

The Role of Cation Exchange Capacity on the Formation of Polystyrene-Clay Nanocomposites by In-situ Intercalative Polymerization

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ABSTRACT

The effect of cation exchange capacity (CEC) on the formation of polystyrene clay nanocomposites is reported. Two types of 2:1 layered silicate having different CEC's, Wyoming (SWy, 97 meq/100g of clay) and Bentonite-H (BNH, 131 meq/100g of clay) were investigated. The organoclay was prepared by mixing purified clay with octadecyldimethylammonium chloride (ODA) in aqueous solution. The packing of the intercalated ODA surfactant was found to depend on the CEC and the degree of solvent extraction. Two possible phases of the interlayer packing, solidlike and liquidlike, were detected for the extracted BNH due to the charge heterogeneity of the clay. The liquidlike phase shows a good affinity toward styrene monomer which promotes a formation of exfoliated nanocomposites. On the other hand, the solidlike phase shows a restricted dispersion in styrene monomer. The organoclay interlayer shows a limited expansion by the styrene monomer. This leads to the formation of intercalated nanocomposites. An increase in the percentage of organoclay loading hinders a formation of the exfoliated nanocomposites.

Keywords: nanocomposites, polystyrene, surfactants, montmorillonite, intercalation

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INTRODUCTION

Polymer-clay nanocomposites have emerged as a promising new class of high performance composite materials. They exhibit several unique properties such as improved permeability, flame retardance, and high temperature stability (Alexandre, *et al.* 2000; Giannelis, 2000; and LeBaron, *et al.* 1999). Several types of polymer clay nanocomposites have been extensively investigated such as polystyrene Fu, *et al.* (2000), and Okamoto, *et al.* (2000) polymethyl methacrylate Okamoto, *et al.* (2000), and Lee, *et al.* (1996), polypropylene Ma, *et al.* (2000), nylon Usuki, *et al.* (1993) etc. Three major approaches have been applied to the preparation of the nanocomposites. They are melt intercalation, in-situ intercalative polymerization and exfoliation-adsorption and template synthesis (Alexandre and Dubois, 2000). The nanocomposites formed can be characterized according to the degree of dispersion of the clay in the polymeric matrix as a phase separated, intercalated, and exfoliated nanocomposites (Alexandre and Dubois, 2000). The difference in the type of polymer-clay dispersion leads to a difference in the observed physical properties (Alexandre and Dubois, 2000).

The surface properties of the 2:1 layered type aluminosilicate is hydrophilic in nature while most of the commodity polymers are organophilic. This presents a difficulty in the mixing of the polymer and the clay. The problem can be overcome by modifying the clay surface with an organic surfactant. Depending on the type and the amount of the surfactant coverage and its chemistry, the properties of the clay surface can be controlled. The surfactant was found to play a crucial role in determining the organoclay dispersion in the polymeric matrix (Okamoto, *et al.* 2000). This affects the final properties of the nanocomposite.

The goal of this work is to investigate the role of the cation exchange capacity of the

layered silicate on the formation of polymer clay nanocomposites. Two types of layered silicate with different cation exchange capacity were investigated.

EXPERIMENT

Swy-1 and bentonite H (BNH) were a gift from Ceramic 'R' Us Co.' Ltd., Thailand. Octadecyldimethylamine (95%) and benzoyl peroxide were kindly provided by Thai Specialty Chemical, Thailand. Hydrochloric acid was purchased from LabScan, Thailand. Deionized water was obtained from Nanopure, Millipore.

Impurities were screened by precipitation in deionized water. Only the suspended clay was selected for further treatment. The clays were converted into sodium saturated clay by treatment in 1.0 M sodium chloride solution. The clay precipitate was washed in a dialysis tube and tested with silver nitrate solution. The test was done until no white silver chloride precipitate was detected. The clay was dispersed in deionized water for a particle selection by a centrifuge (Sorvall RC-5C equipped with GSA250 mL tube rotor) at 750 rpm for 15 minutes.

Organoclay preparation: A solution of 5.0 g of ODA in ethanol was acidified with dilute hydrochloric acid to yield a white precipitate. The precipitate was filtered, washed with cold water, and dried in a desiccator.

Organoclay was prepared by dispersing 1.0 g of the pure clay in warm deionized water. In a separate container, 1.15 g of ODA in 60.0 mL deionized water was heated to 70°C. ODA solution was poured into the clay suspension. The reaction was achieved by vigorously stirring at 70°C for another 2 hrs. The precipitate was warm filtered. Part of the sample was separated for vacuum drying and will be referred further to as "unextracted" sample. The organoclay is dispersed in 50.0 mL of warm water at 70°C

and stirred for 20 min. The suspension was warm filtered. The washing was repeated for 5 times prior to drying at 70°C under vacuum yielding the “extracted” sample.

Organoclay dispersion: The dispersion was achieved by dispersing a proper amount of the organoclay (percent weight by volume) in styrene monomer. The mixture was sonicated for 15-30 minutes in an ultrasonic bath. 2% benzoyl peroxide initiator was added to the solution and sonicated for an additional 10 minutes. The mixture was sealed under a nitrogen atmosphere before polymerization. The polymerization was achieved by heating the suspension at 100°C for 12 hours.

X-ray diffraction was carried out by a Bruker D8 ADVANCE with CuK α radiation (1.5406 Å). The voltage and current were 40 kV and 40 mA. Transmission electron micrograph was taken by JEOL 2010 TEM at an accelerating voltage of 200 kV. The sample was cut by ultramicrotome using a glass knife.

RESULTS AND DISCUSSIONS

An observed d-spacing for the unextracted organoclay are shown in Figure 1 and Table 1. Higher order of d_{001} maxima are observed for unextracted ODA-BNH which suggest a coherent stacking of the individual organoclay layers along their crystallographic z-axis. The corresponding d_{001} -spacing are 40.2 Å for ODA-BNH and 17.7 Å for ODA-SWy. The amount of the surfactant withheld by the clay was determined by TGA [Table 1]. The percent mass loss, in the range of 100-600°C, for unextracted ODA-BNH is 44%. This is equivalent to the 229 meq of the ODA molecule absorbed in 100g of clay. The number is far beyond a typical CEC value of smectite clay (Yang, *et al.* 2001; Vaia, *et al.* 1994; Yui, *et al.* 2002; Xu, *et al.* 1995; Lee, *et al.* 2002; and Ho, *et al.* 2001). This suggests that there should be an extra amount of the ODA molecules, physisorbed, present in the clay. The area occupied by the

surfactant molecules on the surface can be estimated from the amount of the ODA absorbed and the total surface area of the clay (Yui, *et al.* 2002). The total surface area of BNH and SWy clay, both having a particle size less than 2 μ m, are around 750 m²/gram (Yui, *et al.* 2002). The estimated area occupied by an ODA molecule on the clay surface is 54 Å². The contribution of the absorption of the ODA molecule at the edge of the clay surface is considered negligible. The evidence of solidlike packing can be supported by XRD where the observed interlayer spacing is 40.2 Å. The possible packing of the corresponding interlayer ODA is believed to be a tilted bilayer. The mass loss for unextracted ODA-SWy is 25% and corresponds to the amount of ODA absorbed in the clay of 97 meq/100g of clay. The area occupied by ODA on the clay surface is estimated to be 128 Å²/molecule. The area is about 2 times larger than in ODA-BNH which suggests a higher tilting angle of the ODA molecule with respect to the clay surface. This results in a smaller change in the interlayer spacing, 17.7 Å for ODA-SWy. The packing will be referred to as the liquidlike phase.

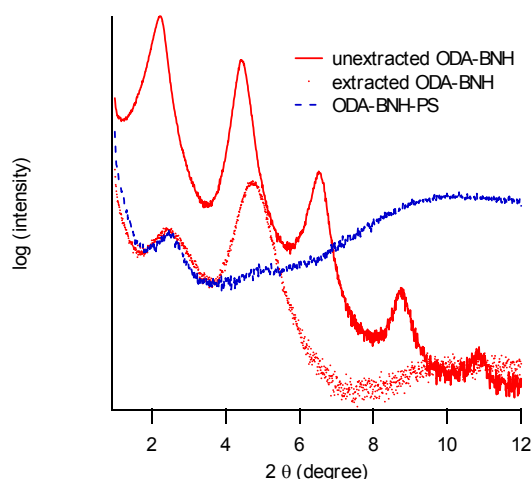


Figure 1 XRD patterns of unextracted ODA-BNH organoclay (solid line), extracted ODA-BNH (dot), and ODA-BNH-PS nanocomposite (dash).

Table 1 The dispersion property of the organoclay in styrene monomers and nanocomposites type.

Organo-clay	d-spacing of organoclay (Å)	% weight loss	amount of ODA absorbed (meq/100g of clay)	appearance in styrene monomer	d-spacing of the nanocomposites (Å)	Nanocomposites type.
ODA-BNH (unextracted)	40.2	44	229	Cloudy	35.8	Intercalated
ODA-BNH (extracted)	35.7, 18.6	31	131	Cloudy	35.8	Intercalated
ODA-SWy	17.7	25	97	Transparent	NA	Delaminated

The samples were subjected to the solvent extraction process (Ho and Briber, 2001). No change in the spacing was detected for the ODA-SWy after solvent treatment as determined by the XRD. A new phase of the organoclay with a smaller interlayer spacing, 18.6 Å, is observed along with the higher spacing phase, 35.7 Å, in ODA-BNH. The intensity of the 18.6 Å peak was increased as the clay was subjected to a longer extraction process while an opposite trend was observed for the peak at 35.7 Å. The higher d-spacing phase corresponds to the solidlike packing of the intercalated ODA. For the liquidlike packing, the ODA molecule is tilted at a higher angle with respect to the clay surface (Yui, *et al.* 2002). The spacing is comparable to those observed in ODA-SWy. An extracted ODA shows a weight loss of 31%. The difference in the weight loss of the unextracted and extracted ODA-BNH is believed to be accounted for by physisorbed ODA. This is only observed in a solidlike phase. The ODA-SWy organoclay does not show any difference in the mass loss for the unextracted and the extracted sample. The amount of the ODA absorbed in the extracted phase is considered as the CEC.

The major difference for these two phases of the organoclay is in the degree of the surface coverage. The loading of ODA in the cation exchange reaction is about 2 times higher than an estimated CEC of the clay (Yui, *et al.* 2002; and Xu, *et al.* 1995). The closer packing of the surfactant in ODA-BNH may promote the amount of absorbed ODA.

This is consistent with the observed d-spacing of the unextracted sample where the intercalated molecules consist of an ionic bond molecule and physically absorbed molecule. The surfactant can be imagined as a solidlike packed surfactant layer covering the clay surface. The physisorbed surfactants which are not tightly bound to the anionic sites of the clay surface can be washed away. The remaining surfactants are the ionic bonded surfactant. The loss of the physisorbed surfactant results in a reduction of the weight loss and a decrease in the d-spacing. The split of the peak in the extracted ODA-BNH suggests that the BNH clay possess the charge heterogeneity (Yang, *et al.* 2001). The amounts of the absorbed ODA in the clay were determined from the TGA weight loss of the extracted sample in the extracted process. They are 97 meq/100g of clay for SWy and 131 meq/100g of clay for BNH. The number represents an average value for CEC of the organoclay because both are cationically bonded molecules. The difference in the amount of the absorbed ODA between an extracted and an unextracted sample should represent the difference in the amount of the higher intercalated higher layer charge clay (Yang, *et al.* 2001). The area occupied by an ODA molecule in extracted ODA-BNH is the result of averaging between the solidlike and liquidlike packed phase.

Organoclay dispersion: The dispersion of the organoclay in the styrene monomer is shown in Table 1. Two main types of dispersion, which are cloudy

dispersion and transparent dispersion, are observed for the ODA organoclay. All the organoclay dispersion in the styrene monomer appears as a cloudy dispersion except for the ODA-SWy where the transparent dispersion is observed. The cloudiness is the result of the light scattered by a primary particle of the organoclay suspended in the styrene monomer (Ho, *et al.* 2001; and Vaia, *et al.* 1995). The transparent suspension suggests that the organoclay platelets are very well dispersed in the styrene monomer. This implies that the ODA-SWy has a good affinity toward the styrene monomer (Ishida, *et al.* 2000). The washing of the organoclay does not have any affect on the appearance of the organoclay in the styrene monomer.

Nanocomposites: The polymerization was done at elevated temperature by using benzoyl peroxide as the initiator. The spacing of PS-clay nanocomposites are shown in Table 1. The nanocomposites of unextracted BNH-PS show a reduction in the interlayer spacing from 40.2 Å to 35.8 Å. The reduction in the spacing may be due to the styrene monomer which leaches out some physisorbed ODA. This causes a decreased in the interlayer spacing. The peak is also an indication that the nanocomposite is an intercalated nanocomposites.

The extracted ODA-BNH-PS nanocomposite shows a diffraction maxima at 35.8 Å and 17.9 Å which are indexed as the d_{001} and d_{002} . The observed peaks are the result of the intercalated PS in the solidlike phase of the organoclay. The peak due to the nanocomposite disappears in the liquidlike packed phase. This can be explained by a better match in the affinity of the styrene monomer toward the loosely packed ODA organoclay. The layers of liquidlike ODA-BNH were swelled or delaminated in styrene monomer while the layers of the solidlike packed ODA-BNH remain intact. This observation suggests that the clay possess the charge heterogeneity. The result from ODA-

SWy-PS nanocomposite also consistent with the result observed from the liquidlike phase of ODA-BNH-PS organoclay. The ODA-SWy organoclay forms only a liquid-like phase. The disappearance of the d_{001} peak in ODA-SWy-PS nanocomposites may be due to any of the following effects. The crystal size may be too small to be detected by XRD. The second possibility is the fact that the spacing may be higher than the detection limit of the XRD at 88.0 Å. The nanocomposites may form as exfoliated nanocomposite where the organoclay is delaminated and dispersed in the polymer matrix. The exact phenomena can be revealed by the TEM micrograph (Kornmann, *et al.* 2001).

The micrograph of ODA-SWy-PS nanocomposite shows that an individual clay platelet is in fact dispersed into a thinner stacking throughout the polymer matrix [Figure 2]. The dark line represents the silicate layer while the grey background represents the organoclay or polymer. The spacing is estimated to be around 80 Å with a few layers of organoclay platelet. This indicates that the composite is indeed an exfoliated nanocomposite (Alexandre and Dubois, 2000).

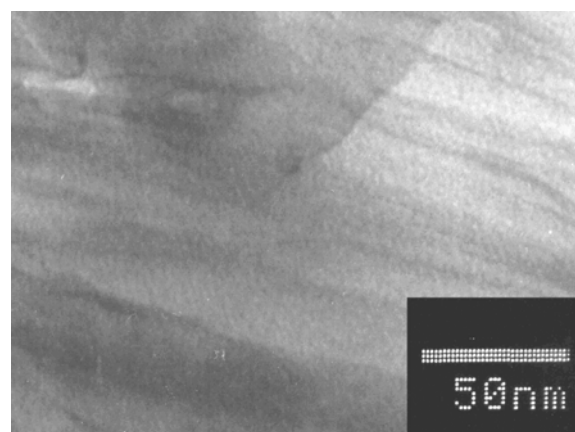


Figure 2 TEM micrograph of 1% ODA-SWy-PS nanocomposites.

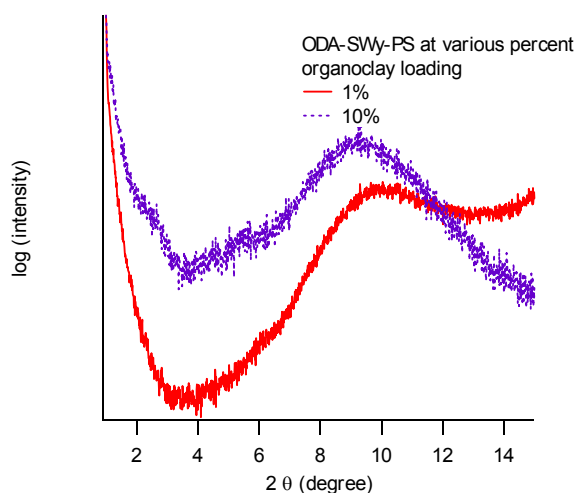


Figure 3 XRD patterns of ODA-SWy-PS at 1% ODA-SWy loading (solid line), and 10% ODA-SWy loading (dot)

An effect of the organoclay loading: As the percentage of clay loading is increased for the ODA-SWy-PS nanocomposite, two very broad peaks start to emerge in the range of $2\theta = 2.0^\circ$ - 3.5° and $2\theta = 4.1^\circ$ - 6.0° [Figure 3]. This is believed to be due to a limited expansion of the organoclay in the styrene monomer. The amount of the organoclay loading is increased while the volume of available for the expansion, and the volume of the styrene monomer, is fixed. The ODA-SWy organoclay is delaminated and dispersed throughout the styrene monomer. Each of the individual organoclay layers would have less available space in the solution of styrene monomer as its percentage loading is increased. Thus the expansion of the organoclay is suppressed. This effect is even more pronounced as the amount of the organoclay is increased. This is consistent with the emerging new peak which becomes more prominent as the percent loading is increased. The broad peak indicates a distribution of the interlayer spacing of the ODA-SWy-PS nanocomposite. This supports the idea that the ODA-SWy organoclay may be delaminated in the styrene monomer prior to reforming an aggregation. This is different from the case of the solidlike phase ODA-

BNH organoclay where the peaks originated from the low affinity of the organoclay toward the styrene monomer. This hinders the delamination of the organoclay.

CONCLUSIONS

The type of the nanocomposites formed by the in situ intercalation polymerization is controlled by the organoclay dispersion in the styrene monomer. A good dispersion of the organoclay was observed only in the case of the liquidlike packing of the ODA molecules on the clay surface where the formation of the exfoliated nanocomposite was observed. The clay with a solidlike packing of the ODA molecule does not have a good affinity toward the styrene monomer. Thus resulting in the intercalated nanocomposites. An increase in the percentage loading of the organoclay results in a limited expansion of the organoclay in the styrene monomer which hinder the exfoliation of the organoclay platelet in the PS matrix.

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