

Effect of the Clay Size on the Dispersion Morphology and Emulsion Stability of ABS/Layered Silicate Nanocomposites

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ABSTRACT: ABS/layered silicate nanocomposites were synthesized through an emulsion polymerization with different sizes of silicates. The particle sizes of Laponite, Cloisite-Na and Kunipia-F are about 20–30, 70–150, and 300–500 nm, respectively. When ABS was synthesized by the emulsion polymerization in the presence of Laponite and Cloisite-Na, ABS/layered silicate nanocomposite emulsion showed a stable suspension without the precipitation of solid particle. On the other hand, ABS/layered silicate nanocomposite synthesized with Kunipia-F showed the precipitation of large aggregated particles and the phase separation. Smaller sizes of silicates like Laponite and Cloisite-Na than polymerized particle worked as resided barrier preventing the emulsion particle from coagulation. Larger size of silicate like Kunipia-F than emulsion particle was not able to enclose the

emulsion particle delicately because of its stiffness and large aspect ratio. The monomers inserted into the intercalated Kunipia-F connected the ABS particles and clay particles. The Kunipia-F particles anchored ABS particles around them inducing the aggregation and precipitation of ABS particles. ABS copolymer emulsion and aqueous silicate dispersion were mixed to compare with synthesized ABS/layered silicate nanocomposites and showed a stable suspension. With small amount of Laponite or Cloisite-Na, nanocomposite emulsion of Kunipia-F was also stabilized. Laponite and Cloisite-Na worked as a steric stabilizer. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1287–1296, 2011

Key words: nanocomposites; clay; graft copolymers; acrylonitrile–butadiene–styrene (ABS); size effect

INTRODUCTION

ABS is a copolymer made by polymerizing acrylonitrile and styrene in the presence of polybutadiene.^{1–5} Compositions of commercial ABS materials range from 15 to 30% acrylonitrile, 5 to 30% butadiene, and 45 to 75% styrene. The name ABS is based on the first letter of each monomers. ABS is found in an extensive range of applications because of its excellent balance of processibility, mechanical property, recyclability, and economics.

Most commercially important ABS products consist of blends of a grafted terpolymer, acrylonitrile-butadiene-styrene, dispersed in a glassy matrix of styrene-acrylonitrile (SAN) copolymer. The ABS consists of a polybutadiene (PBD) rubber core and grafted SAN shell.^{6–10}

Nanofillers such as exfoliated silicates are expected to be effective at a small amount of filler loading about 5 wt %, introducing only a

minor increase in material cost. They provide significant improvement in modulus, thermal stability, fire retardancy, dimensional stability, surface hardness, heat-distortion temperature, and barrier properties.^{11–25}

ABS emulsion shows the stable suspension. When clay layers are added to ABS emulsion, clay layers may deter colloidal stability of the polybutadiene latex depending on their sizes because of the interaction between surface charges of clay layers.

The aim of this article is to synthesize ABS/layered silicate nanocomposites with different sizes of clays and to investigate the size effect of clay layers on stabilizing ABS latex in emulsion polymerization. ABS/layered silicate nanocomposites are prepared through *in situ* polymerization. Particle sizes were measured with dynamic light scattering. Wide-angle X-ray diffraction was used to analyze the interlayer distances. Thermogravimetric analysis was performed to evaluate the thermal stability of nanocomposites. FE-SEM and FE-TEM were used to show the states of ABS/layered silicate nanocomposites particles.

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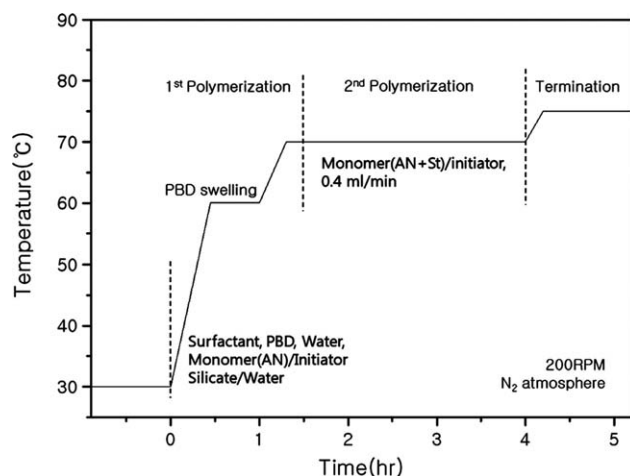


Figure 1 Thermal history of ABS/layered silicate nanocomposite polymerization.

EXPERIMENTAL

Materials

The layered silicates are Kunipia-F from Kunimine Co., Cloisite-Na and Laponite from Southern Clay Products. Kunipia-F, Cloisite-Na, and Laponite have a cation exchange capacity (CEC) of 119 meq/100 g, 92.6 meq/100 g, and 73 meq/100 g, respectively. Usually a clay layer has about 1 nm thickness. Kunipia-F has about 300–500 nm range in length and Cloisite-Na has about 70–150 nm. These are pristine silicates. Laponite is a synthetic smectite silicate with a layered structure with 20–30 nm. Layered silicates were dispersed in deionized water for 24 h at room temperature before polymerization.

Acrylonitrile (AN), Styrene (St), Cumene hydroperoxide as an initiator, and Dodecylbenzenesulfonic acid sodium salt (DBS-Na) were purchased from Aldrich and used without further purification. Polybutadiene (PBD) (52 wt % in water, average particle size is 250 nm) was supplied from Samsung Cheil Industries. DBS-Na was used as a surfactant to eliminate unknown additional effect because it has well-

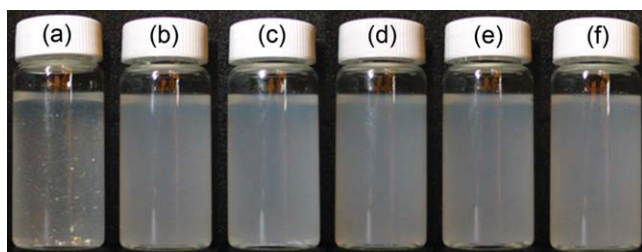


Figure 2 Photographs of diluted ABS/layered silicate nanocomposite emulsions synthesized using different sizes of clays. (a) K3D2.5, (b) C3D2.5, (c) L3D2.5, (d) K2.5C0.5D2.5, (e) K2.5L0.5D2.5, (f) ABS (00D2.5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

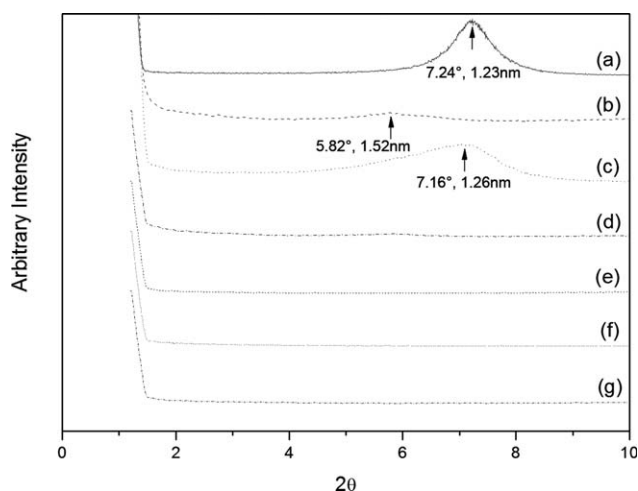


Figure 3 X-ray diffraction patterns of pristine silicates and ABS/silicate nanocomposites synthesized: (a) Kunipia-F, (b) K3D2.5, (c) Cloisite-Na, (d) C3D2.5, (e) L3D2.5, (f) K2.5C0.5D2.5, (g) K2.5L0.5D2.5.

known structure and molecular weight when compared with conventional rosin soap.

Polymerization of ABS/silicate nanocomposites

Polymerization was carried out as below, and the reaction thermal history was presented in Figure 1. Deionized water (200 g), 10% DBS-Na aqueous solution (25 g), aqueous silicate dispersion (variable), and PBD latex (76.9 g) emulsion, cumene hydroperoxide (0.2 g) dissolved in AN monomer (15 g) were mixed at room temperature in a 1 L four-neck reactor equipped with a baffle stirrer, a nitrogen inlet, a reflux condenser, and a rubber septum. The mixture was stirred at 200 RPM for 30 min under nitrogen atmosphere at 30°C. To make PBD swollen with AN monomer, the reactor was heated to 60°C and stirred for 30 min. Initial polymerization was performed at 70°C for 15 min, the mixture of St, AN monomers (St/AN = 30 g/15 g) and cumene hydroperoxide (0.4 g) were fed at a rate of 0.4 mL/min into the reactor by using a syringe pump for 2.5 h for the 2nd

TABLE I
Dynamic Light Scattering Data of Diluted ABS/Layered Silicate Nanocomposite Emulsions Synthesized Using Different Sizes of Clays. K3D2.5 Size Was Determined with SEM

Material	Particle size
PBD Latex	251 nm
ABS(00D2.5)	329 nm
K3D2.5	360 nm
C3D2.5	358 nm
L3D2.5	368 nm
K2.5C0.5D2.5	361 nm
K2.5L0.5D2.5	365 nm

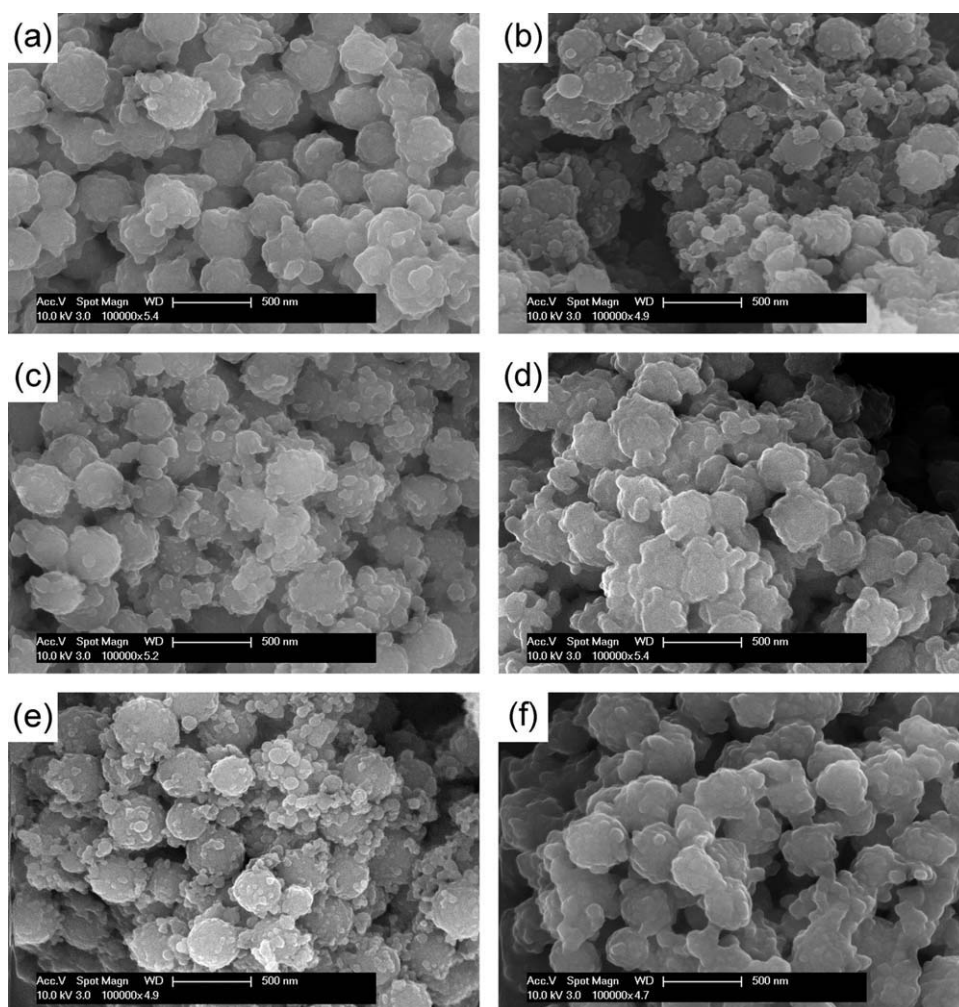


Figure 4 SEM images of ABS/silicate nanocomposites synthesized: (a) ABS (00D2.5), (b) K3D2.5, (c) C3D2.5, (d) L3D2.5, (e) K2.5C0.5D2.5, (f) K2.5L0.5D2.5.

polymerization. Finally, the polymerization temperature was increased to 75°C, and maintained for 1 h for termination. The sample was taken out from the flask and coagulated with MgSO₄ aqueous solution (3 wt %) at 60°C, and then freeze-dried for 3 days and further dried in a high vacuum oven at 50°C for 3 days.

The samples are named as K#D#, C#D#, L#D# or K#C#D#, K#L#D#. The letter K, C, L, and D denotes Kunipia-F, Cloisite-Na, Laponite, and DBS-Na respectively. Numbers followed by each letter stand for the added amount of each material in PHM (part per hundred monomers).

Characterization

The average particle size of the emulsion polymerization particle was estimated with a dynamic light scattering (DLS) (Zeta plus, Brookhaven) at room temperature at constant scattering angle of 90°, and

emulsion samples were diluted with deionized water. Aggregated particle (K3D2.5) size was determined with SEM. Wide-angle X-ray diffraction (WAXD) analysis was performed on a Rigaku X-ray generator (CuK α radiation with $\lambda = 0.15406$ nm, 30 kV, and 60 mA) at room temperature. A sample was prepared in the pellet form. The diffractograms were obtained at the rate of 2°/min in 2 θ range from 1.2° to 10°. The d-spacing of silicate was calculated from the peak position (d_{001} -reflection) of WAXD traces by using Bragg's equation: $2d_{001} \sin \theta = \lambda$, where d_{001} is the interplanar distance of (001) reflection plane, θ is the diffraction angle and λ is the wavelength. Thermogravimetric analysis (TGA) was performed on a TA Instruments Thermogravimetric Analyzer with a thermal analysis over a temperature range from 40°C to 900°C at a scan rate of 20°C/min under nitrogen atmosphere. Images of the prepared emulsion particles were obtained using a Sirion field emission scanning electron microscope (FE-SEM). Samples for SEM analysis were prepared by affixing

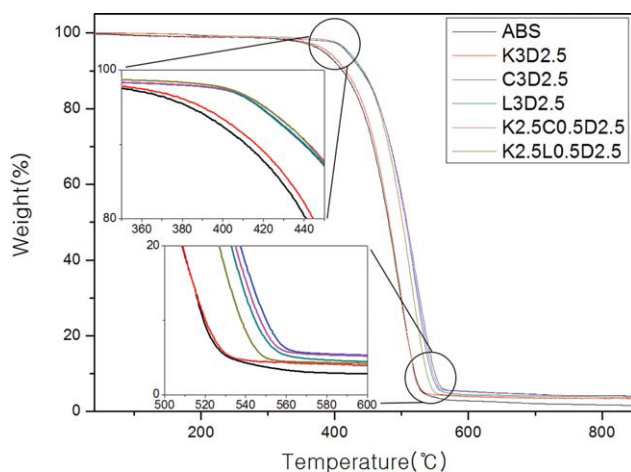


Figure 5 TGA curves of ABS/layered silicate nanocomposites using different sizes of silicates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ABS nanocomposite powder on carbon tape. And then the sample was coated with Pt film of 10 nm thickness under ultra-high vacuum. The microstructure of nanocomposite was imaged using a field emission transmission electron microscope (FE-TEM), JEOL JEM-2100F. Acceleration voltage of TEM was 200 kV. The nanocomposite was sectioned into ultrathin slices (<100 nm) using RMC ultramicrotome equipped with a diamond knife. All the

TABLE II
TGA Residue Percentages of ABS/Layered Silicate Nanocomposites

Material	Residue
ABS(00D2.5)	1.49%
K3D2.5	3.39%
C3D2.5	4.15%
L3D2.5	3.99%
K2.5C0.5D2.5	4.09%
K2.5L0.5D2.5	3.63%

samples were stained with OsO_4 for 2 h to indicate PBD latex.

RESULTS AND DISCUSSION

Figure 2 represents the images of the diluted ABS/layered silicate nanocomposite emulsions using different sizes of clays. Nanocomposite emulsion of 0.1 g were diluted with 50 g of deionized water. In this figure, the image of (b) C3D2.5 and (c) L3D2.5 show stable emulsion states. However (a) K3D2.5 which includes Kunipia-F shows some precipitations owing to the poor stability of emulsions. On the contrary, (d) K2.5C0.5D2.5 with Cloisite-Na and (e) K2.5L0.5D2.5 with Laponite show stable emulsion states even though they contain high proportion of Kunipia-F to other clays.

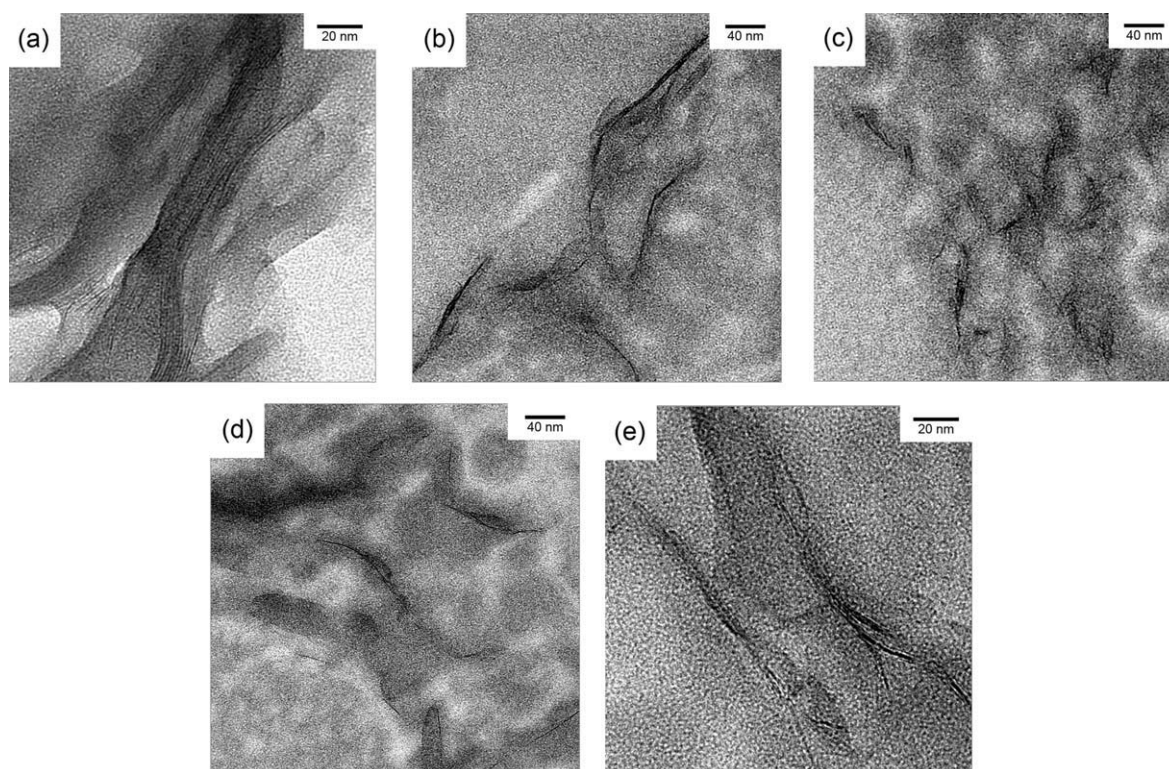


Figure 6 Transmission electron microscopy of (a) K3D2.5, (b) C3D2.5, (c) L3D2.5, (d) K2.5C0.5D2.5, and (e) K2.5L0.5D2.5.

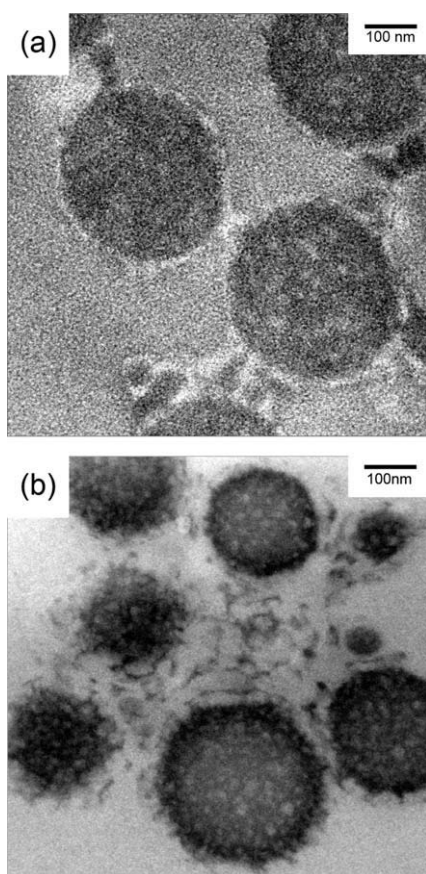


Figure 7 Transmission electron microscopy of (a) ABS and (b) ABS/layered silicate nanocomposite (C3D2.5).

Figure 3 shows thin film WAXD patterns of the silicates and the nanocomposites. The interlayer distances of pristine Kunipia-F and Cloisite-Na are 1.23 and 1.26 nm, respectively. In generally Laponite shows no peak on WAXD pattern.²³ ABS/Kunipia-F nanocomposite (K3D2.5) shows little intercalation. But other prepared ABS/silicate nanocomposites show no peak indicating the exfoliation of silicates.

Particle sizes of ABS/clay nanocomposites were measured by Dynamic light scattering. They are listed in Table I. Polybutadiene Latex and ABS (00D2.5) particle sizes were about 250 and 330 nm, respectively. It is recognized that ABS has the polybutadiene latex covered with SAN and the structure of core-shell. Particle sizes of ABS/clay nanocomposites are about 360 nm. With these results, the layers of Laponite (20–30 nm) and Cloisite-Na (70–150 nm) have smaller lengths than Polybutadiene Latex and ABS (00D2.5) particles. Kunipia-F (300–500 nm) have larger lengths than ABS particles.

Figure 4 shows SEM images of the nanocomposites. The particle sizes of nanocomposites are about 360 nm. In the case of (a) g-ABS (00D2.5), the particles have smooth surfaces. The sample (d) L3D2.5 and (f) K2.5L0.5D2.5 containing Laponite also show similar particle images with smooth surface. And the samples (c) C3D2.5 and (e) K2.5C0.5D2.5 that contained Cloisite-Na showed rough surface status but these two samples showed no peaks on WAXD pattern. But the sample (b) K3D2.5 that contained only Kunipia-F showed rougher surface. This indicates that as the

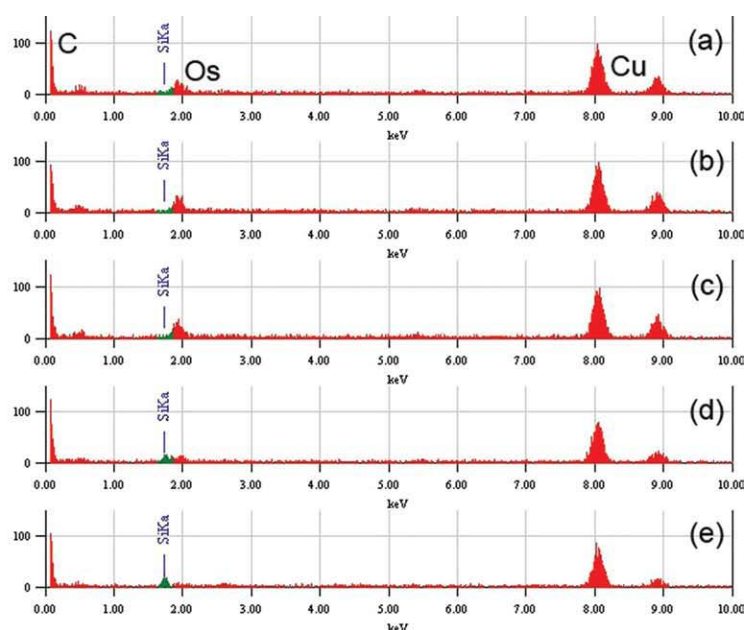
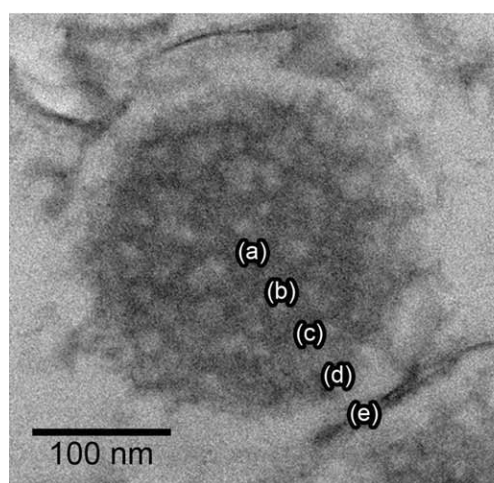


Figure 8 Transmission electron microscopy of an ABS/layered silicate nanocomposite (K2.5L0.5D2.5) and EDAX spectra indicating elemental compositions of the selected areas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

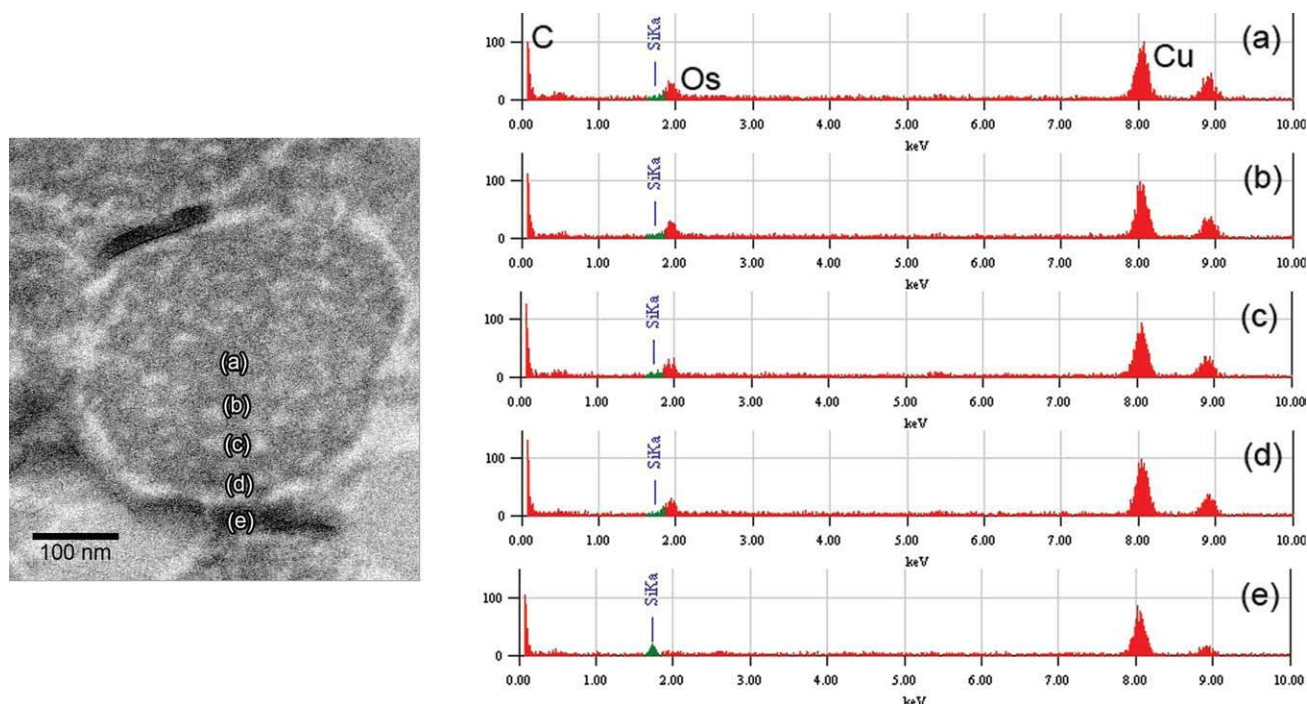


Figure 9 Transmission electron microscopy of an ABS/layered silicate nanocomposite (K3D2.5) and EDAX spectra indicating elemental compositions of the selected areas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

size of silicate goes bigger the surface of the ABS/silicate nanocomposites become rougher.

The TGA of ABS/clay nanocomposites are shown in Figure 5. TGA temperatures of the residues were 850°C. The nanocomposites show high weight percent of residue, (a) 3.39% for K3D2.5, (b) 4.15% for C3D2.5, (c) 3.99% for L3D2.5, (d) 4.09% for K2.5C0.5D2.5 and (e) 3.63% for K2.5L0.5D2.5 when compared with 1.49% for pure ABS. The residue percentages are listed on Table II. This result means that reasonable amount of clay remains in the matrix considering the

initial silicate content for the polymerization. The onset temperature of thermal decomposition moves toward a higher temperature for all the exfoliated

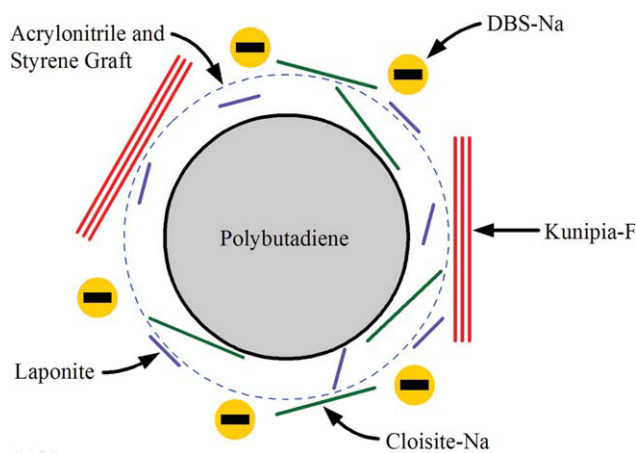


Figure 10 Schematic representation for synthesized ABS/layered silicate nanocomposite emulsion particle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

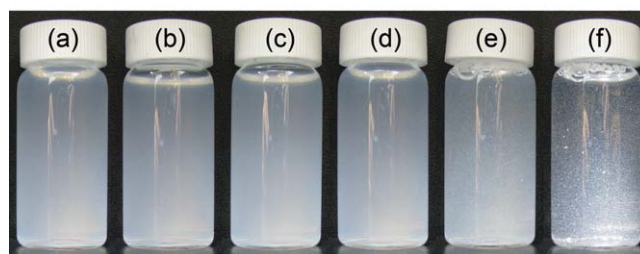
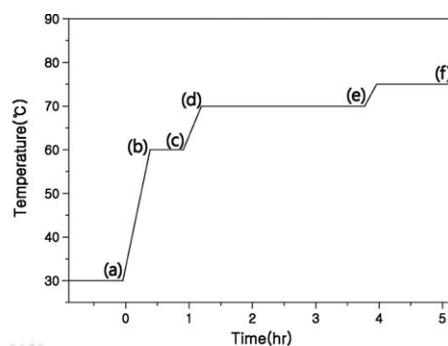


Figure 11 Photographs of thermal history of ABS/Kunipia-F polymerization (above diagram) and the solution diluted from K3D2.5 nanocomposite emulsion collected during the polymerization at the time (a) 0 minute, (b) 30 min, (c) 1 h, (d) 1 h 30 min, (e) 4 h, (f) 5 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

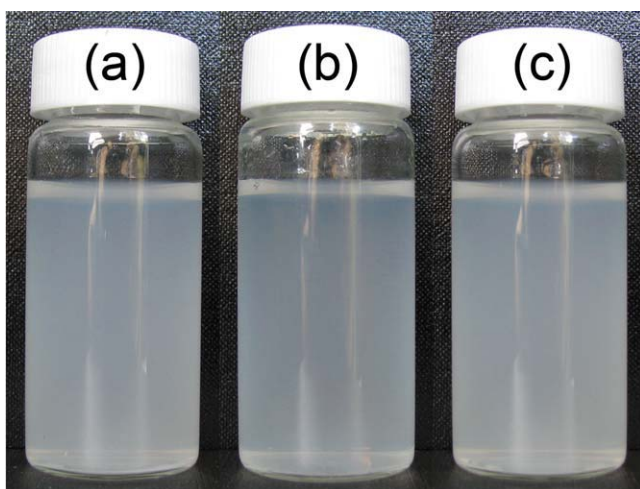


Figure 12 Photographs of diluted ABS/silicate mixture emulsions using different sizes of clays. (a) ABS/Kunipia-F, (b) ABS/Cloisite-Na, (c) ABS/Laponite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanocomposites relative to pure ABS. But K3D2.5 shows the same onset temperature of pure ABS because it has not the exfoliated structure of clay.

Figure 6 shows TEM images of silicates in ABS/layered silicate nanocomposites. ABS/Kunipia-F nanocomposite (K3D2.5) shows the intercalated structure of clay layers. Other ABS/silicate nanocomposites showed the exfoliation of silicates. TEM images are shown in Figure 7 to indicate the difference of ABS/layered silicate nanocomposite from ABS copolymer. Silicates exist around the ABS particles in Figure 7(b).

Natural clays are hydrophilic but PBD latex is a cross-linked rubber and very hydrophobic. Hence

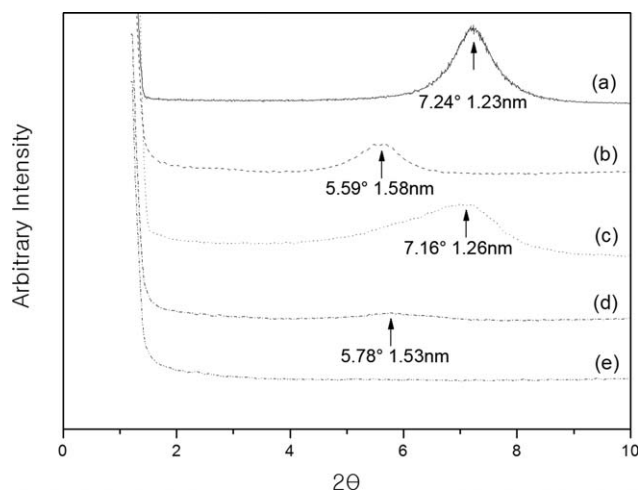


Figure 13 X-ray diffraction patterns of pristine silicates and ABS/silicate mixtures: (a) Kunipia-F, (b) ABS/Kunipia-F mixture, (c) Cloisite-Na, (d) ABS/Cloisite-Na mixture, (e) ABS/Laponite mixture.

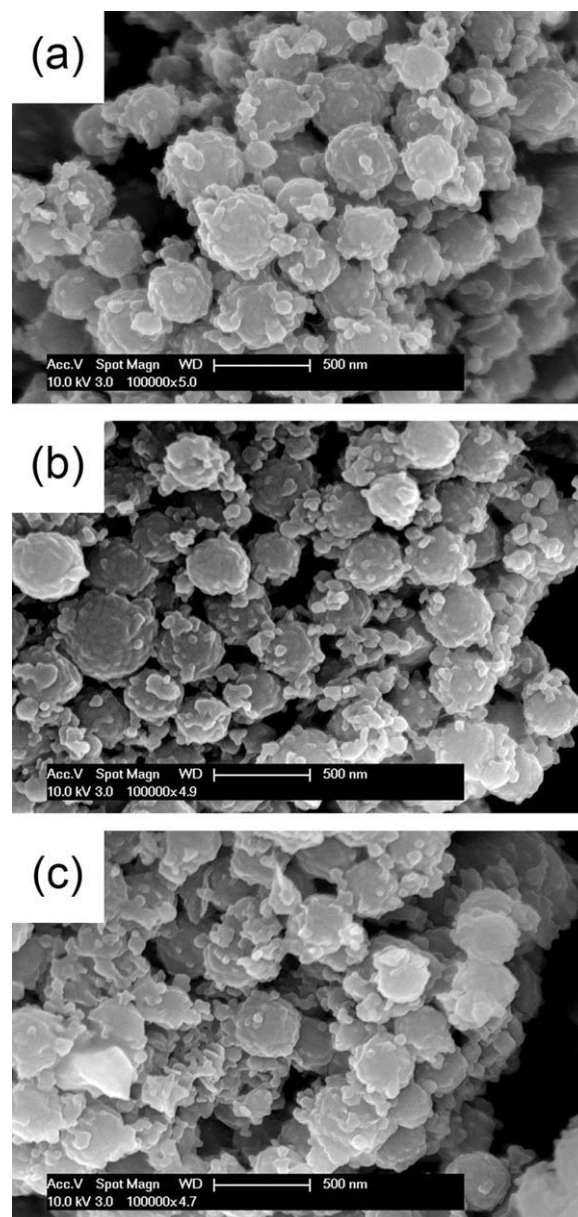


Figure 14 SEM images of ABS/silicate mixtures: (a) ABS/Kunipia-F, (b) ABS/Cloisite-Na, (c) ABS/Laponite.

we expected that clay layers may not penetrate into PBD interior. In the Figures 8 and 9, the compositions of ABS/layered silicate nanocomposites were analyzed by using TEM EDAX detector. Five different areas from the core to the surface of the particle were selected. Cu peaks (about 8.1 and 8.9 keV) are from the copper TEM grid and carbon (about 0.2 keV) is from the ABS copolymer and the carbon black coated on the copper grid. And the Os peak (about 1.9 keV) is from the OsO_4 that is used to stain the polybutadiene. The Si peak (about 1.7 keV) exhibits clay layers. The clay layers are attached to the ABS surface. Laponite with small length layers exists in the shell of acrylonitrile and styrene grafted polymer as shown in Figure 8. However, Kunipia-F

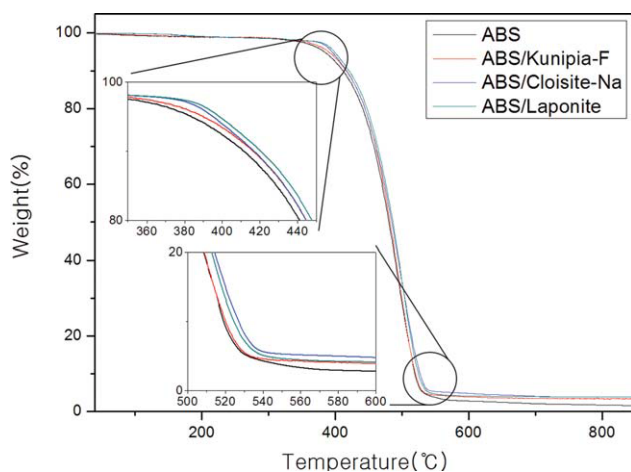


Figure 15 TGA curves of ABS and layered silicate mixtures using different sizes of silicates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is unable to penetrate into ABS interior because of its stiffness and large aspect ratio and exists on the surface of the ABS particle as shown in Figure 9.

Electrostatic charges on the surfaces of ABS particles may cause the repulsion between particles.²⁶ They prevent ABS particles from coagulation, and the ABS emulsion is a stable suspension. When the clays are added to the ABS emulsion, the clay layers may block the repulsive forces and result in the

TABLE III
TGA Residue Percentages of ABS/Silicate Mixtures

Material	Residue
ABS(00D2.5)	1.49%
ABS/Kunipia-F	3.34%
ABS/Cloisite-Na	3.79%
ABS/Laponite	3.74%

coagulation. For an ABS/layered silicate nanocomposite with Kunipia-F, silicate layers are too large to enclose the whole surface of the emulsion particle, so the particles are coagulated. On the contrary, Laponite and Cloisite-Na layers are smaller than ABS particle, hence some of silicate layers can surround the ABS particle and some layers exist in the shell preventing from the coagulation of ABS particles. Figure 10 shows schematic representation for synthesized ABS/layered silicate nanocomposite emulsion particle. The Cloisite-Na and Laponite exists in the shell of ABS particle but Kunipia-F with large length layers is attached to the surface of ABS particle.

In Figure 2, K3D2.5 composite showed coagulated particles. The experiment was done to confirm when the particles were aggregated and precipitated during the polymerization. Figure 11 shows the solution diluted from ABS/Kunipia-F nanocomposite (K3D2.5) emulsion sampled during the polymerization. The images of (a) 0 minute, (b) 30 min, (c) 1 h

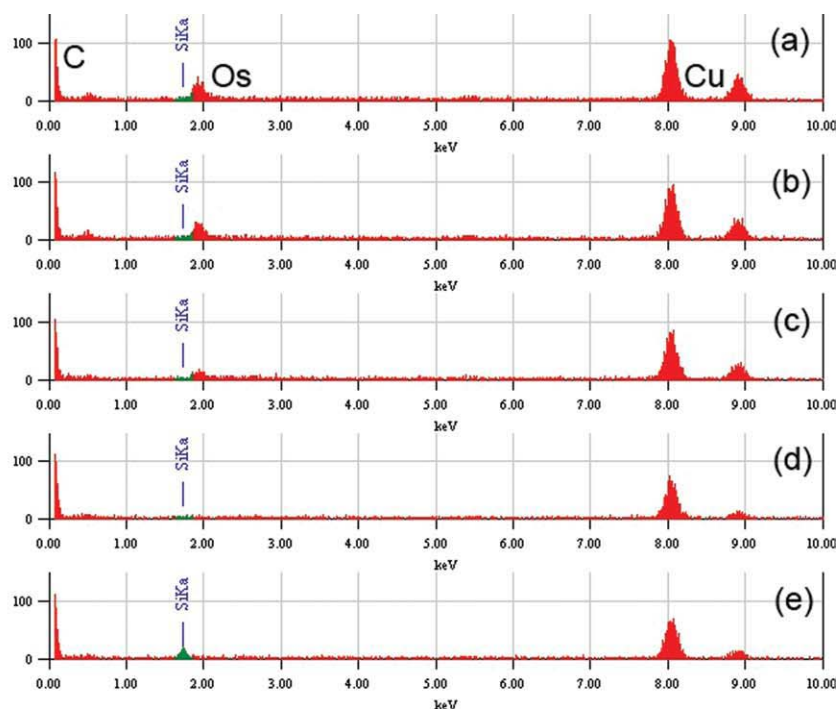
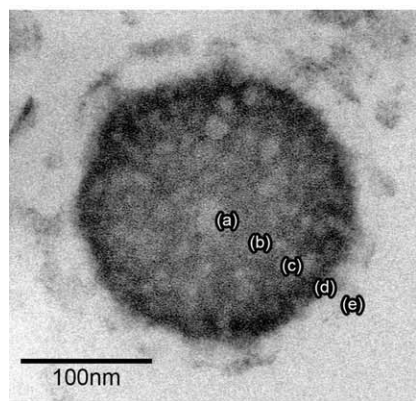


Figure 16 Transmission electron microscopy of an ABS/layered silicate mixture (ABS/Kunipia-F) and EDAX spectra indicating elemental compositions of the selected areas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

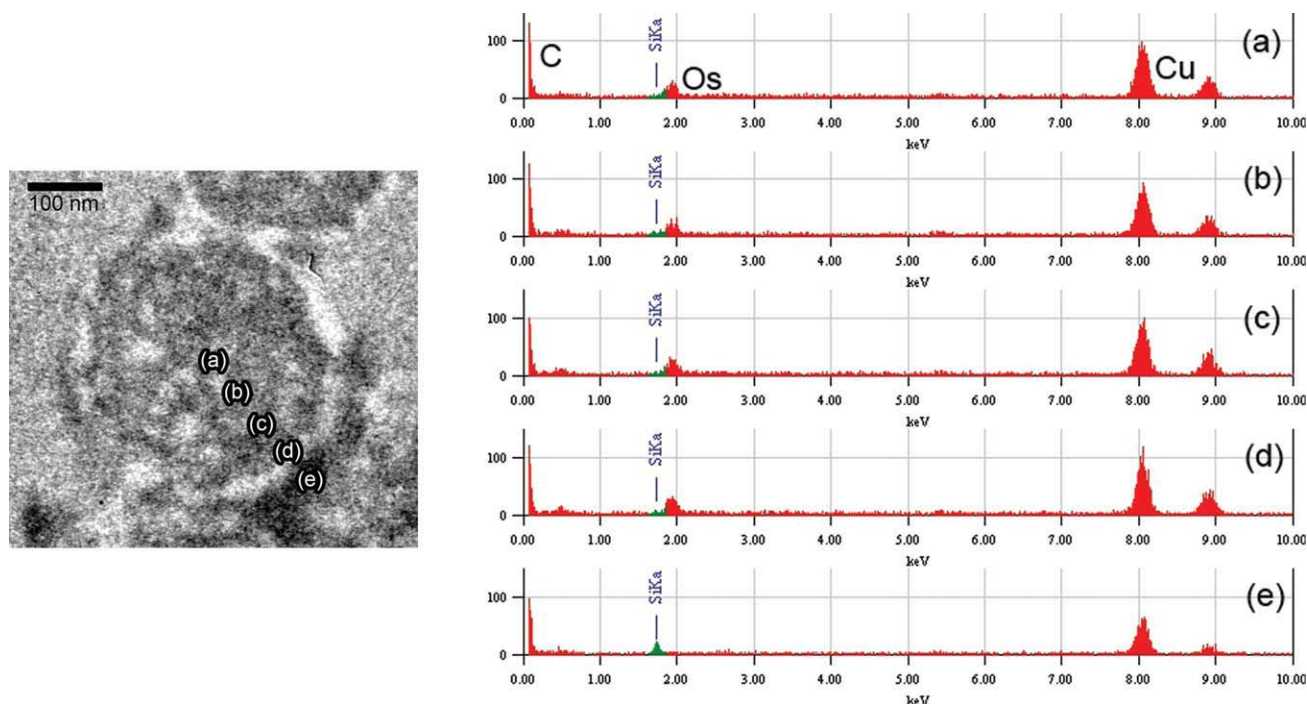


Figure 17 Transmission electron microscopy of an ABS/layered silicate mixture (ABS/Laponite) and EDAX spectra indicating elemental compositions of the selected areas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and (d) 1 h 30 min show stable emulsion states. On the contrary, the image of (e) 4 h shows a little precipitations and (f) 5 h shows much precipitations owing to the poor stability of emulsion.

ABS copolymer emulsion and aqueous silicate dispersion were mixed to compare with the synthesized ABS/layered silicate nanocomposites. Figure 12 represents the diluted solution of the mixture. The images of (a) ABS/Kunipia-F mixture, (b) ABS/Cloisite-Na mixture and (c) ABS/Laponite mixture show stable emulsion states. ABS/Kunipia-F mixture does not show the aggregation and precipitation of particles, which is distinguished from the emulsion of K3D2.5 shown in Figure 2.

Figure 13 shows thin film WAXD patterns of the mixture of ABS and aqueous silicate dispersion. The (001) plane peaks of silicate of ABS/Kunipia-F mixture and ABS/Cloisite-Na mixture can be seen around $2\theta = 5.59^\circ$ and $2\theta = 5.78^\circ$. Interlayer distances of ABS/Kunipia-F mixture and ABS/Cloisite-Na mixture are calculated to be 1.58 and 1.53 nm, respectively. The mixtures have intercalated morphologies of silicate. The ABS/layered silicate nanocomposite obtained by emulsion polymerization showed the exfoliated structure except K3D2.5 nanocomposite shown in Figure 3

Figure 14 shows SEM images of the mixture of ABS and aqueous silicate dispersion. ABS/Kunipia-F mixture and ABS/Cloisite-Na mixture show the rough surfaces of ABS particles covered with silicate

layers similar to K3D2.5 and C3D2.5. ABS/Laponite mixture also shows rough surfaces differently from L3D2.5 with smooth surfaces in Figure 4.

Figure 15 represents thermo gravimetric analysis of the mixture of ABS and aqueous silicate dispersion. Mixtures of ABS/silicate show high weight

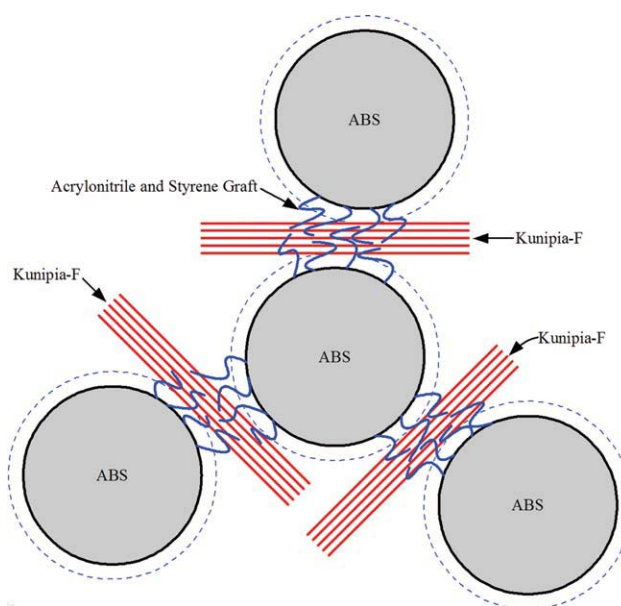


Figure 18 Schematic representation for aggregation of synthesized ABS/Kunipia-F nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

percent of residue, (a) 3.34% for ABS/Kunipia-F mixture, (b) 3.79% for ABS/Cloisite-Na mixture, and (c) 3.74% for ABS/Laponite mixture, which are listed on Table III. Reasonable amount of clay remains in the matrix the same as the initial silicate contents. All the mixtures show almost the same TGA curves as the pure ABS.

In the Figures 16 and 17, the compositions of ABS/layered silicate mixture were analyzed by using a TEM EDAX detector. The clay layers of any sizes are attached to the surface of ABS particles and no clay is detected inside of ABS particles.

The problem is why K3D2.5 showed the unstable emulsion and the precipitation of aggregated particles. It may be explained by the schematic representation of Figure 18. The monomers or oligomers inserted into the intercalated Kunipia-F are connected to the ABS particles by the reaction. So the intercalated Kunipia-F particles induce the aggregation and the precipitation of ABS particles.

CONCLUSIONS

ABS copolymer/layered silicate nanocomposites were prepared through *in situ* emulsion polymerization using three types of silicates with different sizes. From the above results, ABS/layered silicate nanocomposites obtained by using Cloisite-Na and Laponite showed exfoliated states of silicates and stable emulsions. On the other hand, the nanocomposite with Kunipia-F had aggregated particles and separated phases. The nanocomposite with the mixture of Kunipia-F/Cloisite-Na or Kunipia-F/Laponite showed stable emulsion. This result was caused by the small sizes of Cloisite-Na and Laponite. Cloisite-Na and Laponite showed good efficiency to stabilize the emulsion particle during polymerization.

The mixtures of ABS copolymer emulsion and aqueous silicate dispersion showed the stabilized emulsion without the precipitation of particles. The nanocomposites obtained from these mixtures showed the intercalated structure of silicate layers. The ABS/Kunipia-F nanocomposite emulsion obtained by the polymerization showed the aggregation and the precipitation of particles. Kunipia-F had a large length of layer, which could not exist in the shell of an ABS particle but attach on the surface of the particle. The monomers inserted into the interca-

lated Kunipia-F connected the ABS particles and clay particles. The Kunipia-F particles anchored ABS particles around them inducing the aggregation and precipitation of ABS particles. When Cloisite-Na and Laponite were added to ABS/Kunipia-F emulsion, the emulsion showed the stabilized state. Clays with small sizes worked as a steric stabilizer.

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