Role of the Cation-Exchange Capacity in the Formation of Polystyrene–Clay Nanocomposites by *In Situ* Intercalative Polymerization

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ABSTRACT: An effect of the cation-exchange capacity (CEC) on the formation of polystyrene–clay nanocomposites is reported. Two types of 2:1 layered silicates with different CECs, Wyoming (97 mequiv/100 g of clay) and bentonite H (BNH; 131 mequiv/100 g of clay) were investigated. The organoclay was prepared through the mixing of purified clay and octadecyldimethylammonium chloride (ODA) in an aqueous solution. The packing of the intercalated ODA surfactant depended 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 because of the charge heterogeneity of the clay. The liquidlike phase showed a good affinity toward the styrene monomer, which promoted the formation of exfoliated nanocomposites. On the other hand, the solidlike phase showed a restricted dispersion in the styrene monomer. The organoclay interlayer showed limited expansion by the styrene monomer. This led to the formation of intercalated nanocomposites. An increase in the organoclay loading hindered the formation of the exfoliated nanocomposites. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 785–789, 2005

Key words: nanocomposites; polystyrene; surfactants

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 retardancy, and high temperature stability.[1–3] Several types of polymer–clay nanocomposites have been extensively investigated, such as polystyrene (PS),[4,5] poly(methyl methacrylate),[5,6] polypropylene,[7] and nylon.[8] 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.[1] The nanocomposites can be characterized according to the degree of dispersion of the clay in the polymeric matrix as phase-separated, intercalated, and exfoliated nanocomposites.[1] The different types of polymer–clay dispersions lead to differences in the observed physical properties.[1]

The surface of 2:1 layered aluminosilicate is hydrophilic, whereas most commodity polymers are organophillic. This presents a difficulty for the mixing of polymers and clay. The problem can be overcome by the modification of the clay surface with an organic surfactant. Depending on the type and amount of the surfactant coverage and its chemistry, the properties of the clay surface can be controlled. The surfactant plays a crucial role in determining the organoclay dispersion in a polymeric matrix.[5] This affects the final properties of the nanocomposite.

The goal of this work was to investigate the role of the cation-exchange capacity (CEC) of a layered silicate on the formation of polymer–clay nanocomposites. Two types of layered silicates with different CECs were investigated.

EXPERIMENTAL

Wyoming (SWy) and bentonite H (BNH) were gifts from Ceramic 'R' Us Co., Ltd. (Bangkok, Thailand).

Octadecyldimethylamine (95%) and benzoyl peroxide were kindly provided by Thai Specialty Chemical (Bangkok, Thailand). Hydrochloric acid was purchased from LabScan (Bangkok, 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 a treatment in a 1.0*M* sodium chloride solution. The clay precipitate was washed in a dialysis tube and tested with a silver nitrate solution. The test was performed until no white silver chloride precipitate was detected. The clay was dispersed in deionized water for particle selection by a Sorvall RC-5C centrifuge (equipped with a GSA 250-mL tube rotor) at 750 rpm for 15 min.

Organoclay preparation

A solution of 5.0 g of octadecyldimethylammonium chloride (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 the dispersion of 1.0 g of the pure clay in warm deionized water. In a separate container, 1.15 g of ODA in 60.0 mL of deionized water was heated to 70°C. An ODA solution was poured into the clay suspension. The reaction was achieved by vigorous stirring at 70°C for another 2 h. The precipitate was warm-filtered. Part of the sample was separated for vacuum drying and is called the unextracted sample. The organoclay was 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 five times before drying at 70°C *in vacuo*, which yielded the extracted sample.

Organoclay dispersion

The dispersion was achieved by the dispersion of a proper amount of the organoclay (w/v) in styrene monomer. The mixture was sonicated for 15–30 min in an ultrasonic bath. A benzoyl peroxide initiator (2%) was added to the solution, and the solution was son-
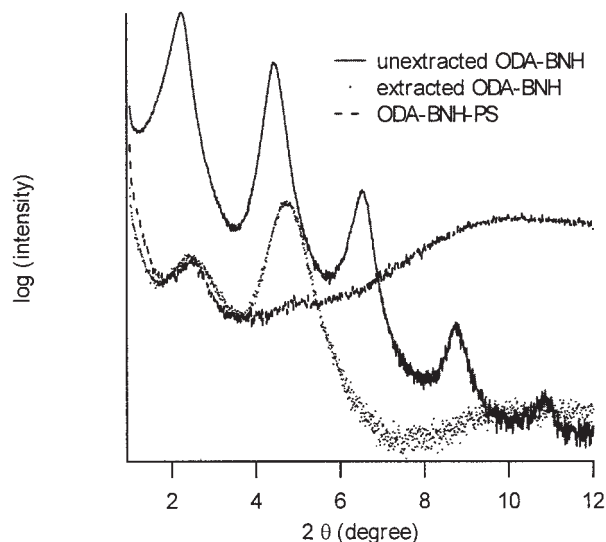

Figure 1 XRD patterns of unextracted ODA–BNH organoclay, extracted ODA–BNH, and ODA–BNH–PS nanocomposites.

icated for an additional 10 min. The mixture was sealed under a nitrogen atmosphere before the polymerization. The polymerization was achieved by the heating of the suspension at 100°C for 12 h.

X-ray diffraction (XRD) was carried out with a Bruker D8 Advance with Cu Kα radiation (1.5406 Å). The voltage and current were 40 kV and 40 mA. Transmission electron microscopy (TEM) micrographs were taken with a JEOL 2010 transmission electron microscope at an accelerating voltage of 200 kV. The samples were cut with an ultramicrotome with a glass knife.

RESULTS AND DISCUSSIONS

Observed d-spacings for the unextracted organoclay are shown in Figure 1 and Table I. A higher order of d_{001} maxima was observed for unextracted ODA–BNH and suggested a coherent stacking of the individual organoclay layers along their crystallographic z axis. The corresponding d_{001}-spacings were 40.2 Å for ODA–BNH and 17.7 Å for ODA–SWy. The amount of

TABLE I
Dispersion Properties of the Organoclay in the Styrene Monomers and Nanocomposite Type

Organoclay	d-spacing of organoclay (Å)	Weight loss (%)	Amount of ODA absorbed (mequiv/100 g of clay)	Appearance in the styrene monomer	d-spacing of the nanocomposites (Å)	Nanocomposite 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	Not applicable	Delaminated

the surfactant withhold by the clay was determined by thermogravimetric analysis (TGA; Table I). The mass-loss percentage, in the range of 100–600°C, for unextracted ODA–BNH was 44%.[9,10] This was equivalent to 229 mequiv of ODA molecules absorbed in 100 g of clay. The number was far beyond a typical CEC of smectite clay.[9–16] This suggested 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 could be estimated from amount of the ODA absorbed and the total surface area of the clay.[13] The total surface area of BNH and SWy clay, both with a particle size of less than 2 μm, was around 750 m^2/g.[13] The estimated area occupied by ODA molecules on the clay surface was 54 Å^2. The contribution of the absorption of the ODA molecule at the edge of the clay surface was considered negligible. Solidlike packing was supported by XRD; the observed interlayer spacing was 40.2 Å. The possible packing of the corresponding ODA interlayer was believed to be a tilted bilayer. The mass loss for unextracted ODA–SWy was 25% and corresponded to the amount of ODA absorbed into the clay (97 mequiv/100 g of clay). The area occupied by ODA on the clay surface was estimated to be 128 Å^2/molecule. The area was about 2 times larger than that in ODA–BNH and suggested a higher tilting angle of the ODA molecule with respect to the clay surface. This resulted in a smaller change in the interlayer spacing (17.7 Å for ODA–SWy). The packing is called the liquidlike phase.

The samples were subjected to the solvent-extraction process.[16] No change in the spacing was detected for ODA–SWy after the solvent treatment, as determined by XRD. A new phase of the organoclay with a smaller interlayer spacing, 18.6 Å, was observed along with a 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, whereas the opposite trend was observed for the peak at 35.7 Å. The higher d-spacing phase corresponded to the solidlike packing of the intercalated ODA. For the liquidlike packing, the ODA molecule was tilted at a higher angle with respect to the clay surface.[12,13] The spacing was comparable to that observed in ODA–SWy. Extracted ODA showed a weight loss of 31%. The difference in the weight loss of the unextracted and extracted ODA–BNH was believed to be accounted for by physisorbed ODA. This was only observed in the solidlike phase. The ODA–SWy organoclay did not show any difference in the mass loss for the unextracted and extracted samples. The amount of ODA absorbed in the extracted phase was considered as CEC.

The major difference in these two phases of the organoclay was in the degree of surface coverage. The loading of ODA in the cation-exchange reaction was
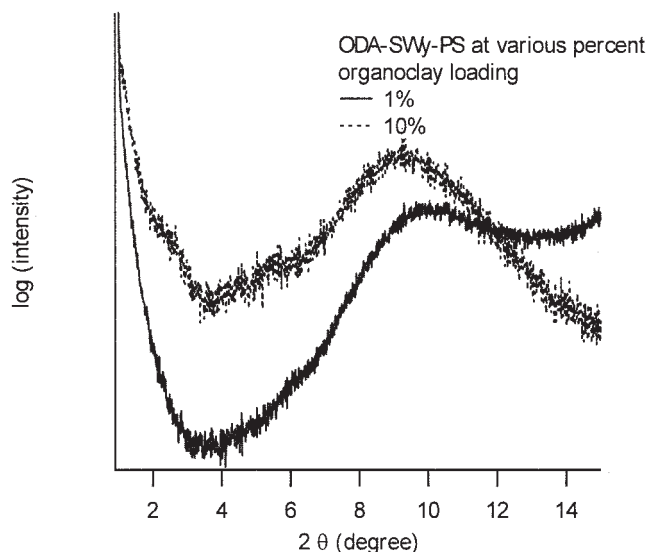

Figure 2 XRD patterns of ODA–SWy–PS at 1 and 10% ODA–SWy loadings.

about 2 times higher than the estimated CEC of the clay.[12–14] The closer packing of the surfactant in ODA–BNH may have promoted the amount of absorbed ODA. This was consistent with the observed d-spacing of the unextracted sample, in which the intercalated molecules consisted of an ionic-bonded molecule and a physically absorbed molecule. The surfactant could be imagined as a solidlike, packed surfactant layer covering the clay surface. The physisorbed surfactants, which were not tightly bound to the anionic sites of the clay surface, could be washed away. The remaining surfactants were the ionic-bonded surfactants. The lost of the physisorbed surfactant resulted in a reduction of the weight loss and a decrease in the d-spacing. The split of the peak in the extracted ODA–BNH suggested that the BNH clay possessed charge heterogeneity.[11] 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 were 97 mequiv/100 g of clay for SWy and 131 mequiv/100 g of clay for BNH. The numbers represent an average value for CEC of the organoclay because both were cationically bonded molecules. The difference in the amount of the absorbed ODA between the extracted and unextracted samples should represent the difference in the amount of the higher interstratified higher layer charge clay.[11] The area occupied by the ODA molecules in extracted ODA–BNH was the result of averaging between the solidlike and liquidlike packed phases.

Organoclay dispersion

The dispersion of the organoclay in the styrene monomer is shown in Table I and Figure 2. Two main types

of dispersions, cloudy and transparent, were observed for the ODA organoclay. All the organoclay dispersions in styrene monomer appeared to be cloudy, except for ODA–SWy, for which a transparent dispersion was observed. The cloudiness was the result of light scattered by primary particles of the organoclay suspended in the styrene monomer.[16,17] The transparent suspension suggested that the organoclay platelets were very well dispersed in the styrene monomer. This implies that ODA–SWy had good affinity toward the styrene monomer.[18] The washing of the organoclay did not have any affect on the appearance of the organoclay in the styrene monomer.

Nanocomposites

The polymerization was performed at an elevated temperature with benzoyl peroxide as the initiator. The spacings of the PS–clay nanocomposites are shown in Table I. The nanocomposites of unextracted BNH–PS showed a reduction in the interlayer spacing from 40.2 to 35.8 Å. The reduction in the spacing may have been due to the styrene monomer, which leached out some of the physisorbed ODA. This caused a reduction in the interlayer spacing. The peak was also an indication that the nanocomposites were intercalated nanocomposites.

The extracted ODA–BNH–PS nanocomposite showed diffraction maxima at 35.8 and 17.9 Å, which were indexed as d_{001} and d_{002}. The observed peaks were the results of intercalated PS in the solidlike phase of the organoclay. The peak due to the nanocomposite disappeared in the liquidlike packed phase. This could 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 the styrene monomer, whereas the layers of the solidlike packed ODA–BNH remained intact. This observation suggested that the clay possessed charge heterogeneity. The result from the ODA–SWy–PS nanocomposite was also consistent with the result observed from the liquidlike phase of the ODA–BNH–PS organoclay. The ODA–SWy organoclay formed only the liquidlike phase. The disappearance of the d_{001} peak in the ODA–SWy–PS nanocomposites may have been due to any of the following effects. The crystallize size may have been too small to be detected by XRD. The spacing may have been higher than the detection limit of XRD at 88.0 Å. The nanocomposites may have formed as exfoliated nanocomposites in which the organoclay was delaminated and dispersed in the polymer matrix. The exact phenomena could be revealed with TEM.[18,19]

The micrograph of the ODA–SWy–PS nanocomposite shows that an individual clay platelet was in fact dispersed into a thinner stacking throughout the poly-
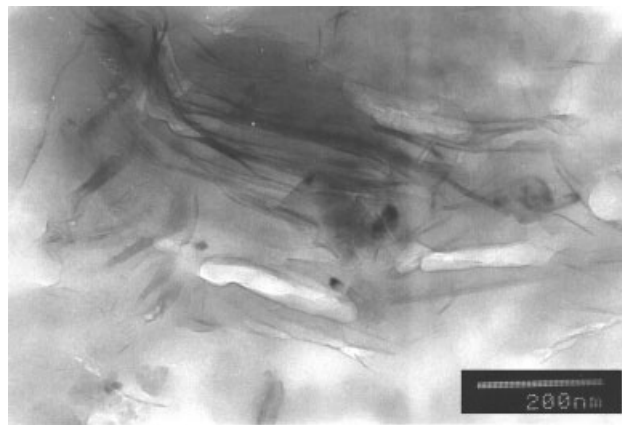

Figure 3 TEM micrograph of 1% ODA–SWy–PS nanocomposites.

mer matrix (Fig. 3). The dark line represent the silicate layer, whereas the grey background represent the organoclay or polymer. The spacing was estimated to be around 80 Å with a few layers of organoclay platelets. This indicated that the composite was indeed an exfoliated nanocomposite.[1,19]

Effect of the organoclay loading

As the clay loading was increased for the ODA–SWy–PS nanocomposite, two very broad peaks started to emerge at $2\theta = 2.0–3.5°$ and $2\theta = 4.1–6.0°$. This was believed to be due to a limited expansion of the organoclay in the styrene monomer. The amount of the organoclay loading increased, whereas the volume available for the expansion, the volume of the styrene monomer, was fixed. The ODA–SWy organoclay was delaminated and dispersed throughout the styrene monomer. Each of the individual organoclay layers would have less available space in the solution of the styrene monomer as its percentage loading increased. Thus, the expansion of the organoclay was suppressed. This effect was even more pronounced as the amount of the organoclay was increased. This was consistent with the emerging new peak, which became more prominent as the loading was increased. The broad peak indicated a distribution of the interlayer spacing of the ODA–SWy–PS nanocomposite. This supported the idea that the ODA–SWy organoclay may have been delaminated in the styrene monomer before reforming an aggregation. This was different from the case of the solidlike phase ODA–BNH organoclay, in which the peaks originated from the low affinity of the organoclay toward the styrene monomer. This hindered the delamination of the organoclay.

CONCLUSIONS

Two types of PS–clay nanocomposites, exfoliated and intercalated, were found to depend on the clay surface

treatment. The exfoliated nanocomposite was observed when an organoclay with a liquidlike packing of ODA molecules (low surface coverage) was used. The intercalated nanocomposite was found for an organoclay with solidlike packing (high surface coverage). An increase in the loading of the organoclay resulted in a limited expansion of the organoclay in the styrene monomer. This hindered the expansion of the individual organoclay layer in the PS matrix.

References

1. Alexandre, M.; Dubois, P. Mater Sci Eng 2000, 28, 63.
2. Giannelis, E. P. Appl Organomet Chem 2000, 12, 675.
3. Lebaron, P. C.; Wang, Z.; Pinnavaia, T. J. Appl Clay Sci 1999, 15, 11.
4. Fu, Z.; Qutubuddin, S. Mater Lett 2000, 42, 12.
5. Okamoto, M.; Morita, S.; Taguchi, H.; Kim, Y. H.; Kotaka, T.; Tateyama, H. Polymer 2000, 41, 3887.
6. Lee, D. C.; Jang, L. W. J Appl Polym Sci 1996, 61, 1117.
7. Ma, J.; Qi, Z.; Hu, Y. J Appl Polym Sci 2000, 82, 3611.
8. Usuki, A.; Kojiyama, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1179.
9. Xie, W.; Gao, Z.; Pan, W.-P.; Hunter, D.; Singh, A.; Vaia, R. Chem Mater 2001, 13, 2979.
10. Xie, W.; Gao, Z.; Lui, K.; Pan, W.-P.; Vaia, R.; Hunter, D.; Singh, A.; Hunter, D.; Singh, A. Thermochim Acta 2001, 367, 339.
11. Yang, J. H.; Han, Y. S.; Choy, J. H.; Tateyama, H. J Mater Chem 2001, 11, 1305.
12. Vaia, R. A.; Teukolsky, R. K.; Giannelis, E. P. Chem Mater 1994, 6, 1017.
13. Yui, T.; Yoshida, H.; Tachibana, H.; Tryk, D. A.; Inoue, H. Langmuir 2002, 18, 891.
14. Xu, S.; Boyd, S. A. Langmuir 1995, 11, 2508.
15. Lee, S. Y.; Kim, S. J. J Colloid Interface Sci 2002, 248, 231.
16. Ho, D. L.; Briber, R. M.; Glinka, C. J. Chem Mater 2001, 13, 1923.
17. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Gainnelis, E. P. Macromolecules 1995, 28, 8080.
18. Ishida, H.; Campbell, S.; Blackwell, J. Chem Mater 2000, 12, 1260.
19. Kornmann, X.; Lindberg, H.; Berglund, L. A. Polymer 2001, 42, 1303.