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A novel polyethylene/palygorskite nanocomposite prepared via in-situ coordinated polymerization

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Summary

A novel polyethylene/palygorskite nanocomposite with excellent processability was prepared via in-situ coordination polymerization. A mixed catalyst of $TiCl_4/MgCl_2/AlR_3$ was employed. Firstly the Ziegler-Natta catalyst of $TiCl_4/AlR_3$ was loaded on the surface of the nanoscale whiskers of palygorskite to prepare the "macromolecular comb". Secondly the $MgCl_2$ catalyst was introduced into the reaction system to prepare the ordinary PE molecular chain. The polyethylene/palygorskite nanocomposites thus obtained possessed excellent mechanical properties.

Introduction

Nanostructured composites consisting of inorganic particles embedded within various polymer matrices have been intensively studied in recent years.[1-3] Technological interest in these types of nanocomposites is spurred by their enhanced mechanical strength, toughness, formability and barrier properties compared to conventionally prepared filled composites. Several nanostructured inorganic particles, such as clay, mica, silicon dioxide, bentonite, palygorskite etc, have been used in the field of producing polymer matrix nanocomposites via polymerization pathway.[4-10] The polymer matrix includes polystyrene, poly (butyl methacrylate), nylon and polyesters etc, but seldom Polyethylene (PE) matrix is included. Sometimes, polypropylene nanocomposite can be obtained by adding maleic anhydride-modified polypropylene via melt compounding.[11] However the presence of agglomeration of organophilic clay particles indicated poor dispersion, which decreased the mechanical properties obviously. For these kinds of nanocomposites mentioned above, the key factor is to prevent the agglomeration of inorganic particles during preparation of nanocomposites.

Recently, a nanocoposites incorporated with palygorskite into polyethylene (PE) matrix have been found to give enhanced mechanical strength by this group.[12] Furthermore, this type of mamocomposites exhibit new functional properties, for example, the better mechanical property and thermostability. In order to fabricate PE/ palygorskite nanocomposites, phase compatibility between the matrix and the dispersoid is important. In this paper, a novel method - in-situ coordinated polymerization was proposed. In the past study, we have chosen PE as matrix, and the palygorskite as dispersoid, and succeeded in preparing a PE/palygorskite nanocomposites, which possessed better dispersibility. For that system, $TiCl_4/AlR_3$ as the catalyst, was loaded in the surface of palygorskite, from which the polymer chain was generated. Therefore a nanocomposite with better compatibility and dispersibility was produced. The processability, however, was poor, and the gel content was high. For this reason, a better method was proposed. In this paper, a mixed catalyst, $TiCl_4/MgCl_2/AlR_3$ was employed. Firstly the Ziegler-Natta catalyst of $TiCl_4/AlR_3$ was loaded on the surface of the nanoscale whiskers of palygorskite. Subsequently ethylene was supplied to the reaction system. During the polymerization, the catalyst of $MgCl_2$ was introduced into the reaction system. During the preparation of PE/palygorskite nanocomposites, the palygorskite loaded with $TiCl_4/AlR_3$ was a support of the catalyst for initiating the polymerization of ethylene, and a reinforcement material for PE/palygorskite nanocomposites after polymerization; simultaneously the ordinary PE molecular chain was generated initiated by the $MgCl_2$ catalyst. During the polymerization, control of the activation of $TiCl_4/ MgCl_2/AlR_3$ mixed catalysts was the key factor. As a result, two kinds of molecular chain existed crosswise via in-situ coordinated polymerization in the PE/palygorskite nanocomposite. This nanocomposite thus obtained possessed better processability and dispersibility, which was characterized by rheometric testing and transmission electron microscope (TEM) respectively.

This novel in-situ polymerization approach with $TiCl_4/ MgCl_2 /AlR_3$ mixed catalysts provides a new method for the production of PE/palygorskite nanocomposite. In addition to the interest of basic science, there is significant interest in producing materials for engineering application, especially for the production prepared via extrusion and injection process.

Experimental

Materials

Ethylene was obtained by Beijing Yanshan Petrochemical Co. (China). Palygorskite was supplied by department No. 14 of RIPP (Jiashan, Anhui Province, China), and was used after being soaked in a muffle at the temperature range 100-1000℃ for 6h. Titanium tetrachloride ($TiCl_4$) and magnesium chloride ($MgCl_2$) was obtained from Beijing Zhonglian Chemical Co. (China); 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).

Activation of palygorskite

Firstly the palgorskite was calcined at 800℃ for 4h. 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℃.

Polymerizations

A 500mL-glass reactor equipped with stirrer and oil bath was purged with N_2. Subsequently, hexane, $MgCl_2$, AlR_3 and activated palygorskite in various wt. ratios were introduced into the reactor, and then the ethylene was supplied under a pressure from 1atm to 6atm. 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 6h.

Characterization

The solvent extraction test of PE/palygorskite nanocomposites was carried out with a soxhlet extractor at 135℃ for 20h using decalin as the solvent. The intrinsic viscosity of PE/palygorskite nanocomposites in decalin solvent was determined by an ubbelohde viscometer. The molecular weight was calculated according to the formula: $[\eta]=6.77\times 10^{-4}M\mathrm{w}^{0.67}$. The rheometric testing of PE/palygorskite nanocomposites was conducted to measure the processability at a temperature of 250℃ and a rotation speed of 20rpm, with a brabender rheometer(PLV-151). Transmission electron microscopy (TEM) was used to investigate the morphology of PE/palyskite 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 microscopy (Hitachi, H-800-1). 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 25mm/s and 23℃ respectively.

Results and Discussion

Preparation of PE/palygorskite nanocomposites

In this paper, the mixed catalysts of $TiCl_4$/ $MgCl_2$ /AlR_3 were employed to produce PE/palygorskite nanocomposites. $TiCl_4$ catalyst was loaded on the whisker of palygorskite. The dispersed shape of palygorskite in water is shown in Figure 1. We can notice that the club-shaped whiskers of palygorskite are dispersed randomly. This better dispersibility in water is due to the "building" hydroxyl group (-OH) in the structure of palygorskite, which is disadvantageous to the loading of catalysts. This is why a calcination process is necessary.

Figure 1. TEM micrograph of palygorskite

During the polymerization, two kinds of PE molecular chain generated simultaneously. Firstly, PE chains grew directly from the surface of the palygorskite. Because of the multi-activated points on each whisker of the palygorskites, a great number of PE molecular chains generated on each whisker. For this reason, a "macromolecular comb" was produced. Secondly, ordinary PE molecular chains generated initiated by $MgCl_2$ catalyst. As a result, the network combined with "macromolecular comb" and ordinary PE molecular chain was produced (Figure 2). The "macromolecular comb" possessed a poor processability because of the excessive entanglement of chain brush. But the processability was improved greatly because of the introduction of ordinary PE molecular chains. As shown in figure 2, the ordinary PE molecular chain dispersed in the "macromolecular comb" became a processability enhancer. As a model system of figure 2, it can help us to test the methods we use, as well as to validate and interpret the characterization results of PE/palygorskite nanocomposites.

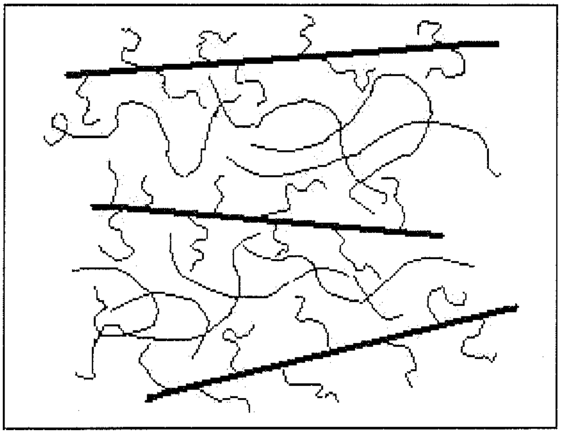


Figure 2. Schematic representation of the possible hybrid formation with palygorskite and polymers

Characteristics of the PE/palygorskite nanocomposites

As shown in figure 2, the unbounded PE molecular chain and the "macromolecular comb" are coexistent. Because of this special structure, the molecular weight and gel content of nanocomposites were measured using a soxhlet extractor with decalin as solvent. The extracted results and the molecular weight can be taken as a measure of characterizing the interaction between palygorskite and PE. The results of the solubility measurements are shown in Table 1.

Table 1. Characteristics of the PE/palygorskite nanocomposites

Sample	Content of the samples before extraction Wt.-%		Extracted PE %	Gel content %	Molecular weight ($M_\eta \times 10^{-4}$)	Catalytic system*
	PE	palygorskite				
PE	100	0	100	0	2.6	B
NCM-1	99.1	1.0	89.9	10.1	2.8	B
NCM-2	98.6	1.4	86.8	13.2	3.2	B
NCM-3	91	9.0	79.4	20.6	5.4	C
NCM-4	95	5.0	33.6	66.4	8.0	A

*Catalytic system: A represents $TiCl_4/AlR_3$, which were loaded on the whisker of palygorskite; B represents $TiCl_4/MgCl_2/AlR_3$, in which the catalysts of $TiCl_4/AlR_3$ were loaded on the whisker of palygorskite; C represents $TiCl_4/MgCl_2/AlR_3$, in which no catalyst was loaded on the whisker of palygorskite.

For the pure PE sample, we can notice that its gel content is zero, and the molecular weight is 2.6×10^4. The gel content and molecular weight increase with the increasing of palygorskite content. When the content of palygorskite is 9.0%, the gel content and molecular weight are 20.6% and 5.4×10^4. But for the sample of NCM-4, the gel content and molecular weight are 66.4% and 8.0×10^4 respectively. This is because only "macromolecular comb" exists in samples of NCM-4. These comb polymers increase the entanglement of molecular chains. As a result, the gel content and the molecular weight are high.

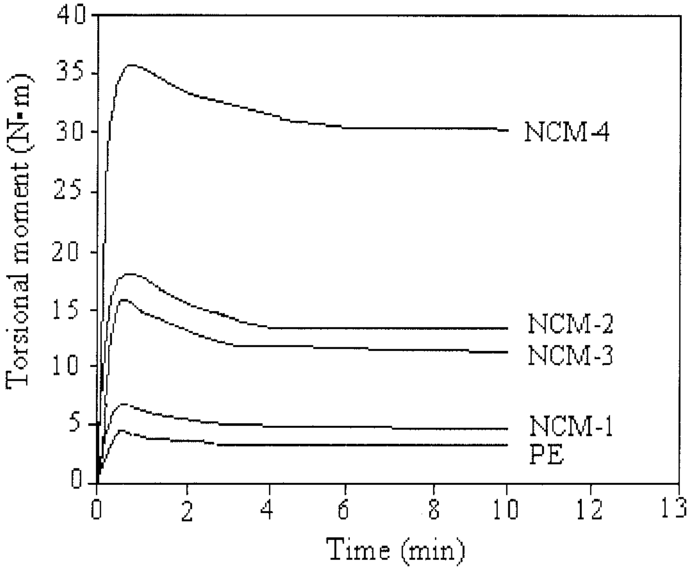
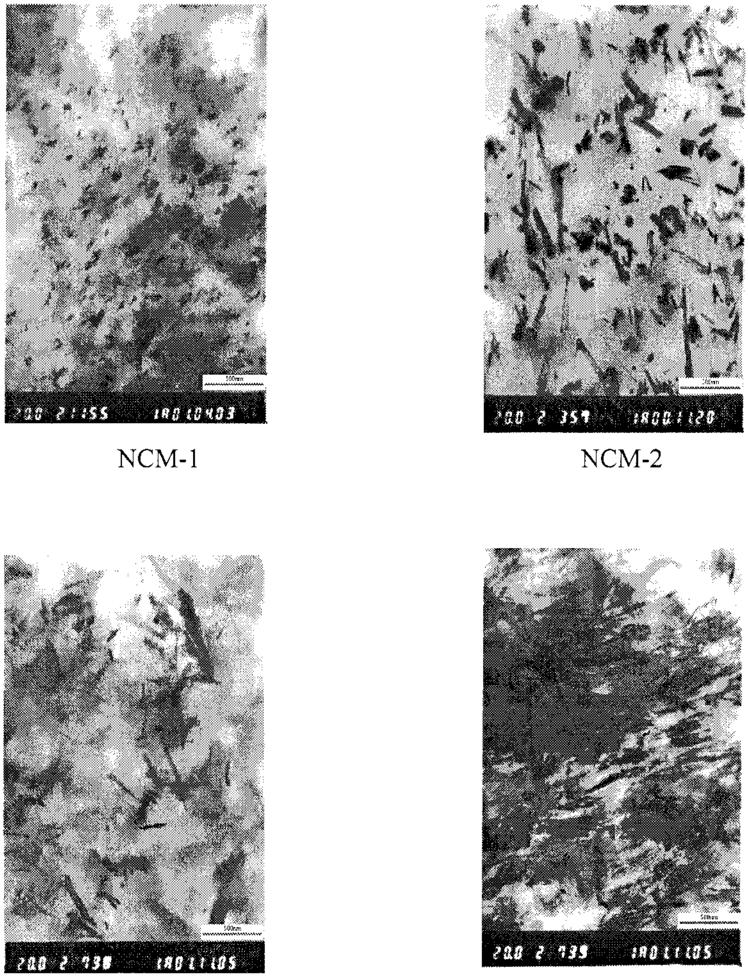


Figure 3. Rheometric curves of different systems

In order to examine the processability of samples prepared via mixed catalysts, the rheometric testing was conducted. The result of rheometric testing was shown in Figure 3. One can notice that pure PE without any palygorskite has the lowest moment, including maximum and balanceable moment. The moment value of NCM-1, NCM-2 and NCM-3 is higher than that of PE, but it is lower than that of NCM-4 greatly. The samples of NCM-1, NCM-2 and NCM-3 with the moment value lower than 20 N• m possess better processability during process. The sample of NCM-4 has a poor processability because of its excessive entanglement.

The morphology of PE/palygorskite nanocomposites was characterized by transmission electron microscopy (TEM). The dispersion aspect of palygorskite in nanocomposites is shown in Figure 4. Figure 4 (NCM-1) and (NCM-2) shows the micrographs of PE/palygorskite nanocomposites catalyzed via mixed catalysts ($TiCl_4$/ $MgCl_2$/AlR_3, in which the $TiCl_4$ is loading on the whisker of palygorskite); Figure 4 (NCM-3) shows the micrograph of PE/palygorskite nanocomposite catalyzed via mixed catalysts ($TiCl_4$/ $MgCl_2$/AlR_3, in which no catalyst was loaded on the whisker of palygorskite); Figure 4(NCM-4) shows the micrograph of PE/palygorskite nanocomposites catalyzed via $TiCl_4$/AlR_3, in which the $TiCl_4$was loaded on the whisker of palygorskite. The white and the black represent PE phase and palygorskite respectively. We can notice that samples of NCM-1 and NCM-2 possess better dispersibility and compatibility, in which the whiskers of palygorskite are dispersed uniformly in the PE matrix.



NCM-1

NCM-2

NCM-3

NCM-4

Figure 4. TEM micrographs of different PE/palygorskite nanocomposites

As a contrast, a poor dispersibility of palygorskite in PE matrix is found for NCM-3, in which a distinct aggregation of palygorskite occurred in PE matrix. This is because the whisker of palygorskite has a high surface energy, which results in the poor compatibility between palygorskite and PE matrix. In addition, NCM-4 exhibits a better dispersibility of palygorskite in PE matrix, but a poor processibility and fluidity constricts its application. As a result, we can find that the loading of $TiCl_4$ catalyst on the whisker of palygorskite is necessary. During polymerization some amount of PE molecular chain is generated on the whisker of palygorskite, which constitutes the compatilizer of palygorskite and PE matrix.

Table 2. Mechanical properties of the PE/palygorskite nanocomposites

Sample	Palygorskite content Wt.-%	Impact strength KJ/m^2	Tensile strength MPa	Elongation at break %
PE	0	22.4	29.6	413
NCM-1	1.0	42.2	32.1	382
NCM-2	1.4	56.2	33.4	127
NCM-3	1.6	9.6	27.5	528

As mentioned above, the entanglement of molecular chain went against the ability of processability, but it will increase the mechanical strength. The results of mechanical properties of the PE/palygorskite nanocomposites are shown in Table 2. One can see that the impact strength and tensile strength of NCM-1 and NCM-2 were improved greatly compared to those of pure PE, and the elongation at break is lower than that of pure PE. But for sample of NCM-3, the impact strength and tensile strength are much lower that those of pure PE. This indicates that introducing of the palygorskites loaded with $TiCl_4/AlR_3$ catalysts is helpful for the improvement of mechanical strength.

Conclusion

A novel polyethylene/palygorskite nanocomposite was prepared via in-situ polymerization. The outstanding merits of polyethylene/palygorskite nanocomposite thus obtained were its excellent processability and mechanical properties, which were resulted from the mixed catalytic system of $TiCl_4$/ $MgCl_2/AlR_3$. The results show that the in-situ coordination polymerization pathway is suitable for preparation of polyethylene/palygorskite nanocomposites.

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