Synthesis of polymer hybrid latex poly(methyl methacrylate-co-butyl acrylate) with organo montmorillonite via miniemulsion polymerization method for barrier paper

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Abstract. Hybrid polymer latex based on combination of organic-inorganic materials, poly(methyl methacrylate-co-butyl acrylate) (PMMBA) and organo-montmorillonite (OMMT) were synthesized via miniemulsion polymerization technique. Modification of montmorillonite (MMT) through the incorporation of myristyltrimethylammonium bromide (MTAB) into the clay's interlayer spaces were investigated by Small-Angle X-ray Scattering (SAXS), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Transmission Electron Microscopy (TEM). Barrier property and thermal stability of polymer latex film sample were investigated through its Water Vapor Transmission Rate (WVTR) and Thermogravimetric Analysis (TGA). The results indicated that addition of OMMT as filler in PMMBA increased the barrier property and thermal stability of the latex film. Addition of 8.0% (wt) OMMT increased the barrier property and thermal stability. Miniemulsion polymerization process with higher addition (>8.0 wt%) of OMMT resulting in high latex viscosity, particle size, and high amount of coagulum. The utilization of this hybrid polymer could benefits paper and board industries to produce high quality barrier paper for food packaging.

1. Introduction

During the past decades, polymer science has entered the field of organic-inorganic polymer hybrids due to its remarkable barrier property, high cation exchange capacity, high platelet aspect ratio and good thermal stability[1]. Organoclays form an important type of modified clay material; clays such as montmorillonite (MMT) are widely used in various areas of sciences due to its ability to be modified with organic molecules [2].This modification can be carried out by exchanging the clay inter layer cations by organic cations which transform from organophobic to organophilic materials and also increase the basal spacing of the clay layers[3]. The use of OMMT in polymers offers improvement of its barrier property, thermal and physical stability. Modification of MMT by quaternary ammonium salts were used as intercalated agents and the intergallery distance d(001) plane of the clay is relatively small, and the intergallery environment is hydrophilic[4]. In this study, MMT was modified using myristyltrimethyl ammonium bromide (MTAB).
Numerous approaches and methodologies have been developed to synthesize inorganic-organic polymer hybrids. Among various polymerization techniques, the hetero-phase polymerization system, particularly the miniemulsion polymerization technique, is widely used. Miniemulsion polymerization is a type of polymerization which takes place in each of the stabilized monomer nano-droplets [5]. The stable nano-droplets (50-500 nm) are dispersed in the continuous phase at the aid of high shear and an effective co-stabilizer to retard Ostwald ripening. The monomer transferring through the water phase to micelles and micelles does not take place as droplets themselves act as the loci of nucleation and latex particle droplets of 1:1 are ideal to copy of original droplets [6]. Every droplet behaves as independent reaction and polymerization inside droplets follows as suspension polymerization behavior.

Thermal stability of polymeric materials is an important key to be considered; the properties may be profoundly affected by the presence of particular sequences of co-monomers or small proportions of additives. Co-monomer such as methyl methacrylic acid (MMA) as well as acrylic acid (AA) lead to increased thermal stability of co-polymers [7]. Thermogravimetry provides rapid method for determining thermal decomposition and thermal hazards of uncharacterized material or mixture (ASTM E2550-17). The scope of the test method describes the assessment of material thermal stability through determination of the temperature at which the material start to decompose or react and the extent of the mass change using thermogravimetry and is applicable over the temperature range from ambient to 800 °C [8].

Theoretical approaches on the barrier properties of polymer hybrids, treats fillers (clays) as impermeable non-overlapping particles, and it is assumed no permeability changes in the polymer matrix [9 - 11]. Permeability of the hybrid polymer will be smaller than permeability of the matrix (assuming the penetrant path does not cross fillers), this path of tortuosity was defined by Nielsen [12]. The key challenge is to obtain an effective dispersion and exfoliation of MMT in polymer matrix in order to obtained well aligned high aspect ratio particles for tortuous diffusion pathway for the improvement of barrier properties, these nanofillers can block gases and increase the tortuosity [13].

The hybrid OMMT/PMMBA latex with different OMMT content were prepared by miniemulsion polymerization method. Addition of OMMT as inorganic filler were expected to improve barrier properties and thermal stability of the hybrid polymer PMMBA latex. These properties could be used as barrier paper material in food packaging.

2. Experiment

2.1. Materials
Styrene, n-butyl acrylate, methyl methacrylic acid (MMA), azobisisobutyronitrile (AIBN) and hexadecane (HD) was supplied by Sigma Aldrich and used as received. Nanoclay montmorillonite (MMT) with CEC 125-130 meq/100g was supplied by FCC, disponil 103 (SDS) by BASF, and myristyltrimethyl ammonium bromide (MTAB) by Pioneer Chemicals, China.

2.2. Surface modification of MMT by ion-exchange
MMT (1.0 to its CEC) [14] was dispersed with stirrer in 750 ml distilled water. The mixture was stirred for 2 hours. MTAB (5.0 g) was dissolved in 250 ml distilled water and stirred for 2 hours. This solution was added drop-wise to MMT clay dispersion under stirring for around 2 hours under regulated drop-wise regulation. The MMT particles were separated by centrifugation (5000 rpm, 10 minutes) and washed with large amount of distilled water until no bromide can be detected by silver nitrate.

2.3. Synthesis of polymer hybrid with miniemulsion polymerization
Oil phase containing hexadecane (co-stabilizer), AIBN (initiator), styrene, n-butyl acrylate, MMA monomers, and required OMMT (0 - 10 wt.%) was sonicated for 20 minutes with 90% amplitude using sonicator (Sonics 750 VCX - Sonics U.S.A). The aqueous phase containing disponil 103 and
water were prepared by dissolving disponil 103 in distilled water at room temperature. The oil phase containing monomers and organoclay was poured into aqueous phase and the mixture was cooled in an icebath. After vigorous stirring for 3 minutes, the solution was sonicated for another 5 minutes with amplitude of 50%. The resultant hybrid minemulsion was transferred into a three-neck round-bottom flask, and temperature was raised to 78 °C for 5 hours for polymerization. Latex film were prepared by casting the latex on plane glass. Samples were allowed to air dry for 24 hours, and after which were dried in an oven for another 24 hours.

3. Results and discussions

3.1. Modification of nanoclay montmorillonite

X-ray diffraction study was carried out using Small Angle x-ray Scattering (SAXS) with Cu-Kα radiation (λ = 1.5406 nm). The diffraction was scanned in the range from 2° to 30° at a scan rate of 1° min⁻¹. As shown in figure 1, MMT has an interlayer spacing of d = 121.677 nm corresponding to 2θ = 7.2659° at d(001) reflection, and the surface modified MMT clay has shifted to d = 250.427 nm corresponding to 2θ = 3.5282°. This confirmed that the MMT is intercalated between the layers as shown in figure 1.

![Figure 1. SAXS picture of pristine MMT (blue line) and modified MMT with MTAB (red line).](image)

In figure 2 (FTIR graph), we could observe bands at 3000-3600 cm⁻¹, 1647 cm⁻¹, and 1000 cm⁻¹, correspond to bands of MMT (blue line). The broad peaks from 3000-3600 cm⁻¹ are attributed to the adsorbed moisture during MMT modification. Peak at 1000 cm⁻¹ indicates the presence of Si-O-Si groups in the octahedral sheets of MMT. Symmetrical and asymmetrical vibrations of -CH₂- from alkyl chains of MTAB appear at peaks 2935 cm⁻¹ and 2863 cm⁻¹. An Asymmetrical C-H vibration of alkyl ammonium appears to shift at peak 1493 cm⁻¹. The peak is attributed to attachment of MTAB surfactant on MMT surface. Peak at 1647 cm⁻¹ is attributed to the coupling of water with octahedral cations and H-O-H bending vibrations. TEM images shows intercalation of MMT with MTAB (figure 3). It indicates that alkyl chains have pseudotrimolecular layer (20.0 - 21.0 Å) with several layers have been deformed.
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**Figure 2.** Comparison of FTIR spectra of unmodified (blue line) and modified MMT (red line).

**Figure 3.** TEM image of modified MMT with MTAB.

### 3.2. Characterization of PMMBA in the presence of OMMT

MMT modified with MTAB in the PMMBA suspension was homogenous solution after sonication from addition of 2.0 - 8.0 wt.%. However, an addition of more than 8.0 wt.% created high amount of gel in monomers solution.

#### 3.2.1. PMMBA/OMMT polymer hybrid viscosity

PMMBA Latex with addition of OMMT from miniemulsion polymerization was measured by Broekfield Viscosimeter RVDV, using spindle No.2 and speed 100 rpm at room temperature. Figure 4 shows an addition of OMMT will increase latex viscosity. An addition at higher OMMT level (> 8.0 wt%) created gel or coagulum during polymerization and limited workability. Latex PSD also increased from 0.4 µm to 0.8 µm as shown in figure 5 following an increase of latex viscosity.

**Figure 4.** Latex viscosity vs OMMT addition.  
**Figure 5.** Particle Size vs OMMT addition.

#### 3.2.2. PMMBA/OMMT latex barrier and thermal stabilities

The standard method for WVTR testing is described by ASTM E96-08. This method measures how much moisture vapor to pass the materials in 24 hours. WVTR for food packaging generally can be accepted at 1 cm$^3$/m$^2$/d for oxygen and 1 g/m$^2$/d for water [15]. These levels of barrier are sufficient for food packaging application. However, further reducing of oxygen and water are needed. Using polymer latex with OMMT as filler could offer a defect free and better barrier property. In figure 6, an addition of OMMT starting 2.0 wt.% level could reduce WVTR value from 3.0 g/m$^2$/d to around 2.4 g/m$^2$/d. Up to 8.0 wt.% is recommended in order to achieve less than 1 g/m$^2$/d WVTR value, or similar to PE coated barrier paper.
The thermal stability of PMMBA/OMMT nanocomposites was analyzed by TGA, where the sample weight loss due to heating and monitored as a function of temperature ramp. Figure 7 shows the thermogram of PMMBA latex with different addition level of organoclay. The graph shows the decomposition behaviour of the materials as the temperature increased from 90 °C to 800 °C. We observed an increase of residual weight at temperature 600 °C, in all addition level of nanoclay.

The decomposition of the PMMBA was observed at 200 - 300 °C. We suggest it is attributed to the thermal degradation of MTAB molecules grafted on the MMT platelets. Improvement of thermal stability is not correlated linearly with addition level of organoclay. Several factors such as degree of nanoclay dispersion in the polymer matrix, morphology and type of interaction at the interface between the clay platelets and polymer matrix need to be considered [16]. Improvement in thermal stability of polymer matrices filled with organoclay acts as mass transport barrier and thermal insulator. And it is attributed to hindered out-diffusion of the volatile decomposition products, which is a direct result observed in the decrease in permeability and is usually observed in exfoliated polymer clay nanocomposite [17].

4. Conclusion
The use of miniemulsion polymerization was found to be an effective method to synthesize polymer hybrid latex poly(methyl methacrylate-co-butyl acrylate) with organo-montmorillonite as inorganic filler. Organo-montmorillonite are well intercalated with MTAB surfactant with 1.0 to its CEC.
Spacing of SAXS give details arrangement of surfactant in the organoclay. Results from TEM analysis shows pseudotrimolecular layer arrangement in the interlayers. Synthesis of PMMBA Latex with OMMT as inorganic filler with miniemulsion polymerization method at 8.0 wt.% addition level resulting an excellent barrier property and thermal stability. Addition at higher level of OMMT (> 8.0 wt.%) will cause high Broekfield viscosity, particle size (0.4 - 0.8 µm) and also high amount of coagulum/gelling on the latex.

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