

Preparation and Properties of Unsaturated Polyester–Montmorillonite Intercalated Hybrid

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ABSTRACT: An unsaturated polyester–organophilic montmorillonite hybrid was prepared by dispersing polymerizable quaternary ammonium-modified montmorillonite in an unsaturated polyester resin, followed by cross-linking reaction. The purpose of this investigation was to discover the role of the polymerizable group of quaternary ammonium in improving interfacial interaction between the silicate layers and polymer chains and the mechanical properties of unsaturated polyester–montmorillonite hybrids. It is found that when the content of organophilic montmorillonite is between 2 and 5%, the tensile strength, impact strength, heat resistance, and swelling resistance of the hy-

brid are obviously enhanced and are better than that of the composites prepared with pristine or nonpolymerizable quaternary ammonium-modified montmorillonite. Results of X-ray diffraction and transmission electron microscopy show that unsaturated polyester and styrene in the resin can be intercalated into the interlayer space of organophilic montmorillonites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2038–2044, 2004

Key words: organoclay; thermosets; polyesters; curing of polymers; nanocomposites

INTRODUCTION

The concept of polymer-layered silicate nanocomposite was first introduced by Kojima and colleagues¹, who discovered the possibility of obtaining a nanocomposite from polyamide-6 and an organophilic clay. It was reported that the tensile strength and heat distortion temperature of the nanocomposite of nylon-6 with only 4.2% of organophilic montmorillonite is 0.5 times and 95°C higher than that of original nylon-6, respectively, but its impact strength does not decrease obviously. Due to their low density, excellent mechanical properties, and outstanding diffusional barrier properties, a lot of nanocomposites based on other thermoplastic polymers, such as poly(1-caprolactone),² poly(ethylene oxide),³ polystyrene,⁴ polypropylene,⁵ poly(ethylene terephthalate),⁶ polyurethane,⁷ polyacrylate,⁸ poly(methyl methacrylate),⁹ and poly(styrene/maleic anhydride)¹⁰ have been investigated. Recently, investigations on the nanocomposites prepared from thermoset polymers, such as epoxy resin,^{11–15} unsaturated polyester,^{16–18} silicone rubber,^{19,20} and polyimide,²¹ have drawn great interest. The research results of Pinnavaia's group¹¹ showed that the tensile strength and modulus of the nanocomposite of epoxide resin with 7.5% of organophilic montmorillonite increase by 10

times. Those materials were produced either by melt intercalation of thermoplastics or *in situ* polymerization of intercalated monomers or by cross-linking (curing) of intercalated oligomers.

Unsaturated polyester resins (UPR) have been widely used in many fields such as fiber-reinforced composites²² and coatings, but its cured products are generally rigid and brittle. In past decades the toughening of UPR have attracted great attention. The conventional toughening routines of UPR involve¹ adjusting the molecular structure of UPR,² filling with inorganic fillers,³ reinforcing with strengthening materials,⁴ and toughening with toughening agents. If the type of UPR, inorganic filler, and reinforcing material are fixed for a desired composite, the toughening with toughening agents is very important. The usual toughening agents are thermoplastics, elastomers, and liquid oligomers with reactive end groups. When the above toughening agents are introduced, the impact strength of UPR composite increases, but the tensile strength, flexural strength, and heat distortion temperature decrease obviously. Recently, Giannelis and colleagues^{16,17} reported that unsaturated polyester resin can be intercalated into the galleries of layers of montmorillonite modified by *p*-vinyl aniline hydrochloride, but there was no report on its mechanical properties. Park and co-workers¹⁸ also investigated the formation mechanism and properties of organic modifier-treated silicate–UPR (MMT-D) nanocomposites prepared by two different mixing methods. The modifiers used are dodecyl ammonium bromide and dimethyl dihydrogenated tallow ammonium, respectively.

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In the present study we focus on how the polymerizable group of alkylammonium ions influences the structure and properties of the resulting nanocomposites of unsaturated polyester. It was considered that the polymerizable group of alkylammonium ions can be cocross-linked with styrene and unsaturated polyester and improve the interaction between the silicate layers and polymer matrix.^{23,24} The effects of organophilic MMTs obtained from different quaternary ammoniums on the mechanical properties and the structure of unsaturated polyester-based nanocomposites were compared. The nanostructure is characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

The polymerizable quaternary ammonium, methacryloxyethyl benzyl dimethyl ammonium chloride (MBDAC), was synthesized in our laboratory according to the method described in earlier articles.^{23,25} The molecular structure of MBDAC was confirmed by elemental analysis, FTIR, and ¹H-NMR. Cetyl trimethyl ammonium bromide (CTAB), an analytical reagent, is directly used without further purification. High-purity Na-montmorillonite used in this study, with a cation exchange capacity of 87 mmol/100 g clay, was obtained from Zhejiang Lin-an Bentonite Mine, China, and was dried at 110°C for 4 h before use. Unsaturated polyester resin, methyl ethyl ketone peroxide, and cobalt naphthenate were all industrial products, directly used without further treatment.

Intercalation modification of montmorillonite

A total of 50 g of Na-montmorillonite was dispersed into 2000 mL distilled water at 80°C. The mixture was stirred until montmorillonite formed a homogeneous gel. A solution of 0.05 mol MBDAC or CTAB in a 1:1 water/ethanol mixture was added to the mixture under 50 or 90°C, respectively, and stirred vigorously for 12 h. White precipitates formed and were isolated by filtration and washed several times with a water/EtOH (50/50) mixture until no chloride or bromide ion was detected in the filtrate by 0.1 N AgNO₃ solution. The obtained organophilic montmorillonites (MBDAC-MMT and CTAB-MMT) were dried under vacuum at 45 or 75°C, respectively, and ground with a planet ball mill and sieved; the 320-mesh fraction was collected.

The infrared spectra of MBDAC-MMT and CTAB-MMT are quite different from that of Na-montmorillonite.^{23,25} An absorption peak appears at 1720 cm⁻¹ belonging to the carbonyl group in MBDAC and the absorption peaks at 2860–2950 cm⁻¹ are assigned to the C–H stretching vibration in the infrared spectrum

of MBDAC-MMT, and there are two very strong absorption peaks at 2850 and 2924 cm⁻¹ assigned to the C–H stretching vibration in the infrared spectrum of CTAB-MMT. It was found from the X-ray diffraction curves that the interlayer distance (*d*₀₀₁) of MBDAC-MMT and CTAB-MMT is 1.47 and 1.87 nm, respectively, while that of Na-montmorillonite is 9.6 nm. The elemental analytical data showed that the contents of quaternary ammoniums in MBDAC-MMT and CTAB-MMT are 13.69 and 20.19%, respectively. According to the cation exchange capacity of Na-montmorillonite, the ion-exchange degrees of MBDAC-MMT and CTAB-MMT are 50.0 and 55.4%, respectively.

Preparation of the treated montmorillonite-UPR hybrids

Prior to curing, 100 g of unsaturated polyester resin was mixed by vigorous stirring with the desired amount of MBDAC-MMT, CTAB-MMT, or Na-MMT at 50°C for more than 24 h until the mixture was transparent. After the addition of 2 g methyl ethyl ketone peroxide and 1 g cobalt naphthenate, the mixture was further stirred severely for 5 min, out-gassed under vacuum for a short period of time, and then poured into polytetrafluoroethylene molds with dimensions of 120 × 120 × 2 and 60 × 60 × 4 mm and cured for more than 24 h at room temperature under a slight press and isolating with air. The obtained sample sheets were cut into testing specimens after a week.

Characterization and property measurement

Hardness of the samples was tested in a HD1–1875 Model Brinell-Rockwell hardness meter. The diameter of the steel ball was 5.0 mm and the load was 62.5 kg. Heat distortion temperature was obtained in a Vicat needle tester; the load was 0.46 Mpa and the heating rate is 5°C/min. DSC measurement was finished in a Perkin–Elmer DSC-2 Model differential scanning calorimeter at a scanning rate of 5°C/min under a nitrogen flow. TG measurement was finished in a Dupont 1090 thermobalance at a scanning rate of 10°C/min under air flow. The tensile and impact strength were tested in a AGS-I 10KN Shimadzu material tester and a Chappy XCJ-40 impact tester, respectively. Powder X-ray diffraction analyses were performed using a D/MAX-III A diffractometer with Cu radiation (50 kV, 40 mA). The scanning speed was 2°/min. Transmission electron micrographs were taken with a JEOL-100CXII transmission electron microscope operating at an accelerating voltage of 120 kV. TEM specimens were cut from composite blocks using an ultramicrotome. Samples with a dimension of 0.5 × 0.5 × 0.3 cm were immersed in toluene and ethyl acetate, respectively, and the swelling degree was calculated according to the increase of the weight of the samples.

TABLE I
Mechanical Properties of the Organophilic Montmorillonite–UPR Nanocomposite

Sample	Content of montmorillonite (%)	Tensile strength (MPa)	Impact strength (KJ/m ²)	Hardness (Barcol)
UPR	0	44.1	6.32	12.4
Na-MMT–UPR	4.0	47.8	4.35	13.3
CTAB–MMT–UPR	4.0	56.4	8.44	13.1
MBDAC–MMT–UPR	4.0	71.2	9.63	13.8

RESULTS AND DISCUSSION

Mechanical property of the organophilic montmorillonite–UPR hybrids

The tensile strength, impact strength, and Brinell hardness of cured unsaturated polyester (UPR) and its composites with various montmorillonites are listed in Table I. The Na-montmorillonite is difficult to disperse in UPR because of the strong aggregation of the layers; therefore, its reinforcing effect is poor. The tensile strength of UPR composite with 4% Na-MMT increases slightly, but its impact strength decreases obviously. The compatibility between the CTAB- or MB-DAC-treated montmorillonite with styrene and polyester is better than untreated montmorillonite; styrene and polyester can be intercalated into the interlayer gallery of treated montmorillonite and can be cured inside and outside the gallery. The role of the silicate layers is similar to that of the glass fiber in fiber-reinforced polyester composite. But the thickness of the layers (10–100 Å) is far smaller than the diameter of the glass fiber; therefore, good reinforcement effect and enhanced tensile and impact strength are reached when a small amount of treated montmorillonite is added. When the content of treated silicate is larger than 6%, the aggregation tendency of the silicate lay-

ers is not to be ignored; the phase dimension of the silicate becomes larger and the mechanical property decreases. The effect of the content of treated silicates on the mechanical property of the composites is shown in Figure 1.

When UPR is toughened by conventional toughening agents, such as liquid rubber or other oligomers, its tensile strength, flexural strength, and hardness decrease obviously as the impact strength is improved. When a quaternary ammonium-treated layered silicate is used, the impact strength is also enhanced slightly while the tensile strength and hardness increase obviously. This will provide a new reinforcing and toughening route for thermoset plastics. But as shown in Table I and Figure 1, the composite is still in the range of brittle plastics.

Heat distortion temperature of organophilic montmorillonite–UPR hybrids

Heat distortion temperature (HDT) is a very important index for unsaturated polyester resin in the application of casting, coating, and laminated plastics. Generally, the HDT of unsaturated polyester toughened by thermoplastics, elastomers and liquid oligomers with reactive end groups decreases obviously.

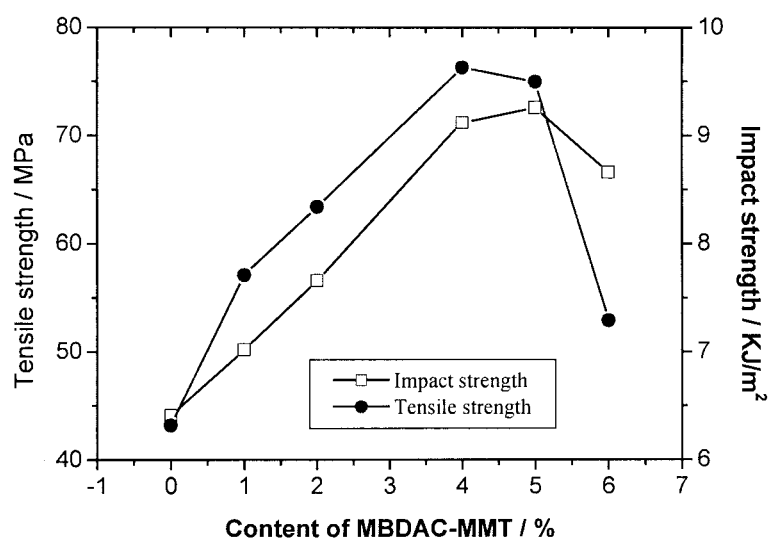


Figure 1 The effect of the content of organophilic montmorillonite on the mechanical properties of the UPR composites.

TABLE II
Heat Distortion Temperature of Organophilic Montmorillonite-UPR Intercalated Nanocomposite

Sample	Content of CTAB-MMT (%)	Heat distortion temperature (°C)
UPR	0	86.2
Na-MMT-UPR	4.0	89.8
CTAB-MMT-UPR	4.0	103.1
MBDAC-MMT-UPR	4.0	110.4

The HDT of the obtained unsaturated polyester-montmorillonite composites is shown in Table II and Figure 2. The HDT of UPR hybrid with 4% organophilic montmorillonite is much higher than that of cured UPR or the composite with Na-MMT. This may be due to the strong interaction or chemical bonding between the inorganic layers and UPR, similar to the affection of a physical or chemical cross-linking agent, respectively. When the unsaturated polyester and styrene is intercalated into the interlayer gallery of the organophilic montmorillonite, the interlayer space can be expanded or even exfoliated. When the UPR-organophilic montmorillonite hybrid is cured completely, the thermal motion of polymer chains or segments is restricted. Figure 2 shows that HDT of a UPR composite increases with the increasing content of MBDAC-MMT when it is less than 5% and doesn't increase obviously when the content is greater than 5%. But most of the unmodified montmorillonite aggregates in a form of many layers forming a domain, the polarity of the layers is much larger than that of UPR, their interaction is weak, and it plays a role of microfiller in the matrix. The effect of 4% Na-MMT on the HDT of a UPR composite is not obvious.

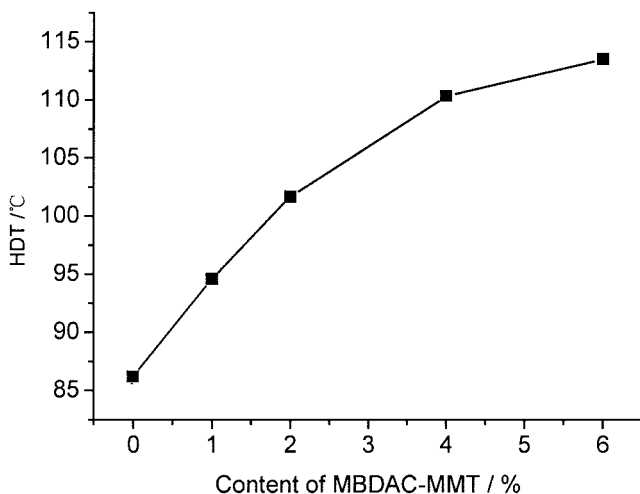


Figure 2 The effect of the content of MBDAC-MMT on the heat distortion temperature of UPR-organophilic montmorillonite intercalated nanocomposite.

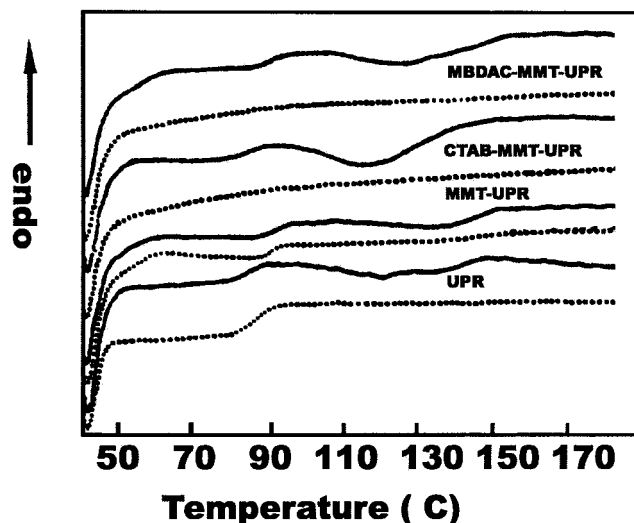


Figure 3 DSC curves of UPR and its composites with various montmorillonites (the solid curves are the first heating curves and the dotted curves are the second heating curves).

Thermal property (DSC and TG) of organophilic montmorillonite-UPR hybrids

The DSC and TGA curves are shown in Figures 3 and 4. On the first heating curves, the glass transition can be observed, the T_g is 75.6, 84.1, 82.6, and 88.2°C for UPR, Na-MMT-UPR, CTAB-MMT-UPR, and MBDAC-MMT-UPR, respectively. At higher temperature, there is an exothermic peak on the first heating curve. It maybe the second curing at a high temperature of the samples that haven't cross-linked completely at room temperature. The second curing temperature is 121.1, 134.9, 116.8, and 126.3°C for UPR, Na-MMT-UPR, CTAB-MMT-UPR, and MBDAC-MMT-UPR, respectively. It is interesting that the glass transition can still be observed at 75.5 and 85.1°C on the second heating curves of UPR and Na-MMT-UPR, but it doesn't appear on the second heating curves of

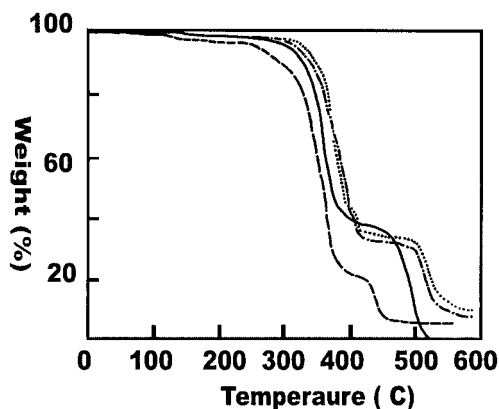


Figure 4 TGA curves of UPR and its composites with various montmorillonites (—, UPR; —, Na-MMT-UPR; —●—, CTAB-MMT-UPR; ···, MBDAC-MMT-UPR).

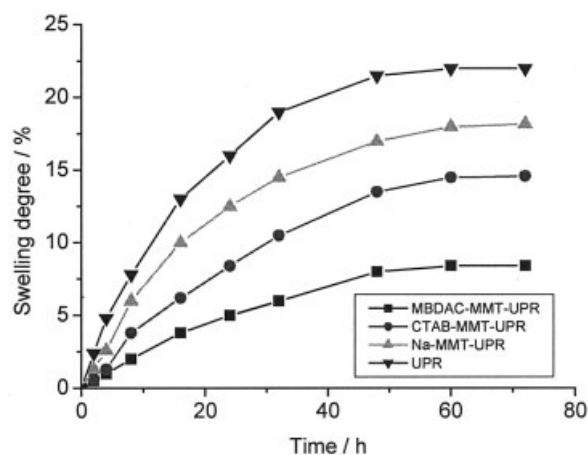


Figure 5 The dependence of the swelling degree of UPR and MMTs-UPR hybrids in ethyl acetate on swelling time.

CTAB-MMT-UPR and MBDAC-MMT-UPR. This indicates that polyester and styrene can be intercalated into the interlayer gallery of CTAB-MMT-UPR and MBDAC-MMT-UPR and there is strong intermolecular interaction or covalent bond between inorganic layers and unsaturated polyester. CTAB-MMT can act as a physical cross-linking agent in the reaction system. MBDAC-MMT is similar to a multi-functional cross-linking agent. When the composites are further cured at high temperature, the thermal motion of the polymer chains and segments is greatly restricted and the glass transition can't be observed again. The result of TGA also indicates the improving of the thermal stability of a polymer that is confined in an interlayer space of organophilic silicate. The weight loss at 243–407°C is due to the decomposition of UPR; the temperature at maximum weight loss for UPR is 357°C. The temperature at starting weight loss of CTAB-MMT-UPR and MBDAC-MMT-UPR is 19 and 11°C higher than that of UPR. The temperature at maximum weight loss is 24 and 30°C higher than that of UPR. The second weight loss temperature of CTAB-MMT-UPR and MBDAC-MMT-UPR also increases obviously in comparison with UPR.

Swelling resistance of organophilic montmorillonite-UPR hybrids

UPR is composed of polar polyester and nonpolar styrene. Although a network is formed after curing, its resistance ability to polar solvents such as ethyl acetate and aromatic solvents such as toluene is poor. The swelling degree of MMTs-UPR intercalated hybrid in ethyl acetate is shown in Figure 5, the relationship of the swelling degree and the content of MBDAC-MMT is shown in Figure 6. It can be found that the resistance to solvent of quaternary ammonium-modified-montmorillonite-UPR hybrid is improved greatly. This indicates that the existence of silicate layers can prevent

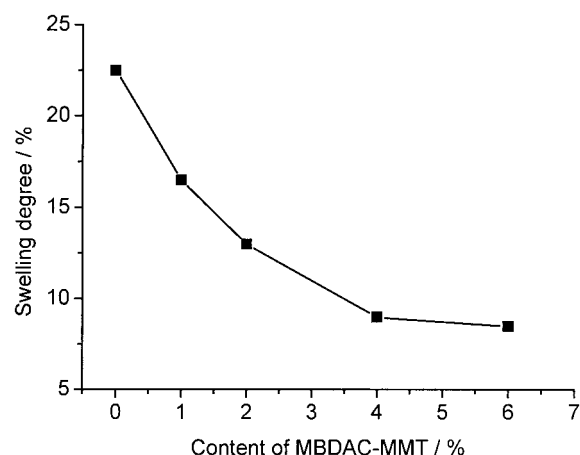


Figure 6 The relationship of the swelling degree of MBDAC-MMT-UPR hybrid in ethyl acetate on the content of MBDAC-MMT ($t = 72$ h, $T = 25^\circ\text{C}$).

the intercalated resin from the diffusion and erosion of solvent; in the meantime, the unsaturated group of MBDAC attached on the silicate can be cocured with UPR to enhance the cross-linking density of UPR.

X-ray diffraction analysis of the organophilic montmorillonite-UPR hybrids

Figure 7 presents the X-ray diffraction patterns from MMTs-UPR hybrids. It can be found that the d_{001} diffraction peak of organophilic montmorillonites ($d_{001} = 18.9$ Å for CTAB-MMT and $d_{001} = 14.7$ Å for

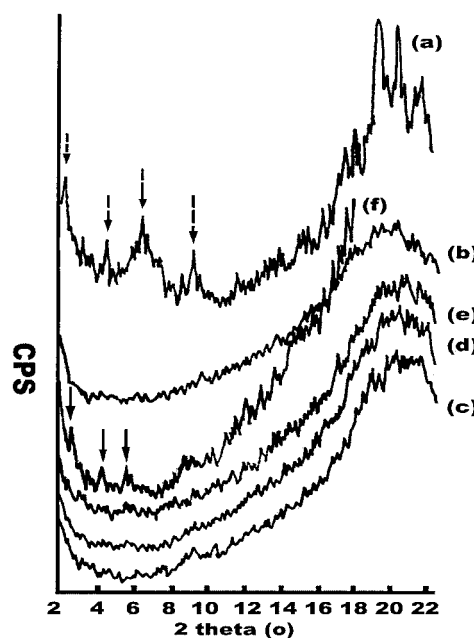
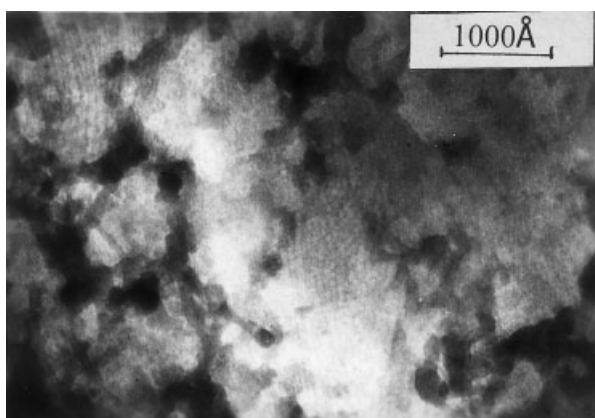
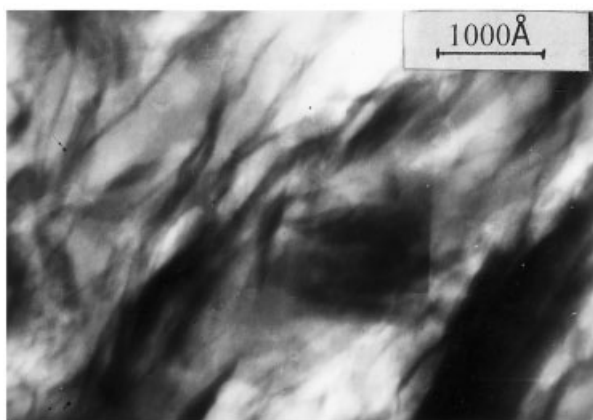


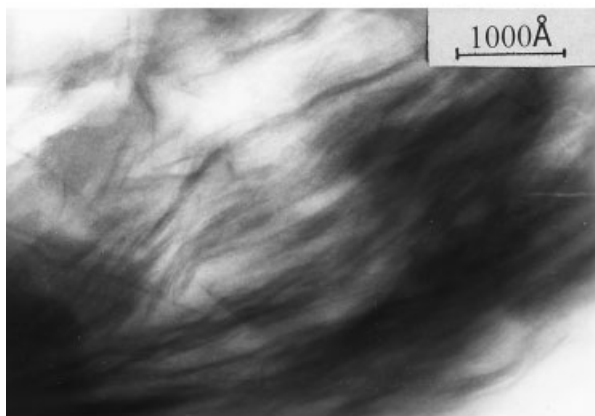
Figure 7 XRD patterns of UPR-MMTs intercalated hybrids (a, Na-MMT-UPR; b, CTAB-MMT-UPR; c, MBDAC-MMT(1%)-UPR; d, MBDAC-MMT(2%)-UPR; e, MBDAC-MMT(4%)-UPR; f, MBDAC-MMT(6%)-UPR).



(a)



(b)



(c)

Figure 8 TEM micrographs of UPR-MMTs intercalated hybrids (a, Na-MMT-UPR; b, CTAB-MMT-UPR; c, MBDAC-MMT-UPR; the content of MMT is 4%).

MBDAC-MMT) is not observed in the measurement range of XRD, that is $d > 88 \text{ \AA}$, when the content of CTAB-MMT or MBDAC-MMT is less than 4%. This indicates that the layers of organophilic montmorillonite are greatly expanded by UPR because of the improved compatibility between the silicate layers and polyester or styrene in UPR. The larger interlayer distance cannot be detected by XRD; it will be directly observed by TEM. When the content of MBDAC-MMT is greater than 6%, there are three characteristic peaks at $d = 29.8, 20.2$, and 15.6 \AA . This shows that the silicate layers are easily aggregated. There are three characteristic peaks at $d = 34.8, 18.8$, and 12.6 \AA in the composite of UPR containing 4% Na-MMT, indicating that only partial interlayer space can be intercalated by the polar polyester or styrene in UPR.

TEM analysis

Figure 8 presents the TEM micrographs of UPR-MMTs intercalated hybrids, showing that most of the pristine montmorillonite was dispersed into pieces in UPR and a small part of it was dispersed into layers (Fig. 8a). The interface between the silicate pieces and polymer is clear. The organophilic montmorillonites were dispersed into layers (silk-like in the graphs) and the interface between the silicate pieces and polymer is blurred. The distance among the layers is between 14 and 30 nm; the length of the layers can reach 1000 nm. But as we can see, the silicate layers tend to aggregate, especially in MBDAC-MMT-UPR (Fig. 8b). The homogeneous dispersion and the nanoscale silicate act as a reinforcing agent to play an important role in improving the tensile strength of the hybrids.

SUMMARY AND CONCLUSION

Intercalated hybrids of which tensile strength, impact strength, and thermal resistance was improved simultaneously can be prepared by cocuring unsaturated polyester resin with montmorillonite modified by polymerizable quaternary ammonium. Polymerizable quaternary ammonium plays a key role in improving the interaction between the silicate layers of organophilic montmorillonites and unsaturated polyester resin and the dispersibility of montmorillonite and the properties of the obtained hybrids.

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