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SHORT COMMUNICATION

# Poly(vinyl acetate)/poly(vinyl alcohol)/montmorillonite nanocomposite microspheres prepared by suspension polymerization and saponification

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**Abstract** Poly(vinyl acetate) (PVAc)–poly(vinyl alcohol)–montmorillonite (MMT) nanocomposite microspheres were prepared through suspension polymerization followed by the heterogeneous saponification. The effects of MMT on the polymerization rate and the saponification rate of PVAc were studied. It was found that the rate of polymerization decreased when MMT content was increased. However, the saponification rate of PVAc significantly increased in the presence of nanoclay particles. The XRD measurement illustrated that the clay particles are intercalated in the polymer matrix.

**Keywords** PVAc–PVA–MMT · Nanocomposites · Microspheres · Suspension polymerization

## Introduction

Nanostructured polymer–inorganic composites are very different from microstructured composites. In polymer–inorganic nanocomposites, strong interactions such as chemical bonding, hydrogen bonding, van der Waals forces, or electrostatic forces often exist between the polymer and inorganic components, which usually lead to some novel nanocomposites with improved properties and large potential applications in the fields of optics, electrical devices, photoconductors, etc. [1–3]. Many useful polymer/clay nanocomposite materials such as nylon/clay and poly(methyl methacrylate)/clay hybrids have been commercially manufactured [4, 5]. These nanocomposites exhibit outstanding improvements in mechanical and thermal properties, generally attributed to the uniform dispersion of the clay silicate nanolayers in the polymer matrix.

Recently, Yeum et al. reported a suspension polymerization system for preparing a high-molecular-weight polymer/inorganic nanocomposite [6–8] with a high yield at a low temperature. Huang and Brittain synthesized poly(methyl methacrylate)/layered silicate nanocomposites by in situ suspension and emulsion polymerization [9]. More recently, Jun and Suh synthesized poly(urethane acrylate)/clay nanocomposite particles by suspension polymerization [10]. According to Hwu et al., polystyrene/montmorillonite (MMT) nanocomposites were obtained by suspension polymerization of styrene in the presence of dispersed organophilic MMT [11].

A flexible poly(vinyl alcohol) (PVA) matrix with excellent optical and mechanical properties can be obtained by blending PVA and nanoclay using a delaminating technology [12–14]. Yu et al. reported an in situ free radical polymerization method for preparing PVA/MMT nanocomposites [15]. It is expected that the mechanism and the kinetics of suspension polymerization are different from bulk polymerization, particularly in the presence of nanoclay in the system. For example, the suspension stability and the final product properties will be significantly affected by the location of nanoclay in the suspension

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system. The polymerization kinetics and conversion will also be affected by the presence of nanoclay particles.

Surface hydrophobicity of the clay particles is important in preparing a polymer–clay nanocomposite using suspension polymerization. It has been well known that the basal surfaces of clay are hydrophobic, and the edge surfaces are hydrophilic. The strong hydropholicity of the edges results in strong hydrogen bonds with water. As a result, unmodified clays tend to stay in the water phase or adsorb on the oil–water interface, but not inside the oil phase. To prepare nanoclay containing poly(vinyl acetate) (PVAc) microspheres, MMT particles must be modified to oganophobic. Furthermore, the hydrophobicity of the basal surfaces is also important in terms of exfoliation of clay particles because the hydrophobic basal surfaces aid the entry of monomer into the intergalleries of the clay. The most common method for clay surface modification and intercalation is to treat clay with a cationic surfactant, such as cetyltrimethylammonium bromide (CTAB) [16, 17].

In this study, PVAc–PVA–MMT nanocomposite microspheres with core/shell structure were prepared through suspension polymerization followed by the heterogeneous saponification. The effects of MMT on the morphology and saponification rate of PVAc/MMT nanocomposite microspheres were examined.

## Experimental

### Materials

VAc purchased from Aldrich was washed with an aqueous solution of $NaHSO_3$ and water and dried with anhydrous $CaCl_2$, followed by distillation in nitrogen atmosphere under a reduced pressure. The initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako) was recrystallized twice in methanol before use. PVA with a number-average molecular weight of 127,000 and a degree of saponification of 88% (Aldrich) was used as a suspending agent. Pristine Na-MMT, Kunipia-F from Kunimine, Japan, was used as received. It consists of exchangeable sodium ions with cationic exchange capacity of ca. 119 meq/100 g. The average particle size and surface area of Na-MMT were 100–1,000 nm and 750 $m^2/g$, respectively. CTAB was obtained from Aldrich. Deionized water was used for all the experiments.

### Preparation of PVAc/MMT nanocomposite microspheres

To prepare PVAc/MMT nanocomposite microspheres, suspension polymerization of VAc was conducted. 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. The ADMVN was added at a fixed polymerization temperature. After predetermined times, the reaction mixture was cooled and kept for 1 day to allow the precipitation and separation of the PVAc/MMT nanocomposite microspheres. The collected PVAc/MMT nanocomposite microspheres were further washed with warm water. Conversion was calculated by measuring the weight of the PVAc/MMT using the average value from three determinations. The detailed polymerization conditions are listed in Table 1.

### Heterogeneous saponification of PVAc/MMT nanocomposite microspheres

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. The alkali solution used for saponification contains 10 g of sodium hydroxide, 10 g of sodium sulfate, 10 g of methanol and 100 g of water. The preprepared PVAc/MMT nanocomposite microspheres (1 g) were slowly added into the alkali solution at 50 °C with gentle stirring. The saponification was stopped at the required time and a PVA shell was formed on the surface of the PVAc/MMT microspheres. After the required reaction time, the mixture was poured into cold water and kept for 1 day to allow the precipitation of spherical core/shell PVAc–PVA–MMT nanocomposite microspheres. Finally, 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). Wide-angle X-ray diffraction (XRD) measurements were per-

**Table 1** Suspension polymerization conditions of VAc

| Condition | Value |
|---|---|
| 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.% |

formed at room temperature on a Rigaku (D/Max IIIB) X-ray diffractometer using Ni-filtered CuK$\alpha$ ($\lambda$=1.54 Å) radiation. The core/shell structure of PVAc–PVA–MMT nanocomposite microspheres was examined using an optical microscope (Leica DC 100). The degree of saponification (*DS*) of PVAc–PVA–MMT nanocomposite microspheres was determined by the ratio of methyl and methylene proton peaks in the $^1$H-NMR spectrometer (Varian, Sun Unity 300).

## Results and discussion

### Preparation of PVAc/MMT microspheres

The formation of PVAc/MMT microspheres that were used as a precursor for preparing PVA/MMT nanocomposite microspheres was studied at different MMT contents. The initiator, ADMVN, that can lower the polymerization temperature to room temperature and increase molecular weight [6–8] was used for the suspension polymerization in this study.

Figure 1a presents the conversion of the polymerization as a function of reaction time in the presence of modified MMT. The initiator concentration used in these reactions is 0.0001 mol/mol of VAc. The results indicate that the rate of the polymerization decreased with increasing MMT addition, which is in agreement with a previous study [11]. The reduction in the polymerization rate is probably due to the reduction of the diffusion rate of both monomer molecules and polymer chains in the intergalleries of nanoclay particles. For the polymerization without MMT, Fig. 1a indicates that the conversion of the polymerization continually increased up to ~40 h, and reached a conversion of ~90% in spite of the low polymerization temperature (30 °C), which suggests that ADMVN is an effective initiator for low-temperature polymerization.

In a free radical polymerization, the rate of polymerization ($R_p$) could be expressed by Eq. 1 [18]

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

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 the rate constants of initiator decomposition, polymer propagation, and termination, respectively. This expression predicts that the rate of polymerization increases as the efficiency and concentration of the initiator are increased.

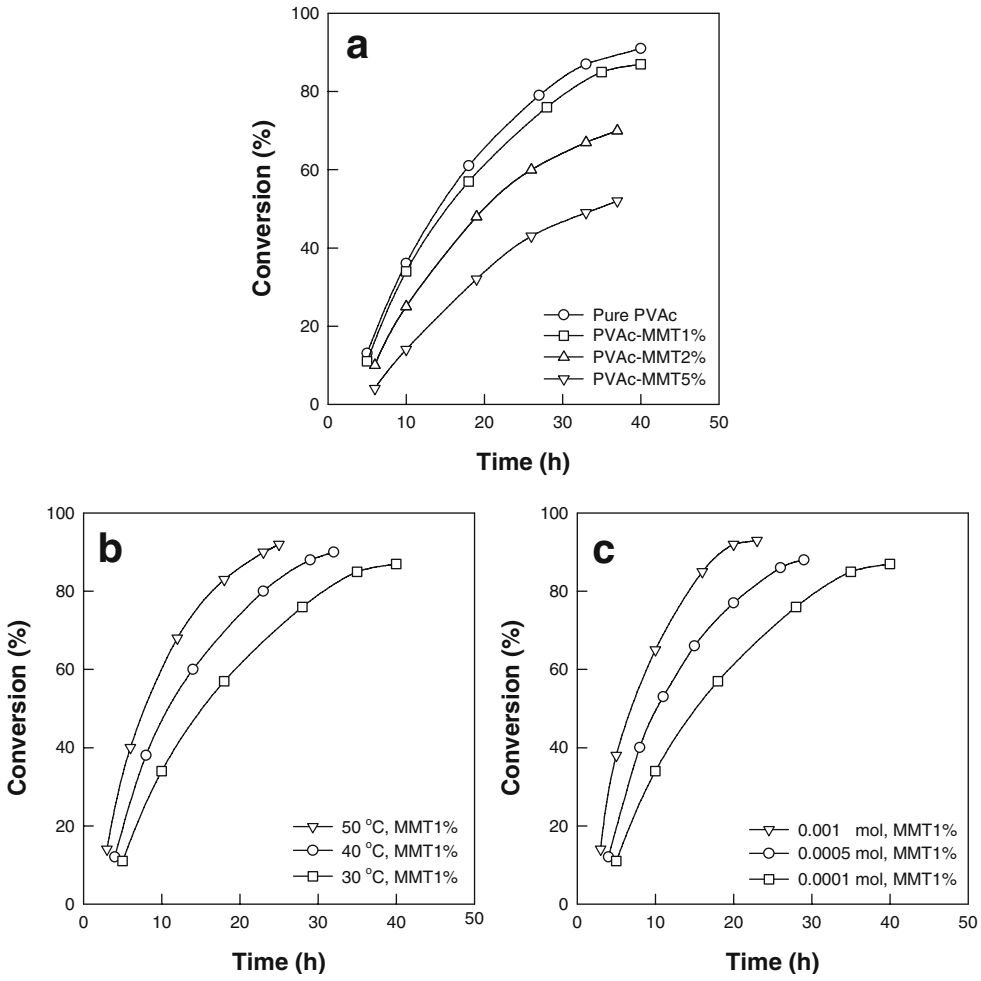


**Fig. 1** Conversions of VAc into PVAc/MMT suspension polymerized using ADMVN concentration of 0.0001 mol/mol of VAc with different MMT contents (**a**), with different polymerization temperatures (**b**), and suspension polymerized using 30 °C with different initiator concentrations (**c**) with polymerization time, respectively

The reduction in the polymerization rate in the presence of MMT suggests that 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 intergallerries may reduce both $f$ and $k_p$ in Eq. 1. It has been known that ADMVN is an effective low-temperature initiator (the 10-h half-life decomposition temperature of ADMVN is 51 °C) for preparing high-molecular-weight polymer with high yield [6, 7]. In this study, ADMVN was used for preparing PVAc/MMT nanocomposite microspheres at room temperature. Figure 1b presents the conversion–time relationship for the reactions carried at different temperatures with a constant initiator concentration. Although a low initiator concentration (0.0001 mol/mol of VAc) and low reaction temperatures were employed, the conversion increased steadily up to 85–95%, depending on the MMT content in the system. The effect of initiator concentration on the polymerization rate is shown in Fig. 1c. It can be seen that the polymerization rate, at a reaction temperature of 30 °C, increased with the increasing initiator concentrations, in accordance with theoretical prediction [6].

SEM photographs of pure PVAc and PVAc/MMT nanocomposite microspheres with 1% MMT contents are presented in Fig. 2. As expected, the surface of pure PVAc microspheres shown in Fig. 2a is smooth. Figure 2b shows that the roughness of the microsphere surface is increased by adding the MMT. To further study the distribution of MMT particles in the PVAc microspheres, the fracture surfaces of the PVAc/MMT nanocomposite microspheres

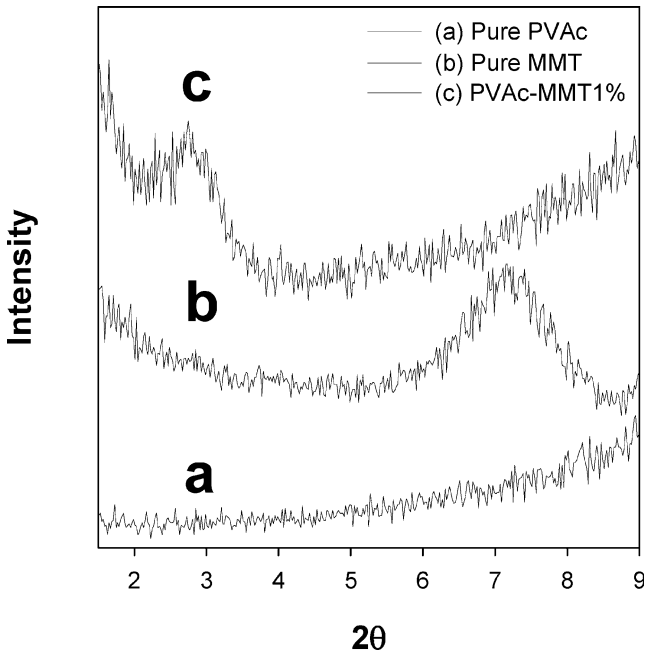


**Fig. 3** XRD patterns of pure PVAc microspheres (**a**), pure MMT (**b**), and PVAc/MMT nanocomposite microspheres with MMT concentration of 1% (**c**), respectively

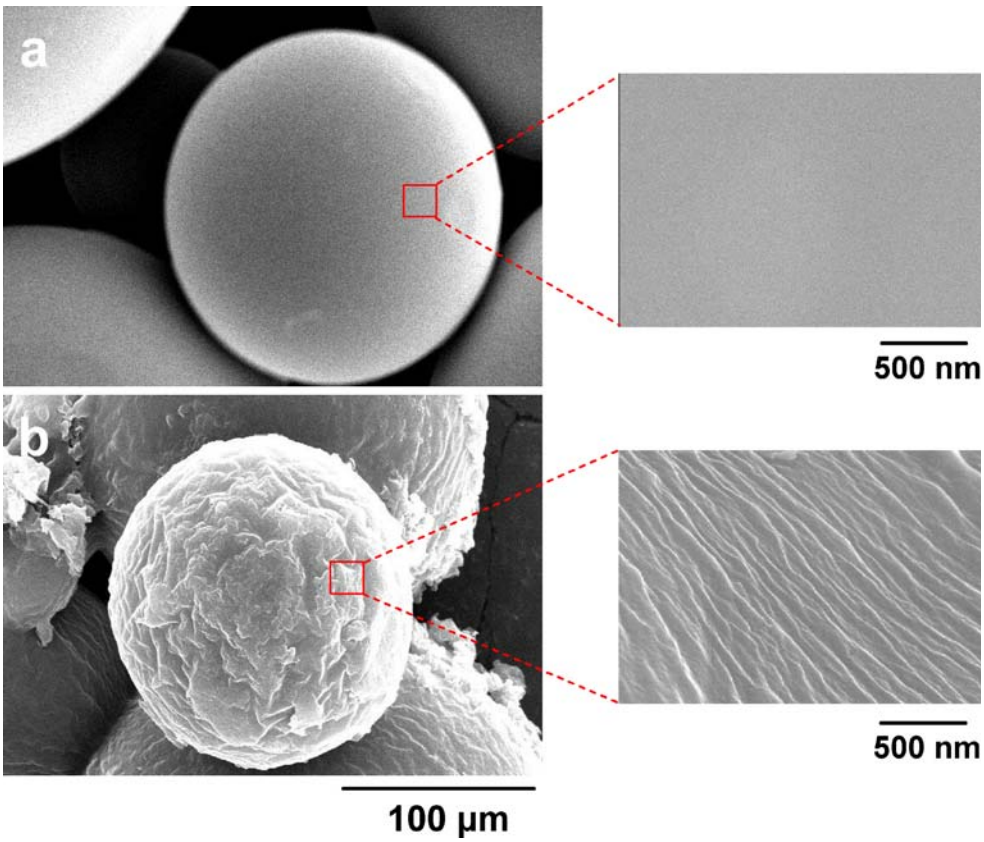


**Fig. 2** SEM photographs of pure PVAc microspheres (**a**) and PVAc/MMT nanocomposite microspheres with MMT concentration of 1% (**b**), respectively

were investigated. Although it is not shown here, MMT particles were embedded inside the composite microspheres, which indicates that PVAc/MMT microspheres could be prepared by in situ suspension polymerization.

The detail structure of the clay nanocomposites has been established using XRD analysis. Figure 3 shows the XRD patterns of the PVAc, MMT, and PVAc/MMT with MMT content of 1%. The MMT shows a diffraction pattern peak at $2\theta=7.2°$, which corresponds to the average basal spacing (d-spacing) of 12.3 Å. In the PVAc/MMT 1% microspheres, the peak moved to a lower angle, i.e., $2\theta=2.7°$. The basal spacing increased from 12.3 to 32.6 Å. This spacing indicates that long alkyl (cetyltrimethyl) 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.

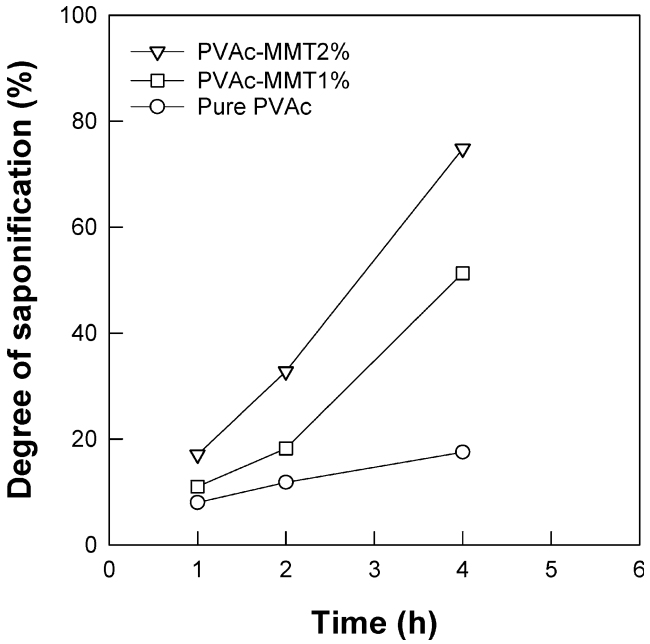


**Fig. 5** Effect of MMT contents on the *DS* of PVAc/PVA with saponification time

## Heterogeneous saponification of PVAc/MMT microspheres

The PVA obtained by the saponification of poly(vinyl ester) is a linear semicrystalline polymer and has been widely used as fibers for textile industries, films, membranes, and drug delivery systems. In this study, the PVA/MMT nanocomposite microspheres were prepared by a simple heterogeneous saponification method. To preserve the spherical shapes of PVAc/MMT nanocomposite particles, the saponificaion was carried out by disperse PVAc/MMT

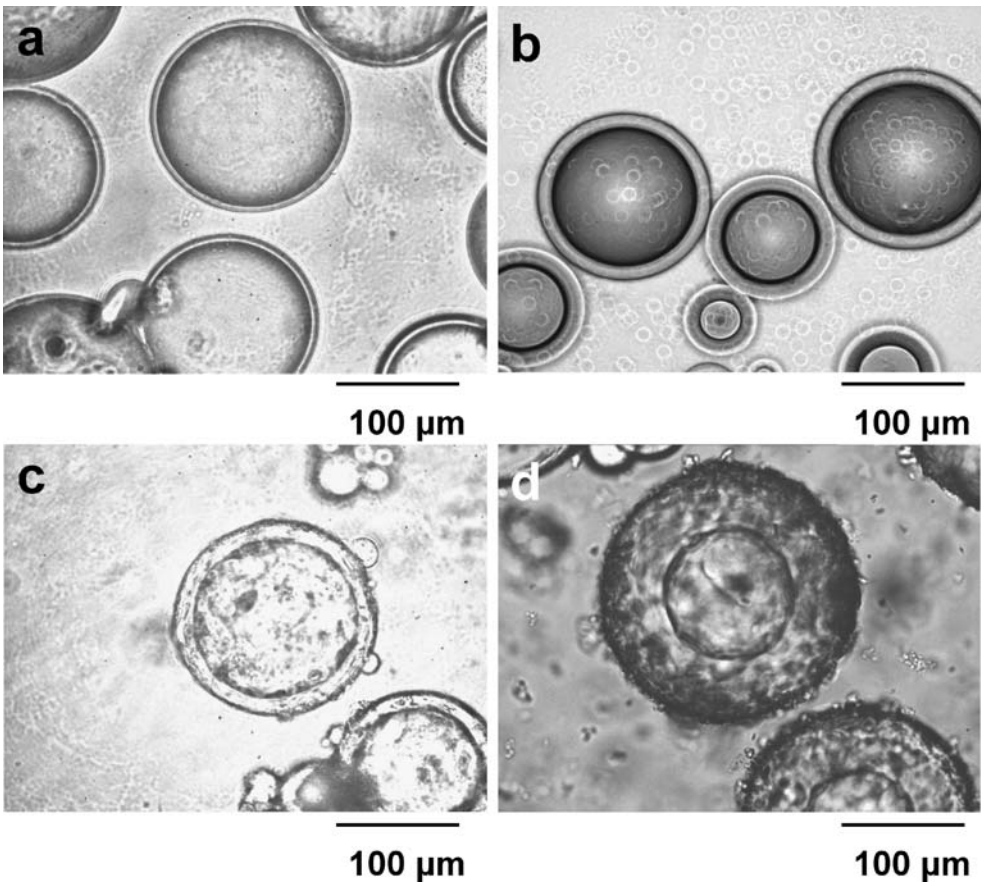


**Fig. 4** Optical micrographs of PVAc/PVA microspheres (**a**, **b**) and PVAc/PVA/MMT nanocomposite microspheres with MMT concentration of 1% (**c**, **d**). The saponification times and *DS* values were 2 h and 14.7% (**a**), 4 h and 17.5% (**b**), 2 h and 18.2% (**c**), and 4 h and 51.3% (**d**), respectively

nanocomposite particles in alkali aqueous solution with very gentle agitation.

The effect of MMT on the PVAc saponification rate was recorded by optical microscope observation. In this study, the heterogeneous saponifications of pure PVAc and PVAc/MMT microspheres were conducted under the same conditions. Degree of saponification (*DS*) is defined by the volume ratio of PVAc/PVA. Figure 4 shows the optical micrographs of PVAc/PVA (Fig. 4a,b) and PVAc–PVA–MMT (Fig. 4c,d) nanocomposite microspheres prepared by heterogeneous saponification at different reaction times. As shown in Fig. 4c,d, partially saponified nanocomposite microspheres (MMT content of 1%, degrees of saponification are 18.2 and 51.3%, respectively) with a PVAc core and PVA shell structure could be obtained by controlling the saponification degrees. It can be seen that the MMT nanoparticles presented in the PVAc microspheres significantly increase the *DS* of PVAc. It is well known that MMT is high swollable in alkaline solution, which results in a faster diffusion of base molecules into the PVAc particles to accelerate the saponification rate of the PVAc microspheres. Figure 5 shows the effect of MMT contents on the *DS* of PVAc microspheres, which indicates that the saponification rate increased remarkably with increasing MMT addition.

FT-IR spectra of saponified PVAc/PVA/MMT nanocomposite microspheres are examined. The absorbanse of the −OH stretching vibration in the region of 3,000–3,600 $cm^{-1}$ after the saponification process further confirmed the saponification of PVAc in the nanocomposite microsphere.

## Conclusions

In this work, PVAc/MMT nanocomposite microspheres, which are a promising precursor of PVA/MMT nanocomposite microspheres, were successfully prepared by low-temperature suspension polymerization of VAc in the presence of organophilic MMT particles. The rate of conversion was decreased with increasing MMT concentration. In the case of 2% MMT, the rate of polymerization decreased largely. However, at 1%, the conversion increased almost linearly up to about 85% in spite of a low polymerization temperature of 30 °C. The SEM study indicates that the PVAc/MMT microspheres could be prepared by in situ suspension polymerization of VAc in the presence of organophilic MMT nanoparticles.

By a heterogeneous saponification method, PVAc–PVA–MMT nanocomposite microspheres with core/shell structure could be prepared. Experiments indicated that the *DS* of PVAc microspheres increased largely with the introduction of the MMT particles. The XRD measurement illustrated that the clay particles are intercalated in the polymer matrix.

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