

Silicate Layer Dispersion in Copolymer/Clay Nanocomposites

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ABSTRACT: Factors of silicate layer dispersions in polymers have been studied with copolymers. The influence of the copolymerization ratio of copolymers and the alkyl chain lengths of organomodified reagents of organophilic clay has been examined. The dispersion of silicate layers in copolymers is dependent on the copolymerization ratios of the functional groups, that is, the polarity of the polymer matrix. The alkyl chain lengths of organomodified reagents

also have an important influence on silicate layer dispersions. From a comprehensive viewpoint, the polarity matching between polymers and organophilic clay is an important factor for silicate layer dispersions in polymers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1554–1557, 2005

Key words: clay; dispersions; nanocomposites

INTRODUCTION

In recent years, organic–inorganic nanocomposites have attracted great attention from researchers because they frequently exhibit unexpected hybrid properties synergistically derived from the two components. Some of the most promising composite systems are nanocomposites based on organic polymers and inorganic clay minerals consisting of silicate layers.^{1–19}

Polymer/clay nanocomposites are classified into three types—immiscible, intercalated, and exfoliated—from the viewpoint of silicate layer dispersions.⁵ Exfoliated-type polymer/clay nanocomposites are industrially desired; they exhibit higher performance in mechanical, thermal, and gas-barrier properties in comparison with the other two types. The intercalation of polymers into organophilic clay galleries generally occurs when the polymers contain some functional groups or aromatic rings,^{5,9} but the exfoliation of silicate layers occurs only in limited polymers, such as nylons,^{1,6} epoxy resins,⁸ and maleic anhydride modified polyolefins.^{14–17} In most cases, such as polystyrene and poly(methyl methacrylate) (PMMA), the molten polymer chains intercalate into organophilic clay galleries until the interlayer spacing expands by approximately 1 nm, but the exfoliation of silicate layers does not occur; this forms intercalated-type nanocomposites.⁹ On the other hand, for nylons and maleic anhydride modified polyolefins, the mol-

ten polymer chains continuously intercalate into organophilic clay galleries, and the layered silicates spontaneously exfoliate even without shear; this gives exfoliated-type nanocomposites.¹⁸ These results probably indicate that thermodynamic stability between the silicate layers and the matrix polymers is very important for obtaining exfoliated-type nanocomposites. The thermodynamic stability between the polymers and silicates depends on strong interactions, such as hydrophilic interactions between polar silicate surfaces and functional groups of the polymer and hydrophobic interactions between alkyl chains of the organomodified reagent of the organophilic clay and polymer chains. Especially in the case of polar polymers, hydrophilic interactions are thought to be very important because silicate layers are polar nanoparticles with electric charges.

Silicate layer dispersions in many polymer/clay nanocomposites with various kinds of polymers and organophilic clay have been reported. However, factors of silicate dispersions in polymers have been scarcely studied systematically. The relationship between silicate layer dispersions in polymers and the solubility parameter of polymers has been examined,¹⁹ but this is not enough to interpret silicate layer dispersions in polymers. In this article, we focus on the polarities of polymers and organophilic clay. The polarities of polymers are generally dependent on the types and ratios of functional groups. To clarify the influence of the polarity of the polymer matrix on silicate layer dispersions, we used copolymers containing one kind of functional group. Copolymers are suitable for this study because the polarities are easily changeable by the copolymerization ratio. The influ-

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TABLE I
Organophilic Clay

Organophilic clay	Organo-modified reagent	Organic content (%)	Interlayer spacing (nm)
C12-Mt	CH ₃ (CH ₂) ₁₁ -NH ₃ ⁺	24.1	1.77
C14-Mt	CH ₃ (CH ₂) ₁₃ -NH ₃ ⁺	26.6	1.79
C16-Mt	CH ₃ (CH ₂) ₁₅ -NH ₃ ⁺	28.1	1.95
C18-Mt	CH ₃ (CH ₂) ₁₇ -NH ₃ ⁺	33.1	2.21

ence of organomodified reagents (alkylammonium ions) of organophilic clay is also examined. The features of organophilic clay are dependent on the clay species (chemical structure), ion-exchange capacity (amount of electric charge), and organomodified reagents. Organomodified reagents are thought to be very important for controlling the polarities of silicate layer surfaces. We chose one kind of montmorillonite and used four primary alkylammoniums, whose carbon numbers of alkyl chains were 12, 14, 16, and 18, as organomodified reagents.

EXPERIMENTAL

Materials

Hydrogenated acrylonitrile butadiene copolymers (H-NBRs) and ethylene-methyl methacrylate copolymers (EMMAs) were used as copolymers. H-NBRs (HY-CAR CT) were purchased from Ube Industries, Ltd. (Ube, Japan), with concentrations of acrylonitrile (AN) groups of 10, 17, and 27 mol %. These H-NBRs were high-viscosity liquids at room temperature. EMMAs (Acryft) were purchased from Sumitomo Chemical (Osaka, Japan), with concentrations of methyl methacrylate (MMA) groups of 6, 18, and 38 mol %. PMMA was purchased from Kuraray Co., Ltd. (Okayama, Japan). Primary alkyl amines dodecylamine, tetradecylamine, hexadecylamine, and stearylamine were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and were used without purification. Purified sodium montmorillonite (Kunipia-F) was purchased from Kunimine Industries Co., Ltd. (Tokyo, Japan), with an ion-exchange capacity of 119 mequiv/100 g.

Organophilic clay

Organophilic montmorillonites were prepared by ion-exchange with primary alkylammonium ions with a typical method.¹⁵ The obtained organophilic clays are listed in Table I. As the alkyl chain lengths of the organomodified reagents increased, the organic contents and the interlayer spacing of the organophilic clay increased.

Preparation of the nanocomposites

H-NBR and a powder of the organophilic clay were put into glass beakers, and the samples were heated at 80°C in an oven and then were stirred with a spatula. The samples were waxy at room temperature. The inorganic concentration in the H-NBR/clay nanocomposites was approximately 10 wt %. Pellets of EMMA and a powder of the organophilic clay were melt-compounded at 150°C with a twin-screw extruder, and the obtained strands were pelletized. The inorganic concentration in the EMMA/clay nanocomposites was approximately 5 wt %. The twin-screw extruder was a TEX30 α -45.5BW from Japan Steel Works, Ltd. (Tokyo, Japan). Its screw length was 1365 mm, and its length/diameter ratio was 45.5.

Evaluation of the dispersion of the silicate layers

The dispersion of the silicate layers in the nanocomposites was evaluated by X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM) observation. XRD measurements were performed for waxes of H-NBR/clay nanocomposites and films of EMMA/clay nanocomposites with a Rigaku RAD-B diffractometer (Tokyo, Japan) with Cu K α radiation generated at 30 kV and 30 mA. The films of the EMMA/clay nanocomposites were prepared by compression molding at 150°C. Their thicknesses were 0.4–0.6 mm. TEM observations were performed for 200-nm-thick ultrathin sections cut from the films. TEM observations were taken with a JEOL 2000EX TEM instrument with an acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the H-NBR/clay nanocomposites. In the XRD patterns of H-NBR-27 compounded with C18-Mt, there are two strong peaks at $2\theta = 2.41^\circ$ and $2\theta = 4.86^\circ$ and a small peak at $2\theta = 7.32^\circ$. The peaks from the low 2θ angle correspond to the (001), (002), and (003) planes of stacked silicate layers of C18-Mt. The interlayer spacing calculated from the peak of the (001) plane is 3.66 nm. In the XRD patterns of H-NBR-27 compounded with C12-Mt, C14-Mt, and C16-Mt, there are also strong peaks corresponding to (001) of the organophilic clay at $2\theta = 3.04^\circ$ (C12-Mt, interlayer spacing = 2.90 nm), $2\theta = 2.76^\circ$ (C14-Mt, interlayer spacing = 3.20 nm), and $2\theta = 2.64^\circ$ (C16-Mt, interlayer spacing = 3.34 nm), respectively. The interlayer spacing of the organophilic clay in H-NBR-27 expands in comparison with the initial ones, and this indicates that H-NBR polymer chains intercalate into organophilic clay galleries and intercalated-type nanocomposites are produced. In the XRD patterns of H-NBR-17 compounded with C16-Mt and

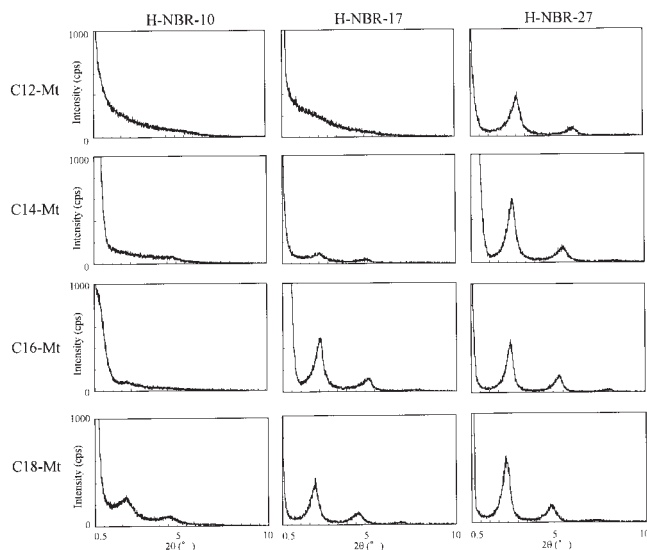


Figure 1 XRD patterns of H-NBR/clay nanocomposites.

C18-Mt, the peaks correspond to stacked layered silicates observed at $2\theta = 2.54^\circ$ (C16-Mt, interlayer spacing = 3.47 nm) and $2\theta = 2.30^\circ$ (C18-Mt, interlayer spacing = 3.84 nm), respectively. In the case of C14-Mt, a broad peak can be observed around $2\theta = 2.5^\circ$, and this indicates that the layered silicate structures are less ordered than samples with C18-Mt and C16-Mt. For C12-Mt, no apparent peak can be observed, and this indicates that an exfoliated-type nanocomposite is produced. In the XRD pattern of NBR-10 compounded with C18-Mt, a broad peak can be observed around $2\theta = 2.3^\circ$, whereas no apparent peak can be observed for C16-Mt, C14-Mt, and C12-Mt; this indicates that silicate layers exfoliate in these nanocomposites.

Focusing on the samples with C14-Mt, in the XRD pattern of the H-NBR-27 nanocomposite, apparent peaks corresponding to stacked silicate layers can be observed; thus, an intercalated-type nanocomposite is formed. As the amounts of AN groups of H-NBR are smaller, the peak intensities corresponding to stacked silicate layers become weaker, and this indicates that the stacking of the silicate layers is disordered. In the XRD pattern of NBR-10, there is no apparent peak, and this indicates that an exfoliated-type nanocomposite is produced. The same tendencies can also be observed for the cases with the other organophilic clay. These results show that the dispersion of silicate layers in H-NBR is dependent on both the AN group ratios of H-NBR and the alkyl chain lengths of the organomodified reagents.

Figure 2 shows the XRD patterns of the EMMA/clay nanocomposites and PMMA/clay nanocomposite. In the XRD pattern of EMMA-38 compounded with C18-Mt, there is a peak at $2\theta = 2.23^\circ$ (interlayer spacing = 3.96 nm) corresponding to stacked silicate layers. The peak is broader and the interlayer spacing

is larger than those of the PMMA/clay nanocomposite shown at $2\theta = 2.72^\circ$ (interlayer spacing = 3.25 nm). The peaks corresponding to stacked silicate layers in EMMA-27 are broader as the alkyl chain lengths of the organomodified reagents are shorter. No peak can be observed in the XRD pattern of EMMA-27/C12-Mt. For EMMA-18, there is a broad shoulder in the XRD pattern with C18-Mt. There is also a broad peak in the XRD pattern with C12-Mt, and it is broader than that of C18-Mt. In the XRD pattern of EMMA-6/C18-Mt, a weaker broad shoulder can be observed in comparison with that of EMMA-18/C18-Mt, and there is no apparent peak in the XRD pattern of EMMA-6/C12-Mt. These XRD patterns show that the dispersion of silicate layers in the EMMA/clay nanocomposites is also dependent on both the MMA group ratios in EMMA and the alkyl chain lengths of organomodified reagents. Figure 3 shows the TEM images of the EMMA/clay nanocomposites and PMMA/clay nanocomposite compounded with C18-Mt. In the PMMA/clay composite, there are aggregates at the micrometer level that consist of stacked layered silicates of 5–20 layers [Fig. 3(c)]. As the ratio of MMA groups decreases in the polymer matrix, the silicate layers disperse more finely with a decreasing number of stacked silicate layers. In the TEM image of the EMMA-6/clay nanocomposite, large parts of silicate layers are found to form disorderly stacked layers composed of several silicates layers, and some silicate layers are found to disperse individually [Fig. 3(a)]. These TEM images also show that the dispersion of silicate layers is dependent on the ratios of MMA groups.

The results for these two copolymer/clay nanocomposites show the following:

- The dispersion of silicate layers in copolymers is dependent on the copolymerization ratios of the functional groups, that is, the polarity of the polymer matrix.

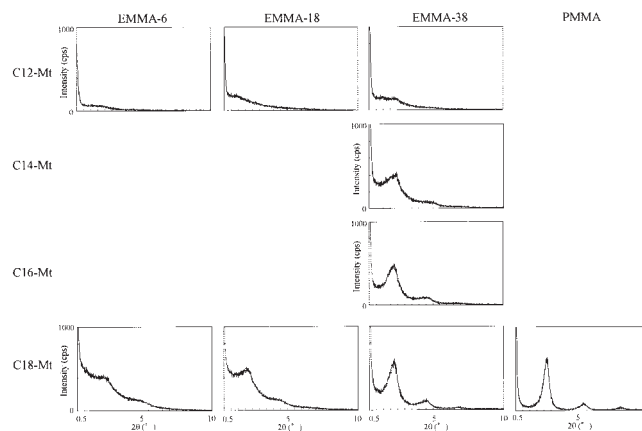


Figure 2 XRD patterns of EMMA/clay nanocomposites.

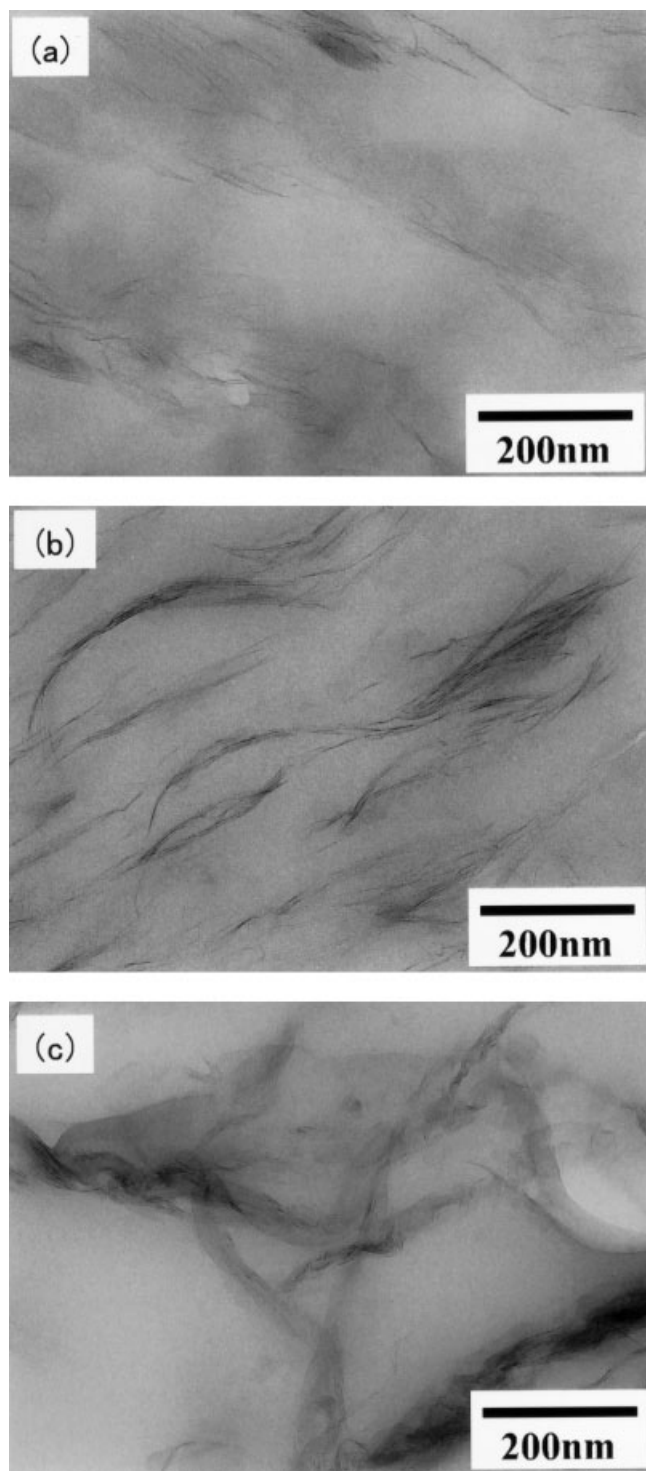


Figure 3 TEM images of the EMMA/clay nanocomposites and PMMA/clay nanocomposite: (a) EMMA-6/C18-Mt nanocomposites, (b) EMMA-38/C18-Mt nanocomposites, and (c) PMMA/C18-Mt nanocomposite.

- The dispersion of silicate layers is also dependent on the alkyl chain lengths of the organomodified reagents. It is suggested that the polarity of the silicate layer surface has an influence on the silicate layer dispersion.
- From a comprehensive viewpoint, it is indicated that the polarity matching between the polymers and organophilic clay is one important factor that determines silicate layer dispersions in polymers.

CONCLUSIONS

The influence of the copolymerization ratio of copolymers and the alkyl chain lengths of organomodified reagents on silicate layer dispersion has been systematically examined. The results indicate that the polarity matching between polymers and organophilic clay is an important factor for silicate layer dispersions in polymers. The factors of silicate layer dispersions will become more precise by further analysis at the molecular level, including the number of functional groups around an ammonium ion and an electric charge on the silicate surface and the interaction between alkyl chains of organomodified reagents and hydrophobic parts of polymer chains.

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