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# The Role of SDS Surfactant in The Synthesis of Polymer Hybrid Latex *Poly-(St-co-BA-co-MMA)* with OMMT as Filler via Mini-Emulsion Polymerization

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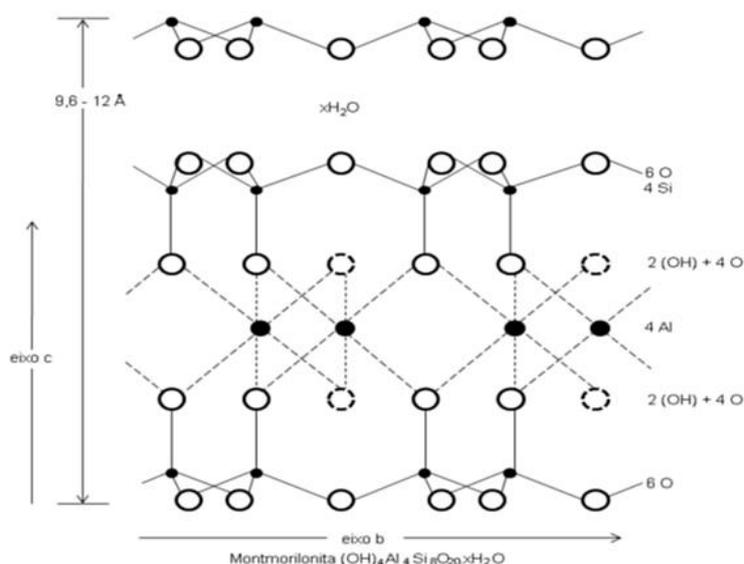
**Abstract:** Polymer hybrid latex *poly-(St-co-BA-co-MMA)* with organo-montmorillonite (OMMT) as a filler were synthesized through a mini-emulsion polymerization technique. To change the nature hydrophilic to organophilic of montmorillonite (MMT), surface modification with cationic surfactant alkylammonium MTAB, CTAB, and OTAB were done through ion exchange process. The results were characterized by X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR). Interlayer layer spacing of OMMT was extended from 1.21 nm to 2.03 nm, and  $2\theta$  decreased from  $7.2^\circ$  to  $4.2^\circ$  resulting in pseudotrilayer structure, FTIR confirmed the XRD results where the amine group from cationic surfactant inserting into MMT interlayer and the surface wettability of MMT changes from hydrophilicity to organophilicity. Mini-emulsion polymerization with 4.0 wt% level of OMMT addition showed the role of SDS surfactant in the mini-emulsion polymerization technique with variation in particle size distributions of hybrid latex, surface tension, and monomer conversion rate. Water-soluble surfactant SDS with the added level from 2.0 to 4.0 wt% contributed to monomer conversion rate (> 99%) with a particle size diameter 80 to 102 nm.

**Keywords:** Mini-emulsion polymerization, organophilicity, hydrophilicity, organo montmorillonite, monomer conversion rate

## 1. Introduction

Polymer hybrid latex or nanocomposites was found in the literature on 1949, credited to Bower convention [1]. The process was based on DNA absorption by montmorillonite (MMT). In 1960, other researches demonstrated montmorillonite application as an initiator in polymerization [2,3]. In 1980, the great leap was done by Toyota researcher by synthesized polymer/clay nanocomposite to be used in cars [4–6]. Montmorillonite (MMT) is a layered silicate clay that belongs to smectite family with 2:1 phyllosilicate structure. The 2:1 structure consists of octahedral layer bonded by aluminium with two sheets of tetrahedral layers of silicon; the layers are formed in continuous formation with *a* and *b* direction and stacked in *c* direction as shown in Figure 1.





**Figure 1.** Schematic structure 2:1 of montmorillonite [7].

In 2:1 structure, trivalent Aluminium cation in the octahedral layer is partially substituted by divalent M-cation [8]. The negative charge is counterbalanced by interlayer sodium ion and calcium ion. However, when two charges unbalanced, the structure will form *mica structure*. One of the exciting features of MMT structure is the cation between the clay layers can be exchanged by other organic cationic molecules, leading to change the characteristic from hydrophilic to hydrophobic [9]. To explain the mechanism of organoclay synthesis, there are many active sites which are available to explain the reaction. The reaction called functionalization based on the interaction of clay surface and surfactant molecules [6]. Surfactant ions are intercalated into interlayer spaces of MMT by conventional ion exchange process and bonded on the surface through electrostatic forces. The cations in some case can be adsorbed onto the external surface of the particles and the surfactant cations [10]. The process creates hydrophobicity and increases the basal clay spacing called “*organophilization*” [11]. The chemical structure, chemical composition, and the amount of carbon atom chains of cationic surfactants may influence the intercalation and exfoliation during the modification process; the common functional group used are alkylammonium, phosphonium, imidazolium, sulfonium or organosilane [12,13].

Colloidal stability of mini-emulsions usually controlled by type and concentration of surfactant; the equilibrium rate of nanodroplets during sonication process influenced by the time of sonication, amplitude and amount of surfactant [14]. Water-based sodium dodecyl sulfate (SDS) surfactant with monomer dispersion rate of 20% affected droplets particle size from 180 nm down to 32 nm [15,16]. As compared to emulsion polymerization process, this amount is considered very small because the latex with particle size 32 nm is already translucent and latex particle size 32 nm is close to latex synthesized with micro-emulsion polymerization [17]. The area of the pre-surfactant molecule on the particle size ( $A_{surf}$ ) was dependent on particle size, the entire range of a dense surfactant monolayer about 0.4 to 7.0 nm<sup>2</sup> [18]. The surface tension of the latex suspension has the range from 36 to 65 mN.m<sup>-1</sup> and the value decreases with the decrease in latex particle size [18]. The maximum area per-surfactant values correspond to surfactant concentration; the value was maintained in order to stabilize droplets against coalescence. Maximum surface areas depend on droplet size and can be stabilized by one molecule of surfactant. The mini-emulsion with a decrease in surfactant will not lead to instability but affected larger particle size distribution [18]. Mini-emulsion polymerization process is a heterophase system consisting of stable nanodroplets in the continuous phase; nanodroplet has the size of 50 to 500 nm which is prepared by shearing a system containing monomers, water, and surfactant/co-surfactant [15,16]. The process of homogenization is usually measured by its turbidity, surface tension, and particle size distribution.

In this study, the first stage was the surface modification of nanoclay montmorillonite performed using MTAB, CTAB, and OTAB surfactants. The basal spacing was investigated by XRD and FTIR. The second step was the synthesis of hybrid latex involving several types of styrene, butyl acrylate, and methyl methacrylate with a ratio of 49/50/1 and 4 wt% of OMMT as a filler via mini-emulsion polymerization technique. The role of surfactant and co-surfactant were studied during the polymerization process.

## 2. Methods

### 2.1. Material

Styrene monomer (St), butyl acrylate (BA), methyl methacrylate (MMA), azobisisobutyronitrile (AIBN) montmorillonite (MMT) with CEC 110 meq/100 g, sodium dodecyl sulfate (SDS), hexadecane (HD), were supplied from Sigma Aldrich. MTAB, CTAB, and OTAB were supplied from Pioneer Chemicals China with 99.9% purity.

### 2.2. Preparation

#### 2.2.1. Surface modification of MMT.

MMT (20 g) was dispersed in 1500 ml distilled water; the solution was stirred for 2 hours until a clear solution was obtained. Organic modifier (based on its CEC) was diluted in 500 ml distilled water; the solution was then stirred for 24 hours at room temperature. The solution was precipitated under mechanical centrifugation at 3500-4000 rpm for 5 minutes, and washing was done several times with distilled water until free of bromide (detected by 0.1 mol silver nitrate solution). The modified MMT and pristine MMT are characterized by x-ray diffraction (XRD) Philips, using  $\text{Cu}\alpha = 1.54060 \text{ \AA}$ , start position from  $3.0^\circ$  to  $15.0^\circ$  and Fourier transform infrared spectrophotometer (FTIR) Shimadzu with KBr, measuring range from  $400\text{-}4000 \text{ cm}^{-1}$ .

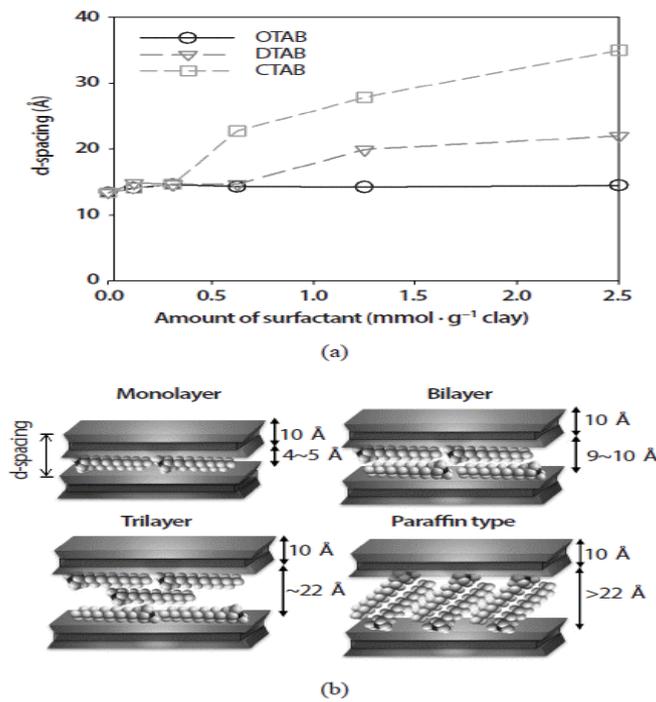
#### 2.2.2. Synthesis of hybrid latex with Miniemulsion Polymerization.

Styrene (St), butyl acrylate (BA), and MMA ratios were based on 40/59/1.0 wt%; the primary ratio was built up based on previous research on synthesis water-based latex polystyrene butyl acrylate latex [15,20]. Mini-emulsion polymerization was done in a mini-laboratory glass reactor, pulse with nitrogen for 15 minutes with a temperature of  $78\text{-}80 \text{ }^\circ\text{C}$  for 8 hours. Mini-emulsion polymerization was carried out by 4 wt% OMMT addition level and variation of SDS surfactant from 0.5 to 4.0 wt% with hexadecane. Polymerization was terminated by addition of one drop of 4-methoxyphenol 2% solution. The latexes were characterized on its particle size with Bettersize 2000, monomer conversion rate, surface tension with Tensiomat model 21 from Fisher Scientific and coagulum content by Sieve Test (ASTM D6913).

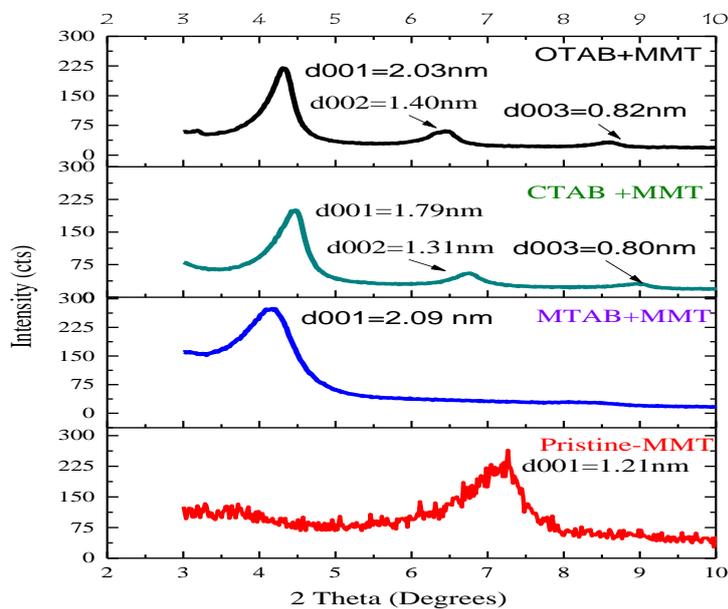
## 3. Results and Discussion

### 3.1. Surface modification of MMT with MTAB, CTAB, and OTAB.

Amount of surfactant used in this study was based on 2.0 of MMT's CEC; this amount was used based on previous research [19]. Figure 3 shows the XRD patterns of MMT and OMMTs. The d001 reflection of MMT which increased from 1.21 nm to 2.00 nm due to inorganic ions in MMT exchanged by the onium group of surfactants through the exchange process. According to previous researches, the basal spacing for aliphatic alkylammonium surfactant with the value of  $\sim 2.0$  to  $2.2 \text{ nm}$  in the form of bilayer or paraffin structure, as shown in Figure 2. [20,21]. MTAB showed a single basal spacing at  $d_{001} = 2.09 \text{ nm}$ . The peaks showed on d002 and d003 on modified MMT with CTAB and OTAB that represent  $\text{CTA}^+$  or  $\text{OTA}^+$  ions in the interlayer of MMT is *pseudotrilayer* arrangement [20,22].



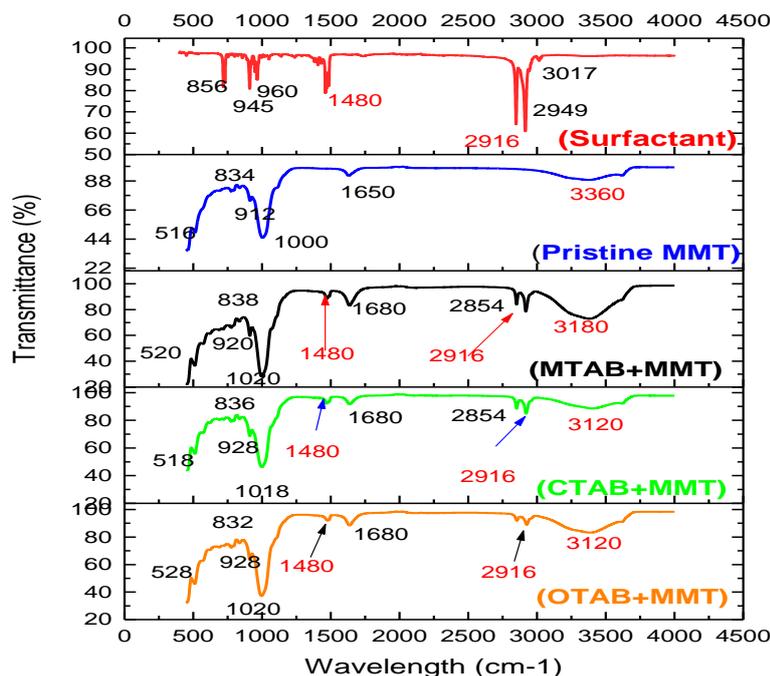
**Figure 2.** Various spacing structures of modified montmorillonite with alkylammonium surfactants [22]



**Figure 3.** X-ray diffraction patterns of pristine MMT and OMMT

Figure 4 shows the IR spectra of cationic surfactant, modified MMT with MTAB, CTAB, and OTAB, cationic surfactant MTAB, CTAB, and OTAB have similar IR spectra pattern. The bands of 3300 to 3500 cm<sup>-1</sup>, 1650-1680 cm<sup>-1</sup>, and 980-1020 cm<sup>-1</sup> correspond to specific bands of MMT. The broad peak centered 3360 cm<sup>-1</sup> in the spectrum of MMT was attributed to the water adsorbed during MMT modification and the peak around 980 to 1000 cm<sup>-1</sup> attributed to the Si-O-Si groups in the octahedral

sheets of MMT [23]. The band at  $1650\text{ cm}^{-1}$  corresponded to the H-O-H bending vibrations that attributed to water in the samples. The broadband of MMT  $3360\text{ cm}^{-1}$  shifted to small shifting to  $3120\text{ cm}^{-1}$  due to the removal of some hydroxyl groups from aluminium and silicon sites and indicated the change of MMT hydrophilic to hydrophobic [24]. The new bands of  $2854$  and  $2916\text{ cm}^{-1}$  attributed to asymmetric and symmetric of C-H stretching vibration of surfactant and the peak at  $1480\text{ cm}^{-1}$  attributed to the  $\text{CH}_3\text{-N}^+$  from alkylammonium surfactant inserted into MMT interlayer. The intensity of new peaks for the three modified MMT are sharp and easily identified, indicated that the adsorbed amount of surfactant with 2.0 CEC is in excess. The ion exchange process with 2.0 ratio of CEC showed adsorbed of cationic surfactant on the external surface [22].

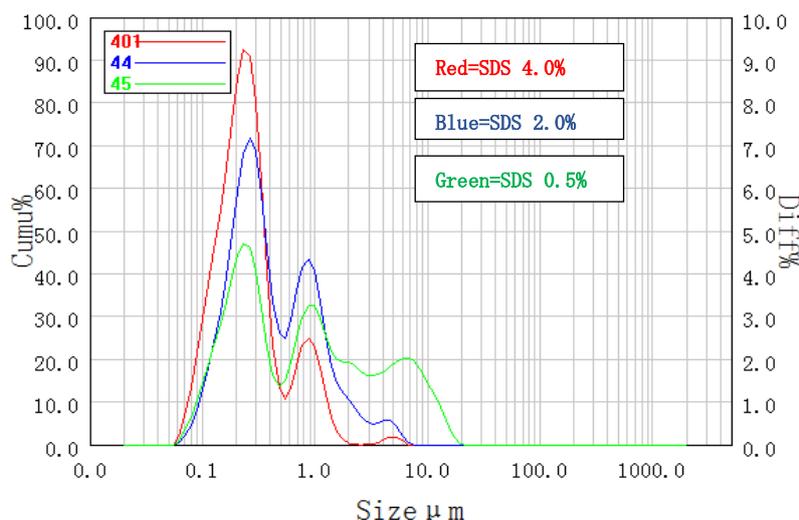


**Figure 4.** FTIR spectra of Pristine MMT and OMMT

Besides, the bands in the range of  $1300\text{--}1500\text{ cm}^{-1}$  of all samples had no significant changes; it indicated that the main bones of MMT had no changes before and after modifications. Both FTIR and SAXS analysis indicated the surfactant had been intercalated into MMT's layers.

### 3.2. The role of surfactants in the synthesis of hybrid latex with mini-emulsion polymerization.

In this research, mini-emulsion was prepared by using different concentration water-based surfactant SDS. Monomer disruption was achieved by using ultra sonication technique; the disruption was indicated by the lower surfactant concentration observed in the mini-emulsion. In this stage, the size of particles depends on the concentration and type of surfactants, not on the ultrasonication process and its parameters [25]. Figure 5, shows the different variation amounts of SDS used, particle size diameter, surface tension, monomer conversion, and the amount of coagulum formed as the function of SDS concentration are shown in Table 1. The latexes particle size ranges from 80 nm to 156 nm were obtained; a higher surfactant concentration results in lower surface tension and smaller latex particle size were observed. Surface tension measurement on the latexes ranged from 35 to 45  $\text{mN}\cdot\text{m}^{-1}$  the values were decreased with decreasing on its particle size [15]. The correlation supported hypothesis of incomplete surface coverage at the increase in particle size due to the equilibrium of surfactant molecules adsorbed in particle interfaces [15].



**Figure 5.** Particle size distribution of hybrid latex with SDS variation concentration.

**Table 1.** Variation of SDS concentration in mini-emulsion polymerization and its influence on latex characteristics.

SDS Concentration (% wt to total mass)	Particle Size (nm)	Surface Tension ( $\text{Mn.m}^{-1}$ )	Monomer Conversion Rate (%)	Coagulum Content Sieve Test (%)
4.00	80	35.3	99.91	0.15
2.00	102	38.8	98.8	1.02
0.50	156	44.6	96.2	3.98

The majority of the recipes in the literature were built up based on anionic surfactant SDS as a model system. However, recent works showed the cationic and non-ionic surfactants were used and formed well to produce narrow size distribution latexes. Previous work reported that nonionic surfactant and hexadecane as hydrophobe were used to synthesize latex with a particle size of 150 nm [26]. Furthermore, the particle size is dependable on the hydrophobe composition in order to avoid Oswald ripening [27]. By varying the composition of the surfactant in mini-emulsion polymerization, it was possible to obtain particle size range of the latex as required [28]. Latex produced with ionic surfactants, cationic surfactants, and non-ionic surfactants following the same size of concentration as mentioned in Table 1, the efficiency of the surfactants is similar. However, the independence of surfactant charge needs to be considered. The efficiency of the nonionic surfactant is much lower compare to ionic ones; this is attributed to the lower efficiency of the steric stabilization in non-ionic surfactant.

#### 4. Conclusion

The MMT was successfully intercalation modified by alkylammonium surfactant through ion exchange. Both the structure and surface properties of the layered MMT changed after modification and showed good compatibility with a polymer matrix. The interlayer spacing of OMMT was extended from 1.21 nm to 2.00 nm; alkyl amine group of surfactant successfully attached on the MMT's surface; the surface wettability of MMT was converted from hydrophilic to hydrophobic after modification. The basal spacing of modified MMT with alkylammonium surfactant MTAB, CTAB, and OTAB showed pseudo-trimolecular layer arrangement. The synthesis of hybrid latex with mini-emulsion polymerization with 4.0 wt% OMMT was successfully done; SDS has an essential role in the synthesis of hybrid latex. Water-soluble surfactant SDS with the addition level 2.0 to 4.0 wt% contributes to monomer conversion rate up to 99% with a particle size 80 to 102 nm.

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