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Emulsifying effect of dimethyldioctadecylammonium-hectorite in polystyrene/poly(ethyl methacrylate) blends

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Abstract

An organically modified clay, dimethyldioctadecylammonium-hectorite (DMDO-Hect.), was used as an emulsifier for the immiscible polystyrene/poly(ethyl methacrylate) (PS/PEMA) pair of polymers. The organoclay in this blend adsorbs selectively the PEMA chains and creates PEMA/DMDO-Hect. intercalated structures within which the PS chains are shaped into separate domains. The size of these domains decreases as the concentration of the inorganic DMDO-Hect. partner increases giving a typical emulsification curve that testifies the emulsifying action of the organoclay. SEM and TEM micrographs reveal efficient mixing of the polymers in the presence of the organoclay. The emulsifying action of the organoclay is also reflected by the presence of only one T_g in the DSC thermograms when the organoclay concentration reaches the equilibrium value in the emulsifying curve. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Organoclay; Emulsification

1. Introduction

Mixing of two polymers for the purpose of obtaining materials with combined superior properties or avoiding the need to synthesize novel structures constitutes an attractive research area. The polymer partners can be derived from used polymers, contributing in this way to polymer recycling and also to the production of new materials of added value. Unfortunately, most homopolymer pairs are immiscible with the result to form separate phases having poor mechanical properties. To overcome the immiscibility problem, a copolymer (block, graft or star) is usually added to the mixture as emulsifier [1–11]. The activity of copolymers relies on their phase separation and the chemical affinity that each constituent presents for one of the homopolymers. Thus, in a mixture of two homopolymers and an appropriate copolymer, each homopolymer associates with the relevant part of the copolymer and their mutual interactions lead to a blend with improved dispersion of the minor phase into the major and with reduced interfacial tension between the components.

Copolymers are often not easily prepared, so their substitution by another efficient phase mixing agent would be highly desirable. In this paper, we wish to report the novel use of organoclays as effective emulsifiers in promoting polymer mixing. Organoclays represent a class of clay derivatives that are easily prepared by exchanging the sodium ions of the pristine mineral with an organic cation, the last being a protonated amine or a quaternary alkylammonium ion [12,13]. The presence of organic cations between the layers affords organophilic behavior to the clay mineral. Organoclays were first employed by Toyota researchers [14–16] to fabricate Nylon/organomontmorillonite composites with improved mechanical, thermal and rheological properties, thereby expanding the applications of Nylon. Following these reports a plethora of publications appeared dealing with different polymer/organoclay composites, such as clay/polystyrene [17,18], epoxy resin [19,20], ε-caprolactone [21], poly(methyl methacrylate) [18], polyethylene oxide [22], polypropylene [23,24], etc.

In general, polymer/clay composites fall into two classes: *intercalated composites* derived from the insertion of one or more polymer chains between the clay layers to give a multilayer with a repeat distance of a few nanometers and *delaminated composites* in which the layers are exfoliated and dispersed in a continuous polymer matrix. In the latter case, the interlayer spacing is comparable to the size of the polymer. The synthesis of polymer/clay composites can be realized by either intercalation of the monomer followed by interlayer polymerization or by polymer intercalation from solution or melt [25].

Extending the polymer/clay physicochemical principles to polymer blends we observe that organoclays are excellent

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emulsifiers for homopolymer mixtures. To demonstrate this action, the immiscible polymer pair polystyrene/poly(ethyl methacrylate) was employed in connection with dimethyldioctadecylammonium-hectorite as the inorganic emulsifier. Recently, diblock and star copolymers of polystyrene/poly(ethyl methacrylate) were used for the emulsification of this homopolymer pair [11]. The emulsifying effect of dimethyldioctadecylammonium-hectorite to polystyrene/poly(ethyl methacrylate) blends was investigated by X-ray diffraction, scanning and transmission electron microscopy and differential scanning calorimetry. Of much importance is that polymer/organoclay interactions, due to the emulsifying effect, are expected to provide composite materials with improved mechanical, thermal, optical and other properties.

2. Experimental part

2.1. Materials

The clay used in this work was sodium hectorite (Na^+-Hect.) from Hector, California, with particles ≤2 μm, obtained from the source clay mineral repository, University of Missouri, Columbia. The cation-exchange capacity (CEC) of hectorite, as determined by the cobalt method, was equal to 78 mequiv./100 g. Dimethyldioctadecylammonium chloride [$DMDO^+Cl^-$: $(CH_3)_2(C_{18}H_{37})_2N^+Cl^-$] was a Kodak product. The homopolymers polystyrene (PS) and poly(ethyl methacrylate) (PEMA) with molecular weights of 2×10^4 and 2.5×10^4 and molecular weight distribution of $M_w/M_n = 1.1$ were obtained from Aldrich Chemicals.

2.2. Preparation of organo-hectorite and polymer/organo-hectorite composites

(a) *DMDO-Hect.* To a 1% w/v aqueous suspension of sodium hectorite a solution of $DMDO^+Cl^-$ in ethanol (5% in excess of the amount imposed by the CEC of the mineral) was added under stirring at 60 °C and the mixture was further stirred at 60 °C for 3 h. The product was isolated by centrifugation, washed first with ethanol to remove any excess of the onium salt, then with water and finally dried in air by spreading on a glass plate at room temperature.

(b) *PS(50)/DMDO-Hect.(50) and PEMA(75)/DMDO-Hect.(25) hybrids* (*in parenthesis* wt%). These hybrids were prepared by adding a tetrahydrofuran (THF) solution of the polymer (approximately 10% w/v) under stirring to a DMDO-Hect. suspension in THF. The mixtures were stirred for 1 h and then spread on glass plates covered with aluminium foil and dried in air at room temperature. Following this technique of drying, the hybrids were received as thin films.

(c) *PS/PEMA/DMDO-Hect. hybrids.* These were prepared as in (b) by keeping the weight ratio of PS/PEMA constant to 1/3 and varying the wt% of the DMDO-Hect. from 5 to 27%. All the composites and their compositions are listed in Table 1.

2.3. Characterization

The X-ray diffraction (XRD) patterns were recorded on a Siemens D-500 diffractometer using Cu Kα radiation. The data were collected in the 2θ region 2–30° with slits 0.3/0.3/0.3/0.15/0.15 and scanning rate 0.03° s^{-1}. Scanning electron microscopy (SEM) micrographs were taken on a Philips model 515 microscope operating at 25 kV. The PS/PEMA/DMDO-Hect. blends were etched for 24 h in cyclohexane, a selective solvent for PS. After prolonged drying the specimens were coated with active carbon prior to electron microscopy. Transmission electron microscopy (TEM) micrographs were obtained on a Philips model CM20 microscope, using an accelerating voltage of 200 kV. The TEM specimens were sections of 90–110 nm thickness of PS(21.2)/PEMA(63.8)/DMDO-Hect.(15) blend encapsulated in epoxy resin and were cut at ambient temperature with the aid of a LKB model 3 microtome (using a glass knife). Owing to different electronic features of PS and PEMA the contrast between the polymer phases is strong enough for successful distinction. The differential scanning calorimetry (DSC) studies were performed using a TA Instruments modulated DSC model 2920. Each sample was heated two times at a rate 5 °C min^{-1}. The illustrated DSC curves are the second runs, the first run being disregarded due to effects of previous thermal histories.

Table 1
Composition, d_{001} spacing (by X-ray diffraction) and PS phase average diameter δ (by scanning electron microscopy) of composites based on PS, PEMA and DMDO-Hect

Sample	Composition (wt%)	d_{001} (nm)	δ (μm)
DMDO-Hect.		2.60	
PS/DMDO-Hect.	50/50	2.94	
PEMA/DMDO-Hect.	75/25	3.43	
PS/PEMA	25/75		9.8 ± 3.8
PS/PEMA/DMDO-Hect.	23.8/71.2/5	3.25	6.7 ± 2.9
PS/PEMA/DMDO-Hect.	22.5/67.5/10	3.50	3.8 ± 1.1
PS/PEMA/DMDO-Hect.	21.2/63.8/15	3.50	6.7 ± 2.9
PS/PEMA/DMDO-Hect.	20/60/20	3.50	1.5 ± 0.6
PS/PEMA/DMDO-Hect.	18.2/54.8/27	3.43	1.6 ± 0.5
PS/PEMA/DMDO-Hect.	63.8/21.2/15	3.43	

3. Results and discussion

Taking into consideration the known ability of organoclays to interact with polymers producing intercalated or delaminated hybrid structures, we were prompted to examine whether organoclays can function also as effective emulsifiers for optimizing polymer blends miscibility. The potential emulsifying action of organoclays was

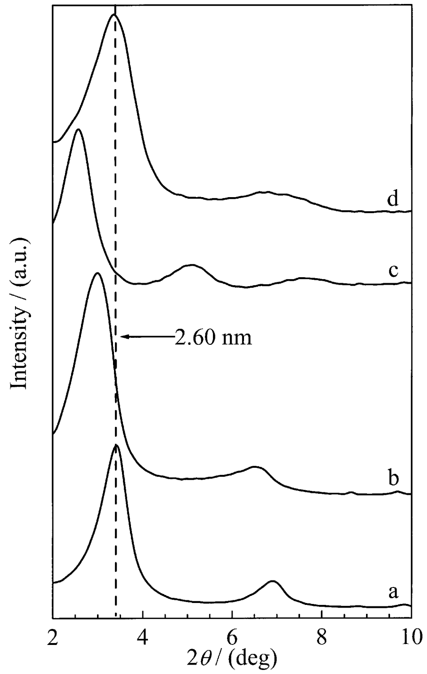

Fig. 1. XRD patterns of: (a) DMDO-Hect., (b) PS(50)/DMDO-Hect.(50), (c) PEMA(75)/DMDO-Hect.(25) and (d) PS(50)/DMDO-Hect.(50) after 24 h of etching in cyclohexane.

evaluated by incorporating different amounts of dimethyldioctadecylammonium-hectorite (DMDO-Hect.) into the immiscible polymer pair of polystyrene/poly(ethyl methacrylate) (PS/PEMA) of constant 1/3 weight ratio. Experimental results from XRD, SEM, TEM and DSC measurements point clearly to the beneficial emulsifying effect of the DMDO-Hect. organoclay.

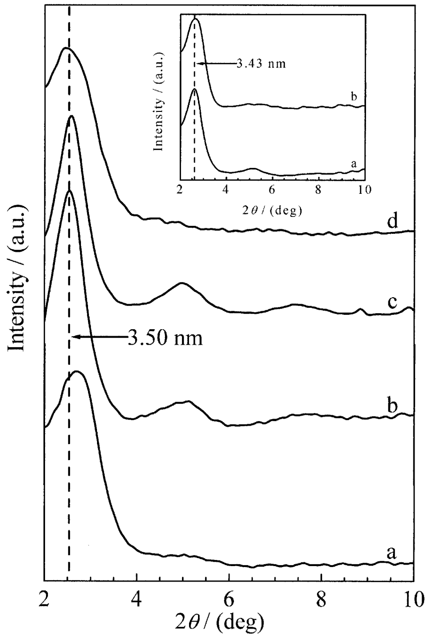

Fig. 2. XRD patterns of PS/PEMA/DMDO-Hect. blends with the following wt% compositions: (a) 23.8/71.2/5, (b) 21.2/63.8/15, (c) 18.2/54.8/27 and (d) 21.2/63.8/15 after 24 h of etching in cyclohexane. The inset includes the XRD patterns of PS(63.8)/PEMA(21.2)/DMDO-Hect.(15) blend: (a) before and (b) after 24 h of etching in cyclohexane.

3.1. X-ray diffraction

The intercalation capabilities of individual PS and PEMA polymers were evaluated by XRD measurements. A series of XRD patterns recorded from: a pristine DMDO-Hect. organoclay **a**, a PS(50)/DMDO-Hect.(50) hybrid **b** and a PEMA(75)/DMDO-Hect.(25) hybrid **c**, are shown in Fig. 1. The intercalation of polymers was conducted in THF solutions. The DMDO-Hect. organoclay has the ability to swell in THF, which means that the silicate stacks break into individual layers forming a three-dimensional network. In this state of exfoliation good mixing with THF solutions of PS or PEMA leads, after solvent evaporation, to restacking of the layers and to the formation of intercalated structures, as shown by the well-defined XRD patterns in Fig. 1(b) and (c).

The insertion of the PS or PEMA chains between the organoclay layers is indicated by the corresponding increase in the d_{001} basal spacing from 2.60 nm for the pristine DMDO-Hect. to 2.94 and 3.43 nm for the PS(50)/DMDO-Hect.(50) or PEMA(75)/DMDO-Hect.(25) hybrid, respectively. Relevant data are listed in Table 1. When a PS(50)/DMDO-Hect.(50) sample was treated with cyclohexane the d_{001} spacing returned to the original value of 2.60 nm for DMDO-Hect. organoclay indicating the deintercalation of PS by this solvent, as shown in Fig. 1(d).

The XRD patterns of various PS/PEMA/DMDO-Hect. blends having constant PS/PEMA weight ratio (1/3) and 5, 15 and 27 wt% in DMDO-Hect. are shown in Fig. 2 (patterns **a**, **b** and **c**). The nearly constant d_{001} values at 3.25, 3.50 and 3.43 nm (Table 1) for the various blends indicate that only the PEMA chains intercalate between the organically modified silicate layers. Confirmation for this preferential adsorption comes from the pattern in Fig. 2(d), which was recorded from sample PS(21.2)/PEMA(63.8)/DMDO-Hect.(15) after 24 h etching in cyclohexane to remove any possible PS hosted in the clay galleries. We observe that the spacing remains unaffected by this treatment, proving the selective intercalation of PEMA from a PS/PEMA mixture. Furthermore, in order to show that this selectivity is not a result of the relative concentration of the two polymers, another PS(63.8)/PEMA(21.2)/DMDO-Hect.(15) blend was prepared and etched with cyclohexane for 24 h. The XRD patterns before and after etching are shown in the inset of Fig. 2. No shift in the d_{001} spacing was observed and the value of 3.43 nm was identical to that of the PEMA/DMDO-Hect. hybrid. The driving force for the selective intercalation of PEMA can be ascribed to hydrogen bonding between the PEMA carbonyl groups and the clay framework hydroxyl groups, as has been proposed for another clay composite with maleic anhydride modified polypropylene oligomers [24].

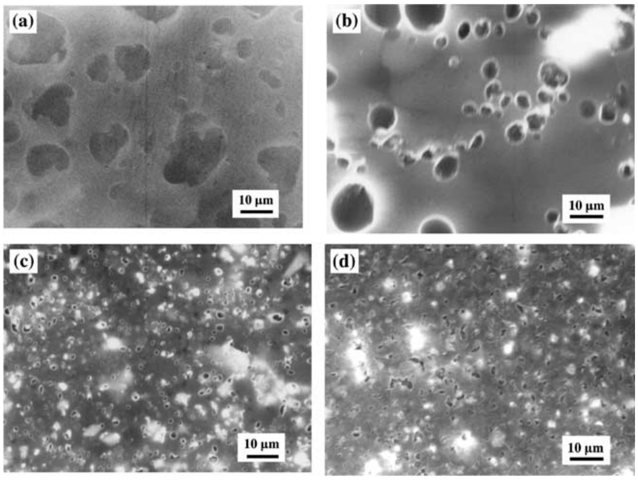

Fig. 3. SEM micrographs of PS/PEMA/DMDO-Hect. blends including the following wt% of DMDO-Hect.: (a) 0, (b) 5, (c) 15 and (d) 27.

3.2. Scanning electron microscopy

The SEM micrographs, shown in Fig. 3, demonstrate clearly the emulsifying effect of the DMDO-Hect. organoclay. All blends were obtained in film form by casting from THF. In order to identify the minor PS phase, the specimens were etched for 24 h in cyclohexane, which removes only the PS. Consequently, in the SEM images the PS phase appears as holes in the matrix of the major PEMA phase. We measured the diameters of about 50 holes for each specimen and the estimated average diameters (δ) and the standard deviations are listed in Table 1.

The immiscibility of the original PS/PEMA blend is evident from the corresponding SEM micrograph in Fig. 3(a), from which a δ value of 9.8 ± 3.8 µm was evaluated. A substantial decrease in the size of the PS domains was observed when the blend was modified with DMDO-Hect. organoclay. In the SEM micrographs of various PS/PEMA/DMDO-Hect. blends with 5, 15 and 27 wt% of organoclay, Fig. 3(b)–(d), the δ was estimated as 6.7 ± 2.9, 1.7 ± 0.5 and 1.6 ± 0.5 µm. The decrease in δ in the presence of the DMDO-Hect. organoclay reflects the enhanced dispersion of PS in PEMA and provides evidence for the emulsifying activity of the organoclay. Regarding the necessary duration for etching, we observe that a 24 h time is sufficient for the total removal of PS. Thus, a blend of 15 wt% in DMDO-Hect., etched for 12 days in cyclohexane gave a δ value almost the same as that obtained from a 24 h etching (1.8 ± 0.6 µm).

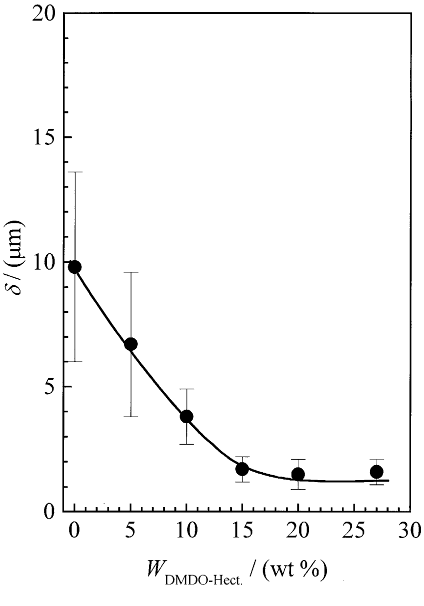

Fig. 4. Plot of the polystyrene phase average diameter δ as a function of wt% of DMDO-Hect. $W_{\text{DMDO-Hect.}}$.

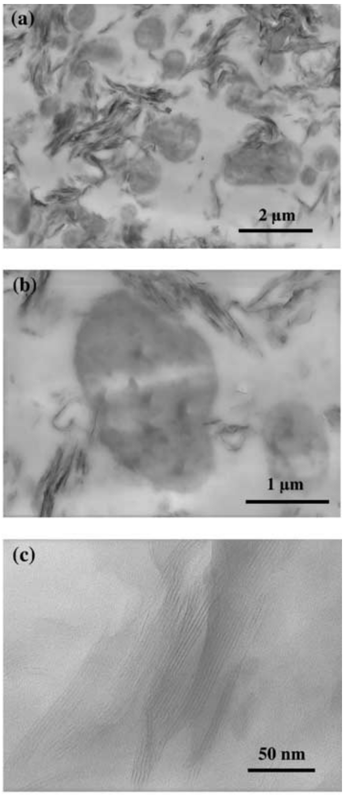

Fig. 5. TEM micrographs of PS(21.2)/PEMA(63.8)/DMDO-Hect.(15) blend: (a) general view, (b) relative position of the three components and (c) intercalated structures of the PEMA/DMDO-Hect.

In Fig. 4 the PS average diameter δ is plotted as a function of the DMDO-Hect. concentration ($W_{\text{DMDO-Hect.}}$), with the bars representing the standard deviations. It is interesting to note that the shape of the curve is a typical emulsification curve. A sharp decrease in the dimensions of the dispersed PS phase with increasing $W_{\text{DMDO-Hect.}}$ is observed up to a critical concentration of 15%, beyond which an equilibrium PS phase with an average diameter of 1.6 ± 0.5 µm predominates.

3.3. Transmission electron microscopy

The technique offers the possibility to register a detailed icon for the position of the organoclay layers

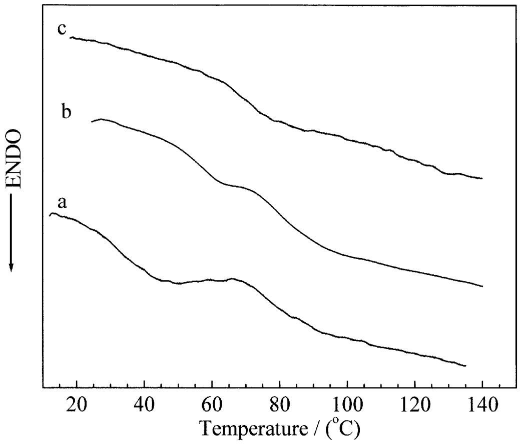

Fig. 6. DSC thermograms of PS/PEMA/DMDO-Hect. blends including the following wt% of DMDO-Hect.: (a) 0, (b) 5 and (c) 15.

in the polymer blend. Fig. 5(a) is a bright field image that gives a general view of the PS(21.2)/PEMA(63.8)/DMDO-Hect.(15) sample. The dark ellipsoid regions correspond to PS domains, the size and shape of which are in agreement with the average diameter and hole modulation determined by SEM micrographs. The TEM micrograph depicts the organoclay particles as elongated and curled areas dispersed in the PEMA matrix and unveils their locations near the PS domains. The relative position of the organoclay particles and the PS domains is better seen in Fig. 5(b). Most of the organoclay particles diffuse through the PEMA matrix and surround the PS domains, while a minor part of layers penetrates the PS domains and in this way, is shared by both polymers. Finally, the intercalated structure of the PEMA chains is clearly seen in the micrograph in Fig. 5(c). From this image the layer separation is easily measured and by substracting the layer thickness of 10 Å, the separation between the layers was calculated to be 2.50 nm, a value very close to that obtained from the XRD results.

The TEM micrographs offer a possible explanation for the emulsifying action of the DMDO-Hect. organoclay. The major part of the organoclay particles gathers around the PS phase, inhibiting in this way the growth of the PS domains. In other words, the organoclay layers act as barriers to the assembly of the PS chains and prevent the expansion of the domain size. This action becomes more intense as the DMDO-Hect. content increases, probably because the space available for domain formation becomes more limited. An inverse action can be considered to take place during the development of the PS domains that compresses the organoclay layers and finally leads to an equilibrium state corresponding to the observed average domain diameter of 1.5 μm.

3.4. Thermal analysis

In order to elucidate the thermal behavior of PS/PEMA/DMDO-Hect. blends, the DSC thermograms of three samples with 0, 5 and 15 wt% of DMDO-Hect. were measured and the relative curves are shown in Fig. 6. From previous findings the glass transition temperature (T_g) of PEMA was found to vary with the microstructure of the polymer chains [26]. Isotactic PEMA has a much lower T_g than the atactic or syndiotactic PEMA. The DSC curve for the pristine PS/PEMA blend, curve in Fig. 6a, shows two distinct T_gs revealing phase separation in agreement with the SEM results. The lower T_g is attributed to an isotactic PEMA-rich phase and the higher T_g to a phase of PS and atactic or syndiotactic PEMA. This last T_g is located at a temperature between those of PS and atactic or syndiotactic PEMA [26]. The DSC curve for the PS(23.8)/PEMA(71.2)/DMDO-Hect.(5) sample, Fig. 6(b), also shows two T_gs which are attributed to the same phases as mentioned earlier. However, this curve is quite altered from that of the original blend, as the T_gs move closer to each other. The approach of the two T_gs is ascribed to the partial mixing of the two polymers which is in agreement with the SEM results. Finally, the DSC thermogram of the sample with 15 wt% of organoclay presents only one T_g, Fig. 6(c). This T_g, lying between those from curves in Fig. 6a or b, implies that a miscible polymer blend is obtained for this quantity of DMDO-Hect. in accord with the SEM and TEM micrographs.

4. Conclusions

PS and PEMA penetrate readily into the DMDO-Hect. layers from THF to form intercalated structures. When the polymers are in blend only the PEMA member is adsorbed by the organoclay layers. The pristine polymers cast from THF separate into two phases. The presence of DMDO-Hect. organoclay in the polymer blend causes an efficient mixing of the polymers. The size of the PS domains in the PS/PEMA/DMDO-Hect. blends decreases with increase in the amount of the DMDO-Hect. component, giving a typical emulsification curve. Above a threshold concentration of 15 wt% the size of the PS domains remains constant at 1.6 ± 0.5 μm. The TEM results guide towards the conclusion that the presence of DMDO-Hect. organoclay in the polymer blend inhibits the expansion of the PS domains thereby providing a miscible mixture of PS/PEMA. This conclusion is also testified by the DSC thermograms.

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