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Synthesis and characterization of maleated polyethylene/clay nanocomposites

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Abstract

Maleic anhydride grafted polyethylene (maleated polyethylene)/clay nanocomposites were prepared by simple melt compounding. The exfoliation and intercalation behaviors depended on the hydrophilicity of polyethylene grafted with maleic anhydride and the chain length of organic modifier in the clay. When the number of methylene groups in alkylamine (organic modifier) was larger than 16, the exfoliated nanocomposite was obtained, and the maleic anhydride grafting level was higher than about 0.1 wt% for the exfoliated nanocomposite with the clay modified with dimethyl dihydrogenated tallow ammonium ion or octadecylammonium ion. The pure LLDPE showed only the intercalation, which does not depend on the initial spacing between clay layers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Nanocomposite; Melt compounding

1. Introduction

Polymer nanocomposites are a class of hybrid materials composed of organic polymer matrix in which inorganic particles with nanoscale dimension are imbedded [1–6]. At this scale, the inorganic fillers improve dramatically the physical and mechanical macroscopic properties of polymer even though their amount is small. The polymer nanocomposite exhibits higher heat distortion temperatures, enhanced flame resistance, increased modulus, better barrier properties and decreased thermal expansion coefficient [7–8]. The enhanced properties are presumably due to the synergistic effects of nanoscale structure and interaction of fillers with polymer. Because of many advantages of the nanocomposites, polymer/clay nanocomposites have been intensely investigated [9].

Polyethylene is one of the most widely used polyolefin polymers. Since it does not include any polar group in its backbone, it is thought that the homogeneous dispersion of the clay minerals in polyethylene is not realized. In general, the clay is modified with alkylammonium to facilitate its interaction with a polymer because the alkylammonium make the hydrophilic clay surface organophilic. However, the organically modified clay does not disperse well in the nonpolar polypropylene or polyethylene since such nonpolar polymers are still too hydrophobic [10–12]. Jeon and coworkers reported the intercalated morphology of HDPE nanocomposites prepared by blending HDPE with sodium montmorillonite cation-exchanged with protonated dodecylamine in solution [10]. However, the presence of fairly large stacks indicated poor dispersion. Only when in situ polymerization was performed, polyethylene/clay nanocomposite showed exfoliated morphology [12–14].

Initial attempts to create the nonpolar polymer/clay nanocomposites by simple melt mixing were based on the introduction of a modified oligomer to mediate the polarity between the clay surface and polymer [15–23]. One of the typical examples is polypropylene/clay nanocomposite system given by Toyota. They used polypropylene oligomer modified with about 10 wt% of maleic anhydride (MA) as compatibilizer and clays exchanged with stearylammonium cation to obtain exfoliated or semiexfoliated clay morphology [17,18,21–23]. In the nanocomposite system with three components, it was pointed out that the miscibility between maleated oligomer and matrix polymer played a key role in composite properties.

Various aspects of polymer/organoclay hybrids obtained by melt intercalation have been investigated in recent years: interlayer structure of modified clays [24], structural evolution during the intercalation [25], mobility of intercalated polymer chains described by both the glass transition behavior [26,27]. The effects of factors such as the length and number of alkyl groups of cationic modifier molecule and the polarity of matrix polymer on the intercalation behavior were also investigated [28]. Some attempts to

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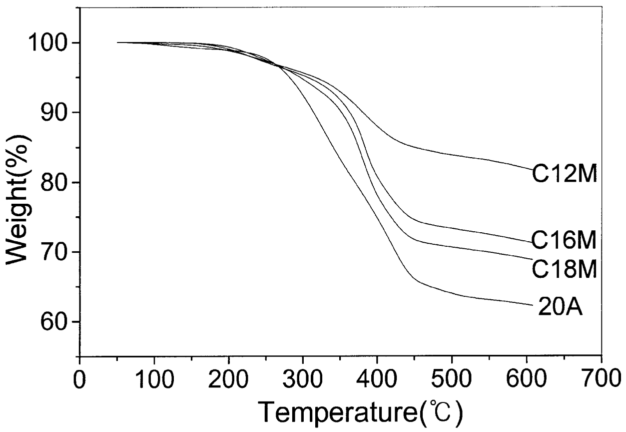

Fig. 1. TGA curve of organophilic clay.

predict the phase diagram and structural characteristics of nanocomposites were performed using thermodynamics based on the lattice model [29], the Onsager based approach [30], the self-consistent field (SCF) theory [31,32] and the molecular simulation method [33–35]. It has been reported that the intercalation of organoclay by polystyrene (PS) takes place in very short time and the equilibrium gallery height is independent of molecular weight of PS, even though the intercalation rate is slower when the molecular weight is higher [27,28].

The equilibrium structure of polymer/layered silicate nanocomposites, in particular with organically modified layered silicates, have been shown to be a strong function of the nature of a polymer (polar or apolar), the charge density of a layered silicate, as well as the chain length and structure of a cationic surfactant.

Balazs et al. have considered the SFC in order to investigate the factors promoting the penetration of polymers into layered silicates [31,36]. They first varied properties related to the nature of tethered surfactant chains. They found out that an increase in the surfactant length (approaching the length of the polymer chains) improved the layers separation by allowing the polymer to adopt more conformational degrees of freedom. On the contrary, increase in the length of polymer chains tends to render the interlayer mixture immiscible. They also reported the effect of the surfactant density on the intercalation process, showing that excessive density of tethered alkyl chains could impede the formation of intercalated structures.

In this study, we investigate the effect of alkylammonium modifier to clay (montmorillonite) and the maleic anhydride (MA) grafted level of polyethylene on morphology of maleated polyethylene/clay nanocomposite prepared by simple melt compounding. The alkylammonium chain length may change the degree of interaction between clay and polyethylene. We also report the intercalation behavior of pure polyethylene, which is not modified with MA, into organically modified montmorillonite.

2. Experimental

2.1. Materials

'Kunipia F' supplied by Kunimine Ind. Co. was a Na + type montmorillonite, with a cation exchange capacity of 119 meq/100 g. Dodecyl, hexadecyl and octadecylamine purchased from Aldrich were used as organic modifier of MMT. Maleic anhydride (MA) and dicumylperoxide (DCP) were used as the modifier of polyethylene and a radical initiator, respectively.

The modified montmorillonite (Closite 20A, abbreviation: 20A) supplied by Southern Clay Products was used, which was ion-exchanged with dimethyl dihydrogenated tallow ammonium ions. (Tallow was composed predominantly of octadecyl chains with smaller amount of lower homologues. The approximate composition was C_{18} 65%, C_{16} 30% and C_{14} 5%.)

Maleic anhydride modified polyethylene (PEMA, 0.85 wt% maleic anhydride grafted, Aldrich) and linear low density polyethylene (LLDPE) from HanWha Chemical Co. were used. All chemicals were used without further purification.

2.2. Preparation of organically modified MMT

Organophilic MMT was prepared using various alkyl ammonium salts according to the reported methods [4,22]. For example, the modification of montmorillonite by octadecylamine was carried out as follows. Sodium montmorillonite (80 g; 119 meq/100 g cation exchange capacity) was dispersed into 5000 ml of hot water (80°C) with continuous stirring. Octadecylamine (31.1 g, 115 mmol) and conc. hydrochloric acid (11.5 ml) were dissolved into 2000 ml of hot water (80°C). It was poured into the hot montmorillonite–water solution under vigorous stirring for 5 min to yield a white precipitate. The precipitate was collected on a cloth filter, washed three times with 2500 ml of hot water (80°C), and freeze-dried to yield a modified MMT with octadecylammonium. This organically modified MMT was termed C18M. The modifications of MMT with hexadecylamine and dodecylamine were similar to the case of octadecylamine except that 71.7 g of hexadecylamine and 55 g of dodecylamine were used instead of 80 g of octadecylamine. The modified MMTs with hexadecylamine and dodecylamine were named as C16M and C12M, respectively.

2.3. Preparation of PEMA/clay nanocomposites and maleic anhydride grafted polyethylene by reactive extrusion

Several types of nanocomposites with different compositions of the organically modified clays and maleated polyethylene were prepared by melt compounding at 140°C, using Brabender mixer with the chamber size of 50 cm^3. Screw speed was 60 rpm and the mixing time was 20 min for all the cases.

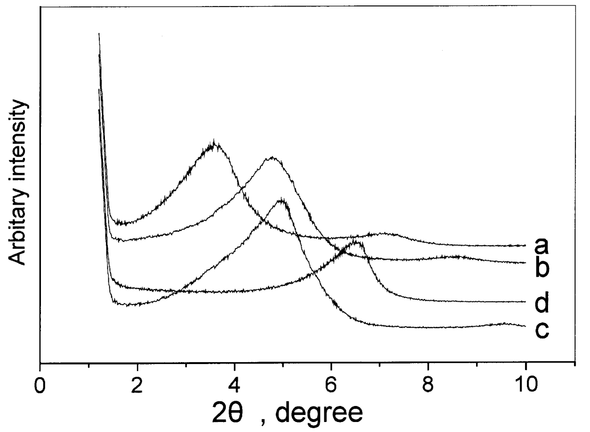

Fig. 2. XRD patterns of organophilic clays: (a) 20A, (b) C18M, (c) C16M, (d) C12M.

We prepared two types of maleated polyethylenes (maleated PE) in twin screw extruder (Gottfert Corp., screw diameter: 19 mm) at a constant rotating speed of 30 rpm and the barrel ($L/D = 25$) temperature profile of 150°–220°C. The first type of maleated PEs was termed Reac-PE-*g*-MA. It was prepared by direct extrusion of MA, LLDPE and peroxide. The second type, PEMA–LLDPE, was prepared by melt blending with PEMA (Aldrich, 0.85 wt% MA grafted) and pure LLDPE. The reaction mixtures were premixed in a Henschel mixer before they were fed into the extruder.

2.4. Measurements

X-ray diffraction (XRD) was carried out by using Rigaku X-ray generator (Cu Kα radiation with $\lambda = 0.15406$ nm) at room temperature. The diffractograms were scanned in 2θ ranges from 1.2 to 10° at a rate of 2°/min. Transmission electron microscope, Pillips CM20, was used to observe the dispersibility of the clay in hybrids using an acceleration voltage of 120 kV. An ultrathin section of 70 nm in thickness was prepared by an ultramicrotome Leica EM FCS. Thermogravimetric analyzer (TGA) was used to observe the exchanged amount of alkylammonium to Na–MMT. Elemental analysis (EA) and FT-IR were used to measure the maleic anhydride (MA) grafting level to polyethylene prepared by melt extrusion. Elemental analysis was performed by CE EA-1110 Elemental Analyzer. The

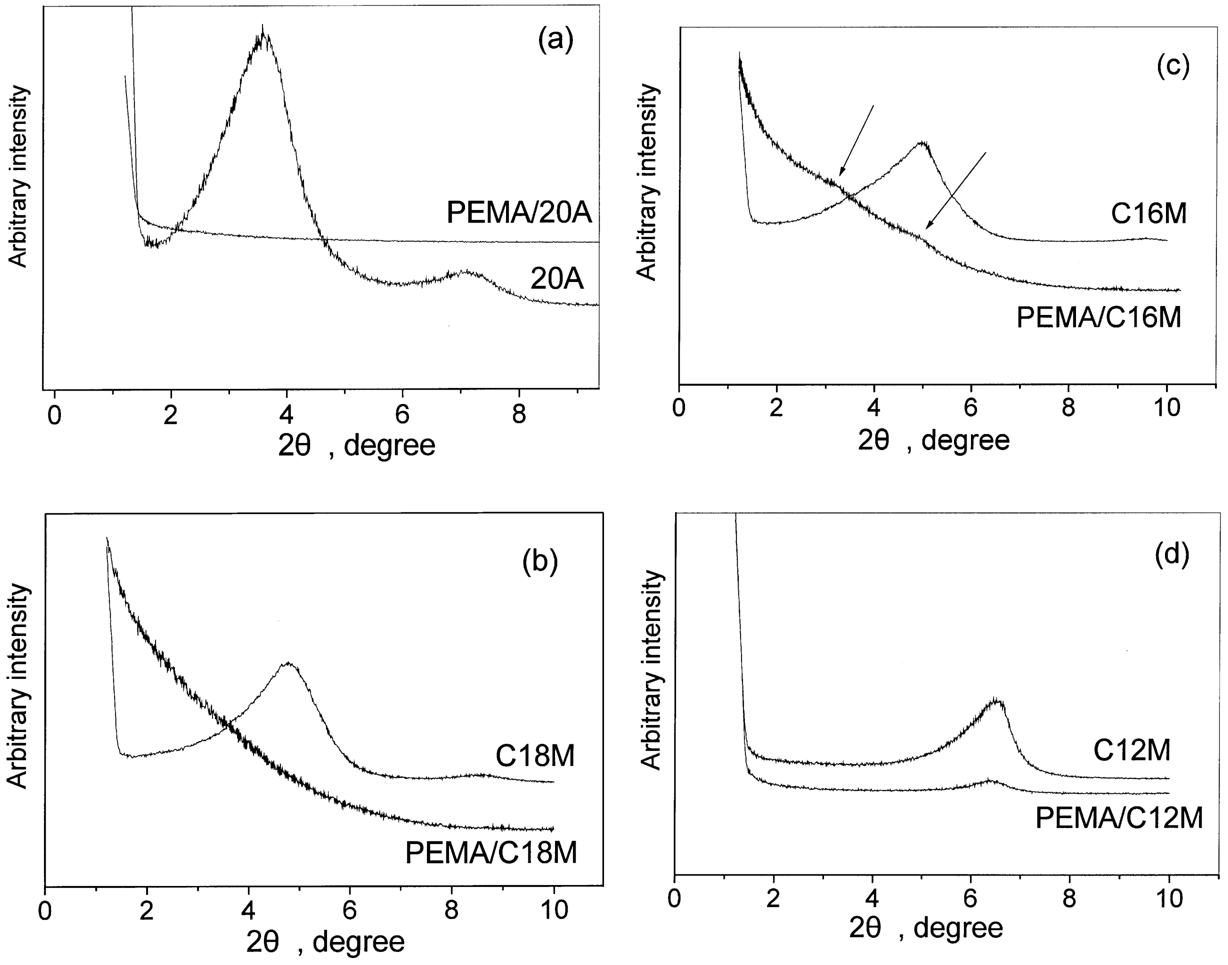

Fig. 3. XRD patterns of hybrids with PEMA and various organoclays (5 wt%): (a) 20A system, (b) C18M system, (c) C16M system, (d) C12M system.

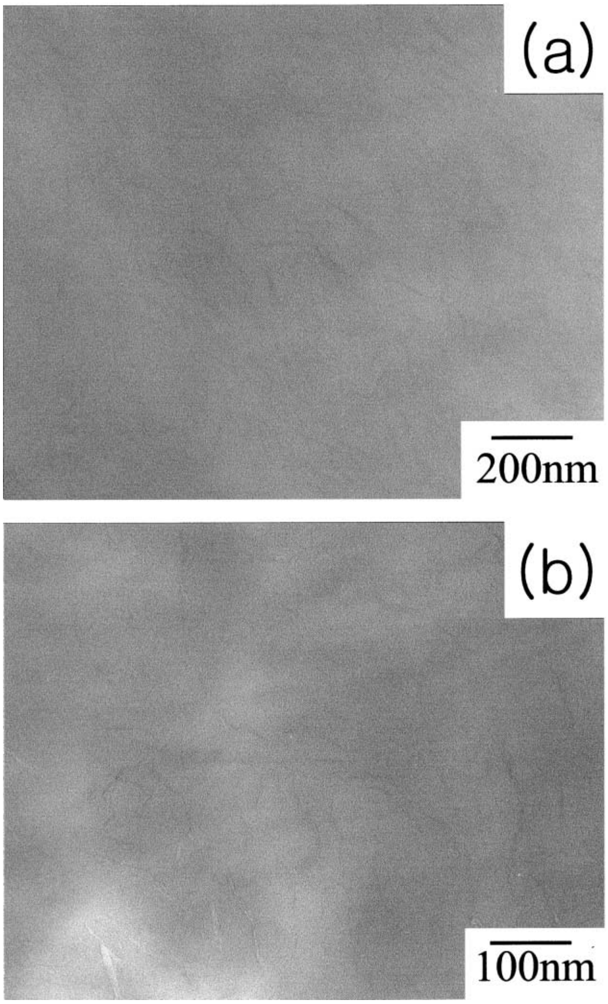

Fig. 4. (a) TEM of hybrid with 20A 5 wt%, (b) TEM of hybrid with C18M 5 wt%.

FT-IR spectra were recorded on a Bomen-MB-100 FT-IR spectrometer with a 4 cm^{-1} resolution. Molecular weight of polyethylene was measured by Gel Permeation Chromatography (GPC, Waters 150 CV) using Shodex linear HT800 column and 1,2,4-trichlorobenzene as eluent.

3. Results and discussion

3.1. Preparation of alkylamine modified MMT

The hydrophilic Na–montmorillonite (MMT) surface layers were modified by dispersing MMT uniformly into an organic modifier solution. As a result, the surface of the MMT had a hydrophobic character [37,38]. The hydrophobic organic modifier can facilitate the intercalation of a hydrophobic polymer into MMT by reducing the surface energy.

To investigate the effect of organic modifier on the morphology of polyethylene/clay nanocomposite, we prepared organoclays such as C12M, C16M and C18M with different alkylammonium chain lengths [4,22]. Also, an organophilic clay, 20A, had two long alkyl chains. Fig. 1 shows the thermo-gravimetric analysis (TGA) of modified clays. The TGA pattern of clays indicates that the clays are well ion exchanged with alkyl amines because the clay with the shorter chain length shows the smaller reduction in weight. Fig. 2 shows the X-ray diffraction patterns of organophilic clays. The interlayer distance is determined by the diffraction peak in the X-ray method, using the Bragg equation:

$$2d_{001}\sin\theta = \lambda$$

where d_{001} is the interplanar distance of (001) diffraction face, θ is the diffraction position and λ is the wavelength. The X-ray pattern shows clearly that the interlayer spacing increases with the increase in size of alkylamine chain length. The interlayer spacings of C12M, C16M, C18M and 20A are 1.36, 1.79, 1.85 and 2.47 nm, respectively. These spacings suggest the successful modification of MMT because the longer the chain length of the modifier becomes the larger the interlayer spacing.

3.2. Preparation of PEMA/clay nanocomposites by melt compounding

We prepared PEMA/clay nanocomposites by melt compounding and investigated the effect of organic modifier on the intercalation behavior of polymer. The MA grafting level of PEMA was 0.85 wt%. Fig. 3 shows the XRD curve of hybrids with PEMA and various modified MMTs. No basal peak reflections are shown for the hybrids with 20A and C18M in Fig. 3 (a) and (b) in the region from $2\theta = 2$ to 10°. This fact reveals that clays in both systems are exfoliated and dispersed homogeneously in the maleated polyethylene matrix. In order to confirm the nanoscale dispersion of clay, the morphology of hybrids with clay weight fraction of 5 wt% was observed by transmission electron microscopy (TEM). In Fig. 4 (a) and (b), the dark lines are the silicate layers. Each layer of clay is disordered and dispersed homogeneously in the PEMA. It is consistent with the absence of (001) plane peak in Fig. 3(a) and (b) due to very large interlayer spacing and the disordered state of silicate layer.

However, in the hybrid with C16M (Fig. 3 (c)), there is a weak peak at a lower angle ($2\theta = 3.2°$) than the basal reflection peak position of C16M ($2\theta = 4.9°$) and there is also a weak peak at the same angle of the modified clay. This indicates that some parts of C16M are intercalated by PEMA but some parts of C16M are not intercalated. Fig. 3(d) indicates that the peak position of original C12M ($2\theta = 6.5°$) is not changed and C12M is not intercalated by the maleated polyethylene. Apparently, a macrophase separation texture was observed (even though TEM is not shown here). It can be concluded that the hybrid with C12M is like a conventional composite.

From these results, it is found that the alkylammonium

Table 1
Grafted MA ratio (wt%) in Reac-PE-*g*-MA prepared by reactive extrusion using twin extruder

Blend ratio before reactive extrusion		Grafted MA wt% in Reac-PE-*g*-MA
LLDPE (wt%)	MA (wt%)	
99.9	0.1	0.068
99.8	0.2	0.11
99.7	0.3	0.22
99.6	0.4	0.29
99.5	0.5	0.33

chain length, i.e. hydrophobicity of organic modifier is an important factor to determine the morphology of PEMA/clay nanocomposite. Exfoliated or intercalated PEMA/clay nanocomposite can be obtained when the number of methylene units in alkylammonium chain is larger than 16.

3.3. Preparation of maleated PE/clay nanocomposite by melt compounding

In addition to the chain length of an organic modifier, the MA grafting level of PE may also be important to the morphology of polyethylene/clay nanocomposite. We prepared the maleated PE with a different MA grafting level by two methods as mentioned in Section 2: the reactive extrusion of LLDPE, MA and peroxide, and the melt blending of PEMA and LLDPE. In order to measure the content of MA grafted on LLDPE, the samples obtained after grafting reaction were pre-dried to remove the unreacted MA monomers in a vacuum oven at 60°C for 5 h. The dried samples were dissolved in xylene at a concentration of 2 wt%. This solution was mixed with acetone and the precipitate was filtered and dried again in a vacuum oven at 60°C for 24 h. The percentage of MA grafted on LLDPE was determined by elemental analysis (EA) and FT-IR spectra. The measured grafted levels of various types of the maleated PE were summarized in Tables 1 and 2.

Table 2
Grafted MA ratio (wt%) in PEMA–LLDPE prepared by melt blend using single extruder (Aldrich PEMA: 0.85 wt% MA grafted, $M_w = 126\,000$ by GPC)

Blend ratio before melt blend		Grafted MA wt% in PEMA–LLDPE
LLDPE (wt%)	PEMA[a] (wt%)	
100	0	0
95	5	0.04
90	10	0.09
80	20	0.17
70	30	0.26
50	50	0.43
0	100	0.85

[a] LLDPE:5MI, 0.930 density, $M_w = 129\,000$ by GPC.

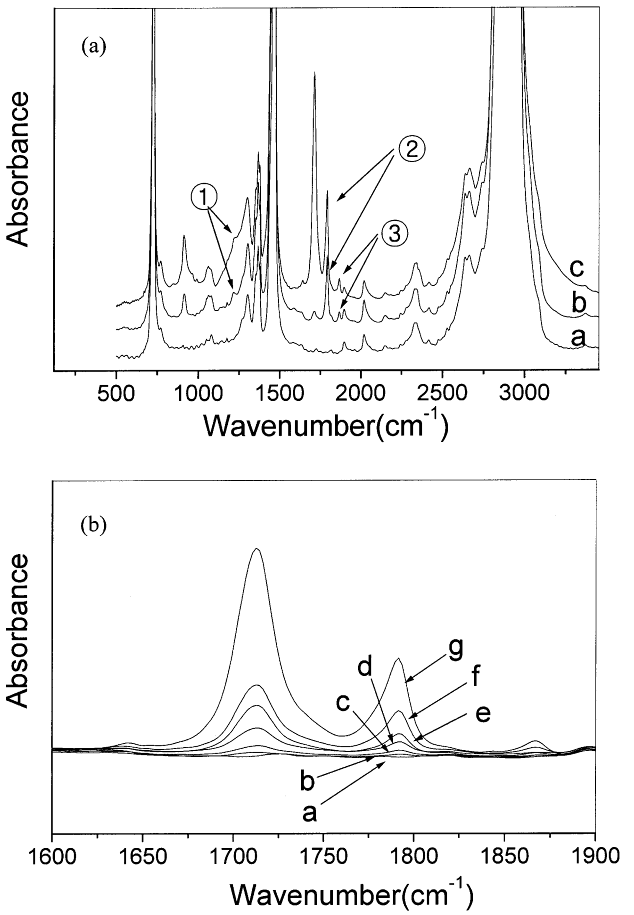

Fig. 5. (a) FT-IR curve of Reac-PE-*g*-MA obtained by reactive extrusion: a: pure LLDPE, b: MA contents: 0.33%, c: PEMA, (1) 1218 cm^{-1}, (2) 1791 cm^{-1}, (3) 1866 cm^{-1}; (b) FT-IR curve of PEMA–LLDPE obtained by melt blending of PEMA and LLDPE: MA contents; a: 0% (pure LLDPE), b: 0.04%, c: 0.09%, d: 0.17%, e: 0.26%, f: 0.43%, g: 0.85%.

Fig. 5(a) shows the FT-IR spectra of LLDPE, PEMA and maleated PE obtained by reactive extrusion. It is found that new peaks appear at 1218, 1791 and 1866 cm^{-1} in Reac-PE-*g*-MA when compared to the pure LLDPE. New peaks indicate that MA has been successfully grafted onto polyethylene chains [39,40]. Fig. 5(b) shows the increase of peak height at 1791 cm^{-1} with the increase of PEMA content. This peak increase is consistent with MA weight percentage, so the MA grafting level was measured from the intensity of 1791 cm^{-1}, and the thickness variation of each sample was corrected by 2019 cm^{-1} intensity for internal reference peak [41].

Maleated PE/clay nanocomposites are synthesized and the effect of grafting level of MA on their morphology is investigated. The contents of organically modified montmorillonite clay are fixed at 5 wt% in all hybrids. Fig. 6 shows the XRD patterns of hybrids with 20A. The original basal reflection peak of 20A disappears completely above a certain grafting level of MA, which is about 0.1 wt%. But below this critical grafting level of MA, a new basal reflection peak with very weak intensity appears

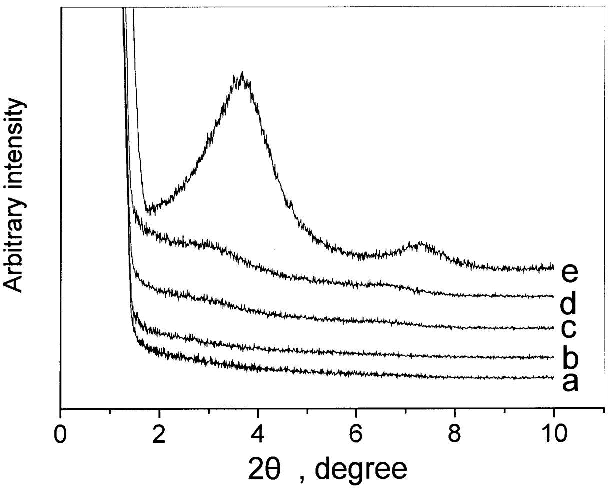

Fig. 6. XRD patterns of hybrids of 20A and Reac-PE-*g*-Mas with various MA grafting levels prepared by reactive extrusion: MA contents; (a) 0.29%, (b) 0.22%, (c) 0.11%, (d) 0.07%, (e) clay 20A only.

at lower angle than the peak of 20A and indicates the intercalation of some Reac-PE-*g*-MA into the clay layers.

Fig. 7 shows no distinct peak of clay C18M for all hybrids above 0.1 wt% of MA grafting level. This critical grafting level of MA is almost the same as the hybrid of Reac-PE-*g*-MA and 20A. In Fig. 8, the hybrids with C16M shows a weak peak at the same position of the original clay peak regardless of the grafting level. This indicates that most of clay is not dispersed into the matrix.

The hydrophobicity of the organically modified montmorillonite increases as the carbon number of organic modifier increases. On the other hand, the hydrophilicity of polyethylene increases as the grafting level of MA in polyethylene. This result suggests that in order to obtain good dispersion of clay in matrix, the polyethylene should have a certain grafting level of MA in matrix.

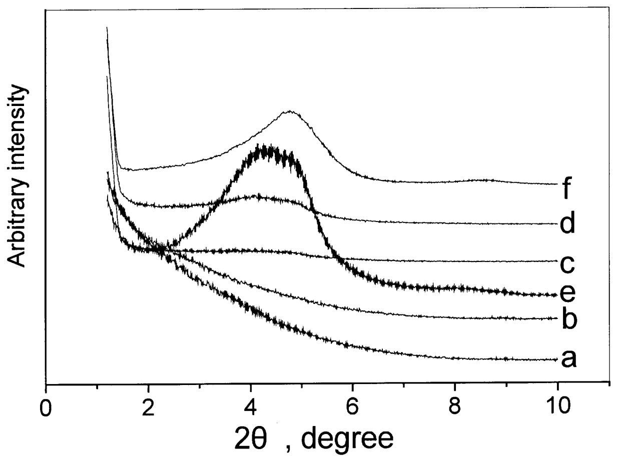

Fig. 7. XRD patterns for hybrids of C18M and PEMA–LLDPEs with various MA grafting levels prepared by melt blending: MA contents; (a) 0.85%, (b) 0.17%, (c) 0.09%, (d) 0.04%, (e) 0% (pure LLDPE), (f) C18M only.

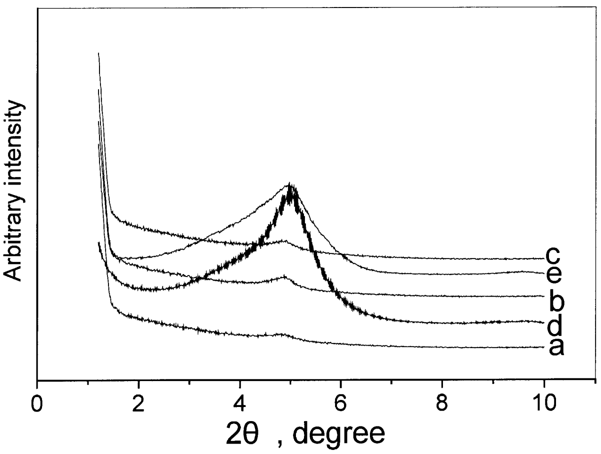

Fig. 8. XRD patterns for hybrids of C16M and Reac-PE-*g*-Mas with various MA grafting levels prepared by reactive extrusion: MA contents; (a) 0.33%, (b) 0.29%, (c) 0.22%, (d) 0% (pure LLDPE), (e) C16M only.

3.4. Intercalation behavior of pure LLDPE

The hybrid of pure LLDPE with C16M shows a clear peak at the same position as that of C16M in the XRD pattern (d curve in Fig. 8). This indicates no intercalation of LLDPE into C16M. On the other hands, the hybrids with 20A and C18M show peaks shifted toward lower angles than those of the clays (Figs. 7 and 9). This clearly indicates the strong intercalation of polymers. Therefore a proper modification of Na–MMT with dimethyl-dehydrogenated tallow (20A) and octadecylamine (C18M) may give an intercalated morphology in the pure LLDPE without grafting of maleic anhydride. Fig. 9 shows the intercalation

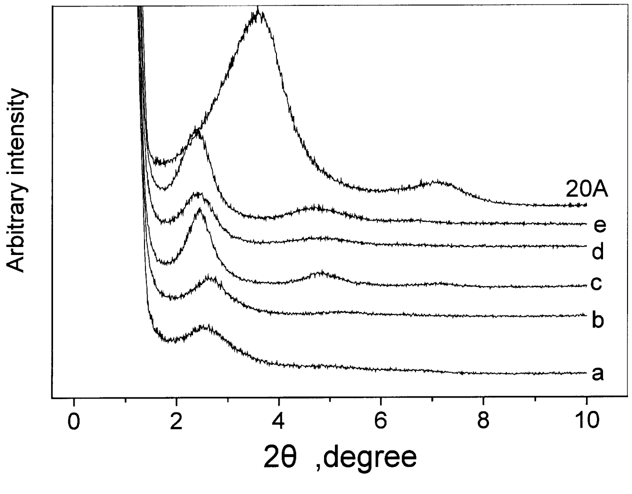

Fig. 9. XRD patterns for hybrids of pure LLDPE with various molecular weights and 20A: M_w of LLDPE by GPC; (a) 15 000, (b) 53 000, (c) 103 000, (d) 129 000, (e) 180 000.

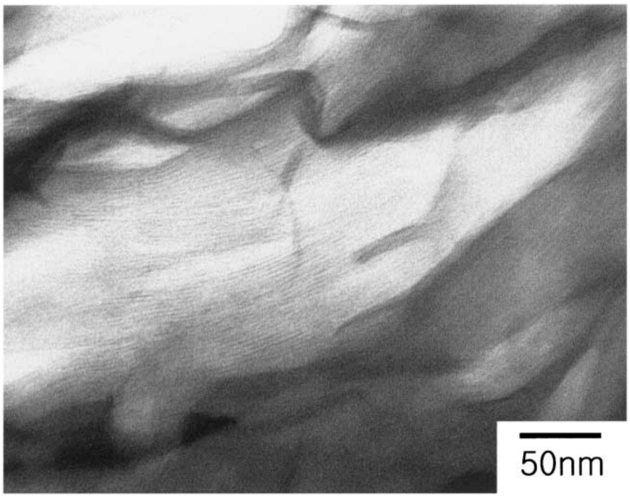

Fig. 10. TEM of hybrid with LLDPE (M_w: 129 000) and 5 wt% of 20A.

behaviors of LLDPE with various molecular weights into 20A (5 wt%). The molecular weight of LLDPE does not significantly affect the morphology of the LLDPE/20A nanocomposite. Hence, it is hard to increase the interlayer spacing of clay by controlling the molecular weight of polyethylene. In order to confirm the dispersibility of 20A clay in pure LLDPE matrix, TEM was used as shown in Fig. 10. The interlayer spacing of clay is about 4 nm, which is almost coincident value expected by XRD peak (Fig. 9). It is realized that polyethylene nanocompoiste can be obtained by only proper modification of clay without modification of polyethylene and can be applied to many application areas with low fabrication cost.

This intercalation behavior of pure LLDPE may be originated from the initially higher interlayer spacing and the more compatible characteristics of the modifiers, 20A and C18M, with LLDPE than that of hexadecyl amine modifier, C16M.

In order to investigate the effect of interlayer spacing of modified clay, Na–MMT was modified with excess octadecyl amine. This new organophilic montmorillonite, C18M(2), has higher interlayer spacing (3.27 nm) than 1.85 nm of C18M used in the experiment (Fig. 11). But in the LLDPE/C18M(2) hybrid, the octadecylamines came out of the layers and the enlarged spacing between layers becomes narrower. This indicates that the intercalation capability has a certain limit. That is, it does not depend on the initial spacing but it seems to be affected by the thermodynamical equilibrium state of the hydrophilicity of clay surface, the hydrophobicity of a modifier and LLDPE.

4. Conclusion

It is quite reasonable to say that the hydrophobicity of the organically modified clay and the hydrophilicity of maleated polyethylene are very important factors to achieve the exfoliated and homogeneously dispersed clay nanocomposites.

When polyethylene has a higher grafting level of MA than the critical grafting level of MA (0.1 wt%) and the number of methylene groups in alkylamine chain has more than 16, polyethylene/clay nanocomposites are completely exfoliated. In the hybrids with pure LLDPE, the intercalation capability depends on the thermodynamical equilibrium state at the clay surface rather than the initial interlayer spacing of organophilic clay.

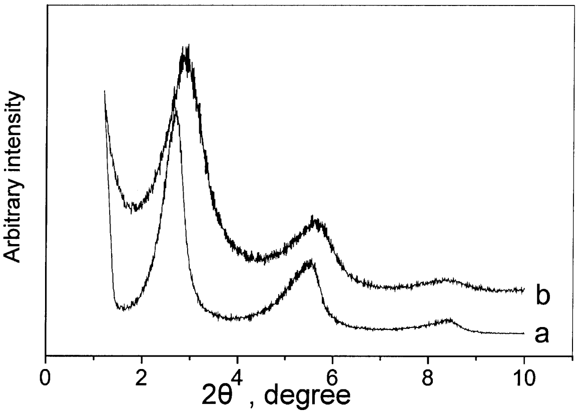

Fig. 11. XRD pattern of hybrid with increased interlayer C18M clay: (a) increased interlayer C18M (C18M(2)), (b) hybrid with pure LLDPE (M_w:129 000) and C18M(2).

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