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Polyethylene/palygorskite nanocomposites with macromolecular comb structure via *in situ* polymerization

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Polyethylene/palygorskite nanocomposites with "macromolecular comb" structure were prepared via *in situ* polymerization. The $TiCl_4$ catalyst was first loaded on the surface of the nanoscale whiskers of palygorskite. Subsequently the ethylene was introduced into the reaction system, and the polyethylene molecular chain was generated directly at the surface of the palygorskite whiskers. As a result, a polyethylene molecular chain with "macromolecular comb" structure was generated. The product thus obtained was blended with regular polyethylene to make a polymer blend, which was characterized by transmission electron microscope (TEM). Finely dispersed palygorskite whiskers in polyethylene matrix were found, which resulted in the improvement of mechanical strength of the polymer blends. Compared with regular polyethylene, the impact strength and tensile strength of the polymer blend were improved by 63.5% and 21.3% respectively at 25°C, when the palygorskite content of the nanocomposite was 20 wt%. © *2003 Kluwer Academic Publishers*

1. Introduction

The creation of polymer composites where the layered silicate can be distributed in the polymer matrix at the nanoscale level has attracted a lot of attention because of their enhanced properties [1–4]. The layered silicates, usually montmorillonite, have been successfully used to prepare the nanocomosites via melt intercalation or monomer intercalation with different matrices, such as polystyrene and nylon 6 [5, 6]. The non-polar polymers, such as polyethylene (PE), cannot form nanocomposites via these methods, because of its non-polarity [7–11]. In this paper, a novel method to prepare a nanocomposite of polyethylene with palygorskite is proposed. In this work, the palygorskite was employed as inorganic filler and $TiCl_4/AlR_3$ was used as catalyst. Palygorskite is a nanoscale whisker. Firstly, the $TiCl_4$ was loaded on the surface of the nanoscale whisker of palygorskite, and then the activated palygorskite, AlR_3, hexane and ethylene were introduced into the reactor. Subsequently the ethylene was initiated directly on the surface of the palygorskite whiskers. Because of the multiple activated points in a palygorskite whisker, several polyethylene molecular chains were generated simultaneously on a palygorskite whisker. As a result, a PE/palygorskite nanocomposite with "macromolecular comb" structure was generated. The products thus obtained possessed a fine dispersibility of palygorskite whiskers in polyethylene matrix. The processability, however, was poor because of the excessive entanglements of the "macromolecular comb." Several linear polyethylene molecular chains in PE/palygorskite nanocomposites were linked together through each palygorskite whisker, and the linking points were chemical bonds. Therefore, in the PE/palygorskite nanocomposites, a recessive crosslinking point existed, which decreased the processability of the PE/palygorskite nanocomposites. But we know that the excessive entanglements of chains

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will give rise to the improvement of the mechanical strength. To overcome the problem with processability, the PE/palygorskite nanocomposites were mixed with regular polyethylene to form a polymer blend. The processability of products thus obtained was improved because of the existence of linear polyethylene molecular chains, and the extent of entanglements of the chains is higher compared with that of unreinforced polyethylene. As a result, a polymer blend with better dispersibility, processability, and mechanical strength can be obtained. The polymer blends were characterized by transmission electron microscope (TEM), Brabender rheometer and mechanical properties. The results showed that a kind of molecular chain with "macromolecular comb" structure was obtained via *in situ* polymerization pathway, and the polymer blends of PE/palygorskite nanocomposites with regular polyethylene provided better dispersibility, processibility and mechanical properties.

2. Experimental

2.1. Materials

Ethylene was obtained by Beijing Yanshan Petrochemical Co.; Palygorskite was supplied by department No. 14 of RIPP (Jiashan, Anhui Province, China), and was used after being soaked in a muffle furnace at the temperature of 800°C for 6 h; Titanium tetrachloride ($TiCl_4$) was obtained from Beijing Zhonglian Chemical Co.; Triisobutylaluminium (AlR_3) was obtained from Beijing Yanshan Petrochemical Co., and used after treatment with molecular sieves; The other compounds, hexane and decalin, were supplied by Beijing Reagent Manufacturer No. 3, China; High density polyethylene (HDPE, 5000S) was supplied by Beijing Yanshan Petrochemical Co.

2.2. Activation of palygorskite

Firstly the palygorskite was calcined at 800°C for 6 h. Subsequently it was reacted with $TiCl_4$ in hexane under N_2 atmosphere for a given period of time. The product thus obtained was washed with hexane and dried under an N_2 at 60°C.

2.3. Preparation of PE/palygorskite nanocomposites

A 500 mL-glass reactor equipped with stirrer and oil bath was purged with N_2. Subsequently, hexane, AlR_3 and activated palygorskite in various weight ratios were introduced into the reactor, and then the ethylene was supplied under a pressure from 1 atm to 6 atm. The polymerization was going on for a certain period of time and terminated by the addition of acidified ethanol. The products thus obtained were dried under vacuum for 6 h.

2.4. Preparation of polymer blends

The PE/palygorskite nanocomposites were blended with regular polyethylene in a mixer for 10 min, and then the mixture was processed using a twin screw extruder machine ($\Phi = 25$ mm, WP, German) at 220°C.

2.5. Gel content determination

The solvent extraction test of PE/palygorskite nanocomposites was carried out with a Soxhlet extractor at 135°C for 20 h using decalin as the solvent.

2.6. Molecular weight measurements

The intrinsic viscosity, η, of PE/palygorskite nanocomposites in decalin solvent was determined by an Ubbelohde viscometer. The molecular weight was calculated according to the formula: $[\eta] = 6.77 \times 10^{-4}\ M^{0.67}$.

2.7. Rheometric testing

Brabender torque rheometry was utilized to characterize the melt flow behavior of the PE/palygorskite nanocomposites. The rheometric testing was conducted to measure the processability at a temperature of 250°C and a rotation speed of 20 rpm, with a Brabender Rheometer (PLV-151).

2.8. Transmission electron microscope (TEM)

Transmission Electron Microscope (TEM) was used to investigate the morphology of PE/palygorskite nanocomposites. Ultrathin sections of the masticated samples were prepared with an ultramicrotome equipped with a diamond knife. The specimens were examined with a Transmission Electron Microscope (Hitachi, H-800-1).

2.9. Mechanical properties testing

The tensile and impact bars were prepared by injection molding machine. Mechanical properties were measured with an Instron 1185 universal testing instrument (ASTM D638-81). The Izod impact test was performed according to GB/T1043-93 with an XJJ-5 impact tester. The tensile test speed and temperature applied was 25 mm/s and 23°C respectively.

3. Results and discussion

3.1. Preparation of PE/palygorskite nanocomposites

PE/palygorskite nanocomposites were prepared via the *in situ* polymerization of ethylene with activated palygorskite using a $TiCl_4/AlR_3$ catalyst. The purpose of loading $TiCl_4$ on the palygorskite whisker was to initiate the polymerization of monomer directly on the surface of palygorskite whisker. The schematic representation of the possible structure of the resulting "macromolecular comb" is shown in Fig. 1. From this model, we can notice that several molecular chains can generate on a palygorskite whisker simultaneously, just like a comb. The linking point of polyethylene molecular chain with the palygorskite whisker forms a chemical bond, which constitutes a recessive linking point between the polyethylene molecular chains and the palygorskite whiskers. Because of the existence of these recessive bonding points, the degree of entanglements of polyethylene molecular chains is improved greatly. As a result, the gel content of PE/palygorskite

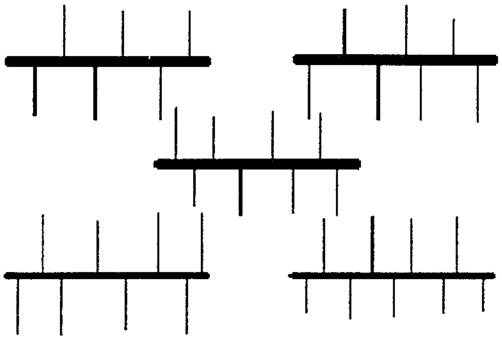


Figure 1 Schematic representation of the possible structure of "molecular comb." ——Represents the polyethylene molecular chain on the palygorskite whisker, ——Represents the palygorskite whisker.

nanocomposites will be increased. Table I shows the results of measurements of the PE/palygorskite nanocomposites.

As shown in Table I, we can notice that the higher the content of palygorskite, the lower the molecular weight of polyethylene generated on the palygorskite whisker. This is a result of *in situ* polymerization of ethylene. Firstly the $TiCl_4$ was loaded on the surface of the palygorskite whisker, and subsequently the ethylene was introduced into the reactor to initiate polymerization. During the polymerization, an equal amount of activated palygorskites was used in the system, which resulted in the equal amount of active centers. As a result, for different systems, the number of molecular chains was equal if an equal amount of activated palygorskite was used, and the greater the amount of ethylene introduced into the system, the higher the molecular weight of polyethylene generated on the palygorskite whisker. Of course the increasing of ethylene decreased the relative content of palygorskite. The molecular weight of PE molecular chains generated on the palygorskite whiskers has a direct influence on the gel content, processability, dispersibility and mechanical properties.

As a result, the gel content was determined for further characterization of the PE/palygorskite nanocomposites with "macromolecular comb" structure. Solubility measurements using decalin as the solvent showed that the weight ratio of the crosslinked structure of the final products was more than 60%. The higher the molecular weight of the PE molecular chains generated on the palygorskite whiskers, the higher the insoluble species content of the products. But the sensitivity of the decrease of the insoluble species with increase in molecular weight was slight for different samples in Table I. During extracting using decalin as the solvent, the polyethylene molecular chain can be broken from the palygorskite whisker, because the linkage between them is weak. The changes of the gel contents were somewhat caused by the molecular weight of PE generated on the palygorskite whiskers. Therefore the gel content was somewhat independent of the content of palygorskites.

TABLE I Measurements results of PE/palygorskite nanocomposites

Sample	Content of palygorskite (wt%)	Gel content (wt%)	Molecular weight ($\times 10^{-4}$)	Balance torque (N·m)
NCM-1	5.0	68.6	8.0	35.3
NCM-2	8.4	66.4	6.4	34.3
NCM-3	11.1	66.5	5.6	34.0
NCM-4	16.3	60.6	5.0	29.4

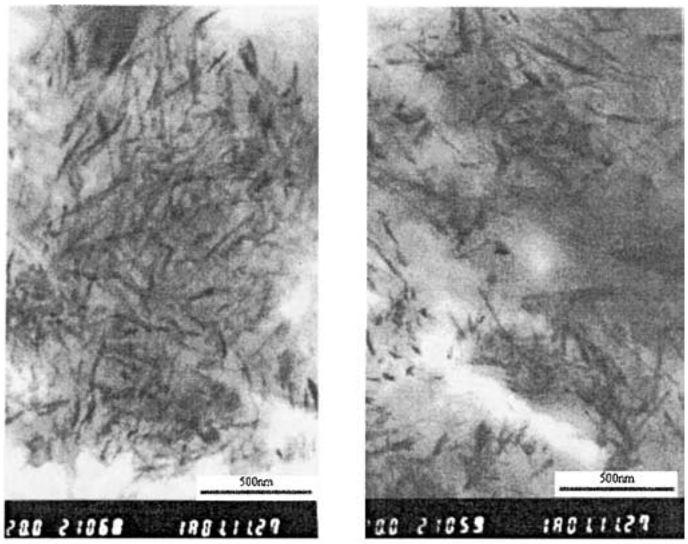
Because of the existence of the recessive crosslinking point of the "macromolecular comb," the entanglements of polyethylene molecular chains resulted in the increasing of the balance torque, which is shown in Table I. We can see that the higher the content of palygorskite, the lower the balance torque, which is related to the molecular weight of polyethylene generated on the palygorskite whiskers. The increasing of the molecular weight enhanced the entanglements of polyethylene molecular chains. As a result, the balance torque was increased.

As shown in Fig. 2 (NCM-1 and NCM-2), transmission electron microscopic analysis clearly confirmed the very effective dispersion for PE/palygorskite nanocomposites where club-shaped whiskers were dispersed finely within the PE matrix. But for samples of NCM-3 and NCM-4, the dispersability of palygorskite whiskers in PE matrix was not as good. This difference in dispersion resulted from the molecular weight of PE molecular chains generated directly on the surface of the palygorskite whiskers. The higher the molecular weight of PE, the better the compabitilization of PE/palygorskite nanocomposites. Among the four samples, NCM-1 has the highest PE molecular weight and the lowest content of palygorskite. As a result, the best compatibilization effect between palygorskite and PE matrix was obtained for NCM-1, which can be seen in Fig. 2. The sample of NCM-4 possessed a relatively poor compatibilization just because of the lower molecular weight of PE.

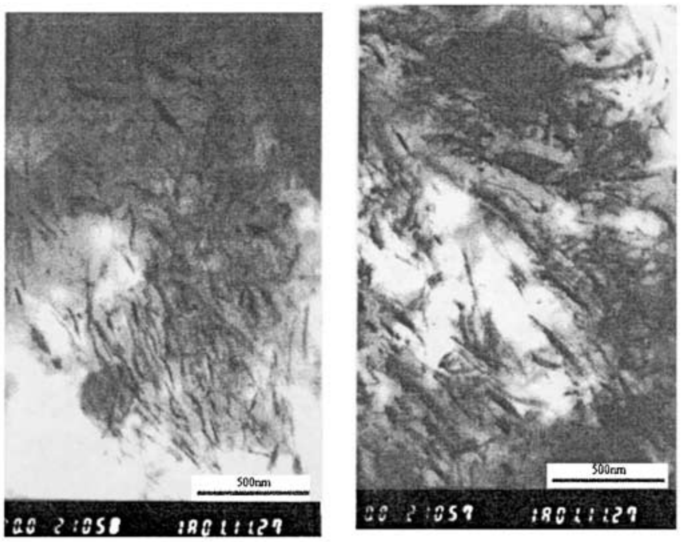
3.2. Polymer blends of PE/palygorskite nanocomposites with regular polyethylene

The PE/palygorskite nanocomposites possessed a poor processability because of the excessive entanglements of polyethylene molecular chains. In order to resolve this problem, a blend of nanocomposites with regular polyethylene was proposed. Schematic representation of the possible structure of polymer blends of nanocomposites with regular polyethylene is shown in Fig. 3. According to the model shown in Fig. 3, we can notice that the molecular chain with "macromolecular comb" structure is blended with molecular chains of regular PE. The extent of entanglements connecting different molecular combs is decreased because of the introducing of regular PE, which constitutes the processability enhancer in the blend system. The existence of PE molecular chains generated on the surface of palygorskite whiskers constitutes the compatibilizers of PE with palygorskite, which results in the fine dispersing of palygorskite in PE matrix.

The nanocomposite samples of NCM-1, NCM-2, NCM-3 and NCM-4 were blended with regular PE with a weight ratio of 2/8. Accordingly, four samples of PB-1, PB-2, PB-3 and PB-4 were thus



NCM-1 NCM-2



NCM-3 NCM-4

Figure 2 TEM micrographs of PE/palygorskite nanocomposites. Content of palygorskite (wt%): NCM-1: 5.0; NCM-2: 8.4; NCM-3: 11.1; NCM-4: 16.3.

obtained. For comparison of the processability, the curves of torsional moment with time of HDPE, NCM-1 and PB-1 are listed in Fig. 4, which represent the regular PE, nanocomposites and polymer blends respectively. One can notice that the regular PE (HDPE) without any palygorskite has the lowest moment. The moment value of NCM-1 is much higher than that of regular PE. This high torsional

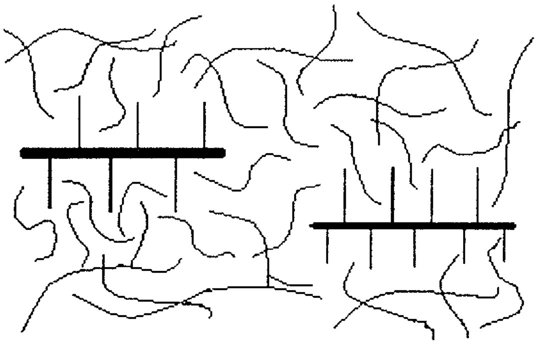


Figure 3 Schematic representation of the possible structure of polymer blends of PE/palygorskite nanocomposites with regular polyethylene. ━Represents the palygorskite whisker, —Represents the polyethylene molecular chain on the palygorskite whisker, and ⁀Represents the liner molecular chain of regular polyethylene.

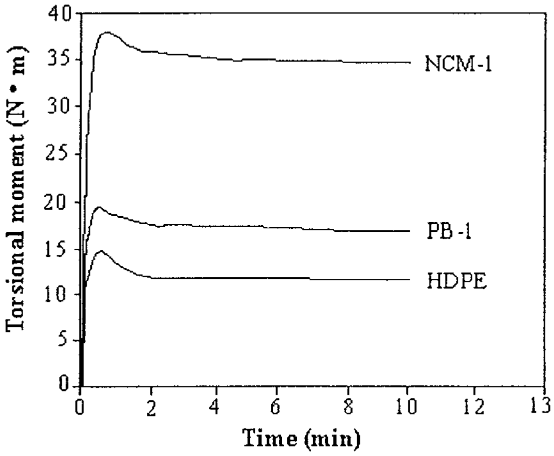
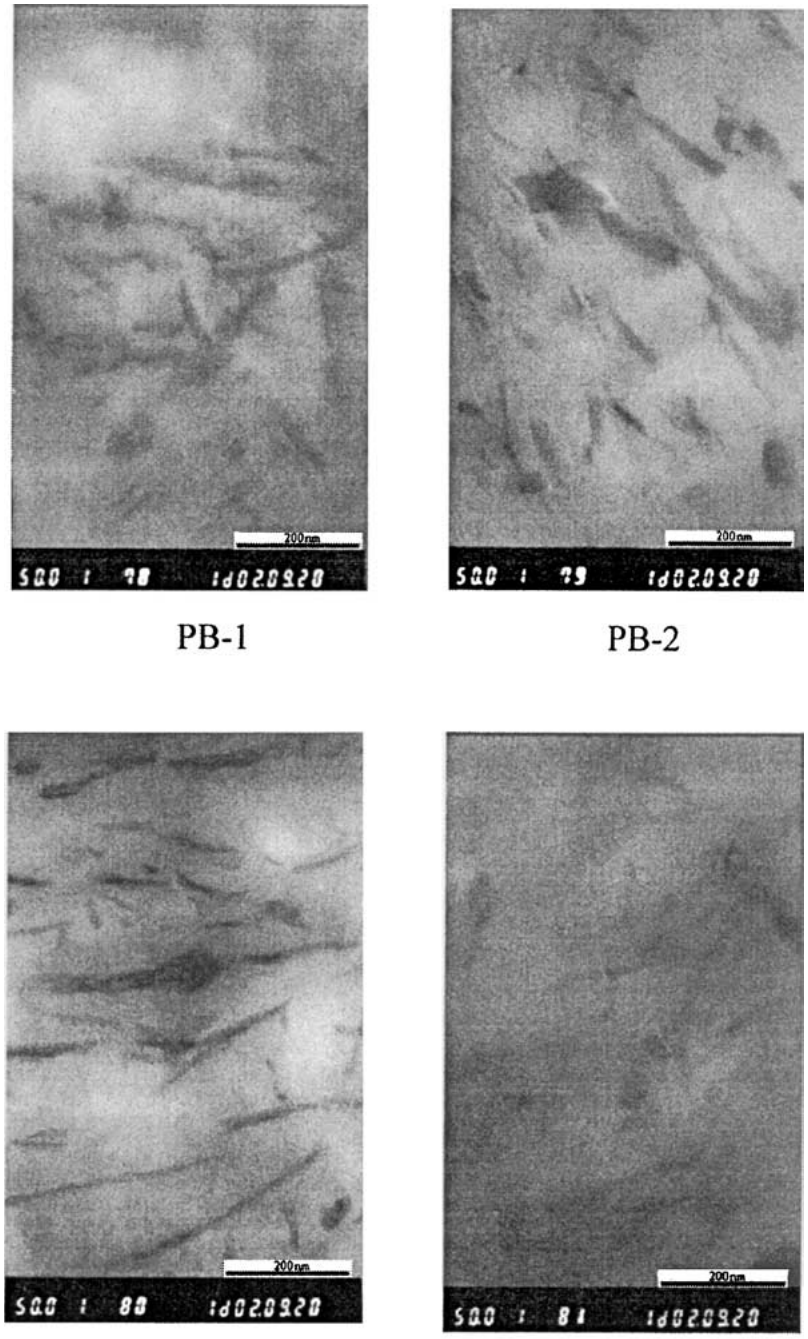


Figure 4 Rheometric curves of different systems.



PB-1 PB-2

PB-3 PB-4

Figure 5 TEM micrographs of polymer blends of nanocomposites with regular polyethylene. PB-1, PB-2, PB-3 and PB-4 are samples of NCM-1, NCM-2, NCM-3 and NCM-4 blended with regular PE with a weight ratio of 2/8.

moment (35.3 N · m) restricts the application of nanocomposites. After the nanocomposite (NCM-1) was blended with regular PE, we can find that the torsional moment is slightly higher than that of regular PE, and is much lower than that of NCM-1. This indicates that the processability of polymer blends thus obtained was improved obviously.

Fig. 5 shows the TEM micrographs of samples of PB-1, PB-2, PB-3 and PB-4. Among the samples of PB series produced by blending, a club-shaped morphology with fine dispersion of palygorskite whiskers in PE matrix can be seen. This excellence in dispersibility is resulted from the compatibilization between PE matrix and palygorskite whiskers. As we know, the PE and palygorskite, just organic/inorganic materials, are incompatible in blends. In this paper, the palygorskite whiskers were enwrapped with PE molecular chains which were generated directly on the surface of the palygorskite whiskers. These PE molecular chains on the palygorskite whiskers constitute the compatibilizer of PE matrix with palygorskite. The observed phase behavior for the blends reflects the compatibilization effect of palygorskite whiskers with PE matrix.

The mechanical properties of the polymer blends obtained were evaluated through impact strength, tensile testing and elongation at break and are presented in

TABLE II Mechanical properties of polymer blends of nanocomposites with regular polyethylene

Sample	Impact strength (kJ/m^2)	Tensile strength (MPa)	Elongation at break (%)
PE	50.7	31.4	180.2
PB-1	82.9	38.1	172.1
PB-2	70.9	32.3	170.2
PB-3	60.2	26.1	166.7
PB-4	42.8	22.4	160.8

Table II. Compared with the PE matrix, a clear-cut difference occurred between the regular PE and polymer blends as far as the impact strength was concerned. We can see that the impact strength of PB-1, PB-2 and PB-3 was improved by 19 to 64%, leading to toughened materials. This is a result of increasing entanglements of molecular chains caused by the introducing of PE/palygorskite nanocomposites with the "macromolecular comb" structure. The impact strength of PB-4, however, was lower than that of regular PE. Because the PE molecular weight generated on the palygorskite whisker was decreased, as shown in Table I, the lack of entanglement is likely to adversely affect the impact strength. Accordingly, the improved entanglements of PE molecular chains caused the improvement of tensile strength of PB-1 and PB-2. But the elongation at break was affected slightly for the four samples. This indicated that the higher the molecular weight of the PE molecular chains on the palygorskite whiskers, the higher the mechanical strength of the samples.

4. Conclusions

A novel polyethylene/palygorskite nanocomposite was prepared via *in situ* polymerization. Because of the loading of $TiCl_4$ catalyst on the surface of palygorskite whisker, the products thus obtained possessed a "macromolecular comb" structure, which resulted in poor processability during molding and processing. The processability was improved by blending the nanocomposites with regular polyethylene. The results showed that a blend of nanocomposite with 80 wt% PE was beneficial to the impact strength and tensile strength of blending products.

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