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Synthesis and structure of smectic clay/poly(methyl methacrylate) and clay/polystyrene nanocomposites via in situ intercalative polymerization

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Abstract

Via in situ intercalative free-radical polymerization, we prepared clay/poly(methyl methacrylate) (PMMA) and clay/polystyrene (PS) nanocomposites from lipophilized smectic clays. The intercalation spacing in the nanocomposites and the degree of dispersion of these composites were investigated with X-ray diffraction and transmission electron microscopy, respectively. Under some conditions, the intercalative nanocomposites exhibited flocculation because of the hydroxylated edge–edge interaction of silicate layers. The nanocomposites had higher storage modulus and higher T_g compared to without clay systems. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocomposite; Clay; Intercalation

1. Introduction

In recent years much attention has been paid to layered clay/polymer composites with nanometer dimensions, the so-called nanocomposites as advanced plastic materials prepared via in situ intercalative polymerization [1–4]. In such nanocomposites, the interfacial effect between the silicate layers and matrix polymers is a key factor leading to high stiffness, high modulus and heat resistant composites [2] which can be by far superior to conventional glass fiber reinforced plastics, provided that the silicate layers are completely exfoliated and thoroughly homogenized into the polymer matrix. However, usually very strong electrostatic interactions between silicate layers through intergallely cations make it extremely difficult to achieve complete exfoliation of the layers. A recent successful attempt to avoid this difficulty was to replace such cations by some quarternized ammonium salts (QAs) preferably with long alkyl chain, i.e. lipophilization of the clays [4]. Such alkylammonium cations reduce the surface polarity (hydrophilic) of the silicate layers and enhance the affinity between the silicate and the matrix [2,3].

Recently we tried to synthesize the clay/poly(methyl methacrylate) (PMMA) nanocomposites using a lipophilized smectic clay which was modified by oligo(oxypropylene)-, diethyl-, methyl-ammonium cation. Interestingly, the dispersed structure of the clay into matrix was quite different between before and after the polymerization of MMA [5]. A better understanding of the structural analysis of suspensions and subsequent preparation of nanocomposites is of fundamental importance in controlling the nanoscale structure.

In this paper, we examine the inter-relation of this kind of lipophilized smectic clays and matrices and discuss the structure and mechanical properties of the nanocomposites.

2. Experimental

The organically modified smectic clays used in this study were supplied by CO-OP Chemical Co. Ltd., which were synthesized by an ion exchange reaction between Na^+-smectite (cation exchange capacity of 86.6 meq/100 g) and QA, oligo(oxypropylene)-, diethyl-, methyl-ammonium chloride, $[(C_2H_5)_2(CH_3)N^+(O{-}i\mathrm{Pr})_{25}]Cl^-$ and methyl-, trioctil-ammonium chloride, $[CH_3(C_8H_{17})_3N^+]Cl^-$. Both lipophilized smectic clays were (SPN and STN) dispersed in MMA and styrene (St) via ultrasonication (Ultrasonic 250, Hey Co.) at 25°C for 7 h to obtain suspensions. Here,

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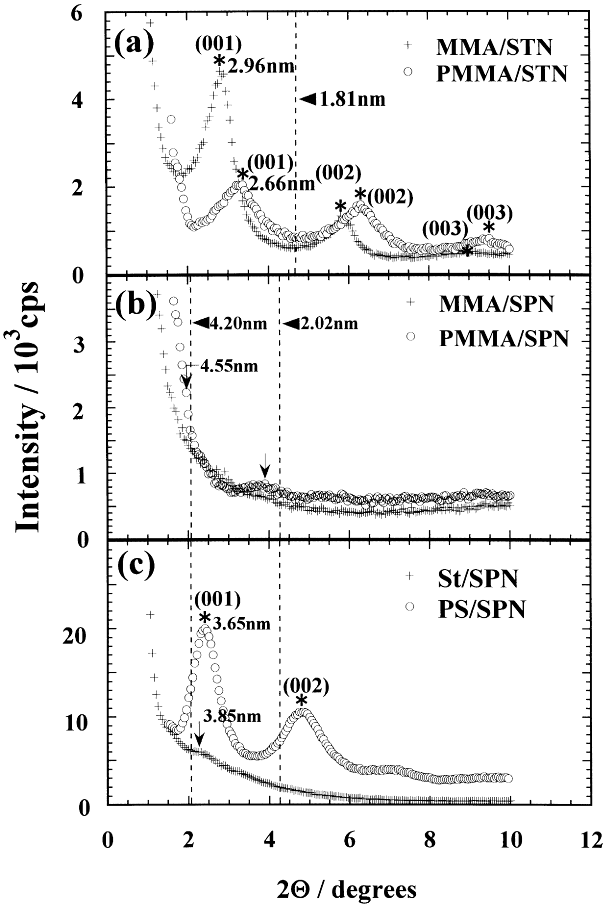

Fig. 1. XRD patterns of suspensions and the corresponding nanocomposites. Th dashed lines indicate the location of the silicate (001) and (002) reflections in (a) STN ($d_{(001)} = 1.81$ nm) and in (b) and (c) SPN ($d_{(001)} = 4.20$ nm, $d_{(002)} = 2.02$ nm). The asterisk indicates the position of (00*l*) reflections from the suspensions and nanocomposites. The arrows indicate a small shoulder or a weak peak.

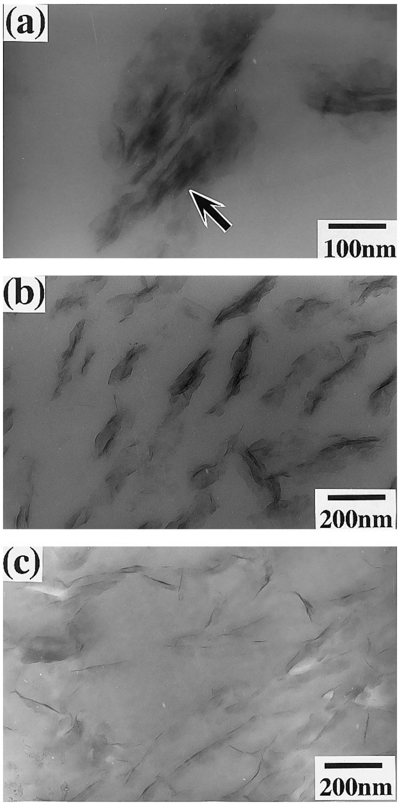

Fig. 2. TEM micrographs of thin section of nanocomposites: (a) PMMA/STN; (b) PMMA/SPN; and (c) PS/SPN. The arrows in panel (a) indicate the oriented collections of STN silicate layers.

t-butyl peroxy-2-ethylhexanate and/or 1,1-bis(*t*-butyl peroxy)cyclohexane) as an initiator was mixed in the suspensions (0.1 wt%) and then free-radical polymerization was carried out in the dark at 80°C for 5 h (for MMA) and at 100°C for 16 h (for St) in a silicone oil bath. For comparison we prepared PMMA and/or PS including QA as the references under the same manner. X-ray diffraction (XRD) experiments were performed directly for the MMA/SPN, MMA/STN and St/SPN suspensions and corresponding nanocomposites (PMMA/SPN, PMMA/STN and PS/SPN) by a PW3050, Philips using Cu K_α radiation (0.154 nm) and a Ni filter, at 40 kV and 50 mA [6]. A transmission electron microscope (TEM, JEM 100CX, JEOL), applying an acceleration voltage of 100 kV, was used to clarify the nanostructure. Dynamic properties of the nanocomposites were measured with Reometrics Dynamic Analyser (RDAII) in tension–torsion mode. Measurements of storage modulus were made at a constant frequency of 6.28 rad/s with strain amplitude of less than 0.05% in the temperature range of 25–130°C with heating rate of 2°C/min. For the suspensions, rheological behavior was examined on a stress-control type rheometer, Reometrics Stress Rheometer (DSR200) at 25°C.

3. Results and discussion

3.1. XRD patterns and TEM observation

The mean interlayer spacing of the (001) plane ($d_{(001)}$) for the solid SPN and STN obtained by XRD measurements is 4.20 and 1.81 nm, respectively [5]. Fig. 1 shows a series of XRD patterns of the suspensions (MMA/STN, MMA/SPN and St/SPN containing 10 wt% lipophilized smectic clays in each case) and the corresponding patterns of the nanocomposites in the range of the diffraction angle $2\Theta = 1$–10°. For MMA/STN suspension, the higher-order peaks corresponding to $d_{(002)}$ and $d_{(003)}$ are clearly observed, suggesting STN can intercalate MMA monomers without the loss of layer structure. The PMMA/STN nanocomposite exhibits rather broad Bragg diffraction peaks at 2.66 nm corresponding to the basal spacing which decreases about 0.3 nm from the suspension. This reduction of $d_{(001)}$ is bigger than the volume shrinkage of PMMA by polymerization (~3%).

In contrast, for MMA/SPN suspension, the absence of Bragg diffraction peaks indicates that the clay has been

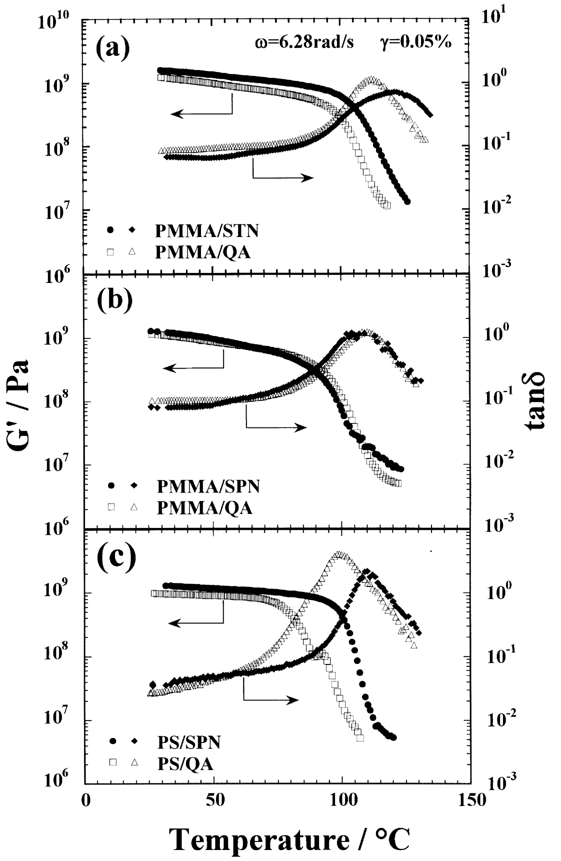

Fig. 3. Temperature dependence of G' and tan δ for the relevant nanocomposites and polymerized polymer/QA compositions without clays.

completely exfoliated (delaminated) in the suspension as revealed by XRD. The diffraction pattern of PMMA/SPN nanocomposite shows a similar profile compared with the suspension but with a small remnant shoulder at $2\Theta = 1.94°$ ($\cong 4.55$ nm) and a very weak peak at $2\Theta = 3.88°$ as indicated by the arrows in the figure.

In the St/SPN suspension, we can also see a small remnant shoulder at $2\Theta \cong 2.3°$ ($\cong$3.85 nm), which is smaller than the basal spacing of solid SPN. The rather weak intercalated structure compared with MMA/STN system may be formed in the St/SPN suspension. On the contrary, in the PS/SPN nanocomposite, the strong diffraction peaks are observed as a well-defined peak and the second peak corresponding to (002) plane. The strong Bragg diffraction peaks reflect the coherent order of the silicate layers, implying that the ordered intercalated nanocomposite is formed during polymerization. The slight reduction of $d_{(001)}$ agrees with the volume shrinkage of PS due to the polymerization (~3%).

Quite different rheological behavior of the suspensions from each other is observed in the frequency (ω) sweep test. Both MMA/STN and St/SPN systems show gel-like ω-dependence of dynamic moduli, i.e. independence of ω, whereas, MMA/SPN shows strong ω-dependence as a sol system. Thus, the rheological behavior drastically alters by the kind of QA and monomers in the system. Owing to the relation between rheology and internal structure revealed by XRD, we may distinguish between intercalating and delaminating.

Fig. 2 shows TEM bright field images corresponding to Fig. 1. In PMMA/STN nanocomposite, individual layers stacked against each other, dispersed in the PMMA matrix (light regions), are visible as a region of alternating narrow, dark and light bands within the particles (fringes). Some areas (as indicated by the arrow in Fig. 2(a)) appear to contain oriented collections of 10–20 parallel silicate layers with basal spacing of about 3 nm, which is consistent with the XRD analysis.

For PMMA/SPN, the stacked silicate layers of about 200 nm length and about 40–50 nm thickness, which consist of about 10 parallel individual silicate layers, are observed randomly in the PMMA matrix but the coherent order of the silicate layers seemed to be lower than that of PMMA/STM. These results are in good agreement with the XRD pattern. Clearly the length of the oriented collections in the range of 100–200 nm is far larger than original clay (mean diameter ≅ 50 nm estimated by laser light scattering analysis [5]). It is most interesting to note that the flocculation takes place owing to the hydroxylated edge–edge interaction of silicate layers. Such flocculation is not clear at the present stage but presumably is governed by the hydrophilic balance of polymer matrix and clays.

In PS/SPN, the stacking of only two, three layers with a distance of less than 4 nm composed of dark band and bright field appears in the PS matrix (light region) as a fine dispersion. Because of the difference between PS and PMMA matrices for the compatibility of SPN, the formation of layered structure in the nanoscale level is strongly affected. The PS chains are intercalated in the narrow space of the oriented collections of parallel silicate layers as revealed by XRD pattern. The mechanism of the intercalation/unintercalation (delamination) and the flocculation of the clay layers seemed to be a complex process of the polymerization controlled by QA–matrix polymer interaction and hydrophile–lipophile balance between clay and matrix polymer.

3.2. Mechanical properties

Giannelis et al. [2] reported previously that nanocomposites exhibit excellent mechanical properties, e.g. the enhancement of the modulus, stiffness and heat resistance [1,2].

Fig. 3 shows the temperature dependence of storage modulus G' and loss factor tan δ of the relevant nanocomposites. For comparison, the data of the corresponding polymerized polymer/QA compositions are shown as a reference because the modulus decreases by the existence of QA low molecule compound as a plasticizer. For PMMA/STN and PS/SPN systems, below glass transition region (25–90°C), both samples exhibit high G' and restriction of a substantial drop in G' with increasing temperature. G' in the glassy region below T_g is approximately 57% (for PS/SPN) and 34% (for PMMA/STN) higher in the nanocomposite compared with the blend systems without clays. The shift of tan δ reaches to higher temperatures and decrease of the value indicates an increase in nanocomposite T_g. The magnitude of the shift estimated by tan δ is about 10°C. Especially, the broadening is observed in the PMMA/STN system. These indicate that the interaction between polymer and silicate layers at the interface of layers and polymer matrix could suppress the mobility in the polymer segments near the interface. That is, in both systems the intercalated nanocomposites are formed.

Further the increase in the rubbery plateau modulus G' of the nanocomposite is slightly seen in each nanocomposite above 120°C. The large aspect ratio of the structural hierarchy in the nanoscale level might lead to such large enhancement in G' throughout the glassy and the rubbery region.

For PMMA/SPN, G' in the glassy region is about 20% higher than that of the reference but the clear change of tan δ is not observed. Presumably, the intercalation of the PMMA segments between the silicate layers does not occur. Its detail and theoretical interpretation will be discussed in a forthcoming paper [7].

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