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Dispersed structure and ionic conductivity of smectic clay/polymer nanocomposites

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Abstract

We examined the correlation between the internal structure and the ionic conductivity behavior of lipophilized smectic clay (SPN)/polymer nanocomposites having various dispersed morphology of the clay layers. Both polystyrene (PS)/SPN and poly(methyl methacrylate) (PMMA)-*co*-acrylamide (AA) (99/1 mol rate)/SPN intercalated nanocomposites, which have finer dispersion of the clay layers, exhibited higher ionic conductivity rather than the other systems such as PMMA/SPN nanocomposite with stacking layer structure. The finer the dispersed morphology the higher was the conductivity of the nanocomposites. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocomposite; Ionic conductivity; Internal structure

1. Introduction

In recent years much attention has been paid to layered clay/polymer nanocomposites as advanced plastic materials prepared via in situ intercalative polymerization [1–3].

In our previous papers [4,5], large improvement was shown in the mechanical properties of clay/poly(methyl methacrylate)(PMMA) and clay/polystyrene (PS) nanocomposites using lipophilized smectic clays (called SPN and STN) modified by organic quarternized ammonium salt (QA). This enhancement of the modulus explains the dispersed structure of clay in the nanocomposites caused by the formation of the large aspect ratio of the clay particles reasonably well.

In recent years, the potential application of polymer electrolytes has been found in a series of poly(ethylene oxide) (PEO)/Li^+-montmorillonite intercalated materials by Aranda et al. [6]. The intercalated PEO molecules between silicate galleries impede the polymer crystallization. This results in higher electrolyte conductivity compared to the system without clays.

A similar electric property is expected in our clay/polymer systems using lipophilized smectic clays. In order to understand the ionic conductivity caused by the presence of ammonium cation (QA^+)s, we first need to know not only the dispersed morphology of the clay particles in the polymer matrix but also the mobility of the interlayer counter cations (i.e. QA^+) in the silicate galleries.

In this paper, we examine the correlation between the internal structure and ionic conductivity behavior of the clay/polymer nanocomposites having various dispersed morphology of the clay particles synthesized in our previous studies [4,5]. Preliminary results concerning the conductive nanocomposites as-revealed by impedance measurement, are discussed.

2. Experimental

The lipophilized smectic clays (called SPN and STN) [7] 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, $[(C_2H_5)_2(CH_3)N^+(O\text{–}iPr)_{25}]Cl^-$ and methyl-, trioctil- ammonium chloride, $[CH_3(C_8H_{17})_3N^+]Cl^-$, respectively.

The clay/polmer nanocomposites used in this study were synthesized by in situ intercalative polymerization [4] or copolymerization of MMA with small amount of polar comonomers (1 mol%) such as *N*,*N*-dimethylaminopropyl acrylamide (PAA), *N*,*N*-dimethylaminoethyl acrylate (AEA) and acrylamide (AA) [5], using SPN or STN in weight fraction of 10% (unless otherwise specified) in our previous studies. The details of the preparation and

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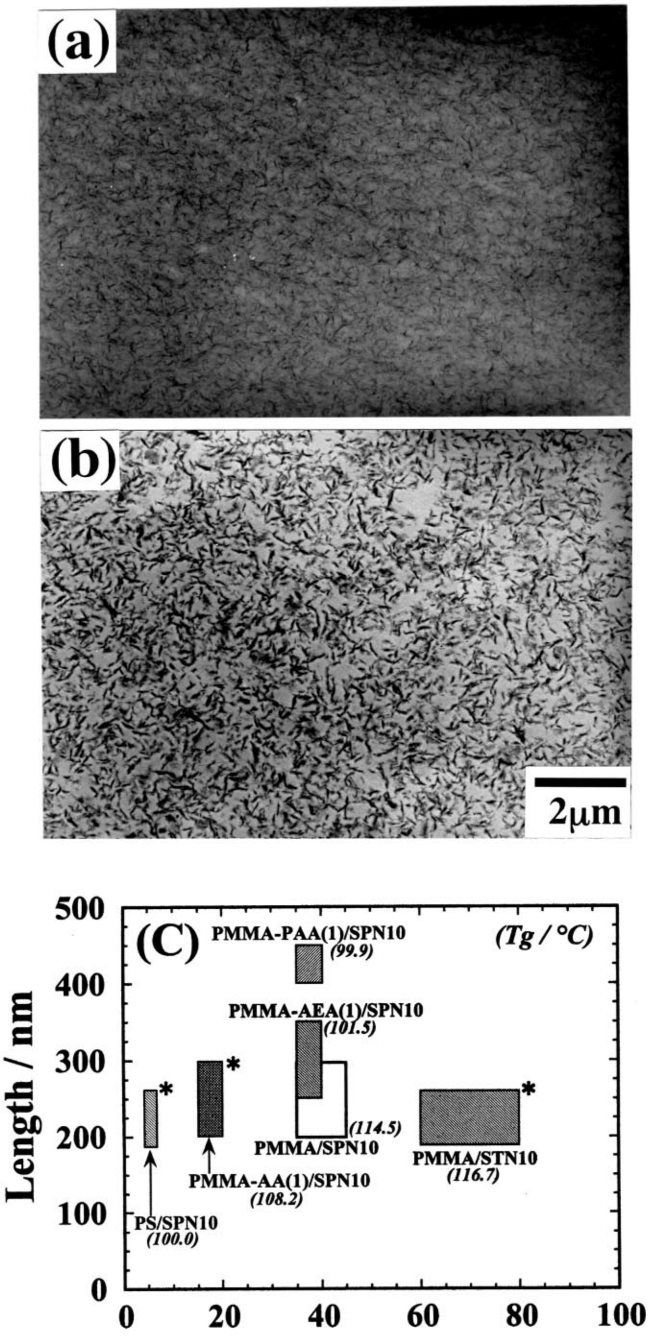

Fig. 1. TEM micrographs showing nanocomposites: (a) PMMA-AA(1 mol%)/SPN10; (b) PMMA-AEA(1 mol%)/SPN10; and (c) plots of length and thickness of the dispersed clay particles in various type of nanocomposites synthesized in our previous studies [1,2]. The glass transition temperature of the matrix polymers was shown with the number in the parentheses. The asterisks indicate the intercalated nanocomposite.

morphology analysis were described elsewhere [4,5]. Here we briefly describe the measurement of the ionic conductivity added to this experiment. For the electrical conductivity, a test specimen was made by compression molding at 5 MPa with a laboratory hot press kept for 100 s at 170–200°C (above the glass transition temperature T_g of PMMA and PS).

The molded sheet was quenched to room temperature and was then cut into a square of 28 mm × 28 mm × 0.8 mm thickness in size and later subjected to tests. This way, the clay layers were more or less laid flat in the plane of the sheet. The sheets were dried under a reduced pressure of 10^{-4} Torr at 80°C for 24 h to remove water before being subjected to conductivity measurement.

The conductivity measurements were carried out at the Ceramic Science Laboratory, Toyota Technological Institute.

The electrical conductivity was measured with an impedance analyzer (YHP4192A; Hewlett–Packard; 5 Hz to 13 MHz range) in the temperature range of 90–150°C under a constant potential of 100 mV. The sample sheet was placed between an indium–tin oxide (ITO) glass electrode in a specially designed electrolysis cell and the current flow was perpendicular to the sample plane controlled with a personal computer [8].

3. Results and discussion

Fig. 1(a) and (b) shows the typical results of transmission electron microscopic (TEM) bright field images of the nanocomposites. Again, the code PMMA-AA(1)/SPN10 represents a nanocomposite containing 10 wt% SPN in a 99/1 (mol rate) mixture of MMA and AA.

PMMA-AA(1)/SPN10 nanocomposite exhibits less stacking of 4–5 layers with a distance of about 5 nm as a fine dispersion in the PMMA-AA(1) matrix. The coherent order of the silicate layers in this system is higher than that in the other systems [5]. For MMA-AEA(1)/SPN10, the stacked silicate layers is observed and the thickness of the layers increases considerably when compared with that of PMMA-AA(1)/SPN10.

To understand the dispersed morphology of the clay particles in various nanocomposites, in Fig. 1(c), we summarized the form factors, i.e. length and thickness of the randomly dispersed clay particles obtained from TEM pictures. The asterisk in figure indicates the formation of the intercalated nanocomposite as revealed by Bragg diffraction peaks of the X-ray diffraction (XRD) experiment [4,5]. In other cases, the intercalation of the polymer chains between silicate galleries dose not occur, but some stacking and/or flocculation of the silicate layers take place [5].

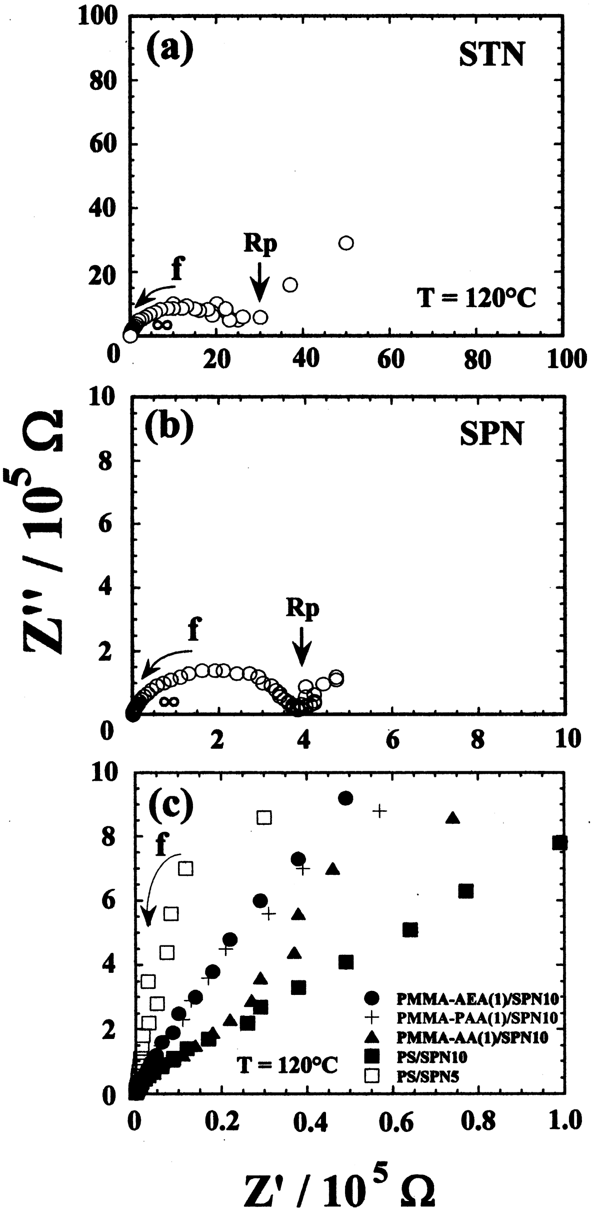

Fig. 2. Cole–Cole plots (a) for STN; (b) for SPN solid; and (c) for various type of nanocomposites at 120°C.

Fig. 2 shows the typical Cole–Cole impedance spectra of the various nanocomposites and lipophilized smectic clay solids, STN and SPN at 120°C. Z' and Z'' are in-phase and out-of-phase components of the impedance, respectively. As seen in Fig. 2(a) and (b), STN and SPN solids show depressed closed arc-like diagrams against frequency f. The systems can be presumably ascribed to ionic conductivity of the organic quarternized ammonium cation (QA^+) but the component of more than one semicircle is contained in the plots, i.e. multicomponent system having several conductivity relaxation time. The intercept of the semicircle with the real axis (Z') at low f region gives the ionic resistance R_p. In STN, the large value of R_p is obtained compared with SPN suggesting that SPN exhibits larger conductivity σ_c (6.7×10^{-8} S cm^{-1}) than that of STN (1.1×10^{-8} S cm^{-1}) because σ_c is directly inverse to the value of R_p. This result means the electrostatic interaction between silicate layers and organic cations in SPN is weaker so that QA^+s in the silicate galleries of SPN are comparatively mobile than in that of STN.

For the nanocomposites, we cannot obtain well-defined Cole–Cole plots as seen in Fig. 2(c). Each spectra show large Z'' value against Z' due to the low conductivity. If we can measure more low f region, we may observe the closed arc diagrams. For PS/SPN nanocomposite, the decrease in the SPN content drastically changes the radius of the Cole–Cole impedance spectra, resulting in a large $R_p$value and a reduced σ_c. This trend is observed in another nanocomposite systems such as PMMA/SPN5 (containing 5 wt% SPN), PMMA-AEA(1)/SPN5 and PMMA-AA(1)/SPN5. This SPN content dependence is presumably because of the ionic conductivity mechanism [9]. For more strict analysis of the diagram, we have to divide the Cole–Cole spectra using several equivalent circuit models with

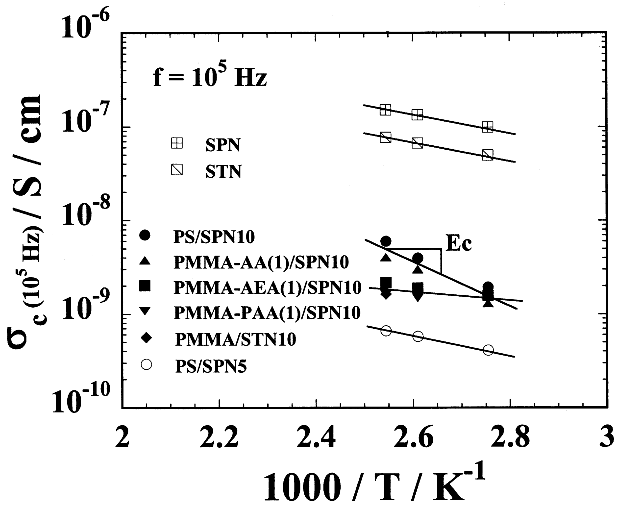

Fig. 3. Arrhenius plots of conductivity at 10^5 Hz σ_c (10^5 Hz) for various type of nanocomposites.

different conductivity relaxation time [10]. A deeper understanding of the conductivity behavior of the nanocomposites will be discussed separately in a forthcoming paper.

In Fig. 3, we show the preliminary results of the conductivity at $f = 10^5$ Hz $\sigma_c(10^5$ Hz) in order to compare each nanocomposite. Here, we constructed an Arrhenius plot of σ_c (10^5 Hz) against reciprocal temperature $1/T$. For comparison, the solid STN and SPN data at $f = 10^5$ Hz estimated from Fig. 2(a) and (b) are also plotted. σ_c (10^5 Hz) in the nanocomposites are decreased by about two order lower of magnitude. At 90°C each nanocomposite having different morphology show almost the same value of σ_c (10^5 Hz). On the other hand, at 120°C, σ_c (10^5 Hz) increases with an increasing T due to the mobility enhancement of the polymer chains above the glass transition temperature T_g. For both PS/SPN10 and PMMA-AA(1)/SPN10 intercalated systems, which are a finer dispersion of the clay particles, these values become higher rather than the other systems. The stacking of the layers may lead to high QA^+ transfer in the silicate galleries (inter- and intra-layers) but low transfer between clay particles as explained by the two contributions of inter- and intra- regions [10]. The finer the dispersed morphology the higher is the conductivity of the nanocomposites.

The slope corresponding to the apparent activation energy of the conductivity (E_c) in finer dispersed morphology systems seems to be slightly larger than the other systems and the corresponding clay solids.

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