Characterization of Polyethylene/Kaolin Composites by Polymerization Filling with Cp_2ZrCl_2/MAO Catalyst System

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ABSTRACT: In this work, the preparation and characterization of metallocene-catalyzed polyethylene (PE)/kaolin composites were presented. The composites was prepared by the so-called polymerization-filling method in which the PE matrix was formed directly on the kaolin surface by ethylene polymerization with the prefixed Cp_2ZrCl_2/methylaluminoxane (MAO) catalyst system on the kaolin surface. SEM, FTIR, and DMA were carried out to characterize the composites. The experimental results showed the new composites had homogeneous distribution of kaolin particles in the PE matrix and strong interfacial interaction between the PE matrix and kaolin particles. At the molecular level, the interfacial interaction caused the decrease of the mobility of PE molecular chains. In addition rheological testing showed that the introduction of kaolin by polymerization filling could improve the rheological behavior of prepared composites. The relationship between the rheological behaviors and the interfacial conditions were discussed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2913–2921, 2002

Key words: composites; metallocene catalyst; interfaces; rheology

INTRODUCTION

The production of filled polymer composites and their processing into all kinds of end products have long been known and used in industry.[1] To date, the most commonly used way of producing filled polymer composites is the mechanical melt-mixing method, in which inorganic filler particles are intensively mixed with the polymer matrix at melt state by mixing equipment such as twin-screw extruder. However, because there is a great gap in polarity, surface tension, and thermal expansion coefficient between polymers, especially polyolefins and inorganic fillers, the filler particles tend to aggregate into agglomerations in the process of preparing filled polyethylene composites by melt mixing. Moreover, because there is no strong interfacial interaction between the polymer matrix and filler particles, the mechanical and thermal properties of the resulting composites are rather low. The problems mentioned above can not be effectively eliminated by conventional interfacial modification methods such as use of coupling agents or compatibilizers. So, to overcome the drawbacks of mechanical melt mixing and to further improve the mechanical and thermal properties of the filled polymer composites, a new method for preparation of polymer–

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inorganic filler composites, the so-called polymerization-filling method was developed in the late 1980s.[2] Essentially, polymerization filling means that monomer polymerization occurs simultaneously with the filling process and the continuous phase of the filled polymer composite is formed directly on the surface of the inorganic filler particles.

Many authors[3–5] have reported the preparation of polyethylene/inorganic filler composites by the polymerization-filling method. Epitomizing the previous works, there are only two steps involved in the preparation of polyethylene/inorganic filler composites by this method, that is, the activation of inorganic filler and ethylene polymerization on the surface of the activated inorganic filler.

So far as the activation of inorganic filler is concerned, most efforts have focused on traditional Ziegler–Natta catalysts. For example, Gorelik et al.[6] applied the $TiCl_4$–$AlEt_3$ catalyst system to the activation of chalk and prepared polyethylene/chalk composites.

In the past decade, the emphasis of the study on the catalyst for olefin polymerization has shifted from the traditional Ziegler–Natta catalyst system to the metallocene-based homogeneous catalyst system. With higher activity and greater control over the properties of the polymers produced, the metallocene/methylaluminoxane (MAO) catalyst system is attracting more attention from scientific researchers. More recently, Kaminsky et al.[7] reported a novel application of the metallocene catalyst, that is, producing polyolefin/filler composites by olefin polymerization in the presence of fillers. In their opinion, MAO is relatively stable against OH– groups or water-covered inorganic metal surfaces; the aluminoxane can be fixed to powders and particles without losing its activity. After treatment with metallocenes and injection of the olefins, the particles can be covered with polyolefin films. This method combines the advantages of the metallocene catalyst and the polymerization-filling method, thus opening a promising way for future progress in the polyolefin composite material science and industry.

In this report we present the preparation of a polyethylene/kaolin composite by polymerization filling with the Cp_2ZrCl_2/MAO catalyst system. The comprehensive studies on the structure and properties of the composites and comparison with their counterpart composites prepared by mechanical melt mixing are also reported.

EXPERIMENTAL

Materials

Kaolin with BET-specific surface area of 9 m^2/g was used. Methylaluminoxane (MAO) was used after removing all volatiles and drying the resulting white powder in vacuum (12 h, room temperature, 0.1 mmHg). Cp_2ZrCl_2 (Aldrich, Milwaukee, WI) was used as received. Toluene was used as solvent during the activation of kaolin after being dried with 4-Å molecular sieves. The polymerization-grade ethylene gas (produced by Beijing Yanshan Petrochemical Corp., China) was used as monomer without further purification. Hexane was used as polymerization solvent after being dried with 4-Å molecular sieves. All operations were carried out under a dry nitrogen atmosphere by using the Schlenk line technique.

Preparation of Polyethylene/Kaolin Composites by Polymerization Filling with the Cp_2ZrCl_2/MAO Catalyst System

Activation of Kaolin Particles with the Cp_2ZrCl_2/MAO Catalyst System

MAO (42 mmol; 1.4*M* in toluene solvent) was added to a suspension of 100 g kaolin in 800 mL toluene. The mixture was stirred at 50°C for 2 h and filtered. The solid part was washed 10 times with 300 mL toluene at 50°C, and then 0.88 mmol of Cp_2ZrCl_2 was added to the suspension of the kaolin–MAO precursor in 800 mL toluene. The mixture was stirred at 50°C for 2 h and filtered. The solid part was washed 10 times with 300 mL toluene at 50°C and dried in vacuum at 70°C for 3 h.

Ethylene Polymerization with the Activated Kaolin Particles

Polymerization was carried out in a 3-L stainless steel autoclave with a blade-type stirrer. A fixed amount of kaolin activated as above was placed into the autoclave. After addition of 1 L hexane, ethylene was introduced. The polymerization was carried out at 80°C and a total pressure of 0.8 MPa, which was kept constant, and a speed of agitation of 40 rpm.

Preparation of Pure Polyethylene by Homogeneous Cp_2ZrCl_2/MAO Catalyst System

Pure polyethylene was catalyzed by the homogeneous Cp_2ZrCl_2/MAO catalyst system. Polymerization was conducted in a 3-L stainless steel autoclave with a blade-type stirrer. After addition of 1 L hexane and a fixed amount of MAO (Al/Zr = 500), 0.005 mmol of Cp_2ZrCl_2 solved in toluene was added and then ethylene was introduced. The polymerization was carried out at 80°C and a total pressure of 0.8 MPa, which was kept constant, and a speed of agitation of 40 rpm for 3 h.

Preparation of Polyethylene/Kaolin Composites by Mechanical Melt Mixing

Polyethylene/kaolin melt-mixing composites were prepared by mixing polyethylene and kaolin for 7 min at 190°C and a rotation speed of 70 rpm in a Haake Rheomix 90 mixer. Before preparation of the mixtures, polyethylene was stabilized by the addition of Irganox 1010 to prevent a thermooxidative degradation process. The polyethylene matrix used was produced by the homogeneous catalyst system Cp_2ZrCl_2/MAO as described above.

Characterization

Kaolin Content Determination

The kaolin contents of the composites were determined in a Perkin–Elmer TG (Perkin Elmer Cetus Instruments, Norwalk, CT). The powder samples of the composites were heated from room temperature to 700°C. There was a mass loss with the temperature and the mass of the residual was recorded. It was found that the residual mass leveled off after the temperature was higher than 500°C, which indicated that all organic substance had been vaporized. The residual mass was regarded as that of the kaolin filler, then the kaolin content was calculated with the ratio of residual mass to the original mass of the sample.

Molecular Weight Determination

Molecular weights of the polyethylene constituents obtained in the presence and absence of kaolin were measured by the viscosity method. The intrinsic viscosity $[\eta]$ of the polyethylene constituent was determined in decalin at 135°C after being extracted from the PE/kaolin composite by decalin at increased temperature. M_w was calculated from the following formula[8]:

$$[\eta] = 4.6 \times 10^{-4} M_w^{0.73}$$

Melting-Point Determination

The melting points of pure PE and PE/kaolin composites were measured by using Perkin–Elmer DSC 7 at a heating rate of 10°C/min.

Scanning Electron Microscopy Investigation

Morphology of the nascent polyethylene/kaolin composite particles, the liquid nitrogen cryofractured surface, and the tensile-fractured surface of the specimens of PE/kaolin composites prepared by polymerization filling and melt mixing, respectively, were studied by using a Hitachi/JEOL scanning electron microscope.

Soxhlet Solvent-Extraction Experiment

To compare the interfacial strength between PE and the kaolin interface, the Soxhlet solvent-extraction experiments were conducted on the composites prepared by both polymerization filling and melt mixing. The solvent used was decalin. The extraction lasted for 20 h at 135°C.

FTIR Characterization

FTIR was used to characterize kaolin and the remaining parts after solvent extraction of the PE/kaolin composites prepared by both polymerization filling and melt mixing. The spectra were recorded on a Perkin–Elmer 599-13 spectrometer.

Dynamic Mechanical Analysis

Dynamic mechanical measurements were carried out with Perkin–Elmer DMA-7 using a heating rate of 5°C/min and a frequency of 1 Hz. The sample preparation corresponds to that for mechanical investigations. Rectangular bars of a dimension of 20 × 3 × 1 mm were cut out from the compression-molded samples.

Rheological Test

A DSR-200 rheometer was used in the dynamic rheology test in the dynamic mode with parallel-plate geometry. The experiment was carried out at 190°C. Sample powder was placed on the lower plate and then the upper plate was loaded down to the powder with a 1-mm gap left between the two plates. After the sample powder was heated for 10 min, the dynamic test started with a frequency ranging from $10^{-0.0.5}$ to 10^2 Hz.

RESULTS AND DISCUSSION

Preparation of PE/Kaolin Composites by Polymerization Filling with the Cp_2ZrCl_2/MAO Catalyst System

To ensure a homogeneous dispersion of kaolin particles in the produced polyethylene matrix, it

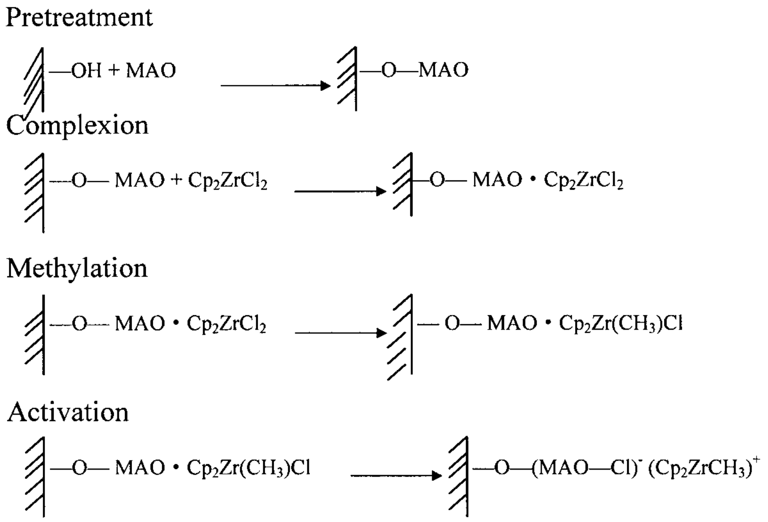

Figure 1 Schematic diagram of the formation of active centers by the Cp_2ZrCl_2/MAO catalyst system immobilized on the surface of kaolin.

is necessary to activate kaolin particles in advance, that is, having active centers for ethylene polymerization formed on the surface of kaolin. Concerning the Cp_2ZrCl_2/MAO catalyst system, it is assumed that there are two main routes for the activation of kaolin: (1) supporting the metallocene compound of Cp_2ZrCl_2 by reaction with –OH and then treating the metallocene-containing kaolin with MAO and (2) supporting MAO first and then treating the MAO-containing kaolin with the metallocene compound of Cp_2ZrCl_2 [which is just the opposite of (1)]. It is well known that kaolin is a rich hydroxyl-containing inorganic filler. When the first route is taken, although metallocene compound can be fixed, it will lose most of its activity probably as the result of an altered structure.[9] However, according to Kaminsky,[6] MAO is relatively stable against –OH groups or water-covered inorganic, metal, or biomass surfaces, and the aluminoxane can be fixed to these particles without losing its activity. Based on this consideration, we took the second route as the kaolin-activation method, that is, fixing MAO to kaolin particles first and treating the MAO-containing kaolin with Cp_2ZrCl_2 second. Figure 1 shows the schematic diagram of the possible activation procedure with this method.

To ensure that the resulting polyethylene chains all grow from the surface of kaolin, as can be seen from Figure 1, all of the active centers must be formed on the surface of kaolin, as was mentioned before, which excludes the addition of external MAO as cocatalyst in the polymerization procedure. In this case, it is presumably the preanchored MAO at the kaolin pretreatment step that functions as cocatalyst of the metallocene catalyst.

Table I gives the results of elemental analysis of Al and Zr contents in the activated kaolin. It can be seen from Table I that, compared with the contents of the same metal elements supported on silica, as Sacchi et al.[9] have shown, the Al and Zr contents are rather low. However, the Al/Zr molar ratio is comparable to that found in Sacchi's study. In metallocene-catalyzed olefin polymerization, the amount of MAO is a key factor that determines the polymerization rate through influencing the complex environment of the central transition metal ion. Ample evidence has proved that the cationic $L_2M(CH_3)^+$ is the active center in olefin polymerization.[10–12] The two main functions of MAO are the alkylation of halogenated metallocene complexes and the reactivation of inactive complexes formed by hydrogen-transfer reactions. Thus, to obtain a high activity, the customarily used amount of MAO is as high as 500–5000 by Al/Zr molar ratio.

Table I Elemental Analysis of Al and Zr Contents in the Activated Kaolin

Element	Content (mol/g)
Al	2.39×10^{-3}
Zr	1.81×10^{-5}
Al/Zr molar ratio	133

Table II Conditions and Results of Ethylene Polymerization with Cp_2ZrCl_2/MAO Catalyst System Free and Immobilized on the Surface of Kaolin

Run	Catalyst	Cocatalyst	Al/Zr Molar Ratio	Polymerization Time (min)	Activity [kgPE/(mol/Zr/h^{-1}/atm^{-1})]	Kaolin content in product (wt %)	M_w ($\times 10^4$)	T_m (°C)
1	Cp_2ZrCl_2[a]	MAO	500	180	2090	0	26.3	132.3
2	Cp_2ZrCl_2–kaolin/MAO[b]	—	—	180	38.6	5.6	25.2	138.2
3	Cp_2ZrCl_2–kaolin/MAO[b]	—	—	108	42.2	8.3	26.6	137.2
4	Cp_2ZrCl_2–kaolin/MAO[b]	—	—	25	54.2	24.0	28.6	137.4
5	Cp_2ZrCl_2–kaolin/MAO[b]	—	—	5	83.3	50.0	25.0	137.5

[a] Polymerization conditions: 0.005 mmol Cp_2ZrCl_2 solved in toluene and 1000 mL hexane at 80°C for 3 h at 0.8 Mpa.

[b] Polymerization conditions: 8 g preactivated kaolin with Zr content of 1.8×10^{-5} mol/g kaolin and 1000 mL of hexane at 80°C and 0.8 Mpa.

Table II gives the experimental results of ethylene polymerization with the kaolin-immobilized and the nonimmobilized homogeneous Cp_2ZrCl_2/MAO catalyst system.

It can be seen from Table II that ethylene polymerization occurs fairly well with the immobilized Cp_2ZrCl_2/MAO catalyst system, which indicates that, on the one hand, having been fixed to the surface of kaolin by reacting with –OH groups, MAO does not lose its activity; on the other hand, the amount of the fixed MAO is sufficient for the formation of an active site. Its activity is somewhat lower than that of the homogeneous catalyst system with the Al/Zr molar ratio of 500, but it is still high enough for the preparation of filled polymer composites. The relatively low activity can be mainly attributed to the decreased amount of MAO used in the formation of active centers, as shown in Table I.

To obtain a series of PE/kaolin composites with different kaolin contents, the polymerization time was changed from 5 to 180 min. As shown in Table II, with the increasing of polymerization time, the kaolin content in the product decreases, which implies that by varying polymerization time, PE/kaolin composites with different kaolin contents can be prepared. The weight-average molecular weight and the melting point of the polyethylene component in the composite do not change remarkably with the polymerization time, the values of which are 2.5×10^5 and 137.5°C on average, respectively. Compared with pure polyethylene produced by the homogeneous Cp_2ZrCl_2/MAO catalyst system with Al/Zr ratio of 500, the values of the molecular weight are in the same order, whereas the values of the melting point are slightly higher. This higher melting point may be attributed to the particular crystallization behavior of PE that is formed on substrate.[13]

Morphology and Interfacial Interaction

To study the structure and properties of PE/kaolin composite produced by polymerization filling, we also prepared PE/kaolin composite by a mechanical melt-mixing method for comparison. For simplicity, we labeled the PE/kaolin composite produced by polymerization filling as PKCP (polyethylene/kaolin composite by polymerization filling), whereas its melt-mixing counterpart was labeled PKCM (polyethylene/kaolin composite by melt mixing). To ensure that the two kinds of composite have almost the same polymer matrix, we chose the pure polyethylene produced with Cp_2ZrCl_2/MAO catalyst system, as previously described, as the polyethylene matrix for the mechanical melt-mixing PE/kaolin composites.

It is well known that the key factors that determine the mechanical properties of a filled polymer composite are the dispersion of filler particles in the polymer matrix and the interfacial strength between filler and polymer matrix. To investigate the dispersion of kaolin particles in the polyethylene matrix and the interfacial behavior of PKCP, the cryofractured surfaces and tensile-fractured surfaces of the specimens were investigated by SEM. For comparison, PKCM was also investigated.

Figure 2 gives the SEM micrographs of cryofractured surfaces of the specimens prepared by PKCP and PKCM at a kaolin content of 24%, respectively. It can be seen from Figure 2 that, for PKCM, large craters left by extracted kaolin aggregates are observed, which indicate a poor dis-

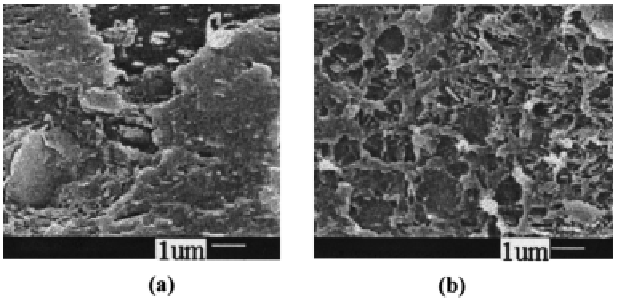

Figure 2 SEM micrographs of cryofractured surfaces of specimens: (a) PKCM 24% kaolin content; (b) PKCP 24% kaolin content.

persion of kaolin particles in the polyethylene matrix. However, for PKCP, the cryofractured surface is covered with smaller craters, which implies a fine dispersion of kaolin particles in PKCP.

Figure 3 shows the SEM micrographs of tensile-fractured surfaces of the specimens prepared by PKCP and PKCM at a kaolin content of 24%, respectively. It can be seen from Figure 3 that, for PKCP, the fractured surface is rough and full of PE fine fibril structures, indicating that there is a strong interfacial interaction between the polyethylene matrix and kaolin particles. However, for PKCM, besides a large kaolin aggregate, there exists a rather smooth fractured surface, which indicates a poor interfacial interaction in PKCM.

To further elucidate the nature of the strong interfacial interaction in PKCP, a solvent-extraction experiment was done on both PKCP and PKCM by employing decalin as the solvent. Remainders of the extracted samples were characterized by FTIR.

Figure 4 shows the FTIR spectra of original kaolin and the remainders of solvent extraction of PKCP and PKCM at a kaolin content of 24%. As shown in Figure 4, for PKCP, after 20 h of extraction, the characteristic peaks of polyethylene at 2918, 2850, 1473, 1463, 730, and 719 cm^{-1} are still strong, whereas for PKCM, these peaks cannot be identified. Because decalin is a good solvent for PE, these results suggest that the strong interfacial interaction between the polyethylene matrix and kaolin particles in PKCP is so strong that it can limit the mobility of the molecular chains of polyethylene. The solvent-extraction experimental results are summarized in Table III.

The dynamic mechanical properties of PKCP and PKCM at a kaolin content of 5.6 and 24% were investigated by Perkin–Elmer DMA at a frequency of 1 Hz and a temperature scan rate of 10°C/min. For comparison, the dynamic mechanical properties of pure PE were also investigated. Figure 5 shows the temperature dependency of loss factor tan δ. The loss factor peak located at about -129°C corresponds to the glass transition of pure PE. It can be seen from Figure 5 that the glass-transition temperature (T_g) of PE in PKCM is nearly the same as that of the pure form, whereas the T_g of PE in PKCP is higher than that of pure PE. Determined from the location of tan δ peaks, the T_g's of PKCM at 5.6 and 24.0% kaolin content were -121.8 and -122.5°C, respectively. The difference between the T_g of pure PE and that of PE/kaolin composites is obviously attributed to the different mobilities of PE molecular chains. Thus, the dynamic mechanical test also provided proof of the strong interfacial interaction in the PE/kaolin composites by polymerization filling.

Rheological Behaviors

The processability of the metallocene-catalyzed polyethylene is a somewhat straightforward problem. The melt tended to exhibit high elasticity, whereupon the unsteady flow took place. In fact, the appearance of unsteady flow is one of the characteristics of linear polymers with tightly entangled molecular chains.[14,15] As discussed above, the polymerization-filling method could offer the composites strong interfacial interaction and the mobility of polyethylene molecular chains was thus decreased. It was reasonable to expect that the PKCP melt had a lower elasticity and would thus lead to better processability.

Figure 6 illustrates the dependency of storage modulus on frequency in the dynamic rheological test of PKCP and its counterpart, PKCM. It is obvious that the storage modulus of PKCP was

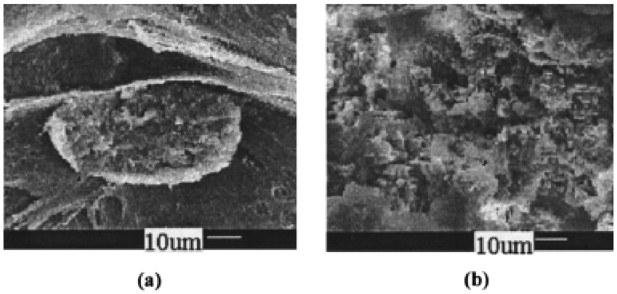

Figure 3 SEM micrographs of tensile-fractured surfaces of specimens: (a) PKCM 24% kaolin content; (b) PKCP 24% kaolin content.

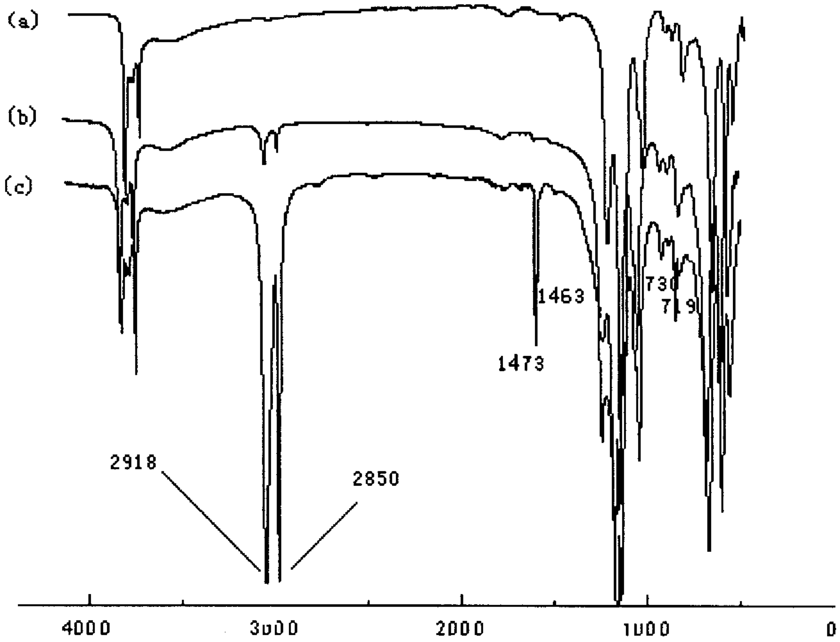

Figure 4 FTIR spectra of (a) original kaolin and the remainders after solvent extraction of PE/kaolin composites prepared by mechanical melt mixing, (b) PKCM, and polymerization filling, (c) PKCP, at a kaolin content of 24%.

lower than that of PKCM and pure polyethylene. Moreover, the storage modulus of PKCP decreased with the mass degree of kaolin. As is well known, the storage modulus is proportional to the energy stored in the elastic deform. Thus the decrease in storage modulus revealed that the introduction of kaolin by polymerization filling weakened the elasticity of metallocene-catalyzed polyethylene.

Similar to the storage modulus, the complex viscosity of PKCP was also lower than that of PKCM and pure polyethylene. The polymerization-filled kaolin decreased the viscosity of PE/kaolin composites, as shown in Figure 7. This

Table III Results of Solvent Extraction[a]

	Preextraction			After Extraction			Results	
		Composition (wt %)			Composition (wt %)			
Sample Name	Sample Amount (g)	PE	Kaolin	Sample Amount (g)	PE	Kaolin	Percentage of Extracted PE (%)	Amount of Residential PE (g PE/g kaolin)
Pure PE	0.1538	100	0	0	0	0	100	0
PKCM[b]	0.1377	94.4	5.6	0.0078	0.6	99.4	99.9	0.006
	0.1166	76.0	24.0	0.0282	0.8	99.2	99.8	0.008
	0.1184	50.0	50.0	0.0596	0.7	99.3	99.3	0.007
PKCP[c]	0.1093	94.4	5.6	0.0300	79.6	20.3	76.8	3.92
	0.1125	91.7	8.3	0.0392	76.2	23.8	71.0	3.2
	0.0883	76.0	24.0	0.0301	29.3	70.7	86.7	0.414
	0.1223	50.0	50.0	0.0650	5.9	94.1	93.7	0.0626

[a] Extraction conditions: decalin as solvent, 20 h.
[b] PKCM, polyethylene–kaolin composite prepared by melt mixing.
[c] PKCP, polyethylene–kaolin composite prepared by polymerization filling.

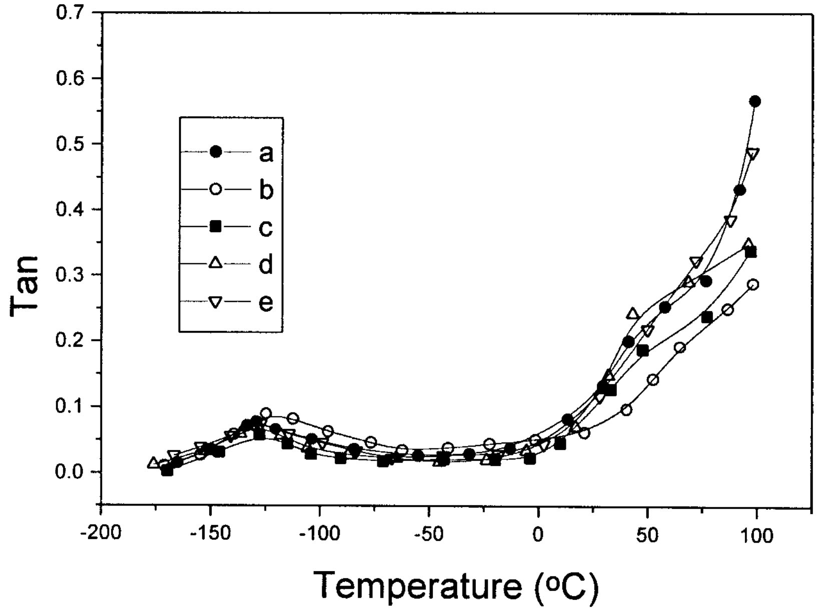

Figure 5 Temperature dependency of tan δ of PE/kaolin composites with different kaolin contents and different preparation methods: (a) pure HDPE; (b) PKCP at kaolin content of 5.6%; (c) PKCP at kaolin content of 24%; (d) PKCM at kaolin content of 5.6%; (e) PKCM at kaolin content of 24%.

phenomenon was similar to the case of the ultrahigh molecular weight PE/kaolin composite by polymerization filling.[16] As a comparison, the case of PKCM was applied to the common rheological rules: the kaolin introduced by the melt-mixing method increased the viscosity of the composites.

As discussed above, the polymerization-filling method provided a strong interfacial interaction to the PKCP and led to the decreased flexibility or mobility of the polyethylene molecular chains. The improvement in rheological property of PKCP could, in brief, be attributed to this special interfacial condition governed by the polymerization-filling method.

CONCLUSIONS

1. The metallocene catalyst system Cp_2ZrCl_2/MAO could be used to prepare polyethyl-

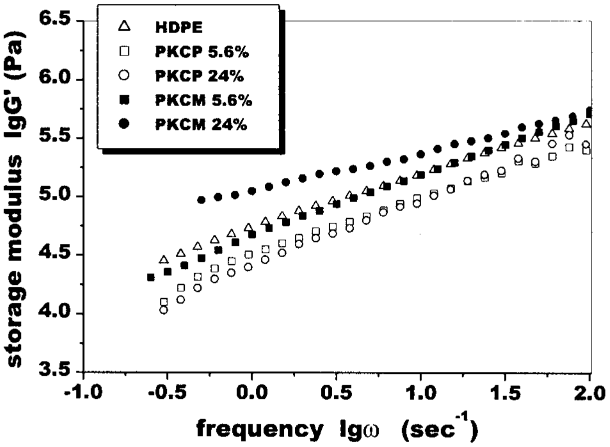

Figure 6 Storage moduli of the melts of PE/kaolin composites.

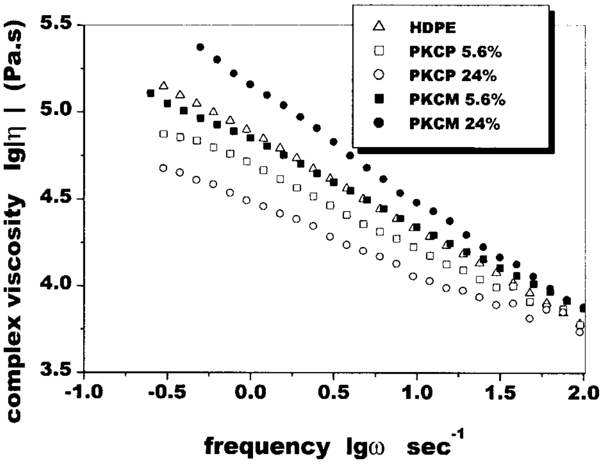

Figure 7 Complex viscosities of the melts of PE/kaolin composites.

ene/kaolin composites by the polymerization-filling method. By first treating the hydroxyl-containing kaolin particles with MAO and, second, treating the MAO-containing kaolin particles with Cp_2ZrCl_2, active centers for ethylene polymerization could be directly formed on the surface of kaolin. After the injection of ethylene, polyethylene could be produced and PE/kaolin composites could also be obtained simultaneously.

2. SEM observations showed that the dispersion of kaolin particles in PE/kaolin composites by polymerization filling was more homogeneous than that of PE/kaolin composites by mechanical melt mixing.
3. The results of extraction experiments and FTIR spectra proved there is a strong interfacial adhesion between the polyethylene matrix and kaolin particles in PE/kaolin composites by polymerization filling. Also indicated by dynamic mechanical analysis, the interfacial interaction was strong enough to influence the mobility of polyethylene molecular chains.
4. The rheological behavior of PE/kaolin composites was improved by the introduction of kaolin by polymerization filling, which is attributed to the special interfacial condition governed by the polymerization-filling method.

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