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Ion exchange reaction in preparation of clay-dispersed polystyrene nanocomposite by emulsion polymerization-coagulation technique

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Summary

In the present work clay/polystyrene hybrids were prepared by emulsion polymerization, and subsequent coagulation technique. Two different coagulants, magnesium sulfate and aluminum sulfate, were used in order to compare the coagulation efficiency, and the final structure and dispersion-state were analyzed by X-ray diffraction method. Aluminum sulfate-water solution is more effective in coagulation of polystyrene emulsion than magnesium sulfate-water solution. Small peaks near $2\theta = 6°$ appear in XRD diffraction patterns of all the hybrids. It is confirmed that these small XRD peaks are ascribed with the ordering of silicate layers between which hydrated metal complex polycations are located with layers of water molecules.

Introduction

Hybrid organic-inorganic composites typically exhibit mechanical properties superior to those of their separate components. To optimize the performance properties of these materials, it is usually desirable to disperse the inorganic components in the organic matrix on a nanometer length scale. One successful approach to achieve such nanocomposites is the *in situ* polymerization of metal alkoxides in organic matrices via the sol-gel process. A good alternative to the sol-gel process for the preparation of organic-inorganic nanocomposites is to disperse in polymer matrix smectite clays and other layered inorganic materials that can be broken down into nano-scale building blocks (1-9). The individual 10 Å thick clay layer in exfoliated nanocomposite is separated in a continuous polymer matrix by the average distance depending upon ceramic loading. Usually, the clay content of exfoliated clay nanocomposite is much lower than that of intercalated nanocomposites. Consequently, exfoliated nanocomposites have monolithic structure with properties related primarily to those of the matrix polymers.

Three different methods preparing clay-dispersed nanocomposites are well known up to now: i) solution drying, ii) monomer intercalation-polymerization, and iii) direct polymer intercalation-shearing methods. Recently, the third method has received an

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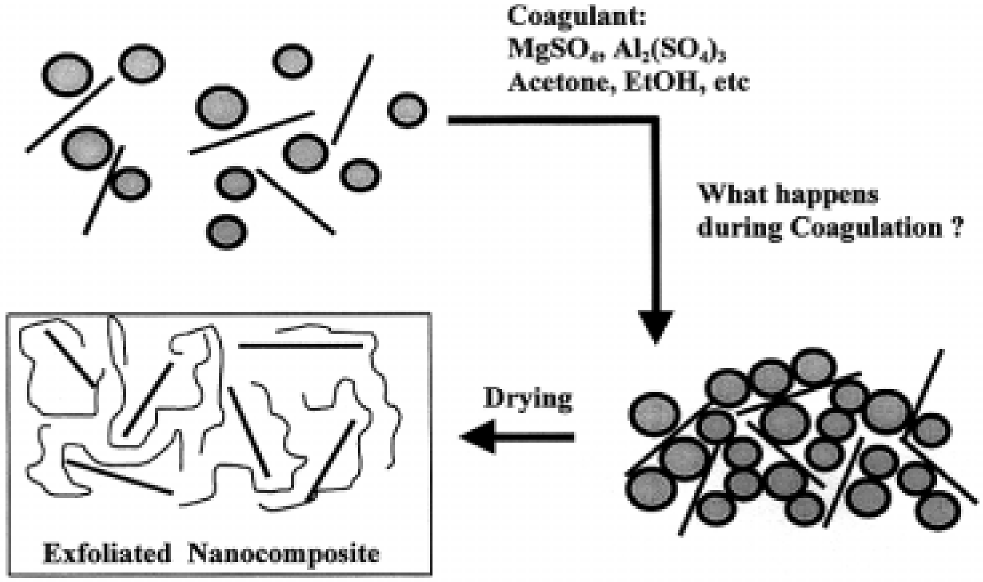

Scheme I. Preparation of clay-dispersed nanocomposite by emulsion polymerization-coagulation technique. Bold circle around a particle represents negatively charged surface of the colloidal particle due to the absorption of anionic surfactant such as sodium lauryl sulfate.

extensive interest because polymers can be inserted directly into the layered material without the aid of a solvent. Subsequent shearing in a melt mixer allows the individual clay layer to be dispersed homogeneously in a matrix polymer. Using this method, however, silicate layers are pretreated with an organic intercalant in the water- or organic solvent-swollen state in order for polymer chains to have favorable interaction with silicate layers of clay. When the Na^+-Montmorillonite is exchanged with an organic intercalant in water-swollen state, it possesses a good swelling capability for water, and its interlayer spacing became large enough to be penetrated by some nano-scale particles, e.g. colloidal particles. Using this concept, Lee *et al*. (4,9) prepared some clay-dispersed polymer nanocomposites by the emulsion polymerization-coagulation technique.

In the present work clay/PS hybrids were prepared by the emulsion polymerization-coagulation technique, which is depicted in Scheme I. Two different coagulants, magnesium sulfate and aluminum sulfate, were used in order to compare the coagulation efficiency, and the final structure and dispersion-state were analyzed by X-ray diffraction method.

Experimental

Preparation of clay-dispersed hybrids

Clay used in this study is "Cloisite®Na^+" supplied by the Southern Clay Products Inc., which is a sodium type montmorillonite. Styrene was emulsion polymerized in the presence of potassium persulfate ($K_2S_2O_8$) and sodium lauryl sulfate ($CH_3(CH_2)_{11}OSO_3Na$) as initiator and surfactant, respectively. A 1 L four-neck resin kettle fitted with a mechanical stirrer, thermometer and condenser was charged with 500 g of distilled water, 10 g of Na^+-Montmorillonite, and 5 g of sodium lauryl sulfate. After the vessel temperature being raised to 75 °C, 100 g of styrene monomer (Kanto Chemical Co., reagent grade) and potassium persulfate were added while applying a constant, gentle agitation. Polymerization was continued for 3 hours to complete the reaction with a stirring rate of 200 rpm. The emulsion colloid after polymerization was poured into distilled water containing an appropriate amount of coagulant under constant stirring. After further stirring for 30 min, white precipitated clay/styrene hybrids were filtered using filter papers (Toyo Roshi Kaisha Ltd., ADVANTEC). The resulting materials were dried in a convection oven at 100 °C. The dried composites were ground with a blade mixer, and dried further in a vacuum oven at 80 °C for a day.

Preparation of Metal Complex Polycation-intercalated Montmorillonite

In a 1 L resin kettle, 10 g of montmorillonite were dispersed in 500 g of distilled water at 75 °C for 3 hours. The montmorillonite slurry was poured into distilled water containing 10 g of magnesium sulfate under constant stirring. After further stirring for 30 min, the mixture was centrifuged and the precipitate was dried at 100 °C.

Evaluation of clay-dispersion in the PS matrix

Dispersion of silicate layers in the hybrids was evaluated using an X-ray diffractometer. The X-ray diffractometer (Model MXP18, MacScience) was adopted to monitor the change in *d*-spacing of montmorillonite in the hybrids. CuK_α (λ = 1.54 Å) was used as an X-ray source at a generator voltage of 40 kV and current of 30 mA. The 2θ scanning rate was 0.2 degree/min in the range of $2\theta = 2\text{~}30°$. The repeat distance in the silicate, d, was calculated using the Bragg's law, $d = \lambda/2\sin\theta_{max}$, where θ_{max} is the position of the (001) peak in XRD pattern.

Results and discussion

Figure 1 shows a plot for the yield of hybrid vs the concentration of two different coagulants in water. As the concentration of metal sulfate as coagulant increases, the weight of obtained hybrid increase above some concentration of metal sulfate. This means that the dried hybrids imbibe the coagulant metal. Meanwhile the weight of obtained hybrid falls down abruptly near the critical coagulation concentration (CCC), which is defined as the metal sulfate concentration at which every interparticle collision is caused to lead to agglomeration. It is also apparent from the figure 1 that CCC for aluminum sulfate is lower than that for magnesium sulfate. According to the Schulz-Hardy rule, coagulation of a colloid by salt depends on both the salt concentration and its formal charge. Because the formal charge for aluminum ion is higher than that for magnesium ion, the CCC for aluminum sulfate is lower than that for magnesium sulfate. This means that the sensitivity of latexes to trivalent cation is greater than that to divalent cation in practical application of emulsion polymerization-coagulation technique for clay-dispersed nanocomposite synthesis.

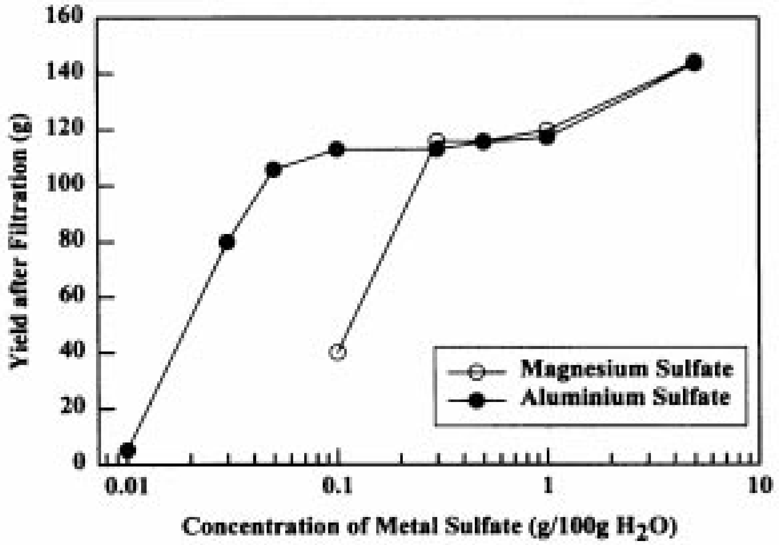

Figure 1. Effect of salt concentration on the coagulation efficiency.

Figure 2 shows XRD patterns of the various hybrids. XRD pattern for the powder of Cloisite®Na^+ is included in the figure for comparison. It is noteworthy that small peaks near 2θ = 6° appear for all the hybrids, and the peak intensity is independent of the salt concentration. According to Lee *et al.* (9), small XRD peak, which appeared around 2θ = 5° from the hybrid prepared by them, might be associated with the crystallographic ordering of some silicate layers intercalated with polymer chains in the hybrid.

Figure 3 shows the XRD patterns of the various hybrids, which were obtained during drying, containing different amounts of water. At higher moisture content, the smaller peak can be found at the diffraction angle near 2θ = 4.5°, which corresponds to repeat distance of the silicate layers (*d*-spacing) of *ca.* 19 Å. This value is similar to those found in aluminum complex polycation-intercalated clay (10-11). It is also noteworthy that the peak intensity increases as the moisture content in the hybrid decreases conserving the peak position of diffraction angle. But the XRD peak position shifts gradually to higher diffraction angle from a moisture content, *ca.* 17 wt.%. This shows that the amount of nano-scale building blocks of silicate layers per unit volume, maintaining the interlayer spacing constant, increases as the hybrid is dried. In other words, only the water molecules outside the gallery of silicate layers migrate at the first stage of drying, and those in the gallery exude at the late stage of drying.

In order to elucidate the origin of the peaks described above, the silicate layers dispersed in magnesium sulfate-water solution was centrifuged and the precipitate was dried as described in experimental part. Figure 4 shows the XRD patterns of the clays which were sampled during drying, so that each hybrid contains different amount of moisture. Only single peak at 2θ = 4.5° is observed from the XRD pattern at the early stage of drying, i.e. at higher moisture content. As the sample is dried further, a shoulder near 2θ = 5.5° appears with increase in the intensity of peak at 2θ = 4.5°. This

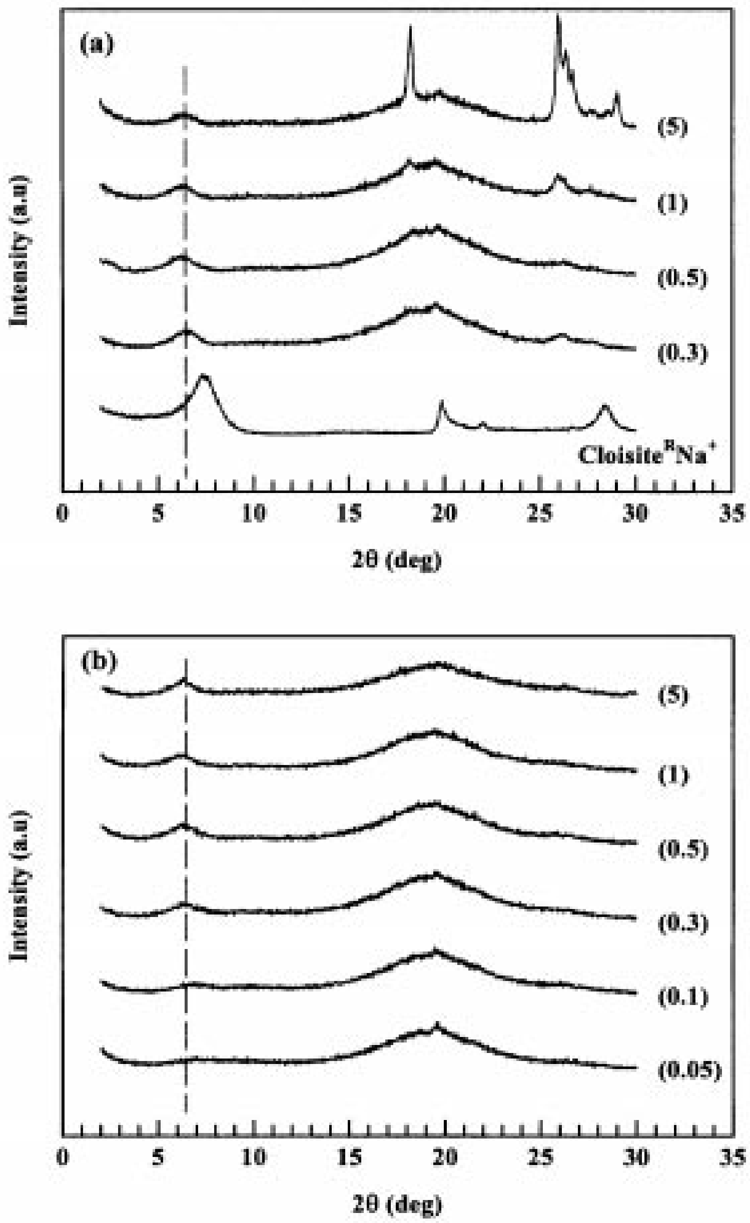

Figure 2. XRD patterns of the hybrids. The numbers in figure indicates the salt concentration in coagulant-water solution, (a) $MgSO_4$; (b) $Al_2(SO_4)_3$. XRD pattern for the powder of Cloisite®Na$^+$ is included in the figure for comparison.

means that some fraction of ion exchanged silicate layers lose their water molecules in the galleries. Only single peak at 2θ = 5.5° is observed below the moisture content of sample (*ca*. 28 wt.%). Finally, the single peak near 2θ = 6° is observed due to the complete exhaustion of water molecules in the galleries by drying. Conclusively, the drying behavior of PS hybrid containing clay is similar to that of the ion exchanged clay. Therefore it can be said that the small XRD peaks near 2θ = 6° are ascribed to the ion exchanged clay formed during coagulation of PS emulsion particles.

In order to investigate effects of the concentration of colloidal particles in emulsion

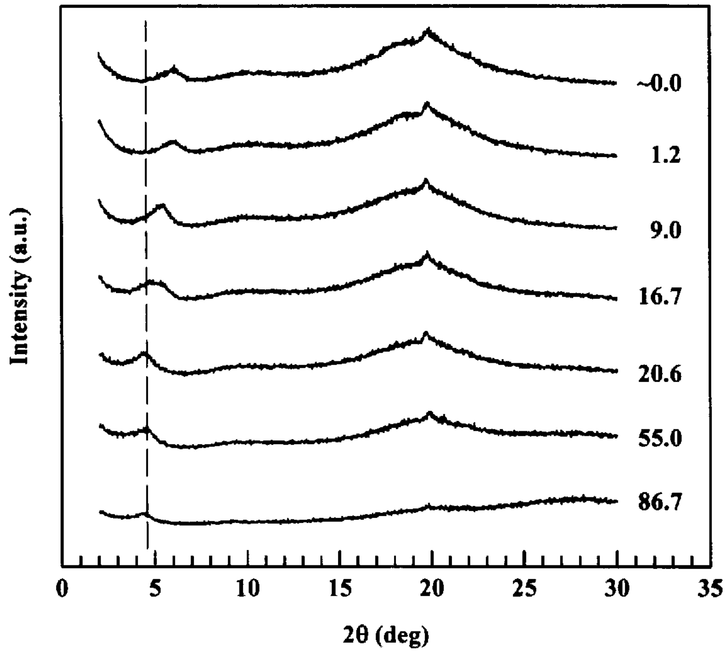

Figure 3. XRD patterns of clay/polystyrene hybrids during drying. The numbers in figure indicate moisture contents of the hybrids.

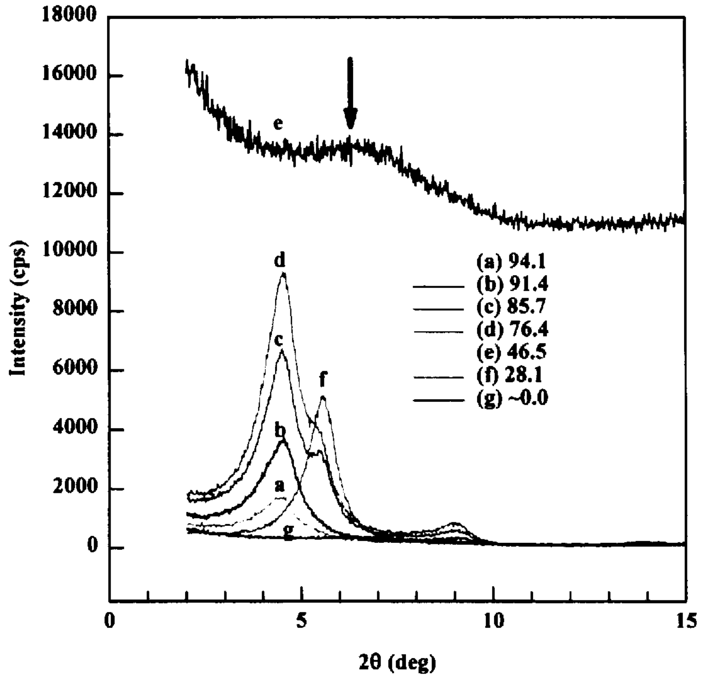

Figure 4. XRD patterns of hydrated magnesium complex polycation-intercalated clay during drying. The numbers in figure indicate the moisture contents of clay. XRD intensity for perfectly dried clay is magnified 10 times and plotted again in the figure for comparison. Arrow indicates the XRD peak position.

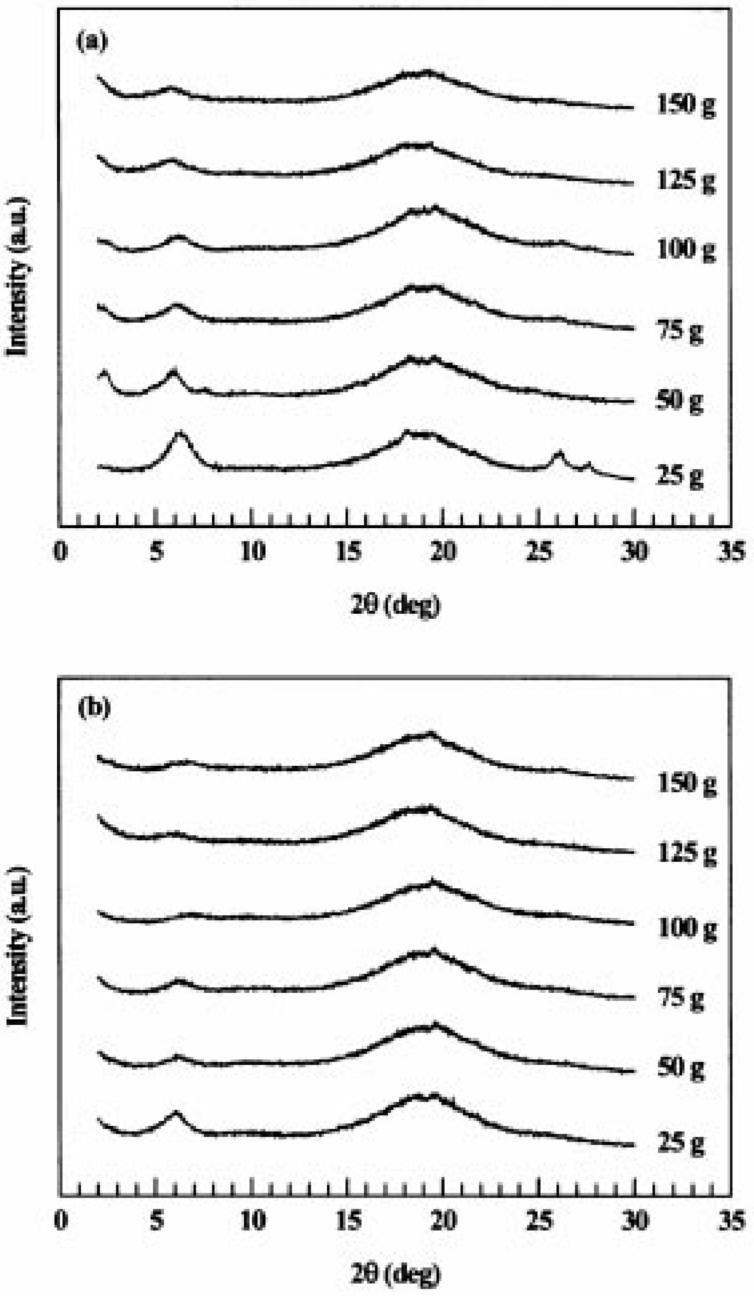

Figure 5. XRD patterns of the hybrids prepared at different concentrations of colloidal particles in emulsion. The numbers indicate the added amounts of styrene monomer in 500 g of distilled water. Two different coagulant water solutions were used, (a) 0.5 g/100g H_2O of $MgSO_4$; (b) 0.1 g/100g H_2O of $Al_2(SO_4)_3$.

on the ordering of silicate layers caused by ion exchange reaction, the added amounts of clay, sodium lauryl sulfate, and initiator are changed to be commensurate with the added amount of styrene monomer in 500 g of distilled water. Therefore clay contents in all prepared hybrids are maintained to be constant. Figure 5 shows that XRD peak intensity around $2\theta = 6°$ increases as the concentration of colloidal particles in emulsion decreases. This may be resulted from the fact that the isolated silicate layers has sufficient time to diffuse out from the aggregate of colloidal particles, resulting in better ordering of silicate layers in clay-rich region, when the colloidal particles in lower concentration are coagulated by metal sulfate.

Conclusions

In the present work clay/polystyrene hybrids were prepared by emulsion polymerization and subsequent coagulation technique. Aluminum sulfate water solution is more effective in coagulation of polystyrene emulsion than magnesium sulfate-water solution. Small peaks near $2\theta = 6°$ appear in XRD diffraction patterns of all the hybrids. It is confirmed that these small XRD peaks are ascribed with the ordering of silicate layers between which hydrated metal complex polycations are located with layers of water molecules. Also, the increase in the concentration of colloidal particles prevents from the ordering of silicate layers in the prepared hybrids. Isolated silicate layers cannot have sufficient time to diffuse out from the aggregate of colloidal particles, resulting in the lower ordering of silicate layers, when the colloidal particles in higher concentration are coagulated by metal sulfate.

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