Synthesis of polymer hybrid latex polystyrene methylmethacrylate-co-butylacrylate with organo-montmorillonite as filler through miniemulsion polymerization for barrier paper application

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Abstract. Nanocomposite have a huge potential in the future technologies and scientific communities. It is possible to design new materials with a simple modification and new materials have different properties and improvement in its mechanical properties and application fields. Hybrid latex based on monomer styrene (St), butyl acrylate (BA) and methylmethacrylate (MMA) have been studied and used for barrier paper applications in food industries in order to replace polypropylene (PP), polyethylene (PE) or polyethylene terephthalate (PET) materials. To achieve better hybrid materials, various techniques and materials have been utilized, montmorillonite (MMT) from smectite family have been selected as filler in order to synthesize polymer clay nanocomposites (PCNs). The selection of MMT as filler due to its high aspect ratio, high modulus and high cation exchange capacity (CEC). MMT was not susceptible to common polymer due to its organophobicity, low basal spacing, and incompatible to common monomers phase. Surface modification of MMT with traditional ion exchange method can be done through ion exchange with quaternary alkyl ammonium surfactants. The objective of surface modification of MMT are to change its nature hydrophilicity to organophilicity, in the same time to increase its basal spacing. Various quaternary alkylammonium cationic surfactants have been used; in this study, three type of alkylammonium were selected to be used due to its different in alkyl carbon chain lengths. Intercalation of surfactants cation in MMT depend on the layer-charge alkyl carbon chains, selection of myristyltrimethylammonium bromide (MTAB) with C17 carbon chains, cetyltrimethylammonium bromide (CTAB) with C19 carbon chains and octadecyltrimethylammonium bromide (OTAB) with C21 carbon chains could give an answer of the selection of organoclay that compatible with St, BA and MMA. This study focuses on the microstructure of organo montmorillonite (OMMT) after surface modification and the potential to be used as filler in synthesis of hybrid latex through miniemulsion polymerization technique. The intercalation or exfoliation of MMT through ion exchange with alkylammonium surfactant were studied, interlayer spacing of OMMT were analysed with X-ray diffraction, small angle X-ray scanning (SAXS) technique, presence of cationic surfactant in the interlayer space and bond character and arrangement of surfactant ions were analysed by Fourier Transform Infrared (FTIR), Thermogravimetric analysis (TGA) and Transmission Electron Microscope (TEM). Synthesis of hybrid latex was done by miniemulsion polymerization technique with selected OMMT filler. Series of experiments were performed to study the polymerization variables such as filler loading, role of surfactant/cosurfactant and filler solubility in monomer emulsions.
results shown that water soluble surfactant SDS in miniemulsion polymerization resulted lower coagulum and smaller particle size compare to non-ionic surfactant (TX405) and cationic surfactant (OTAB). Combination of non-ionic surfactant (TX405) with ionic surfactant (SDS) with ration 1:2 showed the better results than SDS alone, with lowest coagulum, narrow particle size distribution, and lowest Broekfield Viscosity. Scale up loading level of OMMT filler in miniemulsion to 5.0 wt%, resulting instability before and after polymerization with regard to high coagulum content and low monomer conversion rate (<90%). The hybrid latex resulted from miniemulsion polymerization will be applied on paperboard with hand rod coater with coating weight 15-20 gsm. The coated paperboard tested on its water vapour transmission rate (WVTR) together with paperboard coated with PE from melt blending process. Paperboard coated with hybrid latex comparable to paperboard coated with PE, indicated improvement in its WVTR value compare to paperboard coated with latex without filler addition. The main target of this research was to synthesis polymer hybrid latex for super barrier material for food packaging in order to replace unrecyclable PP, PE or PET. The utilization of polymer hybrid latex could benefit paper and paperboard packaging industries.

**Keyword:** montmorillonite, barrier paper, surface modification, miniemulsion polymerization, food packaging, ion exchange methods

1. **Introduction**

Polymer hybrid latex traditionally are reinforced with organic fillers in order to improve their properties as well as to reduce cost. However, this reinforcement with fillers such as talc, calcium carbonate, fibres and clays, required a number of large amount of filler in the polymer materials, which consequently increase bulkiness of composite and leads to lose of transparency. Based on the dimension of phases involved, this type of composite material usually classified as micro composites.

However, to meet the technical challenging and rising of applications of material sciences, research on inorganic fillers and polymeric materials are being continuously developed, particularly on size, type and applications [1, 2]. Polymer nanocomposites are the new class of hybrid material introduced to answer to the challenges. Polymer nanocomposites are dimension in nanoscale or smaller than 80 nm, offering opportunity to explore a new material with different behaviour and able to improve mechanical properties and chemical properties compare to conventional micro-composite materials. In economic view, nanocomposite strongly influence on material properties with only a low addition volume fractions. This mainly due to small inter-particle distances and large amount of fraction of polymer matrix were converted near their surfaces and as consequent, the morphology was being changes [3]. Through all research done with various type of fillers, polymer nanocomposite based on silicate is obtained maximum attention by scientists due to many advantages being offered.

Synthesis polymer nanocomposite based on silicate as filler has fulfilled economic requirement, which is easily available and have low cost, however their application directly into polymer matrix can be straightforward due to its hydrophilic behaviour. In most instances, surface modification of these materials is necessary in order to obtain clay or silicate that are compatible with polymer matrices.

To fully understand the effect of clay reinforcement on the polymer matrix, it is important to understood the clay definition and clay structure. From mineral, clay is material formed from hydrated phyllosilicates with making up from rocks, sediments and soils [4]. From chemicals of view, clay minerals are essentially hydrous aluminosilicates with very fine particles with general formula: (Ca, Na, H) (Al, Mg, Fe, Zn)\(_2\) (Si, Al)\(_4\) O10(OH)\(_2\)\(_x\)H\(_2\)O, where x represents the variable amount of water. Generally, the different clay mineral structure are basically composed of tetrahedral silicate sheets “SiO\(_2\)” and alumina octahedral sheets “AlO\(_2\)” various ratio; when the tetrahedral sheet linked to one octahedral form structure 1:1, known as Kaolinite or Hallysite, when the ratio form 2:1, known as Montmorillonite and Saponite (Fig. 1). The physical dimension of each platelets about 1 nm in thickness and the lateral dimension is varied from 30 nm to micrometer [5].
In the case of 2:1 structure, the trivalent of Al-cations in the octahedral layer is substitute partially by Mg-cation to form montmorillonite structure, given to each layer negative charge generated from their different valence; the bonding forces of attraction them are weak and known as van der walls force [7]. The interstitial water and other polar cations can enter and stay inside the galleries and to replace existing cations via ion exchange reaction in the synthetic rout to change the hydrophilic clay to organophilic [8]. During the exchange process, the basal spacing of clay will be expanded, expansion of the space between two consecutive layers termed interlayer space, imparts high cation exchange capacity (CEC) relative to non-expandable phyllosilicates [9]. CEC is the approximate of the amount of readily exchangeable cations neutralizing negative charge in the clay [9], usually expressed as milliequivalents (meq) per 100 gram of clay. A comparison of CEC for some clays variety with the basal spacing can be found on Table 1.

| Clay Type   | Structure Type | CEC Value (meq/100 g) | D Spacing (Å) | Reference                |
|-------------|----------------|-----------------------|---------------|--------------------------|
| Kaolinite   | 1:1 (TO)       | 3 to 15               | 7.14          | Alkan et al. [10]        |
| Halloysite  | 1:1 (TO)       | 5 to 50               | 7.00          | Sánchez-Fernández et al. [11] |
| Montmorillonite | 2:1 (TOT) | 60 to 150             | 12.4-17.0     | Navratilova et al. [12]  |
| Saporite    | 2:1 (TOT)      | 80 to 90              | 12.4-17.0     | Hussan et al. [13]       |
| Hectorite   | 2:1 (TOT)      | 120                   | 12.4-17.0     | Nguyen and Baird [5]     |

There are many methods to determine CEC, anyone of them are reliable and can be used. However one possible technique that more often used is the method based on cation-saturation, primary the ammonium, sodium, and barium, etc. [11]

Among these clays, montmorillonite (MMT) got prominence over other member nanoclays due to its abundance, environmental friendliness. The literature also provided a lot of information regarding its structure, and well-studied chemistry. The studies revealed that MMT has large surface area ad aspect ratio and also viewed rigid and impermeable filter [14]. Each of individual’s MMT layer has lateral dimensions of 200-600 nm and thickness of a few nanometer that is build up by two tetrahedral sheet and one octahedral sheet, the sheets are linked one to each other as shown on Fig. 1. Individual MMT layers are about 0.96 nm thick and they have lateral dimensions that are more than two orders of magnitude larger. Exfoliation MMT layers in a polymer matrix leads to large interfacial surface area in order to interact with polymer chains. Delamination of each individual was doubtful [15]. However, exfoliation can lead to uniform dispersion of particles corresponding to stack comprising a few clay mineral layers [16]. This the keys issue in order to achieve a good mechanical and barrier properties of nanocomposites. Dispersion of nanoclay particles is difficult due to incompatibility between the hydrophobic polymer matrix and hydrophilic of clay minerals. To solve this problems, this is usually accomplished via ion exchange reactions [17], the inorganic cations in interlayer of clay such as Ca ions,
or Na ions, can directly be exchanged with organic cations by means of an intercalation process. The substitution of cations in interlayers can be partial or complete, in some case it may even exceed the CEC [18]. Intercalation of organic cations is an important, it modifies the clay surface, changing its nature from hydrophilic to organophilic. This renders the MMT compatible with organic polymers and leads the way to the exfoliation of clay minerals layers in the polymer matrix [19, 20].

Quaternary alkylammonium surfactants are the organic cations most often used to intercalate MMTs. Long chain quaternary ammonium ions are preferred as they lead to a large interlayer spacing. This allows the polymer chains into the clay interlayer space, the co-intercalation of polymer chains aids dispersion of distinct MMT particles into the polymer matrix.

To prepare nanocomposite, there are four main routes can be performed: (a). template synthesis (b). synthesis with miniemulsion polymerization (c). in-situ intercalative polymerization (d). melt intercalation [15, 19]. In this research only synthesis of nanocomposite through miniemulsion polymerization are reviewed. Miniemulsion technique is almost a new technique of polymerization, which is formed by high speed homogenization or ultrasonication though droplet nucleation mechanism within the polymerization reaction. There are two destructive processes need to be stabilized: (a) Ostwald ripening degradation and (b) coalescence degradation [21, 22]. Latex instability caused by these two effects has significant effect on number of monomer droplets, rate of polymerization and particle size formation [23, 24]. Hydrophobic materials are introduced to produce virtual osmotic pressure for restricting the monomer migration from droplets. In miniemulsion surfactant concentration should be kept below critical micelle concentration (cmc); nucleation process occurs within the monomer droplets not as micelle nucleation. This phenomenon solved the micellar and homogenous nucleation [24]. To provide the droplets with colloidal stability against coalescence, ionic or non-ionic surfactants were used [25]. van den Dungen et al. [25] used pickering miniemulsion of styrene-co-butyl acrylate and believed that the latex produced were more stable than SDS stabilized latexes; however other nanomaterials had strange effects on the mechanism of polymerization.

Montmorillonite ion exchanged with mixed classical and double bond containing modifier was used to synthesize poly (styrene-co-butyl acrylate-co-methyl methacrylate) nanocomposites via ATRP and clay attached on the system demonstrated a higher molecular weight and lower PDI in comparison with non-hybrid latexes. Partially exfoliated morphology of clay layers observed on low clay loading nanocomposites [26]. Based on surface hydrophobicity of modified MMT, less hydrophobic compounds can be stabilize O/W emulsions, as hydrophobic modified act as stabilizer for W/O emulsions [27]. Armoured structures for particles covered by clay platelets can be act as super-heat barrier and increase thermal stability of polymers [28, 29].

In this research, miniemulsion polymerization was used for making nanocomposites of high solid content (35-40%) with water borne poly(styrene-co-butyl acrylate-co-methyl methacrylate) latex including with loading level of OMMT up to 5 wt%. Kinetic consideration was not studied in this research due to have been studied by Mirzataheri [30]. Miniemulsion polymerization, which is an extension of conventional emulsion polymerization by inclusion of small amount of a monomer soluble, water insoluble material (costabilizer), fulfilled all the requirements for the encapsulation of phyllosilicate layered clay. The costabilizer can significantly reduce the Oswald ripening of monomer and water emulsion as well as reduce the monomer droplet size within the range of 100-500 nm [31]. Hexadecane [32] and cetyl alcohol [31] are the costabilizers most often used in miniemulsion polymerization, however these costabilizers remain in the polymer particles and may have bring a negative effect on polymer end used properties. Alduncin and Asua [33] minimize these negative effect by incorporating into polymer backbone, a series of oil-soluble initiator were evaluated with different water solubility (lauroyl peroxide, benzoyl peroxide, and azobis(isobutyronitrile)) and only lauroyl peroxide was work well to stabilize styrene miniemulsion droplets. The drawback of this system is that lauroyl peroxide (Lp) initiator affect the miniemulsion stability, polymerization rate and low-molecular weight were obtained. Polymers can be used to reduce Ostwald ripening as it has hydrophobes characteristics, Miller et al. [34] found that styrene miniemulsion could be prepared by using 1 wt% of polystyrene as hydrophobe. Reimers and Schork [35] used (poly(methyl methacrylate) to stabilize
methyl methacrylate (MMA). Chern and Liou [36] studied the water-soluble material dye to avoid Oswald ripening, however the shelf life efficiency of dye is less than Hexadecane and cetyl alcohol.

In this research, anionic [37], cationic [38] non-ionic [36] and mixed anionic/non-ionic [39, 40] have been used. The surfactant in miniemulsion should meets the specific requirements as in conventional emulsion polymerization, as following: (i). have a specific structure with polar and non-polar group (ii). it must be more soluble in aqueous phase (iii) it must able to reduce interfacial tension (iv) and it must work in small concentrations. In miniemulsion polymerization it is a potential to enhance the efficiency of the non-ionic surfactants because at the beginning of the process, the total area of the monomer miniemulsion is much larger than that of the monomer droplets in emulsion polymerization. The great versatility of this method arises from the usage of the droplet as a template, meaning the droplets were constant during polymerization and therefore can be adjusted before or during emulsification process. This allows for synthesis of hybrid or copolymerization and encapsulation of solid or liquid particles. Generally, miniemulsions consist of small droplets in continuous phase; the system usually need ultrasonication or high pressure homogenizers to break down the monomer droplets to size 100-500 nm. The stability of the system can be achieved by using proper surfactant and cosurfactant or usually known as osmotic pressure agent [41].

![Figure 2. Processes mechanism of miniemulsion polymerization [42].](image)

The instability of miniemulsion has an influenced on the number of monomer droplets and correlated to the particle size distribution and average molecular weight of final products [43]. As mentioned above, the free surfactant should be kept below its CMC, therefore the nucleation process occurs only in monomer droplets. The morphology of clay-based hybrid latex synthesized by miniemulsion depends on its medium on which the clay is dispersed after modification. If the clay is dispersed in water, it will tend to attach on the polymer surface particles; but if it is dispersing in monomer, the clay tends to be encapsulated. Relatively not so much works in the field of PCNs which is involved in miniemulsion polymerization [44, 45]. The firs miniemulsion polymerization shown only 80% monomer conversion, left 20% unreacted monomers in the systems, and to remove the unreacted monomer, required complicated stripping process. It has been suggested that the clay located at particle surface may act as barrier to radical entries in the encapsulation process. Other problems with encapsulation is the difficult to disperse the clay in all the polymer particles, about 25% of latex particles are found containing clay platelets, the other remaining empty. In general case, nanocomposites show improved in stiffness, mechanical property and heat resistance and decreased gas permeability. All this improvement can be achieved with less than 5% clay loading. Barrier property are great importance in food packaging and coatings. High aspect ratio platelets are very important factor to decrease gas permeability, this may due to increase in “tortuosity path”, the path that molecule must follow to diffuse through a certain thickness. It has been mentioned that the best way to achieve improvement in barrier properties of nanocomposites are to obtain with fully exfoliated morphology rather than partial intercalation or poorly oriented platelets [46, 47]. The effect of filler loading and dispersion also has been analysed, the importance of these parameters has been emphasized by many authors, especially for filler with nanometric dimensions.

In this paper, we present preparation and characterization of organo-montmorillonite clays by using ammonium surfactants, the basal spacing was characterized by XRD measurement and FTIR analysis.
Miniemulsion polymerization was used for making nanocomposites of higher solid contents (up to 35%) water-borne poly(styrene-co-butyl acrylate-co-methyl methacrylate) latex including addition amount of organo-montmorillonite (OMMT) clays (up to 5% loading) in the miniemulsion process [48]. To test and overcome the complexity in barrier properties, the barrier simulation in this study are made with water vapour transmission testing (WVTR). WVTR able to predict as a function of external factors, namely temperature and surrounding humidity rate, while mechanical property required for food packaging are mainly governed by the used of substrate.

2. Experimental.

2.1. Materials
Demineralized water was used throughout the work.
Unmodified MMT with CEC, 110 meq/100 g was supplied by FCC Hangzhou, Chian
Cationic surfactants, MTAB, CTAB and OTAB were purchased from Pioneer Chemicals, China.
Silver nitrate, purchased from Sigma-Aldrich
Styrene monomer from Sigma-Aldrich
Butyl acrylate from Sigma-Aldrich
Methyl methacrylate from Sigma Adrich
Hexadecane from Sigma-Aldrich
Sodium Dodecyl Sulfate from Dow Chemicals.

2.2. Preparation
2.2.1. Surface modification of MMT. MMT (20g) 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 precipitated under 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 mol silver nitrate solution).

2.2.2. Characterization of organo-montmorillonite (OMMT). Characterization of powder samples of OMMT was done by X-ray diffraction, the basal spacing of unmodified and modified samples was determined. To confirmed the XRD results, FTIR analysis was done for all samples.

2.2.3. Synthesis of Hybrid Latex. Synthesis of PMMBA hybrid latex were based on Styrene (St), butyl acrylate (BA) and MMA with ratio 40/59/1.0 wt%, the basic ratio were used based on previous research done by Murima et al. [49] and Tong [50] on synthesis water based latex based on PSBA [55,56]. Sonication conditions for oil phase and emulsion referred to previous studied by [51]. Miniemulsion polymerization was done in mini laboratory glass reactor, pulse with nitrogen for 15 minutes with temperature 78-80°C for 8 hours.

2.2.4. Characterization of Hybrid Latex. Synthesized hybrid latex was characterized for its solid content, surface tension, particle size, coagulum content and latex stability.

2.2.5. Barrier properties evaluation. Evaluation of hybrid latex barrier properties were based on water vapour transmission rate analysis based on ASTM Method E96. Hybrid latex was coated on paperboard by hand rod coater with coating weight 20 gsm, using Laboratory K-Coater.

3. Results and discussion.

3.1. Surface modification of montmorillonite.
The chemical composition of the alkylammonium bromide cationic surfactants is given in Table 2. The surfactants were used on the basis of long hydrophobic carbon chains attached to central atoms.
Table 2. Alkylammonium cationic surfactant used for MMT modification.

| Surfactant                                      | MW (g/mol) | Chemical formula       | Purity (%) |
|-------------------------------------------------|------------|------------------------|------------|
| Myristiltrimethylammonium bromide (MTAN)         | 336.39     | C_{17}H_{38}Br(N)      | 99.80      |
| Cetyltrimethylammonium bromide (CTAB)            | 364.45     | C_{19}H_{42}Br(N)      | 99.80      |
| Octadecyltrimethylammonium bromide (OTAB)        | 392.50     | C_{21}H_{46}Br(N)      | 99.80      |

Based on literature reviews, amount of surfactant weight were based on 2.0 CEC value of MMT (CEC MMT, 110 meq/100g), in order to achieved maximum d-spacing[52]. X-ray diffraction was performed on dried powder samples, XRD of different samples of modified MMT clay give the value of basal spacing. The basal spacing of samples are given in Table 3 and the diffraction patterns of the different samples are given on Fig. 3. The unmodified MMT basal spacing is termed as initial basal spacing.

![XRD patterns of unmodified MMT clay with different alkylammonium surfactants.](image)

**Figure 3.** XRD patterns of unmodified MMT clay with different alkylammonium surfactants.

Table 3. Basal spacing of unmodified MMT and modified MMT.

| Sample               | Position (2θ) | d-spacing (Å) |
|----------------------|---------------|---------------|
| MMT                  | 7.26          | 12.16         |
| MMT+MTAB             | 4.09          | 20.99         |
| MMT+CTAB             | 4.66          | 19.79         |
|                      | 6.74          | 13.19         |
| MMT+OATB             | 4.35          | 20.29         |
|                      | 6.31          | 14.01         |
|                      | 8.61          | 10.26         |
The initial spacing of MMT 12.76 Å with 2θ = 7.26, after modified the basal spacing increased, by treating it with different cationic surfactants. An increase of the interlayer distance, leads to shifting peaks to lower angles. The initial basal spacing of MMT is very important to determine the organoclay intercalation and clay mineral delamination [53]. The unmodified MMT with basal spacing 12.76 Å at 2θ = 7.26, falls within the range of expected values (12.00 to 16.00 Å) for typical smectite minerals. The double chains of alkylammonium surfactant contains minimum 16 carbon atoms, extended to form bilayer or paraffin-like extended chain conformation. Long carbon chains CTAB and OTAB shows additional of small peaks on the diffraction patterns, d(002) and d(003). Organic cations introduced up to the CEC level by ion exchange are electrostatically attached to the clay mineral surface [54], the excess surfactants molecules are intercalated in their neutral salts form [54].

![Figure 4. FTIR Spectra of unmodified MMT, modified MMT and Cationic Surfactant.](image)

**Table 4. FTIR Spectra assignment of MMT, OMMT and surfactant.**

| Assignment          | Frequency (cm⁻¹) |
|---------------------|------------------|
|                     | MMT | MMT+MTAB | MMT+CTAB | MMT+OTAB |
| Structural OH stretching | 3636 | 3600 | 3610 | 3600 |
| Symmetric OH stretching | 3358 | 3360 | 3360 | 3358 |
| Asymmetric CH₂ stretching | 2890 | 2895 | 2890 |
| Symmetric CH₂ stretching | 2825 | 2826 | 2850 |
| H-O-H bending       | 1600 | 1630 | 1640 | 1630 |
| CH₂ scissoring      | 1470 | 1460 | 1458 |
| Si-O stretching     | 1000 | 998 | 999 | 1008 |
| CH₂ rocking         | 910 | 850 | 838 | 830 |
|                     | 778 | 780 | 780 | 779 |
3.2. Synthesis of hybrid latex via miniemulsion polymerizations.

Miniemulsion polymerization is an advantageous process for the encapsulation of insoluble components into polymer matrix. Miniemulsion polymerization consists of two processes; first, emulsification of oil phase and water phase through ultrasonication or high speed homogenation. Second, the polymerization take place in the “nanoreactor”. In this work, miniemulsions with rather hydrophilic monomers were formed by using different amount of surfactants. To reduce secondary particle formation, initiator AIBN was used. To achieved lower surfactant concentration of the miniemulsions, monomer disruption was achieved by ultrasonication.

Table 5. Surfactant concentration and its influence on latex characteristics.

| SDS concentration (%wt to mass) | Particle size (nm) | Surface tension (mN.m⁻¹) | Monomer conversion (%) | Coagulum 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 latexes particle size ranges from 80 nm to 1.0 µm; in general, a higher amount of surfactant resulting in a lower surface tension and smaller particle size. The particle size of the latex depends on the concentration of surfactant not on ultrasonication. However, the surfactant concentration cannot be increased to any amount as micelle are formed, there is a risk of polymerization following the emulsion polymerization principle, which would not keep the droplet inner structure.

![Figure 5](image-url)  

**Figure 5.** Particle Size Distribution as function of SDS concentration (Red) SDS 4.0%, (Blue, SDS 2.0%, (Green, SDS 0.5%).

In continuous miniemulsion polymerization, surfactant concentration has to be high enough to guarantee stabilization of droplets in a short time, but the concentration need to be decrease to avoid micelle nucleation, the concentration should be lower than cmc value. Latex characteristics analysis showed on Table 6.

Broekfield viscosity measured with 50 rpm and spindle no.5, with result around 180 cPs, and coagulum content (sieve analysis) was in normal range 0.03%. Latex stability was measured on 24 hours’ basis and no significant coagulum formed and viscosity was in controlled range.
3.3. Barrier Properties of Hybrid Latex.

In the literature shows that the gas barrier properties of polymers can be significantly enhanced by the addition of inorganics impermeable nanoplatelets. In this review, the synthesis of hybrid latex was filled with 5 wt% loading of organo-montmorillonite (OMMT).

To determine the barrier properties of packaging materials, usually WVTR test was performed. The WVTR measurement were made according to ASTM E96 or SCAN P22:68/143 (cup method). To achieve the steady state of measurement, the R² (linear regression coefficient) should be close to 0.90. The water vapour transmission rate is measured by the slope of the straight line. A coating weight and WVTR-value were measured from the same sample and form a graph on Fig. 6. The coating weight starting from 30 g/m² give WVTR value around 5 g/m²/24 h, increasing coating weight to 35 g/m² and 40 g/m² were not change the WVTR values significantly.

According Fig. 7 results, the influence of temperature is more significant compare to influence of RH, RH does not represent absolute water in samples, it is only absolute water concentration of surrounding. K. Lahtinen and J. Kuusipalo (2010) in his model replaced the humidity rate with mixing ratio which is represents the absolute humidity of surrounding [55].
Figure 7. WVTR as function of Humidity Rate and Temperature (15 g/m² coating weight).

Conclusion
Surface modification of montmorillonite with alkylammonium bromide surfactants MTAB, CTAB and OTAB, has changed the properties of montmorillonite from hydrophilic to organophilic. The basal spacing obtained from X-ray diffraction gave details of arrangement of surfactant in the organoclays. With 2.0 CEC, there was a pseudotrimolecular layer arrangement of MMT with MTAB, CTAB and OTAB. The results confirmed by FTIR spectra and FTIR spectra shows the inserting of alkyl group in the MMT interlayer. Hybrid latex successfully synthesized with miniemulsion polymerization technique. The hybrid latex obtained with 5 wt% loading of OMMT give a stable latex with high barrier properties, indicated by low WVTR results. WVTR have a linear correlation to temperature and coating weight but does not have consistent relationship to humidity rate. Paperboard coated with more than 30 g/m² coating weight showed no significant improvement in WVTR.

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