

## Annual Report [2005-2006]

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During the fiscal year of 2005-2006, the project CTS-0244371 (**Synthesis of Polymer Encapsulated Nano-Clay Hybrid via Miniemulsion**) progressed smoothly forward with distinguished achievements. This report includes two parts: in the first parts, we report the exfoliation and encapsulation of nanoclay in the polymer latex during miniemulsion polymerization process. In the second part, hollow hemispheric polymer/clay nanocomposite particle formation in a miniemulsion polymerization process is presented.

### **Part 1. Exfoliation and encapsulation of nanoclay in the polymer latex during miniemulsion polymerization**

In this part of the work, a stable water-based polystyrene nano-saponite composite suspension was synthesized via mini-emulsion polymerization. The stability of the suspension and the intercalation degree of clay was strongly affected by the pretreatment of saponite-Ca with cationic surfactant OTAB (octadecyltrimethyl-ammonium bromide). This pretreatment process not only intercalated the clay layers but also converted the nanoclay particles from hydrophilic to hydrophobic (monomer-like). The organophilic clay obtained by above treatment could be well dispersed in the monomer phase by sonification at low saponite concentration (< 5 %), but formed high viscose solution or gel in organic monomer at higher concentration of saponite. The effects of saponite modification conditions on the stability of miniemulsion were studied, and the optimum conditions for preparing stable emulsion are reported. The final products resulting from the subsequent polymerization were characterized using light scattering, transmission electronic microscopy (TEM) and X-Ray Diffraction (XRD). It was found that the particle size of such prepared suspension is in the range of 90 nm-120 nm, and the final

latex of nano-saponite composite is stable for months. It was also found that the addition of clay slightly reduced both the reaction rate and conversion.

## 1. Experimental details

See Ref. 1 for details. Brief summary is give as follows:

### 1.1. Modification of Saponite clay

A 5 g saponite-Ca was dispersed into water with 5 mmol OTAB and stirred at 50 °C for 24 hr. The saponite particles were separated by centrifugation (5000 rpm, 10 min) and washed with large amounts of water and ethanol to remove extra (unreacted) OTAB until no bromide can be detected by silver nitrate. The sample was dried in the vacuum oven overnight at 45 °C. The dried organo-clay was ground to a powder with aggregated particle size less than 45 micrometer.

### 1.2. Miniemulsion polymerization

The miniemulsion preparation conditions are given in Table 1. The oil phase A contains 1.2 g hexadecane (co-stabilizer) and 0.24 g AIBN in 12 g styrene monomer and required saponite (0.25 g or 0.6 g). The mixture was then exposed to 2-min sonication (W-385 sonicator, Heat System-Ultrasonics Inc., USA). The viscosity of the system increased if the concentration of intercalated saponite was increased. At a clay concentration higher than 5 %, gel-like suspensions were obtained. The aqueous phase B was prepared by dissolving 2 g TX-405 in 100 g water at room temperature. The intercalated saponite-styrene mixture A was poured into aqueous phase B, and the mixture was cooled in the ice bath. After vigorous stirring of the mixture in the ice bath for 30min, miniemulsion was made by 3-min sonication in the ice bath. This miniemulsion was then ready for either property characterization or for subsequent polymerization.

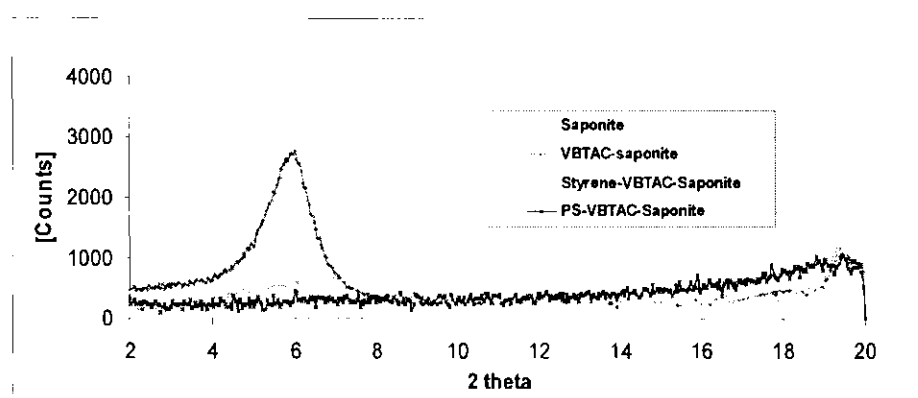
Upon completion of the sonication, the as-prepared miniemulsion was poured into 3-neck flask under bubbling N<sub>2</sub>. The miniemulsion was held at room temperature and degassed for 30 min. After degas, the temperature of the mixture was increased to 70 ± 2 °C, and the polymerization was conducted at this temperature for 6hr under continuous mechanical stirring at 600 rpm and terminated by dropping one drop of 2 % 4-

methoxyphenol solution into the latex. Stable suspension was obtained under favored polymerization conditions.

## 2. Result and discussion

### 2.1. Modification and dispersion of saponite-Ca

The surface properties of clay play a critical role in the dispersibility of intercalated clay in the monomer. The untreated clay particles are organophobic and not easily dispersible in organo-media. The modification of clay using quaternary ammonium cation not only exfoliates the clay galleries but also converts the clay from organophobic to organophilic so the particles can be dispersed in monomer phase. The 18-carbon atom OTAB, which has been used to form the most stable latex in our previous work, is chosen as the modifier. The actual cationic exchange capacity of saponite-Ca using OTAB is 77.32 meq/100 g by incineration experiment, which agrees very well with the provided maximum cationic exchange capacity by the clay supplier (75-80 meq/100 g). This agreement suggests that the exchange of Ca with OTAB is complete in our experiments and no remarkable amount of free OTAB remains in the system. The OTAB treated saponite was intercalated as evidenced by X-ray diffraction measurement. As shown in Figure 1, the pristine Saponite-Ca has an interlayer spacing of  $d$  1.24 nm corresponding to  $2\theta$  at  $7.14^\circ$  ( $d_{001}$  reflection), and the surface modified Saponite clay has shifted to  $d$  1.92 nm corresponding to  $2\theta$  at  $4.6^\circ$

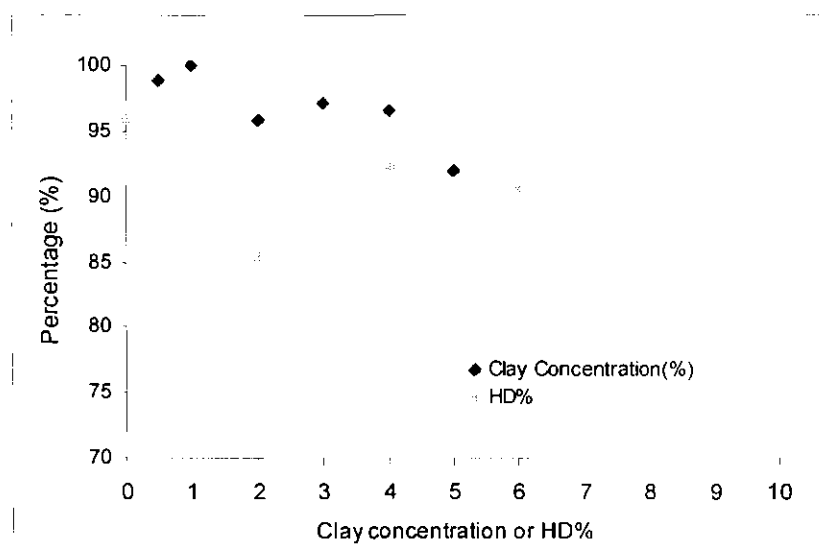


**Figure 1.** XRD spectra of saponite, VBTAC modified saponite, styrene dispersed VBTAC-saponite, and Polystyrene exfoliated VBTAC-saponite.

## 2.2. Distribution of clay in water and oil phase

In order to further understand the surface properties of clay before and after modification, the ratio of pristine and modified clay in oil and water phases was studied. Without the presence of costabilizer hexadecane, the experiment showed that 96 % of the surface modified clay stays in the oil phase, while the pristine clay (81 %) is predominantly present in the water phase.

The effect of co-stabilizer and clay concentrations on the distribution of clay between water and oil phases was also investigated. However, there was no clear tendency observed in the concentration range used in this study. As shown in Figure 2, more than 85 % of OTAB-modified clay particles were in the monomer phase in all hexadecane concentrations although the data is scattered. Meanwhile, more than 90 % of organo-clay particles were in the monomer phase in the all clay concentrations in the absence of hexadecane co-stabilizer.



**Figure 2:** Percentage of organo-clay in the oil and interface as a function of hexadecane (HD) concentration and clay content in the absence of hexadecane co-stabilizer.

It is well known that mechanical homogenization is an important step for preparing a stable emulsion or miniemulsion. Ultrasonication has been commonly used to make stable emulsion or miniemulsion. It was found in this study that the ultrasonification

treatment is a very important factor in obtaining a stable emulsion. However, because a quantitative study of the ultrasonification effect needs well defined equipment and experimental setup and is beyond the goal of this research, only a qualitative study was conducted. The results indicated that, at our experimental conditions, the relative high energy import at short ultrasonic time (3 minutes) benefited the formation of stable and uniform emulsion droplets. Increased ultrasonic time beyond 5 minutes will cause a coalescence of the emulsion particles. It was also found that the stability of final nanoclay composite strongly depended on the stability of pre-polymerization miniemulsion. A large precipitated clay-polymer solid mixture was observed when an unstable emulsion was used in the polymerization.

### 2.3. Effect of hexadecane co-stabilizer on particle size and final latex stability

It has been known that a small amount of hydrophobe builds up an osmotic pressure in miniemulsion droplets which provides stability against Oswald ripening. The required minimum molar ratio of hydrophobe to monomer is about 1:250 for creating enough osmotic pressure in the droplets. Responding to the above empirical content, 2-10 wt. % hexadecane based on the monomer styrene was used in this study. Although Table 2 shows that the particle size of latex after the polymerization slightly depends on the amount of the hydrophobe, it was found that the hexadecane had large influence on the thermodynamical stability of the final latex. When the hexadecane was increased from 2 % to 10 % (based on the monomer styrene), the clay particles in the final product were stable and only a very small portion could be separated by ultracentrifugation. This reveals that the hexadecane not only reduced Oswald ripening as conversional miniemulsion did but also acted as a compatibilizer for stabilize intercalated saponite particles in the system.

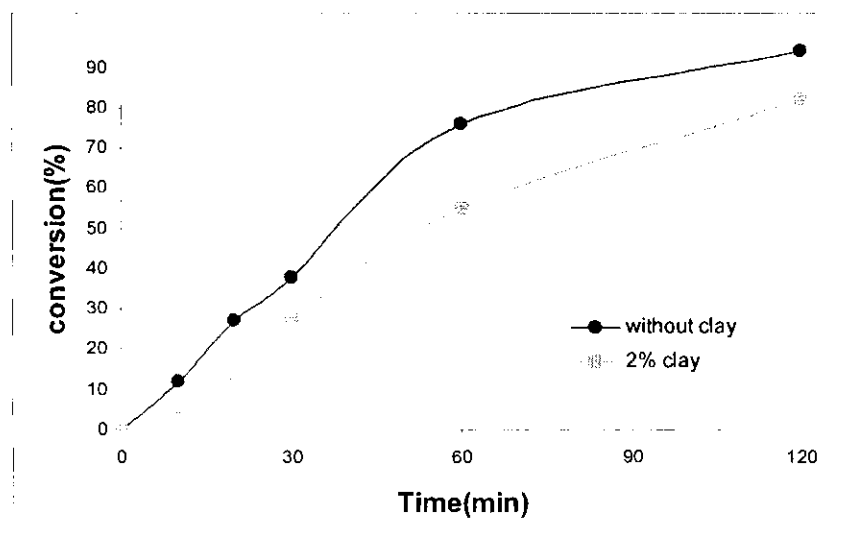
**Table 2: Effect of hexadecane on final latex stability and particle size**

Experiment	HD (%)	Particle size (nm)	Poly. Index	Clay in the precipitate after centrifugation (%)
HD1	10	97.87	0.173	Un-measurable
HD2	6	104.5	0.151	35
HD3	2	109.7	0.171	37.5

#### 2.4. Effect of nanoclay particles on polymerization conversion

In emulsion polymerization, the monomer droplets act as monomer reservoirs to supply monomer to the growing polymer particles. However, in miniemulsion polymerization, the monomer droplets become the principle locus of particle nucleation, which in turn, exhibit different polymerization kinetics and final particle size distributions.

The effect of inorganic particles on the polymerization rate and conversion has been studied in the literature. Generally speaking, the addition of inorganic particles, such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{CaCO}_3$  and Ag, will reduce both monomer conversion and reaction rate in emulsion and suspension polymerizations. Similar results were obtained in this study. The final conversions after 6hr polymerization without and with 2 % clay are 95 % and 85 %, respectively. It was concluded from this data and the results shown in Figure 3 that both polymerization rate and maximum conversion degree decreased with the addition of nanoclay in the miniemulsion. It is believed that the reactivity of radicals and living polymers is lower in the presence of clay particles because of the adsorption of these living species by large nanoclay surface. It was also found that the average particle size and polydispersibility of the final products slightly increased with the addition of nanoclay.



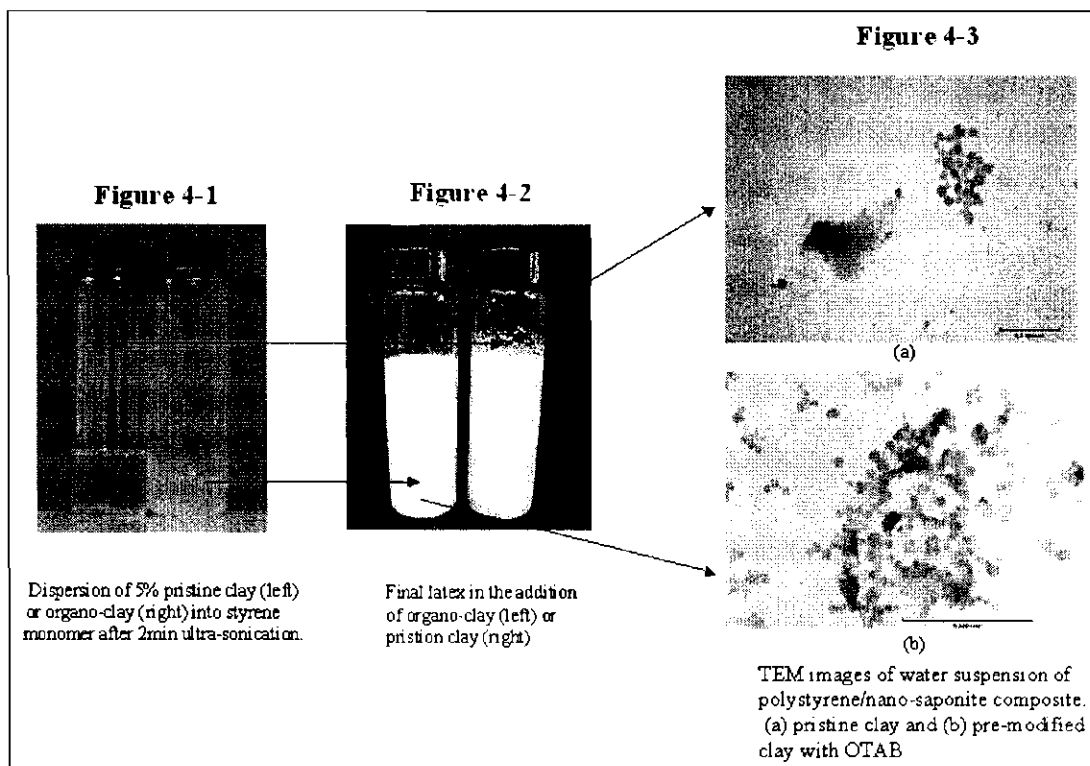
**Figure 3:** Conversion vs. time without clay and with 2% clay

## 2.5. Characterization morphology and stability of the latex in the presence of pristine saponite or pre-modified saponite

As discussed before, pristine clay particles are organophobic and undispersible in the monomer. It was found in this study that pristine clay particles could be partially dispersed in styrene monomer by ultrasonification, but they precipitated out from the monomer quickly after the ultrasonification was stopped as shown in Figure 4-1(left). However, the organo-saponite clay suspension in the monomer obtained by the ultrasonification treatment in the presence of OTAB was an almost transparent homogenous solution at low clay concentration (< 5.0 wt. %). It was also found that OTAB treated clay formed a gel in styrene when the concentration of clay was higher than 5.0 wt. % as shown in Figure 4-1 (right). The gel formation in the monomer combined with the aforementioned XRD results strongly suggest that the saponite particles were intercalated and well swelled by the monomer.

TEM morphology observations of the final product prepared in the presence of 5% pristine and surface modified (organophilic) clays are illustrated in Figure 4-3. It can be seen that the clay particles in the final products are separated from the polymer latexes when pristine saponite was used. However, if the clay particles are pre-modified with OTAB, the nanoclay layers are surrounded and entrapped by latex particles. It is interesting to note that although the clay particles in Figure 4-3b are strongly adhered together with latex particles, they are not perfectly encapsulated by the polymer. This is different from our previous study using modified laponite in which the nanoclay particles were fully encapsulated by polymer molecules. One of the major differences between the saponite used in this study and the laponite used in our previous research is the particle size. It is well known that miniemulsion is comprised of relatively stable oil droplets with a particle size commonly less than 300 nm. Figure 4-3(b) and Table 2 illustrate that the latex prepared is about 100 nm, which is much smaller than intercalated saponite particle size (about 200-300 nm). Obviously, the large platy nanoclay particles cannot be encapsulated by small latex particles. The effort in preparing large and stable miniemulsion droplets in the presence of nanoclay has failed due to the conflict between making stable miniemulsion and increasing the droplet size.

The particle sizes obtained from TEM for the final products with pristine or modified clays are consistent with the data obtained by light scattering measurement, i.e., the average particle size of latex with nanoclay is larger than the latex without clay. Figure 4-3(b) also illustrates that the nano-clay was detected as the irregular, transparent, and high aspect-ratio thin layer. When these very thin particles (1nm thickness) adsorb to latex particles by hydrophobic attraction force, the particles are easily suspended to form a stable suspension even though they are not encapsulated by the polymer. Figure 4-2 illustrated that the final latex suspension made from pristine clay is unstable, but the latex prepared by using modified clay is very stable and no phase separation occurred after centrifugation with 10,000 rpm for 30 min.



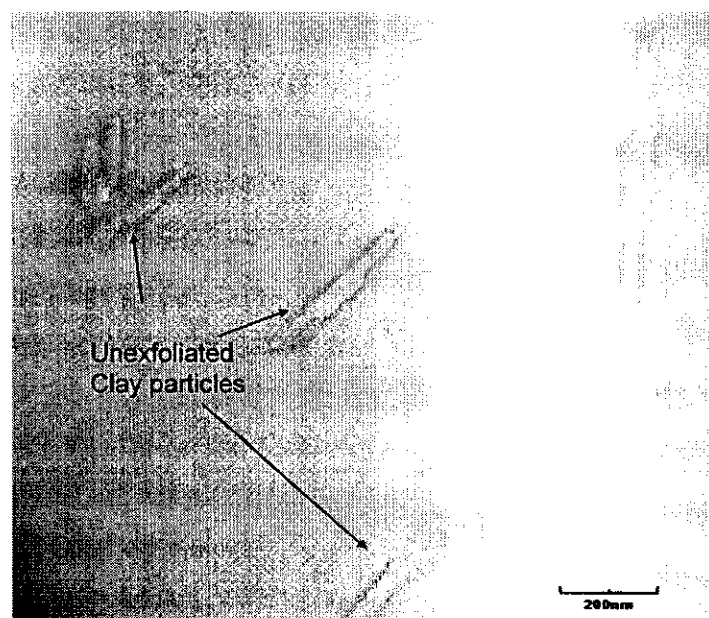
**Figure 4:** Suspensions before and after polymerization and TEM images of final latex in the addition of pristine clay or pre-modified clay.



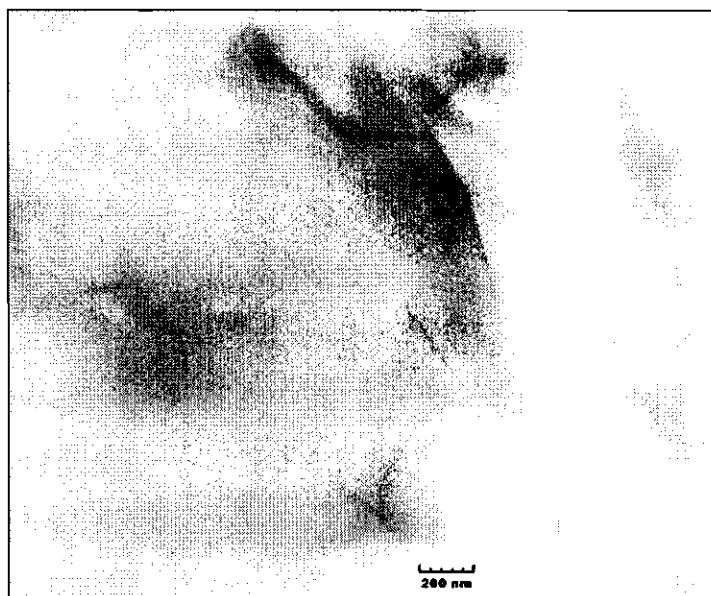
The morphologies of the clay particles in the composites made from both unmodified and modified saponite particles were examined using TEM. To make a thin composite film for TEM observation, the final composite suspension was directly dropped on a TEM grid and allowed it to dry at room temperature. After that, the samples on the grids were heated up to 120 °C (above the glass transition temperature of polystyrene) to form a thin film. As shown in the Figure 5(a), when unmodified clay was used in the polymerization, the saponite particles aggregated together in the polymer matrix. However, if the saponite particles were pre-modified by long hydrophobic surfactant OTAB, the saponite particles were intercalated and uniformly dispersed in the polystyrene matrix. The morphology of the composite made from modified clay is shown in Figure 5(b).

## 2.6. Conclusions

Stable water-based polymer nanoclay colloids containing anisotropic saponite clay platelets have been synthesized by miniemulsion polymerization in this study. The polymer-nanoclay composite contains clay platelets with the intercalated structure, and the final latex suspension is stable up to 5 wt.% of clay in the polymer. Further increase of clay content in the monomer will result in the formation of monomer gel, which is difficult to be used for miniemulsion polymerization. The modification of saponite by cationic OTAB is critical not only for intercalation but also for a hydrophobic surface so that the clay particles can be easily dispersed in the monomer phase during the miniemulsion polymerization. The presence of the costabilizer has a synergic influence on the final latex stability. The result of polymerization kinetics indicates that the addition of nanoclay platelet reduces the polymerization rate. Finally, the TEM observation reveals that the surface modified organophilic clay is entrapped and firmly adheres onto the polystyrene latex particle surface. These entrapped nanoclay plates are stable in the suspension without precipitation for months. TEM observation of the final latex melting films illustrates that the surface modified organophilic clay is intercalated and uniformly distributed into polystyrene matrix after melting at the temperature higher than the  $T_g$  of the polystyrene.



(a)



(b)

*Figure 5:* TEM images of the polystyrene nanosaponite composite film after melting: (a) unmodified saponite, (b) modified saponite in polystyrene matrix

## **Part 2. Hollow hemispheric polymer/clay nanocomposite particle formation in a miniemulsion polymerization process**

In this part, we discovered the unique template role of the platelet saponite clay in forming the hemispherical polystyrene/clay nanocomposite latex particles during a miniemulsion polymerization process following a thermodynamic and dynamic mechanism. The mechanism study is still on the way. In this report, we will present some unique structures of polymer-clay hemispheres. The mechanism will be further studied in our final year study.

### **2.1. Experimental details:**

#### 2.1.1. Materials and characterization

The experimental details can be found in Ref. 4, and as briefed as follows:

**Materials:** Saponite clay (Sumecton SA, kunimine industries Co., Ltd. Japan) is a synthetic clay with a cationic exchange capability of 0.997 equiv./kg and an average particle size of ~ 50 nm when dispersed in water (measured by light scattering). 2,2'-Azobisobutyronitrile (AIBN) was a product of Waco Chemicals USA, Inc., and used as received. (*ar*-vinylbenzyl) trimethylammonium chloride (VBTAC, 99 %), Triton 405 (TX-405, 4-(C<sub>8</sub>H<sub>17</sub>)C<sub>6</sub>H<sub>4</sub> (OCH<sub>2</sub>CH<sub>2</sub>)<sub>40</sub>OH, 70 % solution in water), hexadecane (99 %), and styrene (99 %) were purchased from Aldrich Chemical Inc. Styrene was purified by washing with 5 wt. % NaOH solution followed by deionized water until pH is about 7, and then was distilled under reduced pressure and stored in the refrigerator prior to use. All other reagents were used as received.

**Characterization:** X-ray powder diffraction patterns were recorded on a PW 1800 X-ray diffractometer (Philips, USA) using Cu, K $\alpha$  ray ( $\lambda = 1.54056 \text{ \AA}$ ) as the radiation source. A step size of 0.04 ° and a scan step time of 0.5 s were adopted. The *d* (001) basal-spacing of the pristine clay and the exfoliated clay was calculated using Bragg equation:

$$d = \lambda / 2 \sin \theta$$

FTIR spectra were recorded on a Magna System 560 from Nicolet Company, with samples in pellet form from KBr. The transmission electron microscopy (TEM) observation was conducted on a JEOL 100C transmission electron microscope at an accelerating voltage of 100 KV and a beam current of 70  $\mu$ A. The scanning electron microscopy (SEM) analysis was carried out on a LEO 1530 thermally-assisted field emission (TFE) scanning electron microscope in combination with a thin window energy dispersive spectrometer (EDS) for microanalysis at an operating voltage of 3 KV and a working distance from 6 to 10 mm. The ultrasonification was conducted on a W-385 sonicator from the Heat System-Ultrasonics Inc., USA, at an output power level of 5 with a continuous mode, and a duty cycle of 70 %. The centrifuge separation of the final latex suspension was fulfilled on a Beckman 20 centrifuge at different rate for 30 min at room temperature.

#### Preparation of the hemispherical polystyrene/clay nanocomposite latex particles

##### 2.1.2. Surface modification of saponite clay by VBTAC

In a typical procedure, a suspension of 5 g of saponite in 400 ml of water was continuously stirred at room temperature for 2 hours until a transparent aqueous solution was obtained. Then, an aqueous solution of 1.2 g of VBTAC in 100 ml water was added into above liquor. After continuous stirring of the suspension overnight at room temperature, a white precipitate was collected by centrifugation and washed with water and ethanol to remove the excess VBTAC. The sample was then dried in a vacuum oven at room temperature until constant weight.

##### 2.1.3. Miniemulsion polymerization of styrene in the presence of the modified saponite

In a typical run, as indicated by the recipe as listed in Table 1, oil phase A, composed of 1.2 g of co-stabilizer hexadecane and 0.24 g of AIBN, 12 g of monomer styrene, and varied amount of saponite (from 4-50 wt.% relative to styrene), was subjected to magnetic stirring at room temperature for ca. 30 min. The mixture was then exposed to ultrasonification for 4 min. Following that, oil phase A was poured into an aqueous phase B comprising of 1 g of TX-405 in 100 ml of water under a vigorous mechanical stirring in an ice bath for 30 minutes. The miniemulsion composed of A and B was thus prepared by homogenization under ultrasonification for another 3 minutes and ready for subsequent polymerization.

The miniemulsion polymerization was carried out by degassing the mixture via bubbling N<sub>2</sub> at room temperature for 30 min first, and then increasing the temperature to 80 ± 2 °C for more than 6 h under continuous mechanical stirring (~600 rpm). The reaction was terminated by adding one drop of 2 % 4-methoxyphenol solution into the system.

**Table 1.** The Basic Recipe for the Miniemulsion Polymerization of the Hemispherical Polystyrene/Clay Nanocomposite Latex Particles

Mixtures	Component	Amount added (g)	Percentage in total (wt.%)	Percentage to monomer (wt.%)
Mixture A	Styrene	12.0	10.4	100.0
	Modified-saponite	0.48-6.0	0.4-5.0	4.0-50.0
	Hexadecane	1.2	1.0	10.0
	AIBN	0.24	0.2	2.0
Mixture B	TX-405	1.0	0.9	8.3
	D.I. Water	100.0	87.0	833.3

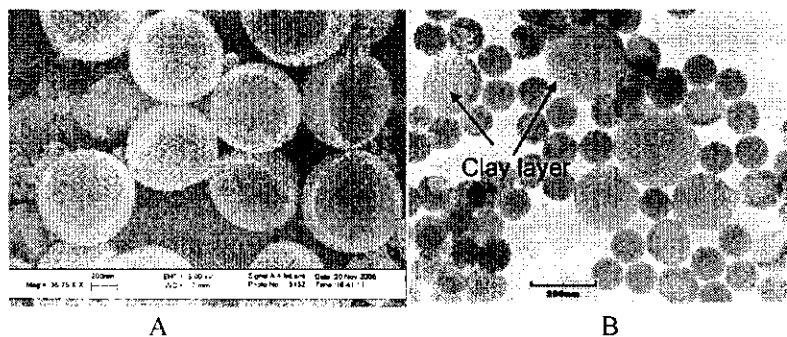
**Table 2.** Elemental Analysis Results of EDS at the Truncated Area of the Polystyrene/Clay Nanocomposite Latex Particles

Element	App. Conc.	Intensity Corr.	Weight (%)	Atomic (%)	Compd. (%)	Formula	Number of ions
C K	3.05	2.0816	1.47	27.26	5.37	CO <sub>2</sub>	3.33
Na K	0.15	1.9136	0.08	0.77	0.11	Na <sub>2</sub> O	0.09
Mg K	0.08	1.3041	0.06	0.60	0.11	MgO	0.07
Al K	0.12	1.1819	0.10	0.86	0.20	Al <sub>2</sub> O <sub>3</sub>	0.10
Si K	0.56	1.1046	0.50	4.00	1.08	SiO <sub>2</sub>	0.49
Fe L	0.79	0.6472	1.21	4.85	1.56	FeO	0.59
O			4.69	65.47			8.00
Totals			7.00				
						Cation Sum	4.22

## 2.2. Results

The hemispherical polystyrene/saponite composite latex particles were successfully synthesized by first pre-modification of pristine saponite clay with the cationic monomer (*ar*-vinylbenzyl) trimethylammonium chloride (VBTAC) and/or a cationic surfactant, and followed subsequently by a miniemulsion polymerization of the modified clay with styrene. Figure 1 A and B shows that the morphologies of the polystyrene nano-saponite composite latex particles with an addition of 4.0 % of the modified organophilic saponite clay. Two groups of particles were observed. One group of the particles consists of spherical particles

less than 100 nm, which is believed to be pure polystyrene particles. The other group of particles consists of truncated or hemispherical particles with a size range from ~100 to 1000 nm, usually

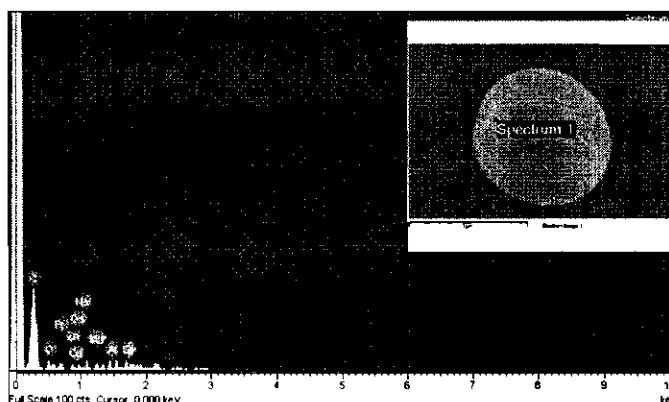


**Figure 1.** SEM (A) and TEM (B) profiles of the hemispherical polystyrene/clay nanocomposite latex particles with 4.0wt.% of VBTAC modified saponite loading. Scale bars: 200 nm

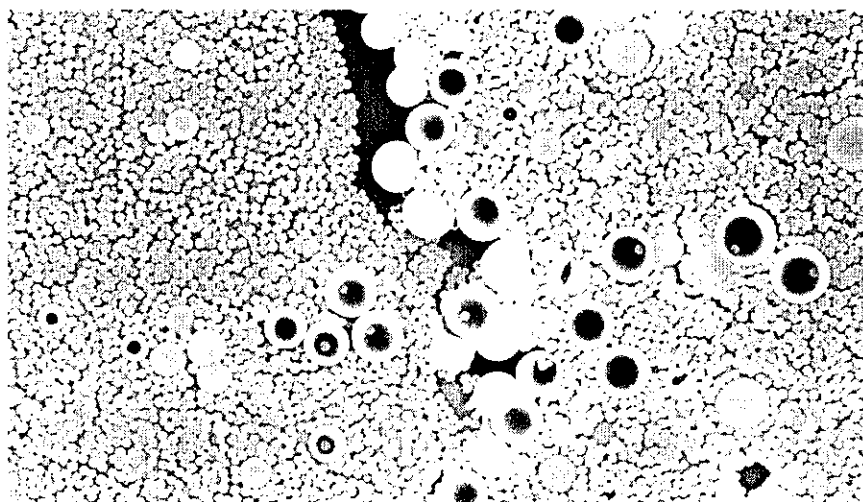
less than one micron. As indicated in the arrowed area of Figure 1B, it was clearly observed that the clay plates were attached to the planar surface of the hemispherical particles as a template. The EDS spectrum as shown in Figure 2 further confirms the existence of clay residues on the truncated surface of the polymer particles, with a weight ratio of Si/Mg/Fe/Al = 0.5/0.06/1.21/0.1.

In order to track the shape evolution of the hemispherical particle formation during the reaction process, the samples were taken out from the reactor at different times during the polymerization, and then the morphologies were observed by transmission electron microscopy (TEM) analysis. It was observed from SEM (not shown here) that only saponite plates were observed after 15-minute polymerization. However, after 30 minute reaction, the polystyrene particles that attached at one or both sides of the planar clay saponite were observed (B). The TEM images of the latex after 45- and 90-minute reactions (Figure 3C and D)

indicated the formation of spherical polystyrene particles. Figures 3 shows bowls of latex particles formed during the polymerization. Other morphologies, such as disk and plates, are not shown here. The mechanism of forming these unique particles is under investigating.



*Figure 2.* EDS spectrum of the hemispherical polystyrene/clay nanocomposite latex particles in the area of truncated profile indicating the existence of elements Si, Mg, Fe, and Al in the saponite clay.



### Part 3. Publications in the fiscal year 2005-2006

1. Z. Tong, Y. Deng, Synthesis of Water-Based Polystyrene-Nanoclay Composite Suspension via Miniemulsion Polymerization *Ind. Eng. Chem. Res.* **2006**, *45*, 2641-2645.
2. Q. Sun, Y. Deng, and Z. Wang, Synthesis and Characterization of Polystyrene-Encapsulated Laponite Composite via Miniemulsion Polymerization, *Macrom. Materials & Eng.*, **2004**, *289*, 288.
3. Q. Sun, J. Shorck and Y. Deng, Water-Based Polymer/Clay Nanocomposite Suspension for Paper Barrier Coating, *Tappi J.*, Submitted
4. Z. Tong, Q. Sun, J. Shorck and Y. Deng, Synthesis of water-based polystyrene-nanoclay composite suspension and hemispherical particles via mini-emulsion polymerization, 4th East-Asia Polymer Conference, Tianjin, China, May 28-31, 2006.
5. Sun, Q.; Deng, Y. Water-Based Nanostructured Composite for Paper Barrier Coating, 2005 Annual AIChE (American Institute of Chemical Engineers) Meeting, Oct. 30-Nov. 4, **2005**, Cincinnati, Ohio, USA.
6. T. Tong and Y. Deng, Synthesis of Water-Based Polystyrene-Nanoclay Hybrid via Miniemulsion Polymerization, AIChE Annual Meeting, Cincinnati, Ohio, November, 2005.
7. Q. Sun, J. Shorck and Y. Deng, Polymer/Clay Nanocomposites for Paper Barrier Coating, 2006 International Conference on Nanotechnology, Atlanta, GA, April 26-28, 2006





# Annual Report [2004-2005]

(NSF Grant No. CTS-0244371)

Through the first stage work from Apr. 2003 to Jun. 2004, during the fiscal year of 2004-2005, we conducted the following researches on project CTS-0244371 (**Synthesis of Polymer Encapsulated Nano-Clay Hybrid via Miniemulsion**), as divided into the following parts:

## **1. Screening of encapsulation and polymerization approaches to encapsulate a broad range of smectite clay into polymer latex particles**

### **1.1. Screening of polymerization approaches**

#### **1.1.1. Miniemulsion polymerization**

On the basis of miniemulsion polymerization approach to encapsulate the laponite clay into polystyrene latex, the following procedures described a new way to encapsulate KSF, a kind of montmorillonite (MMT) clay, into polystyrene latex: We used long chain alkylammonium cations (Cetyltrimethylammonium (CTAB) and Octadecyltrimethylammonium bromide (OTAB) to disperse MMT-KSF in the styrene monomer, in which the clay was converted from hydrophilic (water-like) to organophilic (oil-like) state with surfactant to be intercalated into the interlayer space. A ultrasonification shearing force was then applied to break up the aggregates. Meanwhile, the co-stabilizer (hexadecane) and oil-soluble initiator (AIBN) were also added into this phase prior to being added into aqueous phase. Then this phase was dispersed in the aqueous phase containing water and surfactant (polyoxyethylene (40) isooctylphenyl ether (Triton-405) or Tween-85) by vigorous mechanical stirring and ultra-sonification to form pre-miniemulsion. Then polymerization was carried out at 70 °C under Nitrogen. The direct dispersion of the clay into the oil phase, oil-soluble initiator and characteristic features of the miniemulsion polymerization technique such as the ability to nucleate all of the droplets containing the nano-clay, was expected to provide potential advantages for the encapsulation of nano-clay and formation of stable latex.

After polymerization, some yellowish aggregates were seen on the bottom and on the wall of the reaction flask. After ultra-centrifugation at 5000 rpm for 30min, only very low

percent (3wt % average) of clay (based on the total addition of clay) could be detected within the latex, suggesting most part of the clay had been precipitated to the bottom with extremely low content of polystyrene through calcinations analysis. Another interesting phenomena during the experiment showed that the dispersion of MMT-KSF in the styrene was gel-like solution by using OTAB as modification agent; in contrast, the MMT-KSF could not be dispersed and gelled by using CTAB as modification agent.

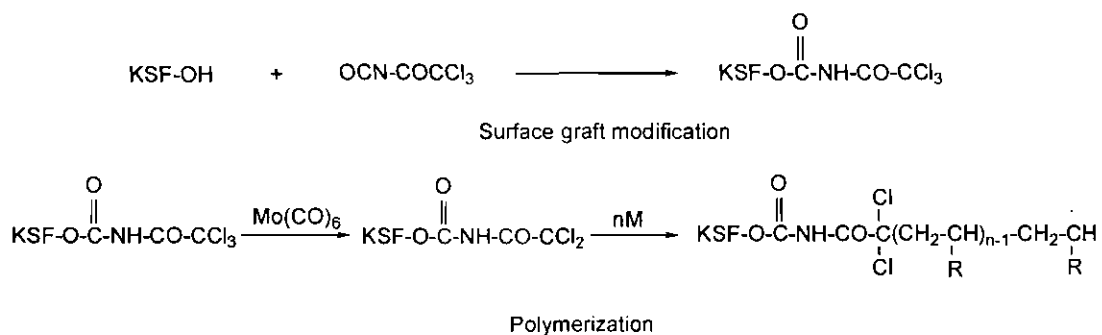
### 1.1.2. High solid miniemulsion polymerization

We adopted the high solid content miniemulsion polymerization approach to solve the collision and aggregation problem often encountered during the research, due to, most probably, the high density of MMT-KSF and the low strength treating of the aqueous dispersion resulting in the aggregates formation in the latex. We increased the solid content of the miniemulsion to 80%, expecting to enhance the viscosity of the latex between the droplets particles so as to suspend the clay with relative high gravimetric density. The procedure was conducted by emulsifying the mixture at high mechanical force (stirring speed as high as 20,000 rpm) for 10min before polymerization, and sodium dodecyl sulfate (SDS) was added as a co-surfactant with the Triton-405 together. As a result, the final latex was stable without any aggregates precipitated out at the bottom the end of the reaction and can be stabilized for several hours. Nevertheless, the aggregates cannot be stable enough and were precipitated out in a few days. We also carried out the experiment to understand the mechanism of a variety of initiators to the stability of the miniemulsion, such as oil-soluble initiator initiator AIBN or water-soluble initiator APS. It was found that a higher content of polystyrene (33%) can be found in the co-precipitates with the clay when an oil soluble initiator was used, comparing with that of 25% by using water-soluble initiator.

### 1.1.3. Grafted miniemulsion polymerization

Except the above approach, we tried the surface grafting of the MMT clay to increase the stability of the latex. Since the stable latex was very hard to achieve and the encapsulation was not also indicated by TEM image, increasing the degree of encapsulation by changing the properties of surface properties was believed to benefit to

get stable latex. The grafted miniemulsion polymerization was carried out. Trichloroacetyl groups were introduced onto KSF particle surface, and then miniemulsion polymerization of styrene was processed using Molybdenum hexacarbonyl ( $\text{Mo}(\text{CO})_6$ ) as initiator. The reactions were shown as following two equations:



The final latex with very low molecular weight and conversion (lower than 60%) of polystyrene was obtained. All amounts of clay were precipitated out on the bottom after the polymerization. The reason was because this polymerization using ( $\text{Mo}(\text{CO})_6$ ) as initiator was not accessible in the aqueous medium.

The stable latex, encapsulation clay inside polystyrene could not be achieved by the above miniemulsion polymerization. The large size of MMT-KSF (the average size about 250-450nm) and the broad distribution (from 100nm to 1 $\mu\text{m}$ ) was believed to be the reason why we failed in the above miniemulsion polymerization since the range of the particle size for the miniemulsion polymerization was 100-500nm. Therefore, the different kinds of emulsion polymerization methods were carried out to be expected to obtain the stable latex for this large-size clay, such as: conventional emulsion polymerization, seeded emulsion polymerization. The following was the details for these two methods.

#### 1.1.4. Conventional emulsion polymerization:

The paper of Dong-Guk Yu etc claimed that titanium dioxide core/polymer shell hybrid composite particles were successfully synthesized by emulsion polymerization. In this study, poly (methyl methacrylate-co-butylacrylate-co-methacrylic acid) [P (MMA-co-BA)-MMA] shell composite particles were prepared with emulsion polymerization of

methyl methacrylate (MMA), butylacrylate (BA), and methacrylic acid (MAA). It was believed that the inorganic/organic composite particles were produced by adding the inorganic particles before polymerization. Due to the different surface properties of TiO<sub>2</sub> and MMT-KSF, this method failed to synthesize the stable core-shell polymer-clay composite.

#### 1.1.5. Seeded emulsion polymerization

Emulsion polymerization is a conventional approach. The seeded emulsion polymerization, however, uses oil soluble initiator and pretreated exfoliated organophilic nano-clay as seeds. Firstly, we obtained an organophilic surface modified KSF (with ca. 10% OTAB) copolymerized with bulk styrene. The surface modified nano-clay with 10-16% surface polystyrene coverage was used as the seed for the following emulsion polymerization. In order to increase the compatibility between the clay and oil monomer phase, a cationic monomer ((vinyl-benzyl) tri-methyl ammonium chloride was also introduced into the bulk solution together with the seeds. Thus these two kinds of seeds were pre-dispersed on the styrene with the addition of the oil soluble initiator 2, 2'-Azobisisobutyronitrile (AIBN), and then following the normal emulsification and polymerization procedures as described above (mixing in D.I. water in the presence of Triton-405). Unfortunately, the results were not satisfactory in terms of phase separation of polystyrene clay composite in the water phase.

#### 1.2. Screening of clays varieties for candidates to be encapsulated

In our preliminary experiments, the polystyrene-encapsulated laponite composites were obtained via miniemulsion polymerization. Due to the high price of laponite, the complexity of laponite dispersion in aqueous phase and difficulties of characterization, it was not considered in the following studying. Therefore, by screening experiment of all kinds of clay minerals, such as: saponite, Montmorillonite (MMT), illite and smectite. Montmorillonite-Na (MMT-KSF) was chosen based on its uniform size distribution

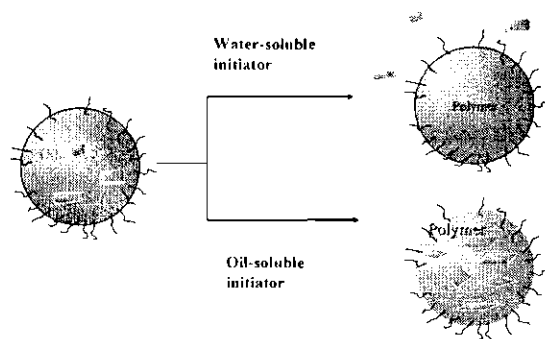
among all kinds of montmorillonite, higher cationic exchangeable capacity comparing with the other clay minerals and its cheaper price in comparison with laponite.

Using MMT-KSF as the clay, the following miniemulsion methods were investigated to synthesize stable water-based latex, such as: miniemulsion polymerization, grafted miniemulsion polymerization, high solid miniemulsion polymerization. The following discussion will show how these methods progressed and what the results made.

## 2. Synthesis and characterization of polystyrene-encapsulated laponite composite via miniemulsion polymerization

A significant progress, along with the screening process during the fiscal year of 2004-2005, is the success in the novel polystyrene-encapsulated laponite composite system via a miniemulsion polymerization approach. The laponite was encapsulated through a miniemulsion polymerization process in which it was predispersed in the monomer phase. The stability of both miniemulsion and latex depends on initiation loci, premixing procedures, intensity and time of ultrasonification, and surfactants and costabilizer used. It was found that the hydrophobicity of the laponite clay played a vital role in both the encapsulation and the stability of the latex. Quaternary ammonium salt, cetyltrimethyl ammonium bromide (CTAB), was mixed with clay in the monomer phase prior to emulsification. As a result, the clay particles were modified to hydrophobic and were intercalated. The hydrophobicity not only favored the clay dispersion in the oil droplets but also aided the entry of the monomer into the clay's intergalleries during polymerization. Meanwhile, CTAB helped stabilize the system when it was used in conjunction with the nonionic surfactant polyoxyethylene (40) isooctylphenyl ether (TX-405).

In this way, the laponite is



Scheme 1. Schematic demonstration of intercalation process of CTAB in the intergalleries of clay and the morphology of clay within an oil phase

effectively encapsulated within a polystyrene shell in stable latex form. More importantly, the polymerization initiated in the intergalleries of the clay effectively expands the clay's platelet array to form an exfoliated structure.

In rationalizing the process, several factors had been taken into account. First of all, suspension polymerization can be excluded from the list of considerations, in terms of the final product form. The conventional emulsion polymerization is also not available in terms of the contradiction between the nucleation mechanism of this approach and the location of clay to be encapsulated, even though it has been a powerful tool in manipulating a wide range of latex products. Our preliminary experiments also verified this judgment. One will naturally be concerned with the loci of the clay before and after polymerization in rationalizing the approach, as depicted in Scheme 1. If a phyllosilicate clay particle must be kept separate within a droplet, it should withstand coalescence and coagulation caused by collision between droplets under high shear. Besides, there should be no transfer of oligomeric radicals from the swollen micelles in the aqueous phase into the oil phase, where the clay exists, for this will unavoidably cause coagulation, if the nucleation mechanism in a normal emulsion polymerization process is followed. In this way, the effective encapsulation could occur. A hydrophobic clay, compared to its intrinsic hydrophilicity, is therefore required to favor its retention within the oil phase before polymerization. This hydrophobicity will aid the entry of monomer into the intergalleries of the clay and exfoliate the clay from a stacked architecture to individually dispersed platelet form after polymerization. Meanwhile, a complete encapsulation of the clay within a polymer shell could be finished.

The basic recipe we adopted is as follows:

Basic Recipe

Mixtures	Component	Amount added (g)	Percentage in total (wt.-%)	Percentage to monomer (wt.-%)
Mixture A	Styrene	6	18.0	100
	Laponite	0.25	0.75	4.2

	CTAB	0.25	0.75	4.2
	CA	0.6	1.8	10
	AIBN	0.15	0.45	2.5
<b>Mixture B</b>	TX-405	0.5	1.5	8.4
	D.I. Water	25	76	417

As illustrated in Table 1-3, and Fig. 1-3, we examined the stability of the miniemulsions as related with the cationic surfactant CTAB, the nonionic surfactant Triton-405, and the costabilizer hexadecane in the system. The chain length of the cationic surfactants was found to be a factor in influencing the stability of the miniemulsion system. WXRd analysis revealed that the insertion of CTAB into the intergalleries allowed not only the pertinent hydrophobicity, helping confine the clay inclusion within the monomer droplets during the droplet formation prior to polymerization, but also aided the continuous monomer's entry in the subsequent polymerization. In this way, the exfoliation of the clay could be fostered and finally achieved. TEM observation suggested that the laponite clay was completely encapsulated within the polystyrene latex particles with stability of the latex solution.

Table 1. Distribution of Laponite Clay between Oil and Aqueous Phase \*

Systems	With CTAB			Without CTAB		
	<u>Added</u> (g)	<u>Measured</u> (g)	<u>Percentage</u> <u>in fed clay</u> (wt.- %)	<u>Added</u> (g)	<u>Measured</u> (g)	<u>Percentage</u> <u>in fed clay</u> (wt.- %)
Oil phase	0.25	0.221	88.3	0.25	0.020	8.1
Aqueous phase	0	0.026	10.4	0	0.224	89.7

- \* The experiment was carried out according to the basic recipe with TX-405 = 2.0 g, after eliminating the post-sonification step for the purpose of clay distribution measuring both in oil and aqueous phase respectively. The samples collected from oil and aqueous phases were dried at 140 °C for 3 hrs first, and then cinerated at 525 °C for 1 hr.



Table 2. Particle Size Dependence on the Content of Costabilizer (CA) and the Stability of Miniemulsions\*

Entry	CA content (wt.-%)	0.0	0.6	1.2	1.8
	Particle size (nm)	1073.9	279.2	267.2	261.6
<i>Before</i>	Polydispersity <sup>a</sup>	0.82	0.78	0.25	0.54
<i>Polymerization</i>	Stability	-	±	+	+
	$W_i$ (g) <sup>b</sup>	4.4	4.3	-	0.3
<i>After</i>	$A_i$ (wt.-%) <sup>c</sup>	5.6	4.5	-	12.2
<i>Polymerization</i>	$C_i$ (wt.-%) <sup>d</sup>	98.5	77.3	-	14.8
	Stability	-	±	N/A	+

\* TX-405 = 0.3 g (0.8 wt.-%) in basic recipe.

<sup>a</sup> Particle distribution by dynamic light-scattering measurement.

<sup>b</sup>  $W_i$  refers to the dry weight (g) of precipitates obtained at the bottom of sample vial after 72 hrs free-standing for latex.

<sup>c</sup>  $A_i$  refers to the weight of clay as obtained in incineration divided by the total weight of  $W_i$  times 100% (wt.-%).

<sup>d</sup>  $C_i$  refers to the weight of clay as obtained in incineration derived from  $W_i$  divided by the total weight of clay fed, then times 100% (wt.-%).

$W_i$ ,  $A_i$ , and  $C_i$  have been defined the same throughout the context

Table 3. Influence of Chain Length of Cationic Surfactants on Particle Size and Miniemulsion Stability\*

Surfactant type	MTAB	CTAB	OTAB
$W_i$ (g)	trace	trace	trace
$W_b$ (g) <sup>a</sup>	0.23	0.004	0.01
Particle size (nm)	257.7	211.6	197.0
Polydispersity	0.41	0.23	0.20
Peak shape (distribution)	Bi-	Mono-	Mono-
Stability	±	+	+

\* The reactions were carried out following the basic recipe and typical procedures as described in the text.

<sup>a</sup>  $W_b$  refers to the dry weight (g) of precipitates obtained at the bottom of centrifuge tube after centrifuge sedimentation for the miniemulsion samples, and with same definition throughout the context.

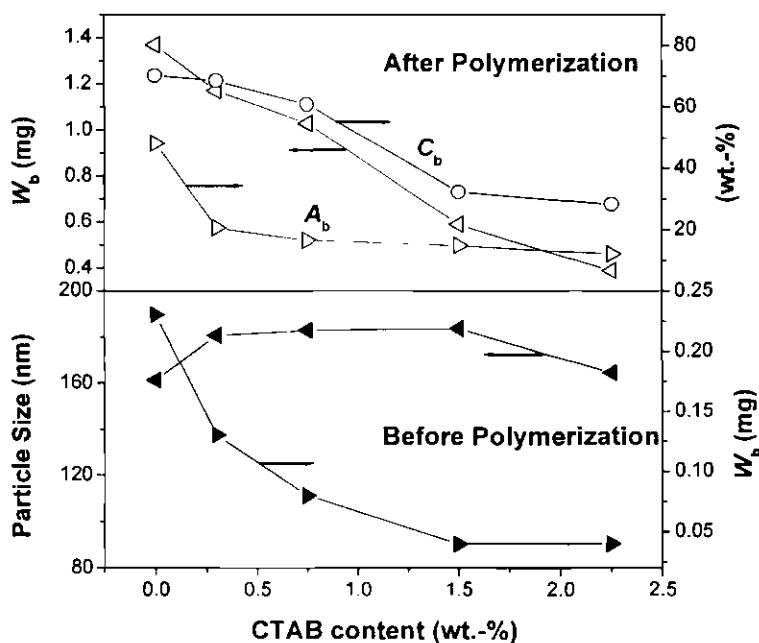


Figure 1. Relationship between CTAB content (wt.-%) and properties. Filled triangles: before polymerization; empty triangles and circle: after polymerization. The stability sequences for the above five specimens were -,  $\pm$ , +, +, and +, respectively.  $W_b$  denotes the dry weight (g) of precipitates obtained at the bottom of the centrifuge tube after centrifuge sedimentation for either emulsion or latex samples.  $A_b$  denotes the weight of clay as obtained in incineration divided by the total weight of  $W_b$  times 100% (wt.-%).  $C_b$  denotes the weight of clay as obtained in incineration derived from  $W_b$  divided by the total weight of clay fed, then times 100% (wt.-%). All of them have been defined the same throughout the context.

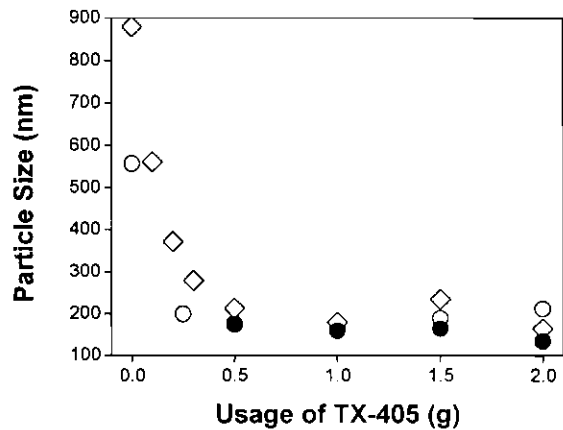


Figure 2. Relationship between particle size and TX-405 usage in the aqueous phase. Empty circle and rectangle: before polymerization; filled circle: after polymerization.  $\diamond$ : CTAB = 0.25 g;  $\circ$ : CTAB = 0.5 g;  $\bullet$ : CTAB = 0.25 g.

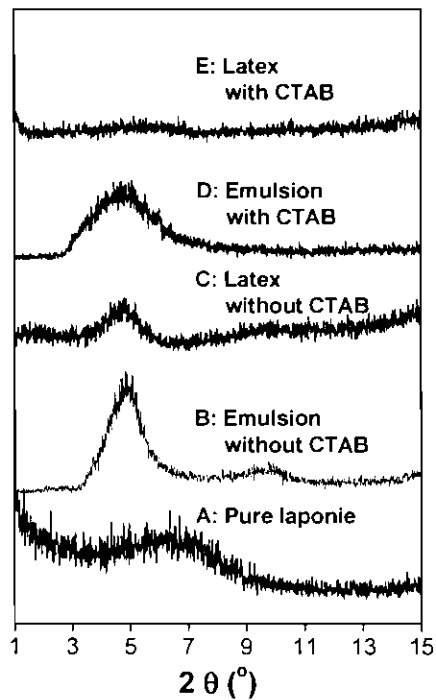


Figure 3. WXR D pattern of **A**: pristine laponite clay; **B**: precipitates collected from sample without CTAB before polymerization (clay content: 90 wt.-%); **C**: precipitates collected from sample without CTAB after polymerization (clay content: 6.0 wt %); **D**: precipitates collected from sample with CTAB before polymerization (clay content: 90 wt %); and **E**: precipitates collected from sample with CTAB after polymerization (clay content: 7.8 wt.-%).

### 3. Significant progress in the encapsulation of Saponite clay via a miniemulsion polymerization approach

Based on the screening and preliminary experiments as described above, it is believed that the particle size and surface properties, the exfoliability of the clay were the key factors, which will finally affect the stability of clay in the monomer, in the emulsion before polymerization, and in the final latex after polymerization. It is also found that the easier the pristine clay to be dispersed in water, the easier to be exfoliated. As a result, the dispersion of modified clay and the stability of the final latex would be improved.

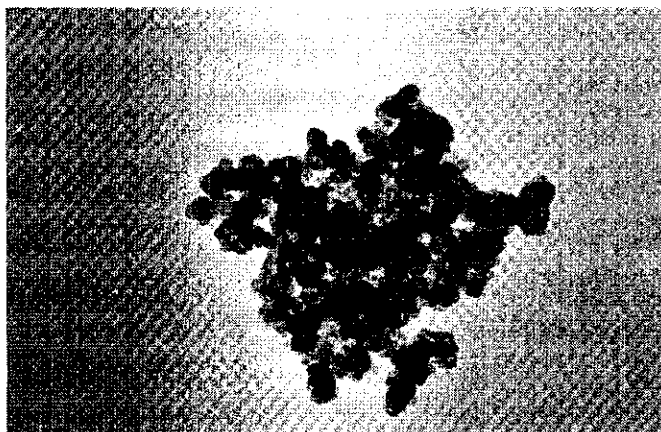


Figure 4. TEM image of saponite-Ca dispersion in water

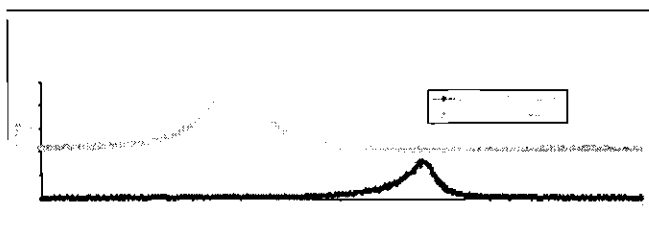


Figure 5. XRD pattern of Saponite before and after OTAB

As shown in **Figure 1**, Saponite-Ca clay, with a relative uniform size distribution and particles size less than 200 nm, can be easily dispersed into water to form a stable aqueous dispersion. After treatment by OTAB at 70 °C for 24hr, the Saponite-Ca clay was found exfoliated. As shown in **Figure2**, it was found that while the pristine

Saponite-Ca had an interlayer spacing of  $d$  1.24 nm corresponding to  $2\theta$  at  $7.14^\circ$  ( $d_{001}$  reflection), the interlayer spacing of the surface modified Saponite clay had shifted to  $d$  1.92 nm corresponding to  $2\theta$  at  $4.6^\circ$ .

A comparative study on the retaining of OTAB on the Saponite clay, as shown in Table 4, revealed that no extra-OTAB existed in terms of a very close matching between the calculated CEC (cation exchangeable capacity) and the real amount measurement of OTAB resided in the interspace of the clay. This is really the case because surface unbonded OTAB residue had been washed away under repeated washing process.

Table 4. The content of OTAB on the surface or interlayer of clay

clay	CEC(meq/100g)	g OTAB/ gOTAB-clay	
		Calculation	Measurement
saponite-Ca	75-80	0.2274-0.2390	0.2323

As illustrated in **Figure 6** (left in the glass vial), the organo-saponite clay obtained by the above treatment exhibiting almost transparent appearance when dispersed in the monomer phase via sonification at low concentration ( $< 5.0$  wt.%). It changed to gel-like solution when

the concentration was increased at around 5.0 wt.% (as shown in right TEM photographs in **Figure 6**). The



Figure 6. Organo-saponite dispersed in the monomer styrene and its TEM image.

latex resulted from the subsequent polymerization provided a stable water-based polystyrene-nano-saponite hybrid with a variation range of organo-saponite from 1.0-5.0 wt.%. As shown in **Figure 7**, under optimum reaction conditions, the latex obtained (left glass vial) exhibited a homogeneous appearance in contrast with that with aggregates formation on

the right. TEM morphology observation between pristine- and surface modified (organophilic) clay, as illustrated in **Figure 8**, revealed that the surface modified organophilic clay was entrapped and firmly adhered onto the polystyrene latex particle surface in contrast with that of pristine clay which was in totally separated state with the PS particles. Although the organophilic clay particles was on the surface of the PS particles in the miniemulsion system, it was still very stable for months under ambient environment and could not be even separated under centrifugation at 10,000 rpm for 1 hr.

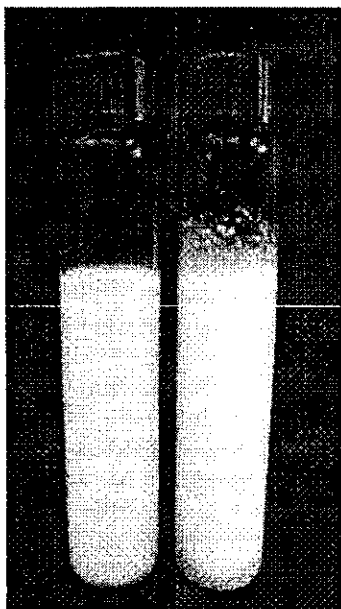


Figure 7. the latex of saponite without (left) and with (right) aggregates

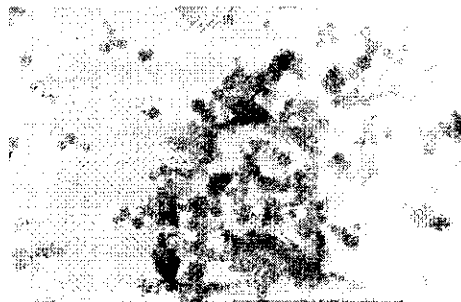


Figure 8. TEM image of water-based stable latex with polystyrene nano-saponite hybrid without (up) and with (down) clay pre-modification

In order to further understand the surface properties of the clay before and after modification, for example, the distribution ratio of pristine and modified clay in oil and water phase respectively, a comparative study was conducted in the absence of surfactant. As shown in Table 5, the surface modified clay exactly exhibited a hydrophobic behavior as staying mainly in the oil phase in comparison with that of the pristine clay which predominantly presented in the water phase.

Table 5. Distribution of pristine Saponite and organo-Saponite in the water and oil phase

clay	the amount of clay staying in the water phase	the amount of clay staying in the oil and interface phase
Saponite-Ca	81%	19%
Saponite-OTAB	4%	96%

The influence of the content of the clay, styrene to water ratio, and the quantity of co-stabilizer hexadecane on the distribution ratio of pristine and surface modified clay in water and oil phase respectively in the absence of surfactant was also investigated. As shown in Figure 9, there observed no significant fluctuation in terms of these influencing factors, ranging from 85 to 95 wt. %..

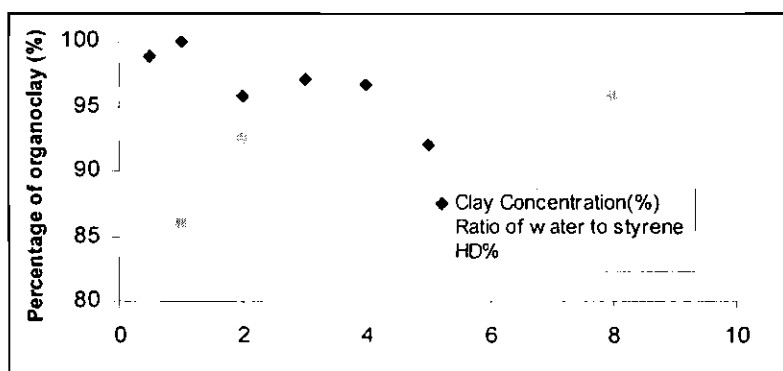


Figure 9. Percentage of organo-clay in the oil and interface with the different percentage of clay concentration, hexadecane and different ratio of water to styrene

#### 4. Work to be conducted in the coming fiscal year

Based on the work performed in 2003-2004 (Task 1: modification of laplonite or montmorillonite into hydrophobic and exfoliated nanoparticles as to obtain a stable organic monomer/nanoclay dispersion system, Task 2: fundamental understanding of modified laplonite or montmorillonite on the miniemulsion stability), and the recent success of the preparation of waterborne latex of polystyrene/organophilic saponite clay hybrid composite in the past year (2004-2005, Task 3: distribution of nanolayered clay particles in water and oil phase before and after polymerization; Task 4: effect of the particle size, aspect ratio and concentration of exfoliated inorganic particle on the

miniemulsion stability and encapsulation efficiency), we planned, according to our proposed research program Tasks 5 and 6, to concentrate on the relationship between the physical properties ( $T_g$ , tensile strength, modulus, heat resistance, water and gases resistances) of encapsulated nanohybrids and structure parameters of inorganic particles (Tasks 5); and the effect of nanoclay particle on the polymerization conversion and kinetics (Task 6) during the fiscal year of 2005-2006. The focus will be on the following aspects:

1. Although to date the waterborne composite latex formed was in the state of co-existence of both surface modified clay and the PS latex, which is a big progress in the field, a complete encapsulation of the saponite clay into the polymer latex particles was contingent. It is postulated that properly increasing the PS latex particle size will be appropriated in terms to completely encapsulate the clay within the latex particles due to the same level particle size between the latex (ca. 100 nm) and the clay particles (ca. 80 nm). To harness the irregular shape of the nano-clay to eliminate the difficulties in encapsulation, mechanical treatment of the clay will be necessary. To further stabilize the surface modified clay, the surface properties of nano-clay needed to be further enhanced in terms of allowing more compatibility to monomer phase. Meanwhile, a deep understanding on the mechanism of miniemulsion polymerization will facilitate the process. As another important impetus, the surface grafting encapsulation approach, especially on the MMT clay, will be launched at due time to allow more space in tailoring the cost effective and source abundant clay utilization in terms of a perfect accomplish of the project. Based on the success of the above mentioned research, we will then investigate the relationship between the physical properties ( $T_g$ , tensile strength, modulus, heat resistance, water and gases resistances) of encapsulated nanohybrids and structure parameters of inorganic particles. If time permits, we will conduct the research of preliminary research on the possible application of this novel waterborne nanoclay composite in paper barrier coating, thus to further broaden the application perspective in papermaking or other related industries.

2. The effect of nanoclay particle on the polymerization conversion and kinetics



Although we have investigated the polymer encapsulation of nanoclay via the miniemulsion polymerization approach, the underlying mechanism, especially the parameters controlling the reaction process and the relationship between them, remained a mystery. Thus in the later part of this research program, we would pay attention on the aspect of effect of nanoclay particle on the polymerization conversion and kinetics to further understand the reaction mechanism and the controlling factors. For example, the nanoclay particle will cause the viscosity change in the system so as to influence the reaction kinetics, conversion, and final products morphology. On the other hand, this performance of the organophilic clay might lead to the properties changing of the oil and water interface, as a result, the function of co-stabilizer and surfactant will be affected.