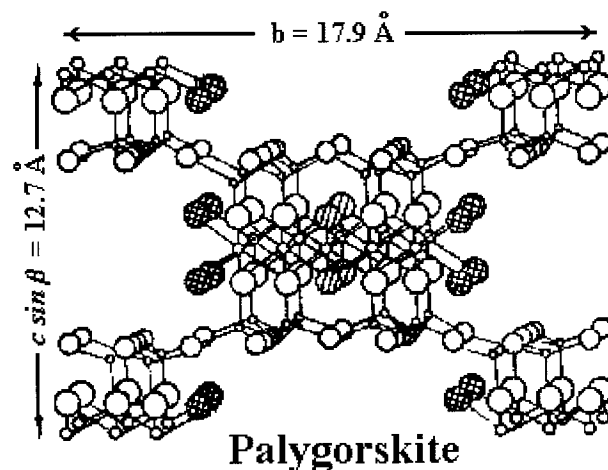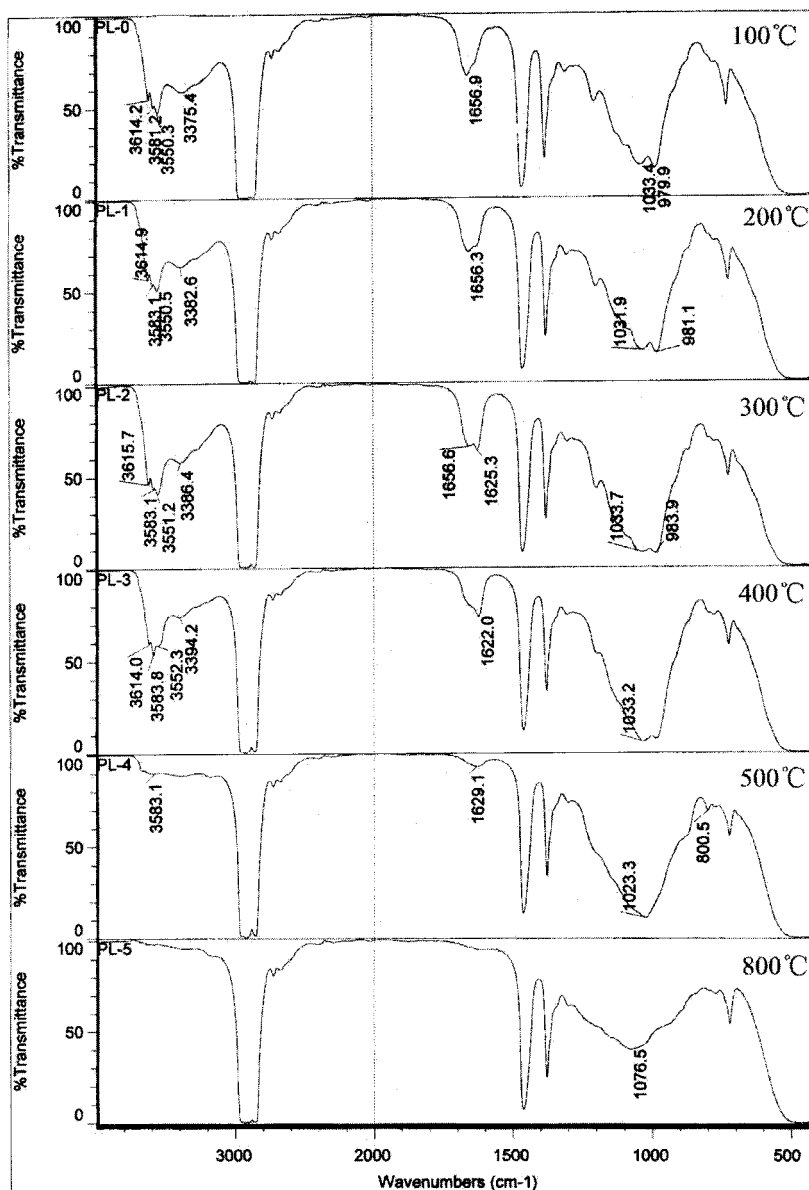

Figure 2 Lattice structure of palygorskite.

Figure 3   FTIR spectra of palygorskite calcined at various temperatures.

(Table I). Further heating to about 800°C gives no change in the fibrous morphology of the clay crystal (Fig. 4). The calcined palygorskite was ready to be activated and thus provides a basis for the production of novel polyolefin/clay nanocomposites.

EXPERIMENTAL

Materials

Palygorskite was supplied by the No. 14 Department of RIPP (from Jiashan, Anhui Province,

Table I   Surface Area and Pore Analysis of Palygorskite Clay

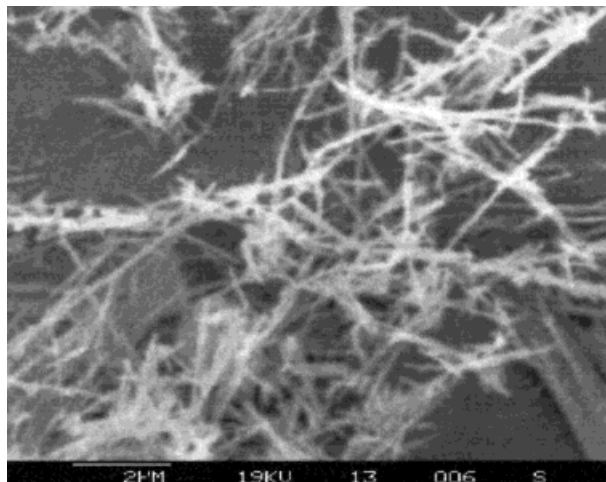| Sample	BET Surface Area $(m^2\ g^{-1})$	Pore Volume $(mL\ g^{-1})$	Average Pore Diameter (nm)
PL-2 (100, 6 h)	88	0.343	157
PL-3 (300, 6 h)	70	0.338	192
PL-4 (500, 6 h)	71	0.349	196
PL-5 (800, 6 h)	32	0.151	187

Figure 4 SEM photograph of palygorskite calcined at 800°C.

China); titanium tetrachloride was purchased from the Beijing Zhonglian Chemical Co. (Beijing, China) and was used without further purification; trimethylaluminum (Aldrich), triethylaluminum (Aldrich), and triisobutylaluminum (Beijing Yanshan Petrochemical Co., Beijing, China) were used after preparation of a hexane solution of 0.8M; and hexane, heptane, octane, and ethylene were purchased from the Beijing Yanshan Petrochemical Co. and were used after treatment with 4-A molecular sieves.

Pretreatment of Palygorskite

Palygorskite samples were soaked in a Muffle furnace at a temperature range of 100–1000°C for 6 h and subsequently stored in N_2.

Activation of Palygorskite

All manipulations of air/water-sensitive compounds were performed using standard high-vac-uum or Schlenk techniques. N_2 was purified by passage through columns of 4-A molecular sieves. Palygorskite was reacted with $TiCl_4$ in a round-bottom flask for a period of time (depending on the experiment plan) in a solvent, which can be hexane, heptane, or octane, depending on the reaction temperature. The product thus obtained was washed with hexane at 40°C three times and dried in N_2 at a temperature of 60°C.

In Situ Coordinated Polymerization

A 500-mL flask equipped with a stirrer and an oil bath was purged with N_2 six times. Subsequently, 200 mL heptane, AlR_3, ethylene, and activated palygorskite in various weight ratios were introduced into the reactor to start the polymerization. Ethylene was supplied under a pressure of 1 atm to maintain the polymerization for a certain period of time. The rate of polymerization was calculated simply by the rate of ethylene consumption. The polymerization was terminated by the addition of an acidified ethanol solution. The composites thus obtained were dried in a vacuum at 60°C for 6 h.

Characterization

The BET surface area and pore volume of the solid samples was measured by a static volumetric measurement on a Micromertics ASAP 2405 instrument. FTIR measurement of the clay samples was conducted on a Nicolet-560 E.P.S instrument. The samples were ground with liquid paraffin and sealed between two pieces of KBr crystal for measurement.

The morphology of palygorskite before and after activation was studied with an ISI-60A SEM instrument. The specimens were sputter-coated with gold before viewing.

The TG analysis of the samples was carried out on a thermal balance (DuPont 2100) in a N_2 flow,

Table II   Titanium Content and Activity of Activated Palygorskite

Measurement	Calcining Temperature (°C)				
	100	200	300	500	800
Titanium content [% (wt)]	8.97	7.14	2.03	1.06	0.54
Activity [gPE (gTi h)$^{-1}$]	32	75	256	966	904

Preparation condition: excessive $TiCl_4$ is added into the reaction system during the activation. Polymerization condition: 40°C, Al/Ti = 15.

Table III   Activity of Activated Clay

Measurement	Calcining Temperature (°C)				
	100	300	500	800	800 (rehydrated)
Activity [gPE (gTi h)$^{-1}$]	Trace activity	390	1755	1633	Trace activity

Polymerization condition: 40°C, Al/Ti = 15.

at a heating rate of 10°C/min. The titanium content of activated clay was measured by the ICP/AES method on a Varian Vista instrument. The samples were weighed and then treated in a titanium solution by sulfuric acid for measurement.
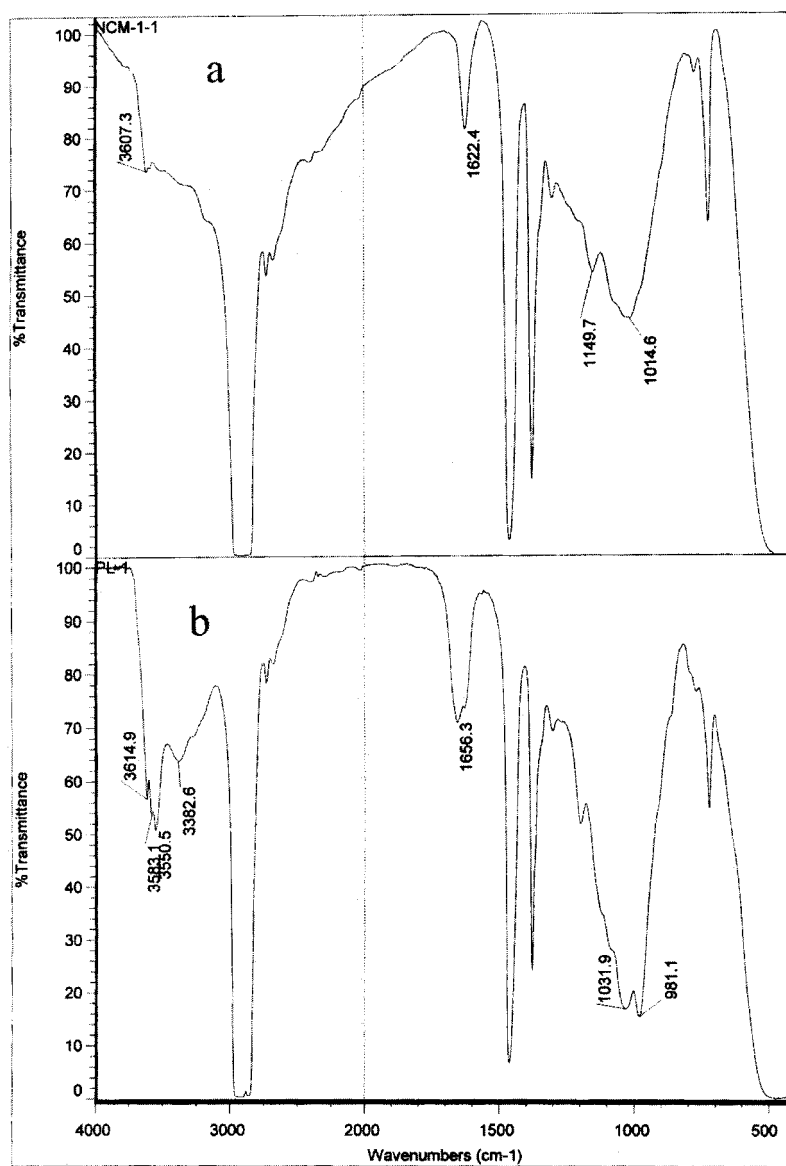

Figure 5   FTIR spectra of (a) activated palygorskite and (b) calcined palygorskite at 100°C.
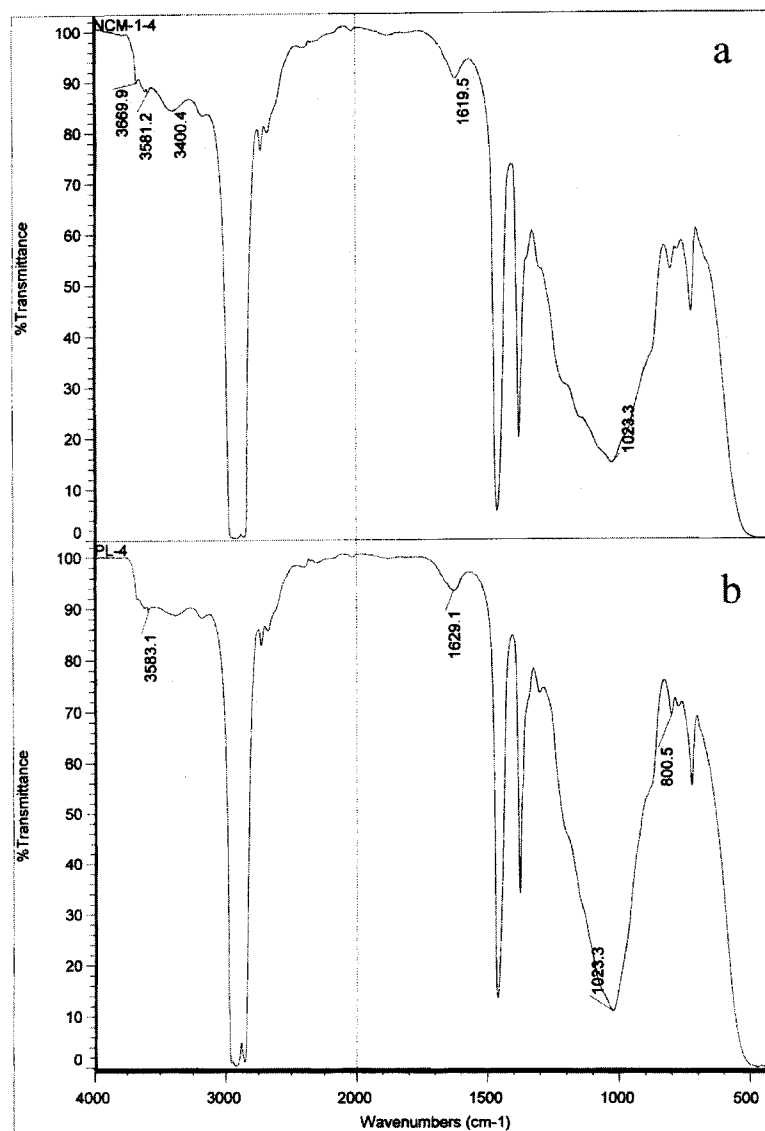
Figure 6 FTIR spectra of (a) activated palygorskite and (b) calcined palygorskite at 500°C.

Viscometry was performed in an Ubbelohde viscometer at 135°C with 0.5% or 0.1% decalin solutions. Molecular weight was calculated with the formula[10]

$$[\eta] = 6.77 \times 10^{-4} M_w^{0.67}$$

RESULTS AND DISCUSSION

Structure and Activities of Supported Titanium Species

The structures and properties of palygorskite calcined at different temperatures are different.
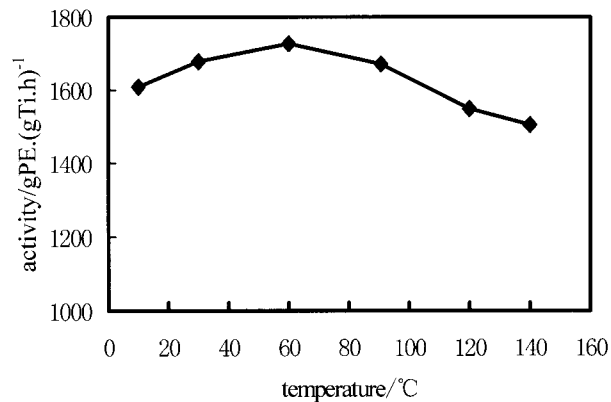

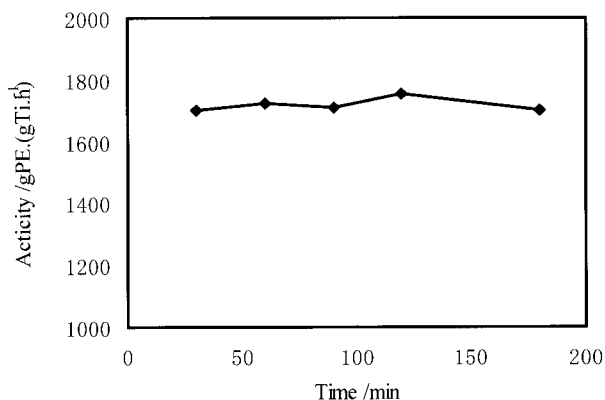**Figure 7** Relationship between activity and reaction temperature.

Figure 8 Relationship between reaction time and activity. Palygorskite was calcined at 600°C for 6 h; Ti content: 0.3 wt%; reaction temperature: 60°C.

When supporting $TiCl_4$, the activated palygorskite will show different catalytic activities. Table II shows the titanium content and polymerization activity of activated palygorskite calcined at different temperatures.

The titanium content decreases with increase of the calcining temperature, but the activity of activated clay increases with it (Tables II and III). Overheating will lead to a decrease of the surface area and pore volume and then affect the activity of the activated clay.

In the process of the activation, three possible reactions between $TiCl_4$ and palygorskite may take place:

(1) $TiCl_4$ reacts with water of palygorskite clay and forms titanium oxides or their derivatives:
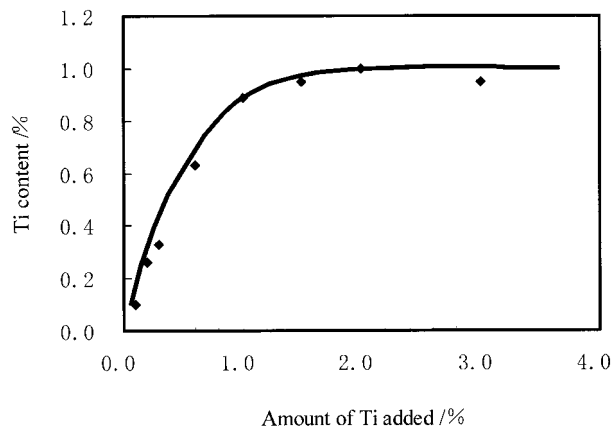

Figure 9 Relationship between the titanium content of activited palygorskite and the amount of titanium added. Palygorskite was calcined at 600°C for 6 h; reaction temperature: 60°C; reaction time: 1 h.
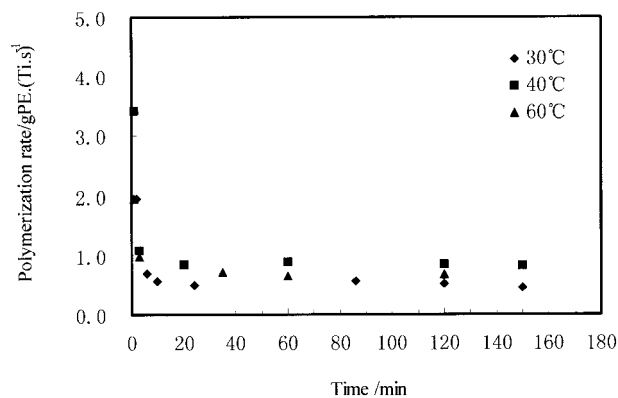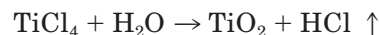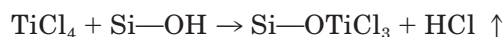

Figure 10 Kinetic curve of activated palygorskite at various polymerization temperatures. Palygorskite was calcined at 600°C for 4 h; Ti content: 0.3 wt %; Al/Ti = 30; cocatalyst: $Al(i-Bu)_3$.

$$TiCl_4 + H_2O \rightarrow TiO_2 + HCl \uparrow$$

(2) $TiCl_4$ reacts with Si—OH located on the surface of the clay fibers and is supported on it:

$$TiCl_4 + Si—OH \rightarrow Si—OTiCl_3 + HCl \uparrow$$

(3) $TiCl_4$ coordinates with the magnesium vacancies in the clay structure and is supported on it:
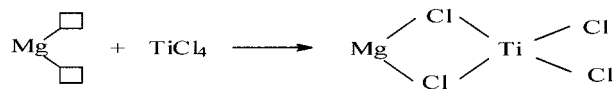
Because the amount of Si—OH in the palygorskite structure is small, reaction (2) can be ignored. If the calcining temperature is low, there is a relatively large amount of water present in palygorskite. When $TiCl_4$ is introduced, water reacts preferably with $TiCl_4$ according to reaction (1) and many noncatalytic titanium species are formed; although a high titanium content is obtained, the activity of the activated palygorskite is still low. Figure 5 shows the change of the infrared spectra of palygorskite samples calcined at 100°C before and after being activated. One may notice that the peaks between 3300 and 3700 cm^{-1}, which stand for zeolitic water and coordinated water, weaken greatly, and the peak at 1656 cm^{-1}, which stands for absorbed water, disappears after activation. These results suggest that water in palygorskite was consumed during the activation and, thus, constitutes proof for reaction (1), providing an explanation for why a

Table IV   Activity, Molecular Weight, and Ethylene Concentration at Different Temperatures

Measurement	Polymerization Temperature (°C)			
	30	40	50	60
Ethylene concentration (mol L^{-1})	0.1405	0.1295	0.1190	0.1080
Molecular weight $(M_w) \times 10^4$	570	502	529	448
Activity [gPE $(gTi\ h)^{-1}$]	1311	1826	2090	1334

Activated palygorskite: 600°C 4 h, Ti content = 0.3% (wt); polymerization condition: Al/Ti = 15, Al(i-Bu)$_3$.

high titanium content was accompanied with low activity.

However, if palygorskite was treated at an elevated temperature, most of the water content was driven out, reaction (3) became the main reaction, and active titanium species were generated. For this reason, high activity was achieved even though the titanium might have been low. Figure 6 shows the change of infrared spectra of palygorskite samples calcined at 500°C before and after being activated. One can see that the IR spectra of the samples did not alter after the activation. This suggests that reaction (3) predominated, which did not consume water.[11]

If palygorskite, calcined at high temperatures, is rehydrated by exposing it to the air, the subsequent activation may still result in low activity. This shows again that the nature of the activation reaction was controlled by the level of the water content.

In the activation reaction, the reaction temperature and the amount of TiCl$_4$ introduced affect the activity of the supported palygorskite. Figure 7 shows the relationship between the polymerization activity and the reaction temperature. It is seen that good activity can be achieved by conducting the reaction at temperatures between 30 and 90°C.

Figure 8 shows the relationship between the reaction time and the activity of palygorskite. It is seen that the reaction time has little influence on the activity of palygorskite.

Figure 9 shows the relationship between the titanium content in the activated palygorskite and the amount of titanium introduced into the reaction system. It is seen clearly that the titanium content in palygorskite increases steadily with the amount of titanium introduced until a constant value is reached (about 1 wt % of palygorskite). This result is easy to understand: For palygorskite calcined at a certain temperature, the number of vacancies that can be used to coordinate with TiCl$_4$ is finite. When all the vacancies on palygorskite are filled with TiCl$_4$, they no longer absorb extra titanium.

Other Factors Affecting the Polymerization Activity

Figure 10 shows the kinetic curves at different polymerization temperatures. It is seen that all the curves show an attenuation trend. The polymerization activity reaches a maximum at the beginning of the reaction and then attenuates quickly until the activity reaches a relatively constant value.

Temperature has a great influence on the polymerization. Limited by the boiling point of the solvent, the polymerization temperature was controlled to be no higher than 60°C under normal pressure. The rate of polymerization initiated by normal Ziegler–Natta catalysts was controlled by two parameters: A higher polymerization temperature results in a higher activity, but a lower ethyl-

Table V   Influence of Al/Ti on Activity and Molecular Weight

Measurement	Al/Ti (mol mol^{-1})				
	2	5	10	30	60
Activity [gPE(gTi h)$^{-1}$]	420	1790	1820	1800	1590
Molecular weight $(M_w) \times 10^4$	506	476	440	386	297

Activated palygorskite: 600°C 4 h, Ti content = 0.3% (wt); polymerization condition: 40°C, Al(i-Bu)$_3$.

ene concentration. For this reason, the overall activity exhibits a maximum, as shown in Table IV.

Table IV shows that the molecular weights of all the samples are very high. This can be attributed to the difficulty of the β-H elimination. Because the active sites are dispersed uniformly on the surface of the clay fibers, the energy for β-H elimination may be improved greatly, so the life of the active chains is prolonged. This case is not the same as with the situation of the unsupported catalyst.

The cocatalyst, alkyl aluminum, also plays an important role. The **e**ffects of the Al/Ti weight ratio on the activity and molecular weight are listed in Table V. It is seen that, as the Al/Ti weight ratio increases, the activity exhibits a maximum. This is normal for Ziegler–Natta catalysts and the decrease in activity at high Al/Ti weight ratios can be explained by the overall reduction of active sites.[12] The molecular weight decreases with the increase of the Al/Ti weight ratio: This can be explained by the chain transfer of alkyl aluminum.[13]

Besides the Al/Ti wt ratio, the type of cocatalyst also affects the activity of the polymerization, as shown in Figure 11 and Table VI. The order of the activity is Al(i-Bu)$_3$ > AlEt$_3$ > AlMe$_3$. The reason may lie in the low reduction capability of Al(i-Bu)$_3$.

CONCLUSIONS

The type of titanium species supported on the surface of palygorskite depends on the water content present in the fiber. Palygorskite fibers should be soaked at a high temperature above 500°C to remove water. An extremely low water
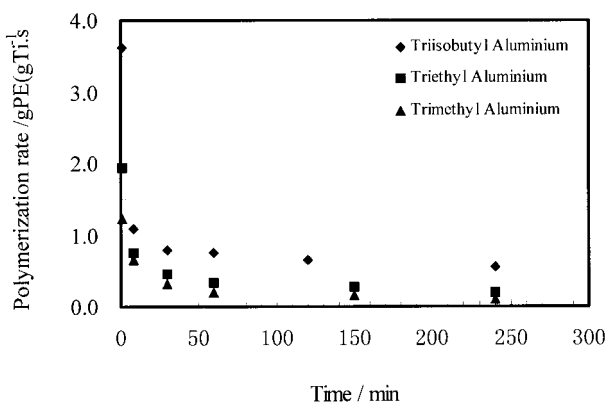
Table VI Influence of Different Cocatalysts on the Activity of Activated Clay

Measurement	Cocatalyst		
	AlMe$_3$	AlEt$_3$	Al(i-Bu)$_3$
Activity [gPE(gTi h)$^{-1}$]	366	847	1826

Activated palygorskite: 600°C 4 h, Ti content = 0.3% (wt); polymerization condition: 40°C, Al/Ti = 30.

content can ensure the formation of the titanium species with the proper activity. TiCl$_4$ should be coordinated with the vacancies on the surface of palygorskite; otherwise, supported TiCl$_4$ possesses no activity. The temperature at which the reaction of TiCl$_4$ and palygorskite is performed affects the activity of the surface of palygorskite, the preferred temperature range being between 30 and 90°C. The cocatalyst, alkyl aluminum, plays an important role in polymerization activity. An optimum Al/Ti weight ratio gives rise to maximum activity. Different cocatalysts exhibit different activities of polymerization, the order of the activity being Al(i-Bu)$_3$ > AlEt$_3$ > AlMe$_3$.

REFERENCES

1. Okada, A.; Kawasumi, M.; Kuranchi, T.; Kamigaito, O. Polym Prepr 1987, 28, 447.
2. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T. J Mater Res, 1993, 8, 1174.
3. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A Polym Chem 1993, 31, 1755.
4. Mehrotra, V.; Gianelis, E. P. Mater Res Soc Symp Proc 1990, 171, p 39.
5. Gianelis, E. P.; Mehrotra,V.; Russell, M. W. In Better Ceramic Through Chemistry; Brinker, C. J., Eds.; Mater Res Soc Proc: Pittsburgh, PA 1990; p 180.
6. Mehrotra, V.; Gianelis, E. P. Solid State Commun 1991, 77.
7. Leifu, R. Clay and Clay Minerals; China Geology: Beijing, 1992.
8. Nagata, N.; Shimoda, S. Clay and Clay Miner 1974, 22, 285–293.
9. Yang, Y.; Zhang, N. Chinese Clay Minerals; China Geology: Beijing, 1994.
10. Polymer Handbook, 3rd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1989.
11. Ellestad, O. H.; Bilindheim, U. J Mol Catal, 1985, 33, 275.
12. Damyanov, D.; Velikova, M. Eur Polym J 1979, 15, 1075.
13. Bacskai, R. J Appl Polym Sci 1988, 35, 321.

Figure 11 Kinetic curve of activited palygorskite initiated by different cocatalysts. Palygorskite was calcined at 600°C for 4 h; Ti content: 0.3 wt %; polymerization temperature: 40°C; Al/Ti = 30.