

## Preparation of Poly(vinyl acetate)/Clay and Poly(vinyl acetate)/Poly(vinyl alcohol)/Clay Microspheres

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**Abstract:** Poly(vinyl acetate) (PVAc)/poly(vinyl alcohol) (PVA)/montmorillonite (MMT) clay nanocomposite microspheres with a core/shell structure have been developed via a suspension polymerization approach. In order to prepare the PVAc/MMT and PVAc/PVA/MMT nanocomposite microspheres, which are promising precursor of PVA/MMT nanocomposite microspheres, suspension polymerization of vinyl acetate with organophilic MMT and heterogeneous saponification were conducted. A quaternary ammonium salt, cetyltrimethylammonium bromide, was mixed with the MMT in the monomer phase prior to the suspension polymerization. The rate of conversion decreased with an increase in MMT concentration. The incorporation of MMT into the PVAc was verified by FT-IR spectroscopy. Organic vinyl acetate monomers were intercalated into the interlayer regions of organophilic clay hosts and followed by suspension polymerization. Partially saponified PVA/MMT nanocomposite microspheres with a core/shell structure were successfully prepared by heterogeneous saponification.

**Keywords:** PVAc/MMT, PVAc/PVA/MMT, Microsphere, Suspension polymerization

### Introduction

Nanocomposite materials, consisting of inorganic nanolayers of montmorillonite (MMT) clay and organic polymers, have evoked intense interest lately because their unique characteristics have the potential to be used in many commercial applications. Nanostructured polymer-inorganic composites, mixed at the molecular level or near molecular level, are much different from the conventional composites with incorporation of a variety of additives in the polymer matrices [1-3]. In the polymer-inorganic nanocomposites, strong chemical bonds or interactions such as van der Waals forces, hydrogen bonding, or electrostatic forces, often exist between the polymer and inorganic components. This usually leads to some novel nanocomposites with improved performance properties, which may be potentially used in fields such as optics [4], electrical devices [5], and photoconductors [6]. Several useful polymer/clay nanocomposite materials have been produced, such as nylon/clay hybrids [7], and poly(methyl methacrylate)/clay hybrids [8]. These polymer-layered silicate nanocomposites exhibit much improved mechanical and thermal properties. There are generally attributable to the uniform dispersion of clay silicate layers in the polymer matrix.

Recently, Yeum *et al.* prepared high molecular weight polymer/inorganic nanocomposite microspheres that had a high yield via suspension polymerization [9-11]. Also, many polymer/inorganic nanocomposites were prepared by suspension polymerization. Huang and Brittain synthesized

poly(methyl methacrylate)/layered silicate nanocomposites by in-situ suspension and emulsion polymerization [12]. More recently, Jun and Suh synthesized poly(urethane acrylate)/clay nanocomposite particles by suspension polymerization [13]. According to Hwu *et al.* [14], polystyrene (PS)/montmorillonite nanocomposites were obtained by suspension free radical polymerization of styrene in dispersed organophilic montmorillonite.

The flexibility and processability of polymer matrices based on water-soluble polymer such as poly(vinyl alcohol) (PVA) with excellent optical properties and good compatibility with additives can provide good mechanical properties. Recently, PVA/clay nanocomposites are found to display novel properties, which can be observed from two dissimilar chemical components combining at the molecular level. There are several publications associated with the preparation and properties of PVA/clay nanocomposites prepared by solution dispersion technique [15-17]. According to Yu *et al.* [18], PVA/MMT nanocomposites were prepared via an in situ free radical polymerization. The preparation of PVA/MMT nanocomposite spheres, however, has not been reported. In order to obtain PVA/MMT nanocomposite spheres for new industrial applications, poly(vinyl acetate) (PVAc)/MMT nanocomposite spheres need to be prepared.

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 an individually dispersed platelet form after polymerization. In the present study,

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organophilic MMT was prepared with cetyltrimethylammonium bromide (CTAB) as a cationic surfactant [19]. In order to obtain PVAc/MMT nanocomposite microspheres, which are promising precursor of PVA/MMT nanocomposite microspheres, suspension polymerization of vinyl acetate (VAc) was conducted. Also, partially saponified PVA/MMT nanocomposite microspheres with core/shell structure were prepared by heterogeneous saponification. The effects of MMT on the morphology and structure of PVAc/MMT nanocomposite microspheres were examined.

## Experimental

### Materials

VAc purchased from Aldrich was washed with an aqueous solution of NaHSO<sub>3</sub> and water and dried with anhydrous CaCl<sub>2</sub>, followed by distillation in nitrogen atmosphere under a reduced pressure. The initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako Co.) was recrystallized twice in methanol before use. PVA with number-average molecular weight of 127,000 and degree of saponification of 88 % (Aldrich Co.) was used as a suspending agent. MMT (KSF) and CTAB were obtained from Aldrich. Water used for all the procedures was deionized.

### Preparation of PVAc/MMT Nanocomposite Microspheres

In order to prepare PVAc/MMT nanocomposite microspheres, suspension polymerization of VAc was conducted. The suspending agent was dissolved in water under a nitrogen atmosphere with constant stirring in a 250 ml reactor fitted with a condenser. CTAB was mixed with the MMT in the monomer phase prior to suspension polymerization [19]. Then, ADMVN was added at a fixed polymerization temperature. After predetermined times, the reaction mixture was cooled and kept for one day to separate and to sink PVAc/MMT nanocomposite microspheres. In order to eliminate residual VAc and suspending agent, PVAc/MMT nanocomposite microspheres were filtered and washed with warm water.

Conversion was calculated by measuring the weight of the PVAc/MMT. Conversions were averages of three determinations. Detailed polymerization conditions are listed in Table 1.

**Table 1.** Suspension polymerization conditions of VAc

Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration	0.0001, 0.0005, 0.001 mol/mol of VAc
Suspending agent concentration	1.5 g/dl of water
VAc/Water	0.5 l/l
Rpm	500
Temperature	30, 40, 50 °C
MMT concentration	0, 1, 2, 5 wt.%

### Heterogeneous Saponification of PVAc/MMT Nanocomposite Microspheres

In order to prepare PVA/MMT nanocomposite microspheres, heterogeneous saponification of PVAc/MMT nanocomposite microspheres was conducted. In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel, and a stirring device, alkali solution (sodium hydroxide/sodium sulfate/methanol/water) was made. Separated 1 g of PVAc/MMT nanocomposite microspheres was slowly added in the flask during stirring. After the reaction, the reaction mixture was poured into cold water and kept for 1 day so as to separate and sink the spherical core/shell PVAc/PVA/MMT nanocomposite microspheres. The solid saponification product was filtered and washed several times with water and dried in a vacuum at 40 °C for 1 day.

### Characterizations

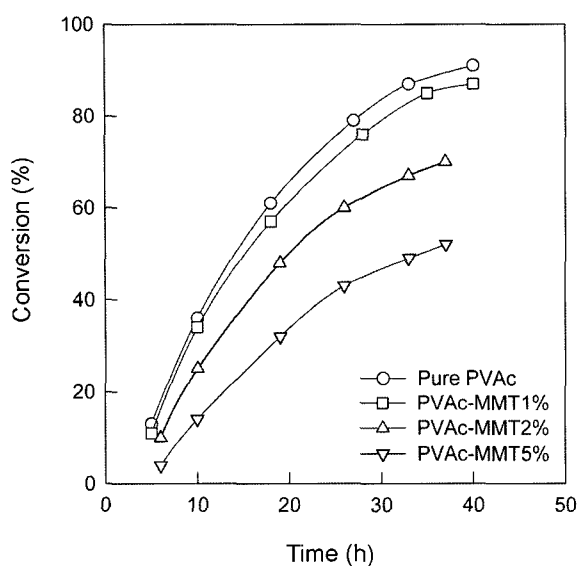
The Fourier Transform Infrared (FT-IR) spectrum of the sample was obtained using a Perkin-Elmer 1650 that cast on potassium bromide. The surface morphology of PVAc/MMT nanocomposite microspheres was examined using a Hitachi S-570 scanning electron microscope (SEM). To precisely examine the fractured surface of microspheres, all samples were fractured in liquid nitrogen. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature with a Rigaku (D/Max III B) X-ray diffractometer using Ni-filtered CuK $\alpha$  Radiation. The core/shell structure of the PVAc/PVA/MMT nanocomposite microspheres was examined using optical microscope (Leica DC 100). The degree of saponification of the PVAc/PVA/MMT nanocomposite microspheres was determined by the ratio of methyl and methylene proton peaks in the <sup>1</sup>H-NMR spectrometer (Varian, Sun Unity 300).

## Results and Discussion

### PVAc/MMT Nanocomposite Microspheres

In this study, the formation of microspheres of PVAc/MMT nanocomposite, for a precursor of PVA/MMT nanocomposite microspheres during the suspension polymerization of VAc, was studied using different MMT concentrations. Quaternary ammonium salt, CTAB, was mixed with the MMT in the monomer phase prior to suspension polymerization. ADMVN, which can lower the polymerization temperature to room temperature, was selected for the suspension polymerization of VAc with modified MMT, in order to obtain PVAc/MMT nanocomposite microspheres with the highest conversions [9-11].

Figure 1 presents conversion-time plots at different MMT concentrations using an initiator concentration of 0.0001 mol/mol of VAc with or without modified MMT. The rate of conversion decreased with an increase in MMT concentration. In the case of a MMT content of 2 %, the rate of polymerization decreased significantly. This can be explained by the fact that MMT has a chain transfer termination effect in the



**Figure 1.** Effect of MMT concentration on the conversion of VAc into PVAc/MMT nanocomposite microspheres.

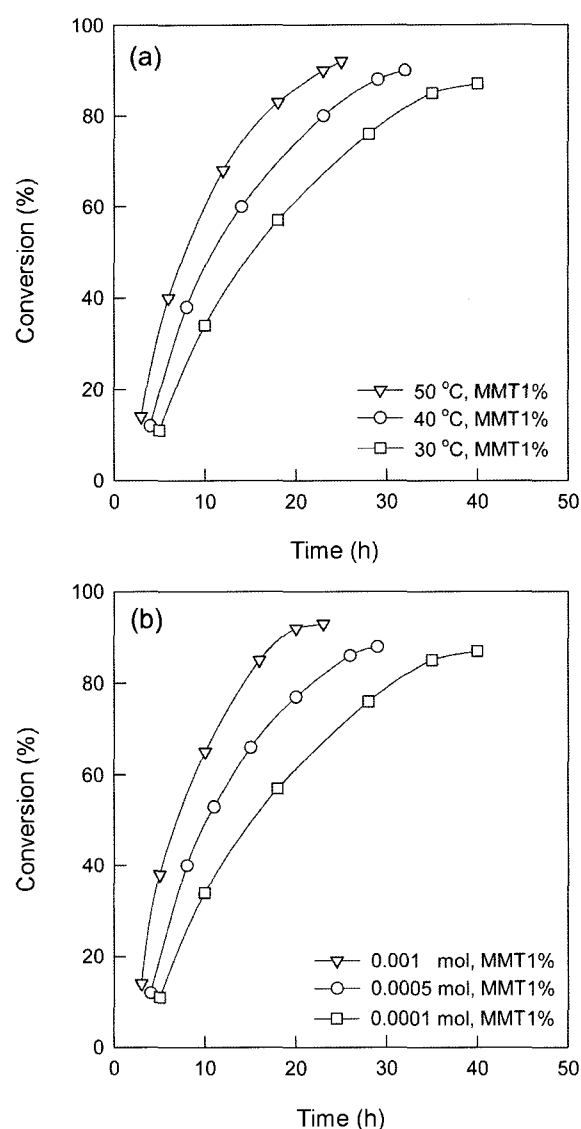
formation of the polymer chain [14]. Also, the precipitation of polymer/MMT can occur quickly due to higher content of MMT. At 1 %, however, the conversion was linearly increased up to about 85 % in spite of low polymerization temperature of 30 °C, in sharp contrast with an only 30 % conversion of VAc under bulk polymerization. This explains the fact that suspension polymerization in the presence of organophilic MMT nanoparticles by ADMVN is useful for producing PVAc/MMT nanocomposite microspheres in high yields.

In a free radical polymerization, the rate of polymerization ( $R_p$ ) may be expressed by equation (1) [20].

$$R_p = k_p[M][I]^{0.5}(fk_d/k_t)^{0.5} \quad (1)$$

where  $f$  is the initiator efficiency,  $[M]$  and  $[I]$  are the concentrations of monomer and initiator, and  $k_d$ ,  $k_p$ , and  $k_t$  are reaction rate constants of initiator decomposition, propagation and termination, respectively. This expression predicts that the rate of polymerization is increased as the efficiency and concentration of initiator are increased. The reduction of the polymerization rate in the presence of MMT suggests that the either the efficiency of the initiator,  $f$ , or the propagation rate constant,  $k_p$ , were decreased when MMT was added into the suspension polymerization system. We believe the reduction of the diffusion rate in the nanoclay intergalleries may reduce both  $f$  and  $k_p$  in equation (1). It has been known that ADMVN is an effective low temperature initiator (10 h half-life decomposition temperature of ADMVN is 51 °C) that can be used to prepare high molecular weight polymer with high yield. In this study, ADMVN was used to prepare PVAc/MMT nanocomposite microspheres at room temperature.

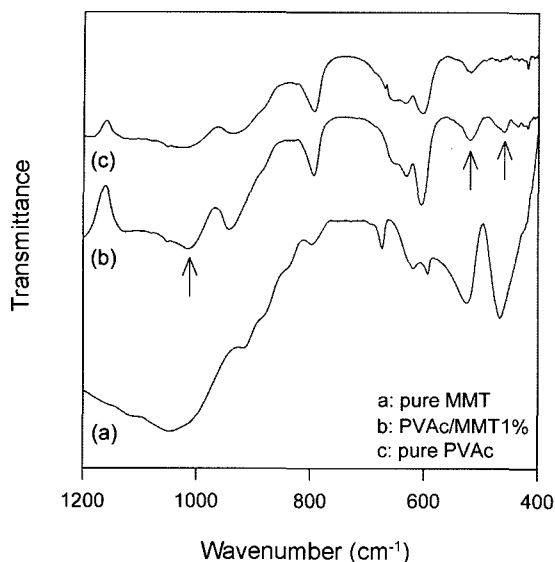
Figure 2(a) presents the conversion-time relationship at



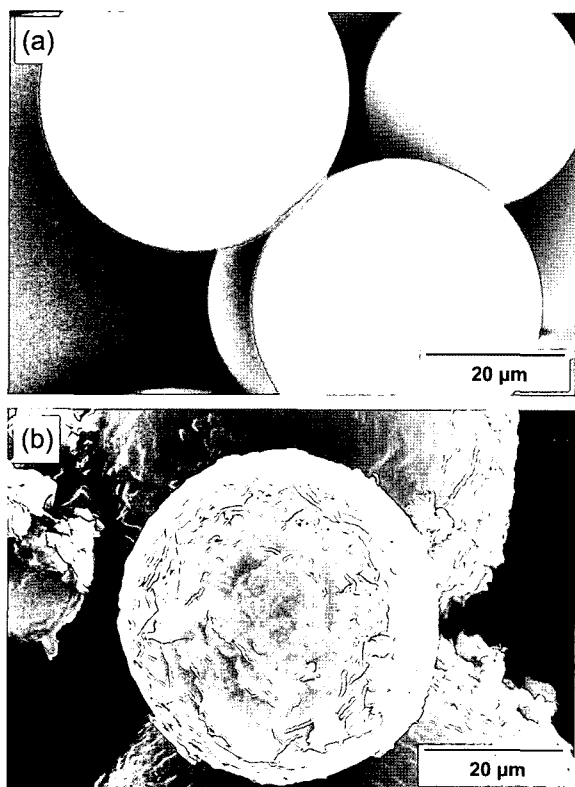
**Figure 2.** Conversion of VAc with polymerization time in the suspension polymerization of PVAc/MMT (a) using ADMVN concentration of 0.0001 mol/mol VAc at different polymerization temperatures and (b) at 30 °C with different initiator (ADMVN) concentrations.

different polymerization temperatures with an initiator concentration at  $10^{-4}$  mol/mol of VAc. Although a low initiator concentration ( $10^{-4}$  mol/mol of VAc) was used, the conversion increased steadily with the reaction time at a reaction temperature of 30-50 °C until ca. 85-95 % of conversion was arrived, in contrast with an only 30 % conversion of VAc under bulk polymerization. The high conversion suggested that the chain transfer and termination reactions were not significant under the conditions used in this study [20]. As the slope of the curve on the conversion-time plot represents the polymerization rate, the bigger the slope (steeper), the higher the polymerization rate. As shown in Figure 2(b), the

polymerization rate, at a reaction temperature of 30 °C, increased with an increase in initiator concentrations, in accordance with theoretical prediction [20].



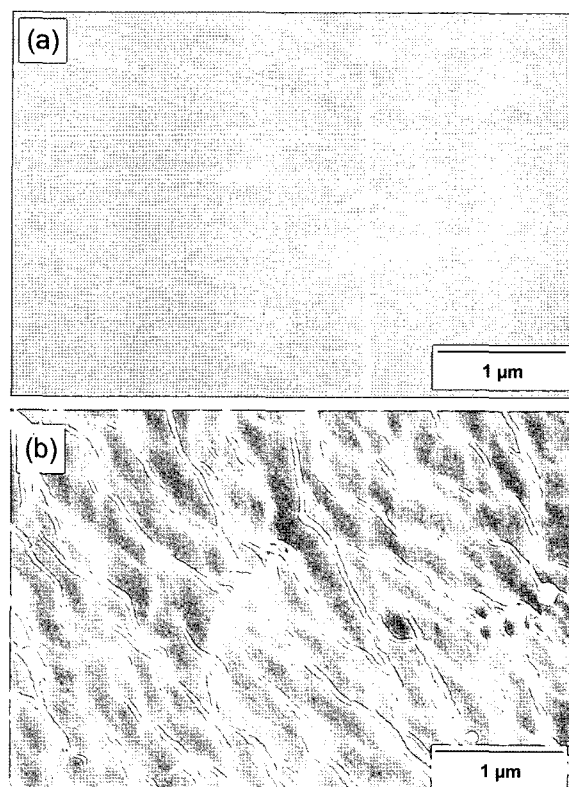
**Figure 3.** FT-IR spectra of (a) pure MMT, (b) pure PVAc microspheres, and (c) PVAc/MMT nanocomposite microspheres with a MMT concentration of 1 %.



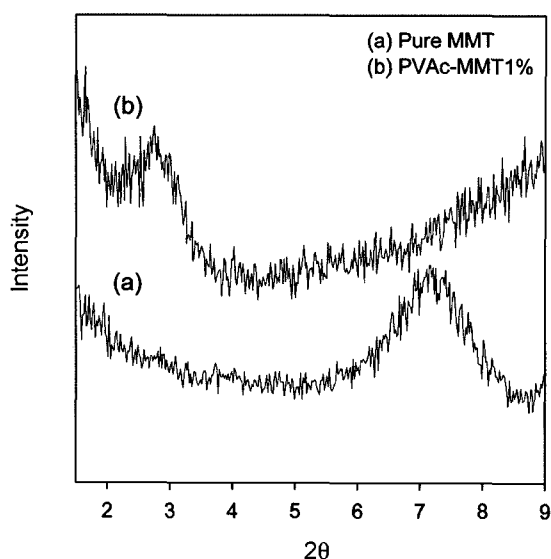
**Figure 4.** SEM photographs of (a) pure PVAc microspheres and (b) PVAc/MMT nanocomposite microspheres with a MMT concentration of 1 %.

In this article, the structure and morphology of polymer/MMT nanocomposite microspheres, with high yield prepared by using MMT concentration of 1 %, were investigated before and after saponification. The structure of the PVAc/MMT nanocomposite microspheres was analyzed by using FT-IR spectroscopy. Figure 3 shows the FT-IR spectra for pure MMT, pure PVAc microspheres, and PVAc/MMT nanocomposite microspheres with MMT content of 1 %. It is well known that pure MMT shows three strong peaks at 455, 520, and 1045  $\text{cm}^{-1}$  [13]. These peaks are associated with the bending mode of Si-O, the stretching vibration of Al-O, and the stretching vibration of Si-O, respectively. One can easily see peaks of both PVAc and MMT component in the spectrum of PVAc/MMT nanocomposite microspheres. It should be noted that MMT-incorporated polymer particles could be prepared by the *in situ* suspension polymerization of VAc in the presence of organophilic MMT nanoparticles.

SEM photographs of pure PVAc and PVAc/MMT nanocomposite microspheres, with a MMT content of 1 %, are presented in Figure 4. As expected, the surface of the pure PVAc microspheres is clean. Also, we can see encapsulated composite microspheres shown in Figure 4(b). In order to ensure the distribution of MMT nanoparticles in the PVAc microspheres, the fractured surface of the PVAc/MMT nanocomposite microspheres were observed. Figure 5(a) and Figure 5(b)



**Figure 5.** SEM photographs of the fractured surfaces of (a) pure PVAc microspheres and (b) PVAc/MMT nanocomposite microspheres with a MMT concentration of 1 %.



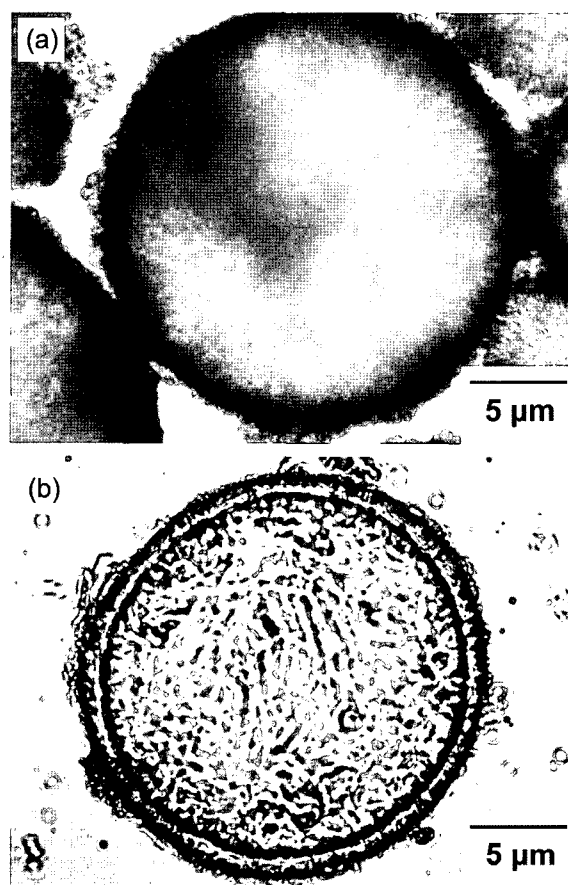
**Figure 6.** XRD patterns of (a) pure MMT and (b) PVAc/MMT microspheres with a MMT concentration of 1 %.

show SEM photographs of fracture surface of pure PVAc microsphere and PVAc/MMT microsphere with MMT content of 1 %, respectively. We can see embedded MMT nanoparticles from the fracture surface. From the observation of fracture surface, it was verified that PVAc/MMT nanocomposite microspheres could be prepared by *in situ* suspension polymerization.

Generally, the structure of clay nanocomposites has been established using XRD analysis. Due to its easiness and availability, XRD is most commonly used to probe nanocomposite structures [21,22]. Figure 6 shows the XRD patterns of the MMT and PVAc/MMT with MMT content of 1 %. The MMT shows a diffraction pattern peak at  $2\theta = 7.2^\circ$ , which corresponds to the average basal spacing (d-spacing) of 12.3 Å. In the PVAc/MMT 1 % microspheres, the peak moved to lower angle, i.e.,  $2\theta = 2.7^\circ$ . The basal spacing increased from 12.3 to 32.6 Å. This spacing indicates that long alkyl ammonium ions were inserted into the gallery of MMT, as a result, an intercalated structure formed. The inserted long alkyl chains caused the hydrophilic nature of the clay to decrease, and this effect improved the dispersion of silicates in the polymer matrix.

#### PVAc/PVA/MMT Nanocomposite Microspheres with Core/Shell Structure

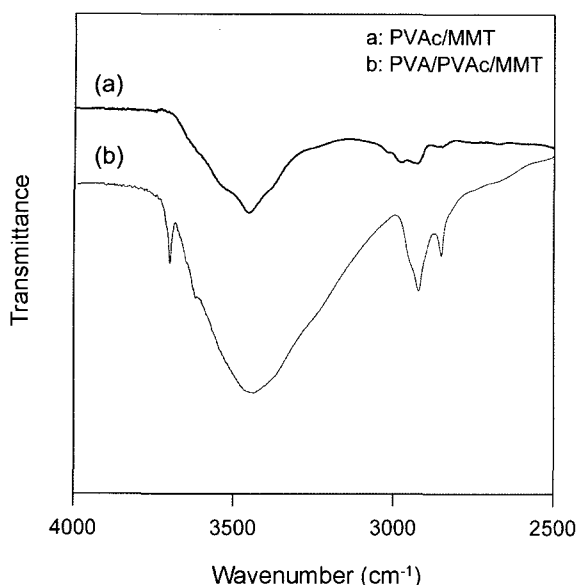
PVAc/MMT nanocomposite microspheres can be saponified by the method of heterogeneous saponification. In order to preserve the spherical shapes of the PVAc/MMT nanocomposite particles, saponification was restricted to the surface of the spheres by suspending PVAc/MMT nanocomposite particles in an aqueous alkali solution, and core/shell structured particles were obtained. Compared with pure PVAc microspheres, the PVAc/MMT nanocomposite microspheres prepared



**Figure 7.** Optical microscope images of (a) PVAc/MMT nanocomposite microspheres and (b) PVA/PVAc/MMT nanocomposite microspheres with a MMT concentration of 1 %.

by using high MMT concentration were not easily saponified. Therefore, the saponification rate of PVAc nanocomposites with different MMT contents may be different. To precisely identify the effect of MMT content on the kinetics of the saponification of PVAc/MMT nanocomposite microspheres, further work in this area is needed.

Figures 7(a) and 7(b) show the optical micrographs of the PVAc/MMT and PVAc/PVA/MMT nanocomposite microspheres, respectively. As shown in Figure 7(b), partially saponified PVAc/PVA/MMT microspheres (the degree of saponification of PVAc/PVA/MMT microspheres is 13.5 %) with core/shell structure were successfully prepared. So, this saponification method is capable of producing PVA/MMT nanocomposites with spherical shape and uniform surface. FT-IR spectrum of the PVAc/MMT and saponified PVAc/PVA/MMT nanocomposite microspheres is presented in Figure 8. From the generation of the -OH stretching vibration in the region of  $3000\text{--}3600\text{ cm}^{-1}$  after the saponification process, it is obvious that the surfaces of the PVAc/MMT nanocomposite microsphere were saponified with the hydroxyl groups. Therefore, it is expected that PVAc/MMT nanocom-



**Figure 8.** FT-IR spectra of (a) PVAc/MMT and (b) PVA/PVAc/MMT nanocomposite microspheres (MMT concentration of 1 %).

posite microspheres, with a high yield, can be used as a precursor for PVA/MMT nanocomposite microspheres.

### Conclusions

In this work, PVAc/MMT nanocomposite microspheres, which are promising precursor for PVA/MMT nanocomposite microspheres, were successfully prepared by low-temperature suspension polymerization of VAc in the presence of organophilic MMT nanoparticles. The rate of conversion decreased with an increase in MMT concentration. In the case of a 2 % MMT content, the rate of polymerization decreased significantly. At 1 %, however, the conversion linearly increased to about 85 % in spite of low polymerization temperature of 30 °C. It should be noted that MMT-intercalated PVAc nanocomposite microspheres could be prepared by *in situ* suspension polymerization of VAc in the presence of organophilic MMT nanoparticles. Also, PVAc/PVA/MMT nanocomposite microspheres, with core/shell structure, were prepared successfully by heterogeneous saponification.

This suggests an easy way of producing PVA/MMT nanocomposite microspheres at high yield by low-temperature suspension polymerization in the presence of organophilic MMT nanoparticles and heterogeneous saponification. In the near future, we will report on the properties of PVA/MMT nanocomposite microspheres with different degrees of saponification.

### Acknowledgement

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