# Synthesis and Characterization of $Al(OH)_3$/Polystyrene Nanocomposite Latex Particles by Emulsion Polymerization

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**Summary:** The inorganic/organic core-shell type nanocomposite particles of $Al(OH)_3$/PSt were synthesized through the emulsion polymerization of styrene (St, shell monomer) with ammonium persulfate (APS, initiator), polyoxyethylene (50) nonyl phenyl ether (NP-1050, nonionic surfactant), and ammonium (POE) alkyl arylether sulfate (EU-S133D, anionic surfactant) in the presence of the modified $Al(OH)_3$ particles. The improved compatibility of $Al(OH)_3$ surface with St achieved by the modification with 3-(trimethoxysilyl) propyl methacrylate ($\gamma$-MPS) enabled to form a polymer shell around the mineral particles. The structure of nanocomposites prepared from different feed ratio of $Al(OH)_3$/St was investigated by scanning (SEM) and transmission (TEM) electron microscopies.

**Keywords:** aluminum hydroxide ($Al(OH)_3$); core-shell; emulsion polymerization; polystyrene (PSt)

## Introduction

Recently, enormous attentions have been paid to such nanoparticles in conformity with the fast development of nanotechnology.[1–3] Encapsulated particles consisting of an inorganic core and polymer shell are of interest in various applications, such as inks, paint and cosmetics because of their better physical properties.[4–6] Though many efforts have been devoted to the preparation of core-shell type polymer/inorganic composites for oxides such as $SiO_2$, $TiO_2$, $Al_2O_3$, and $ZrO_2$,[7–11] few works were done for $Al(OH)_3$. $Al(OH)_3$ is well known to be an environmentally friendly halogen-free flame retardant additive.[12,13]

In this study, we first report the preparation of a new core-shell composite of aluminum hydroxide ($Al(OH)_3$) nanoparticles with polystyrene (PSt) by emulsion polymerization. This can be achieved through the preliminary modification of the aluminum hydroxide surface with a silane coupling agent, $\gamma$-MPS, leading to an organophilic coating and capable of later copolymerizing with the styrene monomers.

## Experimental Part

### Materials

Aluminum hydroxide (provided from Skynics), with average 70 nm, was dried at 110 ° under vacuum for 24 h prior to use. 3-(Trimethoxysilyl) propyl methacrylate ($\gamma$-MPS, from Sigma-Aldrich) and styrene (St, from Junsei Chem.) were purified by reduced pressure distillation. Ammonium persulfate (APS, from Junsei Chem.), polyoxyethylene (50) nonyl phenyl ether (NP-1060, from Dongnam Chem.), and ammonium (POE) alkyl arylether sulfate (Eu-S133D, from Dongnam Chem.) were used without further purification.

### Polymerization of $Al(OH)_3$/PSt Nanocomposites

The grafting of $\gamma$-MPS onto $Al(OH)_3$ was carried out under argon atmosphere by the

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method similar to the literature procedure for $\gamma$-MPS-functionalized $Al_2O_3$.[14] Modified $Al(OH)_3$ was isolated by ultracentrifuge and washed with toluene several times to remove unreacted $\gamma$-MPS. Emulsion polymerization of St was performed using ammonium persulfate (APS) as initiator in the presence of $\gamma$-MPS-functionalized $Al(OH)_3$ particles. To stabilize the emulsion, ammonium polyoxyethylene alkyl arylether sulfate (Eu-S133D) and polyoxyethylene (50) nonylphenyl ether (NP-1060) were used as surfactants. In a 500 mL four-neck round bottom flask equipped with an anchor-like mechanical stirrer and reflux condenser, and surfactants, NP-1060 and Eu-S133D, were dissolved in deionized water. $\gamma$-MPS-functionalized $Al(OH)_3$ was dispersed in St and the resulting mixture was introduced into the surfactant/aqueous solution for 30 min under an argon stream with a stirring speed at 600 rpm. The suspension was purged with argon and heated to 80 °C in water bath before the addition of the initiator (ammonium persulfate, 0.1% w/w with respect to St) to start the polymerization. The polymerization was continued with a stirring speed of 700 rpm for 3 h.

### Characterization

FTIR characterizations of pristine and functionalized powders were performed using a BOMEM Hartman & Braun FTIR spectrometer. TEM analysis was performed with a HITACHI H-7500 microscope (accelerating voltage of 80kV). SEM observation was performed with a HITACHI S2700 scanning electron microscope operating at 20 kV. A Brookhaven laser light scattering (Brookhaven Instruments Co.) was used for DLS measurements. The measurements were carried out at scattering angles of 90° at 20 °C. Brunauer, Emmett, and Teller (BET) areas were calculated from the nitrogen adsorption isotherms at 77 K using a Micromeritics ASAP 2000 surface analyzer. X-ray fluorescence (XRF) results were obtained from a SHIMADZU XRF-1700 with a 4kW Rh-Ka X-ray tube.

## Results and Discussion

The average size of $Al(OH)_3$ nanoparticles were 69 nm and 72 nm by DLS and TEM analysis, respectively. In order to obtain a functionalized surface, $\gamma$-MPS with C=C groups was reacted with Al–OH groups on the surface of $Al(OH)_3$. After the reaction, unreacted $\gamma$-MPS was recovered from the supernatant solution. The reacted $\gamma$-MPS was calculated to be ca. 50% of feed $\gamma$-MPS from a gravimetric analysis. XRF analysis also revealed that the ratio of Al and Si in the modified $Al(OH)_3$ was 74.1408% vs 25.7360%, which is comparable to the composition from the gravimetric analysis. An effective silanisation was evident from the FTIR data where the stretching vibration of $CH_3$, C=O and C=C groups of MPS were found at 2958, 1716, and 1636 $cm^{-1}$. BET analysis of $Al(OH)_3$ particles was performed to determine the grafting density of $\gamma$-MPS on the surface. (see Table 1) The grafting density of $\gamma$-MPS was roughly calculated to be $10.5 \times \mu mol/m^2$ with dividing the mole of reacted $\gamma$-MPS by the specific surface area of the $Al(OH)_3$.

The emulsion polymerization of St was attempted with different ratio of the modified $Al(OH)_3$, St, surfactants, and APS. (see Table 2) In the polymerization, the amount of St and DI water were fixed as 10 g and 50 mL, respectively. When NP-1060 and EU-S133D were used below 0.25 g with 0.5 g of APS, slight aggregation of latexes was found during the polymerization. However the stability of latexes was improved with the increase of both surfactants up to 0.25 g. Furthermore, most stable latexes could be obtained by the decrease of APS from 0.5 g to 0.1 g. Thus, the polymerization for the core-shell nanocomposites was carried out at this reaction condition with different feed amount of the modified $Al(OH)_3$. (ALPS-10, ALPS-10, and ALPS-10 in Table 2) For the control experiment, PSt was also prepared without $Al(OH)_3$. The $Al(OH)_3$/PSt nanocomposite latex particles produced were characterized SEM and TEM analysis. Figure 1 shows a series of SEM image of latex

***Table 1.***
DLS and BET analysis of pristine aluminum hydroxide and $\gamma$-MPS-functionalized $Al(OH)_3$.

| Inorganic powder | Average particle size (nm)[a] | Specific surface area ($m^2g^{-1}$) | $\gamma$-MPS surface density ($\mu$mol $m^{-2}$)[b] |
|---|---|---|---|
| Pristine $Al(OH)_3$ | 72 | 451.7 | – |
| $\gamma$-MPS-fuctionalized $Al(OH)_3$ | 72 | 381.9 | 10.5 |

[a] determined by TEM analysis;
[b] calculated from reacted $\gamma$-MPS and specific surface area of pristine $Al(OH)_3$.

***Table 2.***
Emulsion polymerization of St in the presence of $\gamma$-MPS- fuctionalized $Al(OH)_3$.

| Sample | $Al(OH)_3$ in feed (g) | NP-1060 (g) | EU-S133D (g) | APS (g) | Conversion (%) | Stability of emulsion |
|---|---|---|---|---|---|---|
| PSt[a] | – | 0.25 | 0.25 | 0.1 | 98.2 | stable |
| ALPS-10A | 1 | 0.15 | 0.15 | 0.5 | 36.0 | unstable |
| ALPS-10B | 1 | 0.15 | 0.15 | 0.1 | 38.5 | unstable |
| ALPS-10C | 1 | 0.25 | 0.15 | 0.5 | 41.3 | unstable |
| ALPS-10D | 1 | 0.25 | 0.25 | 0.5 | 36.7 | unstable |
| ALPS-10 | 1 | 0.25 | 0.25 | 0.1 | 90.2 | stable |
| ALPS-20 | 2 | 0.25 | 0.25 | 0.1 | 88.7 | stable |
| ALPS-30 | 3 | 0.25 | 0.25 | 0.1 | 91.1 | stable |

[a] PSt homopolymer by emulsion polymerization without $Al(OH)_3$;
[b] polymerization condition; St = 10 g, DI water = 50 mL, Temperature = 80 °C, Time = 3 h.

particles prepared by increasing feed ratio of the $Al(OH)_3$. The PSt homopolymer particles were in the shape of uniform spherical (average diameter = 198 nm). The morphology of $Al(OH)_3$/PSt composite were also spherical, but the particle size became irregular with increase of amount of $Al(OH)_3$ in feed. (see Figure 1b, c, and d)

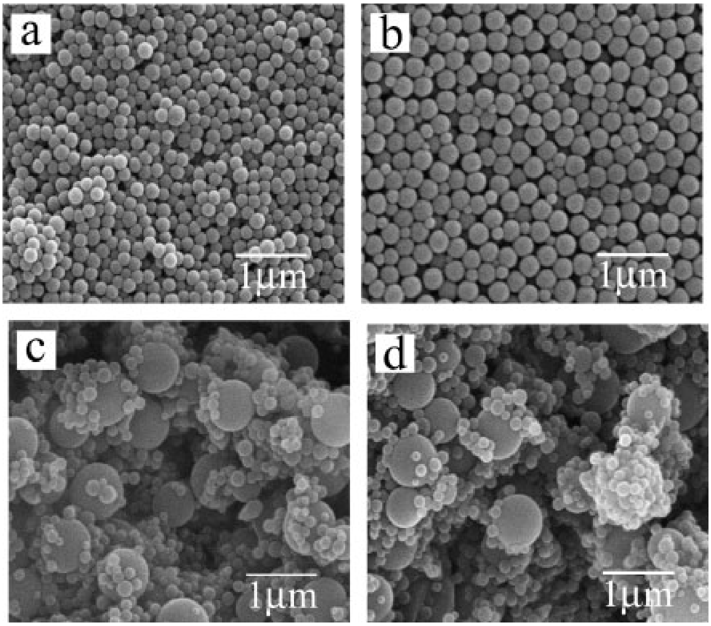

***Figure 1.***
SEM image of (a) polystyrene homopolymer by emulsion polymerization without $Al(OH)_3$ (b) SALPSt-10, (c) SALPSt-20, (d) SALPSt-30.

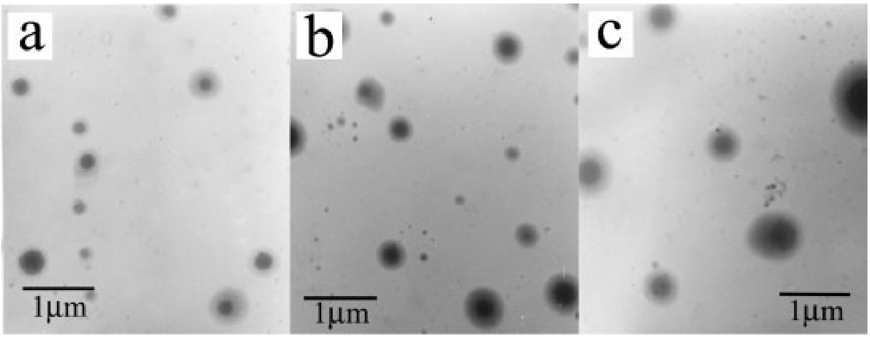

***Figure 2.***
TEM image of (a) SALPSt-10, (b) SALPSt-20, (c) SALPSt-30.

This irregularity may be attributed to the pre-aggregation of the $Al(OH)_3$ at higher concentration.

TEM analysis of nanocomposites was performed to investigate the core-shell morphologies. In the TEM micrograph for $Al(OH)_3$/PSt, it is clearly proved that the morphology of the nanocomposite is core-shell with $Al(OH)_3$ core and PSt shell (see Figure 2a, b, and c). Light PSt shell coats the dark $Al(OH)_3$ cores. A few small particles were also seen in the image. This result suggest that an increase of the affinity of the styrene molecules for the functionalized $Al(OH)_3$ surface can produce mostly the formation of a polymer shell around the mineral particles. At lower $Al(OH)_3$/PSt ratio (SALPSt-10), the particles were well dispersed in the reaction medium and the polymerization proceeded mostly on the surface of particles with maintaining the latex stability. In contrast, at higher $Al(OH)_3$/PSt ratio of SALPSt-20 and SALPSt-30, the size of composite particles was found to increase. This is possibly due to the fact that the pre-aggregation of $Al(OH)_3$ particles at high concentration produces larger cores as well as less homogeneous dispersions.

## Conclusions

Core-shell type nanocomposites of $Al(OH)_3$/PSt where $Al(OH)_3$ is the core and PSt is the shell was successfully prepared by the emulsion polymerization of St in the presence of surface modified $Al(OH)_3$. The microspheres could be obtained as stable latexes in aqueous solution by optimizing the ratio of the initiator and surfactants. At 9.1% of the $Al(OH)_3$ w/w with respect to St monomer, spherical and relatively uniform core-shell nanocomposite were produced, while irregular larger composites were obtained at higher concentration of the $Al(OH)_3$.

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