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Polyethylene–clay hybrid nanocomposites: in situ polymerization using bifunctional organic modifiers

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Abstract

A hybrid polyethylene–clay nanocomposite was prepared using in situ polymerization with bifunctional organic modifiers. Morphological characterization of the product shows that a fraction of the polyethylene chains is chemically linked to the silicate surface. The chemical modification and intercalation of montmorillonite was carried out with alkylaluminum and vinylalcohol. The vinyl groups chemically linked to the silicate surface were copolymerized with ethylene inside the clay galleries using a coordination catalyst. The polymerization leads not only to effective exfoliation of the layered silicate but also to polyethylene chains that are chemically bonded to silicate surface.

Keywords: Clay; Nanocomposites; Polyethylene

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1. Introduction

The development of hybrid polyolefin–clay nanocomposites is a field of rapidly growing industrial relevance [1–6]. Layered silicates can be used to produce polymer nanocomposite materials by in situ polymerization. Organic modifiers may be used to just intercalate the silicate or to intercalate the silicate and take part in the polymerization. The approach of using bifunctional organic modifiers has been explored with nylon–silicate nanocomposites [7]. More recently, coordination catalysts have also been used to prepare polyolefin nanocomposites [8–11]. We propose here a method to synthesize a polyethylene–clay (PE–clay) hybrid nanocomposite prepared by in situ polymerization that has polyethylene chains chemically linked to the silicate surface.

2. Experimental

2.1. Intercalation

MKSF (montmorillonite, Aldrich) (10 g) was dispersed in 100 ml of 0.1 N HCl and then washed with deionized water until no chlorine ion was detected with 0.1 N $AgNO_3$ solution. The filter cake was vacuum-dried at 300 °C for 24 h. The dried exchanged clay (1 g) was transferred to a 100 ml Schlenk tube under nitrogen and treated with 1.7 mmol of AlR_3, (trimethylaluminum TMA, or triisobutylaluminum TIBA) dissolved in toluene for 2 h and dried again under vacuum for 3 h. The resulting solid was then treated with 1.7 mmol of ω-undecylenylalcohol dissolved in 20 ml toluene. The solid was then washed with 15 ml hexane three times and dried for 3 h. Finally, 1 g of the resulted solid was treated with 1.6 mmol of dad-Ni, dissolved in 20 ml of toluene, and washed with 20 ml of toluene and again dried for 3 h under vacuum. (1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) dichloro nickel (dad-$NiCl_2$) was prepared through the known procedure [12].

2.2. Polymerization and characterization

A 100 ml glass reactor was purged and loaded with 20 ml

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monochlorobenzene, 1 g MAO, ethylene (at atmosphere pressure) and dad-$NiCl_2$-impregnated clay in various wt% ratio. After 1 h, the polymerization was terminated by the addition of acidified ethanol. Final composites were dried in the vacuum oven (50 °C) for 6 h. The melting point (T_m) was determined using a Thermal Analysis DSC 2920 differential scanning calorimeter (heating rate of 10 °C/min). The polyethylene/clay loading was determined by thermogravimetric analysis (TGA, Thermal Analysis SDT 2960, heating rate of 10 °C/min, oxygen atmosphere). A Philips CM20 200 kV transmission electron microscope (TEM) with liquid nitrogen cooling stage was used to investigate the morphology of the clay and the phase distribution in PE–clay nanocomposites. A LEO 1530 scanning electron microscope (SEM) with EDX was used to investigate the surfaces of nanocomposites.

3. Results and discussion

Fig. 1 summarizes the synthetic approach. In this first stage of intercalation, the aluminum compounds will react with hydroxyl groups within the clay galleries. After washing out the excess of the alkylaluminum compound and drying in vacuum, the clay is contacted with a vinyl alcohol (ω-undecylenylalcohol). The polar groups (hydroxyl) react with the alkyaluminum compounds on the surface of the clay galleries. This second intercalation process is designed to further enhance intercalation and the organophilic character of the inorganic clay [7]. The loading of intercalated compounds was determined using TGA.

This clay–catalyst compound acts as an effective catalyst for ethylene polymerization, as indicated in Table 1. The yield obtained is comparable to that obtained in the absence of clay (Sample 1, productivity = 843 kg_{pol}/mol_{Ni} h). It was possible to control the ratio between polyethylene and clay by varying the polymerization time or the initial clay loading. For the same initial clay and catalyst loading, increasing the polymerization time decreases the wt% of clay in the final product. For the same polymerization time, increasing the initial clay loading increases the wt% of clay in the final product. These two variables can be used to effectively control the ratio between polyethylene and clay, which is important if such system is chosen for preparing a master batch of hybrid PE–clay for subsequently blending with other polymers. The polymerization temperature also affected the wt% of clay in the final product in the range studied, most probably because decreasing the polymerization temperature decreases catalyst activity and number of branches of the polyethylene chains [13–15]. The clay wt% in the final polymer as reported in Table 1 was determined by TGA, which agrees closely with the loading calculated using the initial clay loading and the polymer yield.

The melting temperature of the final hybrid PE–clay nanocomposite was measured using DSC (Table 1). As expected, the low melting point of the homopolyethylene is attributed to short chain branches originating due the chain walking mechanism [13–15]. However, for polymerizations carried out using the intercalated catalyst at the same polymerization time, temperature and pressure, a higher melting point is obtained, since the clay surface will decrease the rate of chain walking, leading to polyethylene chains with fewer short branches. The lower melting point for sample 6 is due to the short polymerization time. Note that decreasing branching levels with increasing polymerization time has also been observed for homogeneous systems [15]. Similar behavior has been previously reported on the effect of heterogeneous ethylene polymerization with dad-$NiCl_2$ [16].

Extraction of polyethylene chains from the hybrid PE–clay product was carried out using hot solvent (trichlorobenzene and toluene) in a Soxhlet extractor for 24 h. Results on Table 1 show that only part of the polyethylene could be extracted. Homopolyethylene (sample 1) is totally extracted. Sample 7 was prepared by treating the clay with saturated alcohol instead of vinyl alcohol. Although there is no vinyl groups anchored to the surface available for copolymerization, some polymer remained unextracted. Additionally, the TGA profile of the sample after extraction indicates the presence of polyethylene after extraction. SEM images (Fig. 2) of the material after extraction and further identification of distinct silicate and polyethylene phases with EDX also corroborate to the evidence that polyethylene could not be totally removed by hot solvent extraction.

The exfoliation obtained after the in situ polymerization of ethylene was probed using TEM. Fig. 3 compares (a) SEM micrograph of Na-montmorillonite before treatment with organic modifiers, and (b) TEM micrograph of film (typical thickness of 50 nm) produced by melt pressing the nanocomposites directly on grid. The original montmorillonite phase has dimensions on the order of tens of micrometers. In the final nanocomposite, most of the silicate

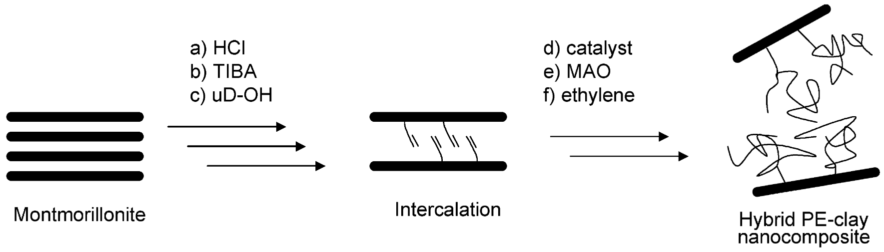

Fig. 1. Synthetic approach using bifunctional organic modifier to produce polyethylene chemically linked silicate layers prepared by in situ polymerization.

Table 1
Preparation of polyethylene–clay nanocomposites by in situ polymerization with dad-$NiCl_2$/MAO catalyst and TIBA/ω-undecylenylalcohol modifier

Sample	Polymerization					Characterization			
	Initial clay loading (mg)	Time (min)	Yield (pol + clay) (g)	Clay (wt%)[a]	Clay (wt%)[b]	Extract in toluene (wt%)	Extract in TCB (wt%)	T_m (°C)	T_D (°C)
1	0	90	1.6	0	0	100	100	114	–
2	100	30	0.4	25.0	25.2	–	74.3	107	458
3	100	90	1.6	6.25	6.3	30.0	72.4	124	461
4	200	60	1.8	11.1	9.4	29.6	76.7	123	457
5	200	60	1.0	20.0	19.1	30.6	58.7	122	461
6	50[c]	30	0.2	25.0	28.5	33.3	–	100	–
7[d]	200	60	0.92	21.7	19.0	86.7	90.2	90.2	–

Polymerization conditions: room temperature, atmospheric pressure of ethylene.

[a] Determined using the initial clay loading and final polymer yield.

[b] Determined by TGA.

[c] Polymerization temperature 0 °C.

[d] MMT/TIBA/undecanol/Ni catalyst.

is homogeneously distributed over the polyethylene matrix and the dimensions are in the order of tens of nanometers (Fig. 3b, arrow 1). The silicate layers are thin enough to produce a diffraction pattern during TEM analyses. There was, however, some indication of partial exfoliation evidenced by the presence of clusters of silicate layers (Fig. 3b, arrow 2). It can be speculated that during the film formation, the polyethylene chains chemically bonded to the surface of the exfoliated silicate drag each individual layer as the polymer flows to homogeneously distribute the silicate layers in the polyethylene matrix. If the layered silicate would not have been exfoliated during the in situ polymerization, clusters of silicate at the micrometer size range would be present after film preparation.

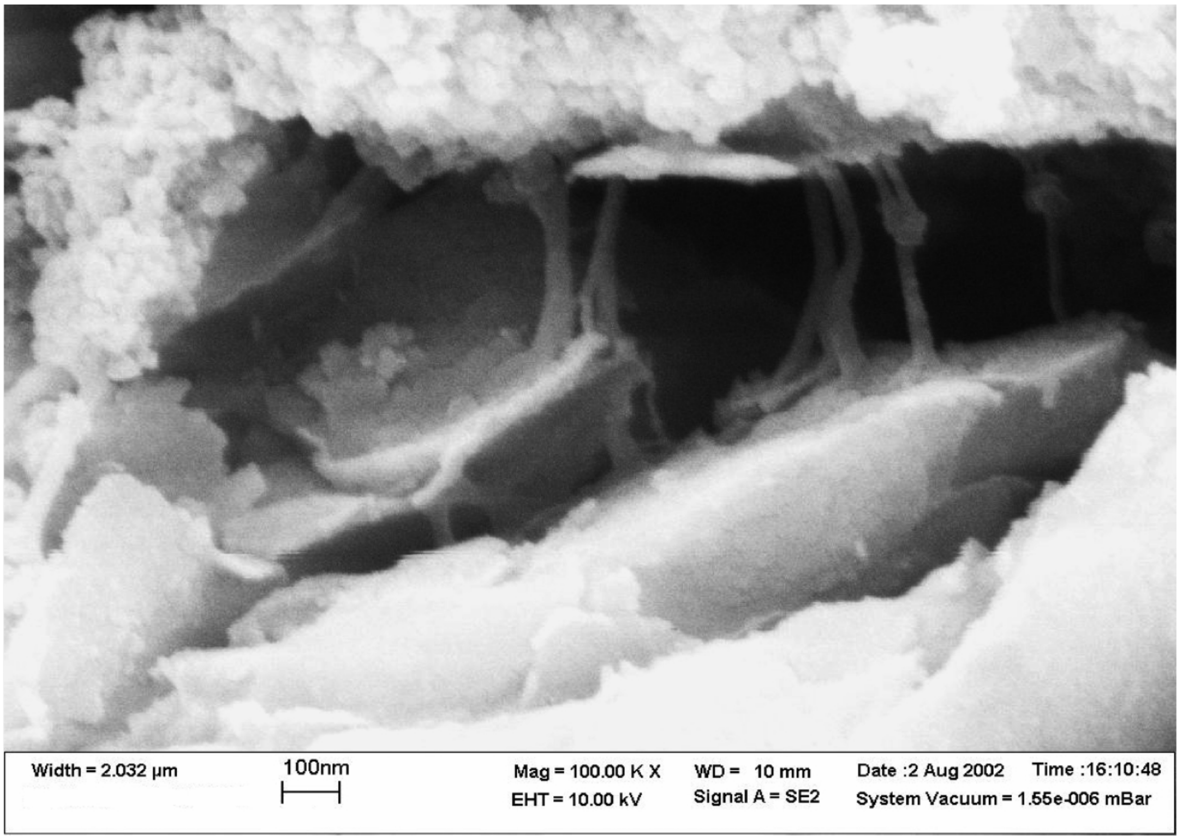

Fig. 2. SEM micrograph of nanocomposite after solvent extraction of polyethylene with boiling trichlorobenzene for 24 h.

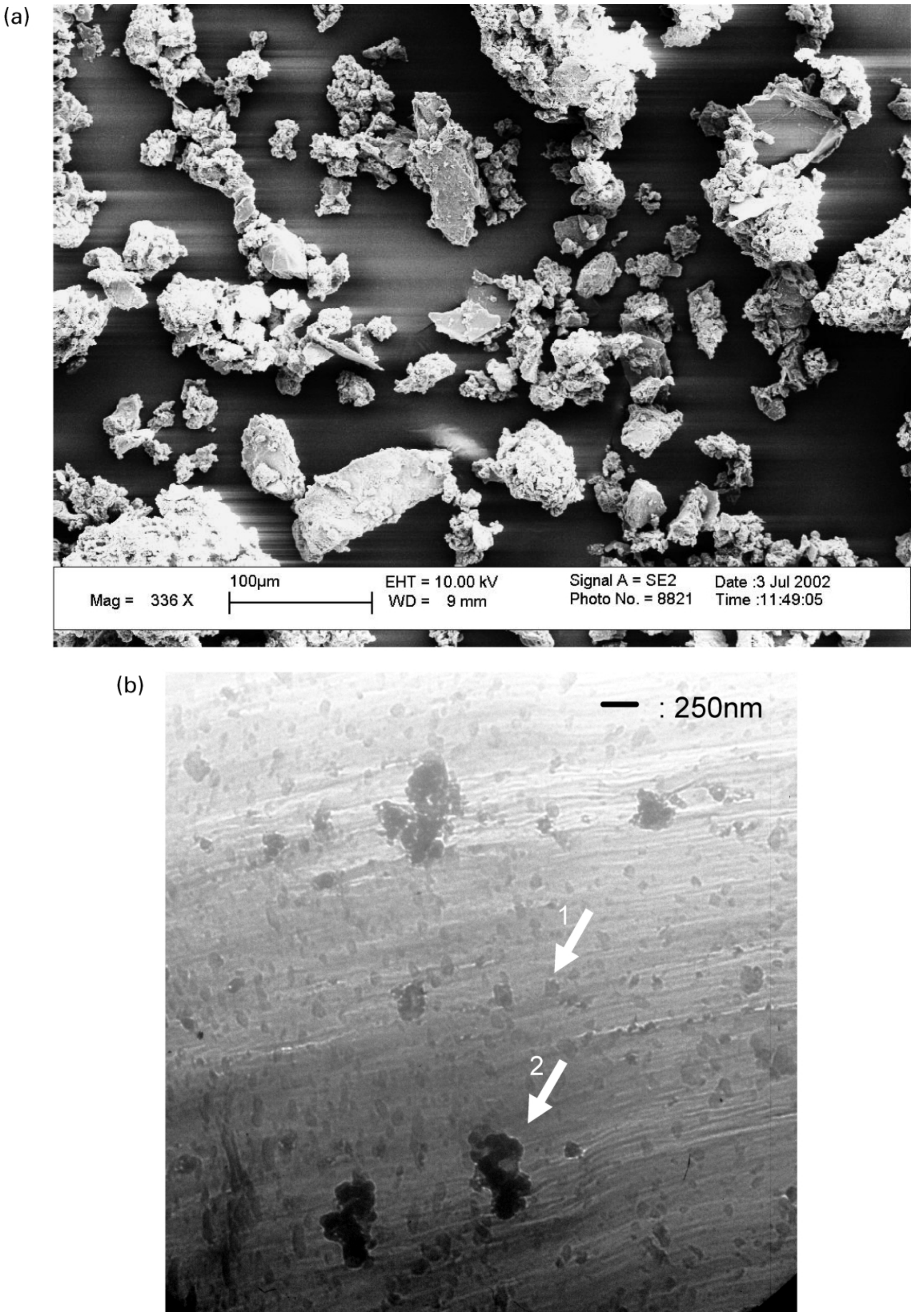

Fig. 3. (a) SEM micrograph of Na-montmorillonite as received; (b) TEM micrograph of nanocomposite film (~50 nm-thick) indicating homogeneous dispersion of individual silicate layers (1) on the polyethylene matrix and isolated clusters (2) of layers.

4. Conclusion

A PE–clay hybrid nanocomposite was prepared using in situ copolymerization with a transition metal catalyst. Montmorillonite was intercalated with triisobutylaluminum and ω-undecylenylalcohol. The intercalation process allows the transition metal catalyst and the activator methylaluminoxane to enter the clay galleries and polymerize ethylene. Formation of polyethylene inside the galleries leads to the exfoliation of the layered silicate. Two types of polymerization are possible: (a) the homopolymerization of ethylene, and (b) the copolymerization of ethylene and the vinyl ends of alcohol modifier connected to the surface during intercalation. The second process produces polyethylene chains chemically connected to the silicate surface.

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