Water vapor transmission rate of polymer hybrid latex poly-(St-co-BA-co-MMA) synthesized via miniemulsion polymerization technique with montmorillonite as filler

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Abstract: Nanocomposites based on poly-(St-co-BA-co-MMA) and organo-montmorillonite (OMMT) were synthesized through miniemulsion polymerization. OMMT was used as filler after modification with cetyltrimethylammonium bromide (CTAB) through ion exchange method. The results were characterized with x-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectrophotometer. Unmodified MMT showed a diffraction peak at 2θ = 7.2° with interlayer spacing of 12.78 Å, shifting to lower angle of 2θ = 4.7° with interlayer spacing increased to 22.31 Å formed pseudotrilayer or paraffin structure. FTIR confirmed the XRD results with the presence of new peaks on modified MMT, indicated the amine groups have inserted into MMT layers. Miniemulsion polymerization with OMMT level up to 8.0 wt% was performed well with less coagulum in the latex; scaling up to higher level of OMMT (>10 wt%) affected instability in polymerization system, created high amount of coagulum and increased the latex Brookfield Viscosity from 150 cP to 528 cP. Water vapor transmission rate (WVTR) of latex with 8.0 wt% OMMT level was compatible to LDPE and PET films but still unable to compete with OPP film.

1. Introduction

One of the most important factor affecting the self-life of food is the moisture exchange between the food and the surrounding atmosphere [1]. The exchange is typically controlled by choosing the proper materials. Poly-(St-co-BA-co-MMA) is one of the typical material or adhesive extensively used in barrier paper [2]. To enhance the barrier properties of the adhesive material, polymer hybrid latex are produced by dispersing impermeable anisotropic filler into polymer base matrix [3, 4]. Compared to the original composites and pure polymer, hybrid latex exhibit enormous enhanced in barrier properties due to high aspect ratio and high surface area [5]. Improvements of barrier properties with inserting small amount of nanoclays have been reported by many research group [6, 7]. However, development of nanocomposites on coating solutions and selection of proper filler required consideration of particle-polymer compatibility, aspect ratio, and coating adhesion [8]. MMT is the most popular choice filler in synthesis PCNs due to its small particle size (less than 2 µm) and high surface area (800-1000 m²/g) [9]. MMT has moderate surface charge, known as cation exchange capacity (CEC) which is expressed in meq/100g and contains hydrated K+ and Na+ ions which is hydrophilic, hence immiscible in polymer matrix [10]. To allow intercalation to polymer chains, the
clay surface must be modified with cationic surfactants such as alkylammonium surfactant through ion exchange process [11]. The modification process decrease the surface energy of the clay platelets and improve the wetting behaviour, resulting in a larger basal spacing [12, 13]. The basal spacing of the resultant organoclay depends on the degree of CEC, chain length and molecular structure of the modifiers [14]. Miniemulsion polymerization technique has been reported to be a versatile tool. The versatile of this technique is the usage of droplet as a template, where the droplet composition remains constant before and during polymerization (Figure 1). Droplets can be adjusted before and after emulsification process, the process allows for copolymerization and encapsulation of solid materials [15, 16]. Generally, miniemulsions consist of small and stable droplets in continuous phase; the small droplet was obtained by high shear homogenizer or by ultrasonication to size around 50-500 nm. To ensure the stability of droplets, the addition of proper surfactant and the osmotic pressure agent (co-stabilizer) should be sufficient enough to keep the miniemulsion droplets with colloidal stability against coalescence and Ostwald ripening [17, 18].

In this study, firstly we focused on surface modification of montmorillonite with CTAB with 2.0 ratio of its cation exchange capacity (CEC) [19]. The basal spacing of pristine-MMT and modified MMT were determined by small angle x-ray scattering (SAXS) analysis, and the inserting of surfactant groups were qualitatively analysed by FTIR. The second steps, synthesis of polymer clay nanocomposite latex PMMBA with several loading level of OMMT through miniemulsion polymerization. The third step, is to determination WVTR based on ASTM E96 of polymer latex films with set to standard test conditions to 37.8°C and 90% HR which is the common standard in North America.

2. Experimental Methods

2.1. Material

Styrene monomer (St), butyl acrylate (BA), methyl methacrylate (MMA), 2,2’Azobisobutyronitrille (AIBN), sodium dodecyl sulfate (SDS), hexadecane (HD), cetyl trimethylammonium bromide (CTAB), silver nitrate and 4-Methoxyphenol Solution were purchased from Sigma Aldrich. Montmorillonite (Nanolin ® DK2 purity 99.8% with CEC 110 meq/100g was purchased from FCC Hangzhou, China. Calcium Chloride powder was purchased from Weifang, Haibin Chemicals China.

2.2. Preparation

2.2.1. Surface modification of montmorillonite (MMT) with CTAB

MMT (20 g) was dispersed in 1500 mL distilled water, the mixture was stirred for 2 hours until a clear solution was obtained. The organic modifier (based on its CEC) was dissolved in 500 mL distilled water, the mixture was stirred for 24 hours at room temperature. The solution precipitate under

![Figure 1. Mechanism of miniemulsion polymerization [20].](image-url)
mechanical centrifugation at 3500-4000 rpm for 5 minutes and several washing was done with distilled water until free of bromide (detected by 0.1 M silver nitrate solution). The precipitate were collected and dried in the oven. The modified-MMT and pristine-MMT were characterized with XRD and FTIR. X-ray diffraction (SAXS) patterns were recorded using CuKα radiation (n=1.5418Å) on a Philips PANanalytical X’Pert Pro, operating at 50 kV and 40 mA between 3 to 15° (2θ) at a step of 0.01 °/s. The functional groups were analysed by using FTIR spectrophotometer of Shimadzu 8201 under a dry air at room temperature by KBr pellets method.

2.2.2. Synthesis of polymer hybrid latex with miniemulsion polymerization.

The miniemulsion polymerization preparation are given in Table 1. Monomer phase contains monomers, co-stabilizer and initiator was exposed to 2 minutes with Sonics 750 VCX. The water phase prepared was poured into the monomer phase and exposed again to 5 minutes in ultrasonication with amplitude 50% and pulse rate 4 seconds. Upon completion of sonication, the emulsion was poured into 3-neck flask under bubbling with Nitrogen. The miniemulsion was performed at room temperature and degassed for 30 minutes. After degassing, the temperature of the mixture was increased to 80 °C; polymerization was done at this temperature for 8 hours under continuous mechanical stirring (600rpm) and terminated by dropping one drop of 4-methoxyphenol 2% solution into the latex. Stable suspension was obtained under favoured conditions.

2.2.3. Determination of WVTR

ASTM E96 was used as a methodology to measure the WVTR. WVTR is the steady state rate at which water vapour permeates through a film at specific conditions of temperature and humidity rate. Values are expressed in g/m²/24 hr in SI units. Test conditions vary, but in this research we 37.8°C and 90% HR was used, which is the most common set of WVTR used in packaging application.

3. Results and Discussion

3.1. Surface modification of montmorillonite

The intercalation of CTAB ion into montmorillonite can be done through ion exchange process based on the chemical reaction:

\[ \text{Na}^+\text{-MMT} + \text{HO}_2\text{-R-NH}_3^+\text{-Br} \rightarrow \text{H}_2\text{O} - \text{NH}_3^+\text{-MMT} + \text{NaCl} \]

Lagaly, et al [21] reported that alkyl chain can be intercalated in three types of structures, monolayer, bilayer and pseudotrilayer (paraffin complex). Monolayer has basal spacing of around 13.6Å, bilayer ~17.7Å and pseudotrilayer ~22.3Å [22]. Figure 2 presents XRD spectra of unmodified-MMT,

| Ingredient       | % wt to monomers |
|------------------|------------------|
| Monomer phase    |                  |
| Styrene          | 40               |
| Butyl Acrylate   | 59               |
| Methyl Methacrylate | 1              |
| OMMMT, % wt to monomer | 0.0 to 10.0  |
| Co-stabilizer (Hexadecane) | 4            |
| Initiator (AIBN) | 0.75             |
| Water phase      |                  |
| Surfactant (SDS) | 4                |
| Water            | as required      |
modified-MMT and exfoliated-MMT. Unmodified-MMT showed a diffraction peak at 2θ = 7.2° with an interlayer spacing of 12.78Å. After treated, the diffraction peak shifted to a lower 2θ value and interlayer spacing increased to 22.31Å. This implied that the MMT interlayer was expanded due to intercalation of MMT. Based on the interlayer spacing result of modified-MMT, the structure intercalation formed pseudotrilayer or paraffin complex. This structure allows to block gas molecule diffusion and extends the diffusion pathway of the permeating gas molecules, resulting lower WVTR [23]. Exfoliated-MMT shows no angle range, it was indicated OMMT has fully exfoliated. Exfoliation is the last stage of dispersion and preferred for optimum efficiency to achieve low WVTR or a better barrier property [24]. FTIR analysis has been carried out in order to confirm the presence of alkyl of ammonium cation between the interlayer MMT. Figure 3 shows the spectra of MMT, OMMT and CTAB. The bands around 2850-2960 cm⁻¹, are the bands to the asymmetric and symmetric vibrations of C-H that confirmed the presence of alkylammonium group after the intercalation. The absorption bands on 1417-1468 cm⁻¹ attribute to the stretching of aliphatic C–C in alkyl chain of ammonium cations. Absorption peaks at 3415 and 3630 cm⁻¹ attributed to the −OH in the Si–OH and Al–OH groups, the broad peaks centred at 3500 cm⁻¹ on MMT and OMMT are attributed to the adsorbed water. The peak appeared in the region 1640 cm⁻¹ contribute to −OH bending of water coupled with octahedral ions. The presence of new peaks on modified MMT conform the CTAB intercalation in the interlayer spaces of MMT and compliment to the XRD analysis results.

Figure 2. XRD pattern of MMT and modified MMT.

Figure 3. FTIR spectra of pristine-MMT and modified-MMT.
3.2. WVTR of Hybrid Latex Film

WVTR is the standard measurement by which films are compared for their ability to resist moisture transmission. Lower values indicate better moisture protection. In this report, WVTR was compared under the same temperature and humidity conditions (37.8 °C, 90%RH).

Hybrid latex without OMMT similar in WVTR to EVOH latex film (1 mil film thickness), addition of 2.0 wt% OMMT caused lower WVTR (68 g/m²/24hr). One of the most valued of WVTR is OPP, which is exceptional in moisture barrier property. OPP provide an excellent WVTR of all common polymer films. Hybrid latex with high loading ratios (10.0 to 12.0 wt%) still unable to compete with OPP. OMMT level 6.0 to 8.0 wt% in hybrid latex gives same WVTR values to LDPE or PET; increasing OMMT level up to 10.0 or 12.0 wt% were able to compete with Cast PP and HDPE. However, to synthesize poly-(St-co-BA-co-MMA) latex with this OMMT level was difficult due to problems in miniemulsion polymerization process. Latex stability became the main concerned with addition of high OMMT level (>8.0 wt%). At 10.0% OMMT addition level, the miniemulsion polymerization showed high coagulum, resulted low latex solid and larger particle size. Latex properties in different addition level of OMMT can be found on Table 2. The limitation of synthesis latex with higher OMMT level can be solved by lowering the solid content of the latex to lower level or choosing the suitable surfactants.

Figure 4. WVTR vs polymer hybrid latex film with various OMMT level.

| Latex Parameter | OMMT Loading Level (wt %) |
|-----------------|--------------------------|
|                 | 0 | 2 | 4 | 6 | 8 | 10 |
| Latex color     | milky white | milky white | milky white | milky white | milky white | milky white |
| Brockfield viscosity cPs, 50 rpm, sdp No.2 | 155 | 162 | 165 | 168 | 220 | 528 |
| Solid content (%) | 38.2 | 38.1 | 38 | 38.1 | 37.2 | 30.2 |
| Coagulum content (%) | 0.025 | 0.032 | 0.038 | 0.049 | 0.098 | 28.625 |
| Particle size (nm) | 80 | 88 | 90 | 98 | 108 | 358 |
| Latex stability after 24 hours | * | * | * | * | ** | *** |

*Good, **Average, ***Poor
4. Conclusions
Nanocomposites latex based on poly-(St-co-BA-co-MMA) and OMMT were successfully synthesized by miniemulsion polymerization. OMMT modified with CTAB could intercalate with diffraction peak of $2\theta = 7.2^\circ$ of unmodified MMT shift to $2\theta = 4.7^\circ$ with basal spacing increased from 12.78 to 22.31 $\AA$, formed paraffin structure. FTIR confirmed the intercalation with new peaks appeared on modified MMT, indicated that ammonium groups inserted into MMT interlayer. Addition of filler in the latex affected for lowering the WVTR value due to the increase of tortuosity of pathway. Latex with 8.0 wt% OMMT has similar WVTR to LDPE and PET films but still unable to compete with OPP film. Hybrid latex with 8.0 wt% OMMT might replace the LDPE or PET films in food barrier packaging application.

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