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Invited paper

Dehydration kinetics of polyvinyl alcohol nanocomposite hydrogels containing Na-montmorillonite nanoclay

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Abstract A series of freeze-thawed, polyvinyl alcohol nanocomposite hydrogels were prepared using various loading levels (0–15 wt%) of hydrophilic natural Na-montmorillonite nanoclay. The morphology of nanocomposite hydrogels, their dehydration kinetics at different temperatures and the effect of Na-montmorillonite on the gelation process were investigated. The results showed a partially exfoliated morphology for the prepared nanocomposite hydrogels. Also by increasing the amount of nanoclay incorporated into the specimens, the gel fraction values of nanocomposite hydrogels were increased. According to the dehydration tests, the dehydration rates of nanocomposite hydrogels exhibited an inverse dependency on the nanoclay loading level and a direct dependency on the dehydration temperature. Finally, it was concluded that the dehydration mechanism of all specimens prepared is non-Fickian at 20 °C, while it is Fickian at 37 °C and 55 °C.

1. Introduction

Hydrogels are three-dimensional polymeric networks that can absorb large amounts of water or aqueous solutions, while maintaining their structure. The networks are composed of homopolymers or copolymers and are insoluble in aqueous solutions, due to chemical or physical crosslinking of the individual polymer chains [1,2]. The application of hydrogels in numerous biomedical and pharmaceutical fields, such as tissue engineering, drug and gene delivery systems, ocular devices, wound healing materials and artificial extracellular matrices, has been reviewed in the literature [2–5].

In recent years, several attempts have been made to reinforce the structure of hydrogels using nanoparticles or nanostructures to obtain nanocomposite hydrogels with enhanced mechanical, physical and chemical properties [6–8]. Most research on nanocomposite hydrogels has been focused on the use of clays, such as laponite [9–12], hydrotalcite [13,14], bentonite [15,16] and montmorillonite [17–20], as nanoparticles. Nanocomposite hydrogels have good potential to be used as functional soft materials in biomedical applications, due to their excellent mechanical properties, high water content and good biocompatibility [18,21,22]. Our research group previously prepared nanocomposite hydrogels on the basis of polyvinyl alcohol (PVA) and organically modified montmorillonite (OMMT), and investigated their potential as novel wound dressing devices; both *in vitro* [23] and *in vivo* [24].

The application of nanocomposite hydrogels might be restricted in biomedical fields, such as drug delivery systems, contact lenses and wound dressing systems, because of their undesired dehydration process [25,26]. It is obvious that a dried hydrogel is not recognized as a soft material in biomedical usage, and its application would be restricted under such conditions. Therefore, having enough information about the dehydration kinetics of nanocomposite hydrogels in order to design optimum medical devices would be required.

In this work, PVA-Na-montmorillonite (MMT) nanocomposite hydrogels were prepared via the freezing-thawing cyclic method. The morphology and gelation process of PVA–MMT nanocomposite hydrogels and the effect of MMT loading levels on their dehydration kinetics were investigated.

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2. Experimental

2.1. Materials

PVA, having an average molecular weight of 74 800 and degree of saponification of greater than 98%, was purchased from Nippon Gohsei. Natural hydrophilic nanoclay (Cloisite Na^+) with the Cation Exchange Capacity (CEC) of 92.6 meq/100 g was purchased from Southern Clay Products Inc. Double Distilled Water (DDW) was used in preparation of all aqueous solutions.

2.2. Preparation of PVA–MMT nanocomposite hydrogels

PVA–MMT nanocomposite hydrogels containing 15 wt% of PVA (based on the total mass of hydrogel) and 0, 3, 6, 9, 12 and 15 wt% of MMT (based on the dried mass) were prepared using the freezing-thawing cyclic method. To prepare each hydrogel, an adequate amount of MMT was added to DDW and mixed to gain a desirable MMT suspension. Then, PVA was gradually added to the MMT suspension and mixed for 4 h at 90 °C to achieve complete dissolution. The obtained solutions were then poured in plastic moulds and placed at −20 °C for 24 h to induce crystallization and gel formation. After the freezing process, they were subsequently allowed to thaw for 24 h at room temperature. The freezing-thawing cycles were repeated three times for each solution.

2.3. Structural characterization

The microstructure and morphology of PVA–MMT nanocomposite hydrogels were characterized using X-ray Diffractometry (XRD) and Transmission Electron Microscopy (TEM) methods. The XRD experiments were conducted on a Philips diffractometer at a scanning rate of 2 °C/min.

All characterized samples (MMT powder and typical nanocomposite hydrogels) were dried in a vacuum oven for at least 24 h before XRD measurements. The microstructure of a typical nanocomposite hydrogel (i.e. 9 wt% MMT) was observed, using a transmission electron microscope (EM 208 S, Philips) with an acceleration voltage of 100 kV. Prior to the TEM experiment, the nanocomposite hydrogel was completely dried under vacuum and then embedded in an epoxy matrix. Subsequently, it was cut into 70–100 nm thick sections using a diamond knife and placed onto a 400 mesh copper grid.

2.4. Gel fraction

The preweighed slice of each hydrogel was dried under vacuum at room temperature until no change was observed in its mass. The nearly identical weight of another slice of the same sample was immersed into excess of DDW for 7 days, to extract uncrosslinked species. Subsequently, the immersed hydrogel was removed from DDW and dried at room temperature under vacuum until the dried mass showed constant weight. The gel fraction test was repeated three times for each hydrogel. The gel fraction value of hydrogels was calculated as follows:

$$\text{Gel fraction (\%)} = \frac{m_f}{m_i} \times 100, \tag{1}$$

where, m_f and m_i are the mass of the dried hydrogel after and before the extraction, respectively.

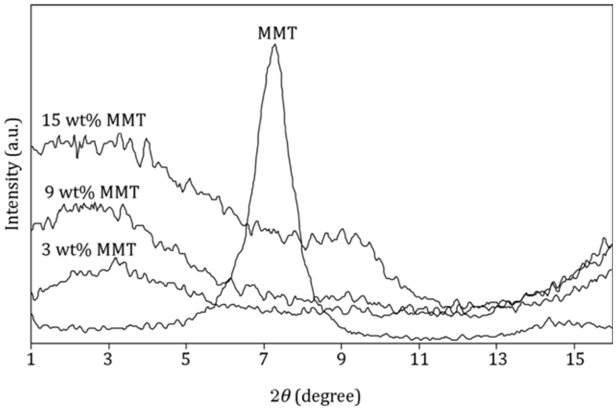

Figure 1: XRD patterns of MMT and nanocomposite hydrogels.

2.5. Dehydration tests

Dehydration tests were performed at constant temperatures of 20°, 37° and 55 °C within a GTH-072TR chamber (Giant Force Instrument). The dehydration kinetics of all hydrogels was determined gravimetrically by weighing their weight at some predetermined time intervals. The fraction of water removed from each hydrogel at time t was calculated as follows:

$$\frac{M_t}{M_\infty} = \frac{m(t) - m(0)}{m(\infty) - m(0)}, \tag{2}$$

where M_t and M_∞ are the cumulative amount of water loss of the hydrogel at any time, t, and the total amount of removable water from the hydrogel (the initial amount of water inside the hydrogel), respectively. $m(0)$, $m(t)$ and $m(\infty)$ are the mass of hydrogel at the initial state, time t and the final state (dried condition), respectively.

3. Results and discussion

3.1. Morphology of nanocomposite hydrogels

XRD and TEM are complementary powerful methods to determine the morphology of polymer-clay nanocomposites. Figure 1 illustrates the XRD patterns of MMT nanoclay and nanocomposite hydrogels containing 3, 9 and 15 wt% of MMT. The XRD profile of MMT has a characteristic diffraction peak at 7.26° corresponding to the d_{001}-spacing of 1.22 nm. On the other hand, there are no characteristic MMT peaks in the XRD patterns of nanocomposite hydrogels. The XRD results suggested a partially exfoliated morphology for the prepared PVA–MMT nanocomposite hydrogels.

To more directly identify the morphology of the nanocomposite hydrogels, the TEM image of a nanocomposite hydrogel containing 9 wt% of MMT was obtained (Figure 2). The dark lines represent the MMT layers and the gray-white area represents the polymer matrix. The image shown in Figure 2 is clearly in accordance with the XRD results. It shows that the MMT silicate layers have been uniformly dispersed in the hydrogel matrix and proves the partially exfoliated morphology of PVA–MMT nanocomposite hydrogels.

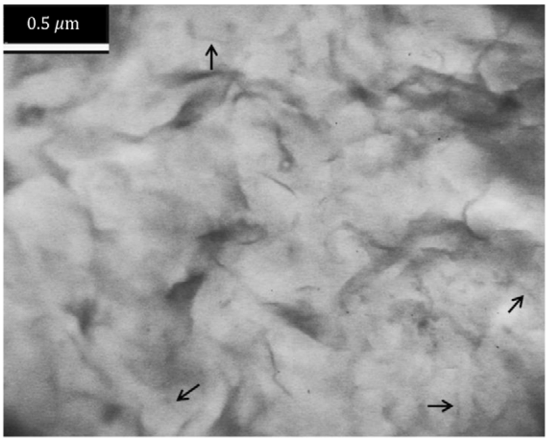

Figure 2: TEM image of nanocomposite hydrogel containing 9 wt% of MMT.

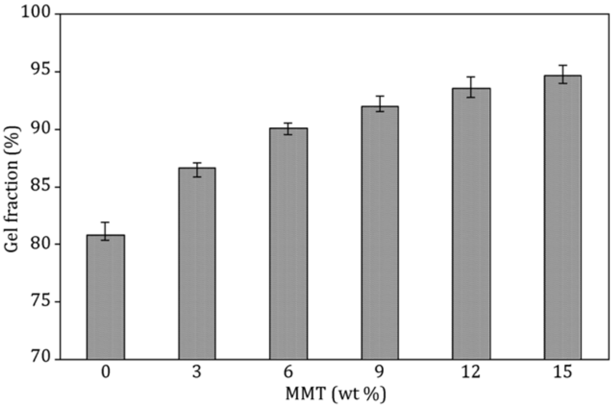

Figure 3: Gel fraction of PVA–MMT nanocomposite hydrogels.

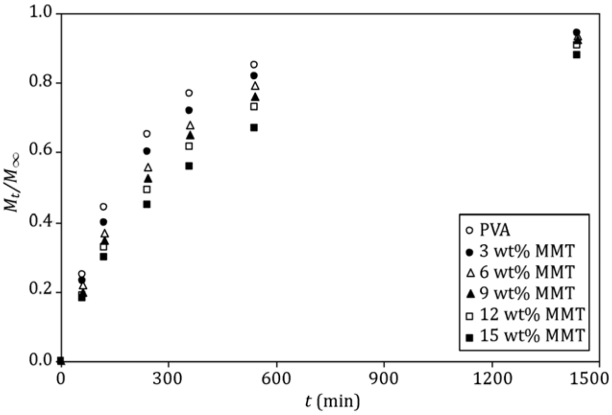

Figure 4: Dehydration kinetics of nanocomposite hydrogels at 20 °C.

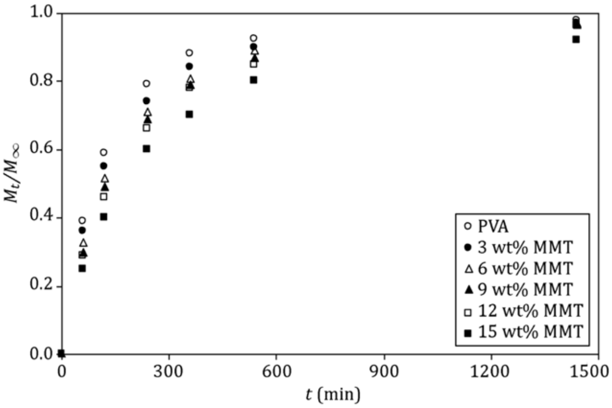

Figure 5: Dehydration kinetics of nanocomposite hydrogels at 37 °C.

3.2. Gel fraction

Figure 3 shows the gel fraction values for the prepared nanocomposite hydrogels versus the weight percentage of MMT. The gel fraction of nanocomposite hydrogels increases by increasing the amount of MMT. As shown, the gel fraction of nanocomposite hydrogels containing 15 wt% of MMT has been enhanced by 17.1%, as compared to pure hydrogel. This reveals the development of some interaction between the MMT layers and PVA chains, and shows the function of MMT as a crosslinking agent in the hydrogel network. The function of MMT, as a physical crosslinker in the network of PVA–MMT nanocomposite hydrogels, has been also confirmed by other research groups [23,27,28]. It can be deduced that the functional hydroxyl groups on the MMT silicate layers could interact with similar groups on the PVA linear chains during the gelation (freezing-thawing) process.

3.3. Dehydration kinetics

Dehydration kinetics of PVA–MMT nanocomposite hydrogels was determined by plotting M_t/M_∞ values versus time for each sample at different drying temperatures. Figures 4–6 show the time-dependent dehydration curves of the prepared nanocomposite hydrogels at 20 °C, 37 °C and 55 °C, respectively. Nearly identical patterns are observed for the dehydration curves of all samples at different constant temperatures. Dehydration curves of specimens at any dehydration temperature show that the dehydration ability of nanocomposite hydrogels decreases by increasing the MMT loading level. In other words, nanocomposite hydrogels containing higher levels of MMT exhibit longer dehydration duration. This is related to the higher gel fraction value and more entangled structure of the nanocomposite hydrogels containing higher levels of MMT. It is obvious that in the specimens with higher gel fraction and crosslinking values, there is less free volume available for transporting water molecules. It means that the mass transfer of water molecules during the dehydration process would be restricted in the PVA nanocomposite hydrogels compared with the pure PVA hydrogel. In addition, the silicate layers inside the nanocomposite hydrogel network could entrap the water molecules and, also, act as a physical barrier against molecule transport, due to the creation of more tortuous paths, which offer controlling steps against mass transfer, as well as the dehydration process. So, it can be remarked that the nanocomposite hydrogel needs more time to reach a specified level of dehydration and, therefore, shows slower dehydration kinetics compared to pure hydrogel.

Figures 4–6 also show that the dehydration rates of hydrogels rise by increasing the drying temperature. This can be attributed to an increase in the diffusion coefficient of water in the hydrogel matrix and its faster shrinkage process, due to the easier relaxation of polymer chains at higher temperatures.

To determine the mass transfer mechanism in the PVA–MMT nanocomposite hydrogels, the following power law equation,

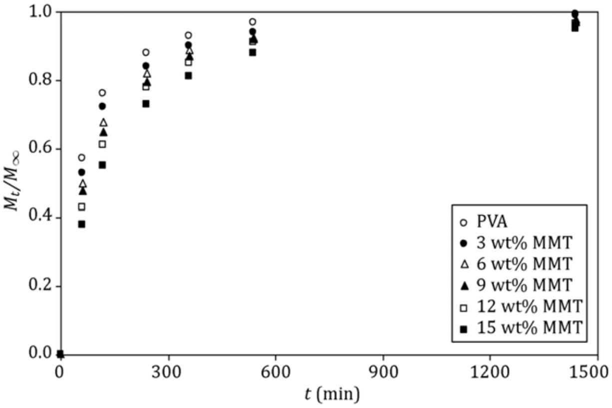

Figure 6: Dehydration kinetics of nanocomposite hydrogels at 55 °C.

describing the time-dependent dehydration process, was used:

$$\frac{M_t}{M_\infty} = Kt^n, \tag{3}$$

where, K is the dehydration characteristic constant and n is the characteristic exponent of the mode transport of the water from hydrogel. According to classification of the diffusion mechanism $n = 0.5$ and $0.5 < n < 1$ indicate the Fickian and non-Fickian (anomalous) diffusion mechanisms, respectively. The values of n and K were calculated for each hydrogel from the slope and the intercept of the plot of $\log(M_t/M_\infty)$ against $\log(t)$ for $M_t/M_\infty < 0.6$, respectively. A good linear relation was observed between $\log(M_t/M_\infty)$ and $\log(t)$ for each specimen at different temperatures. A typical graph showing the $\log(M_t/M_\infty)$ curves versus $\log(t)$ for hydrogels at 37 °C has been presented in Figure 7. The values of constants, n and K, for all hydrogels are shown in Table 1. According to the calculated values for constant n, the dehydration mechanism of all hydrogels is a *non-Fickian* mechanism at 20 °C. In addition, the mechanism of transport for hydrogels in other dehydration temperatures (i.e., 37° and 55 °C) is considered as *Fickian*. As Table 1 shows, the values of constant K, which could be considered as criteria for the dehydration rate of hydrogels, decreases either by increasing the MMT level or by decreasing dehydration temperature. The ratios of K for the nanocomposite hydrogel containing 3 wt% of MMT per K for the hydrogel containing 12 wt% of MMT at the constant temperatures of 20 °C and 55 °C are 1.3 and 1.8, respectively, while the ratios of K at 55 °C per K at 20 °C for the nanocomposite hydrogels containing constant MMT values of 3 and 12 wt% are about 9.4 and 6.8, respectively. This implies that temperature has a more significant effect than MMT loading level on the dehydration process of PVA–MMT nanocomposite hydrogels.

Table 1: Dehydration characteristics for nanocomposite hydrogels at different temperatures.

MMT wt% (Temperature)	n	K
0 (20 °C)	0.6278	0.0202
3 (20 °C)	0.6375	0.0177
6 (20 °C)	0.6313	0.0172
9 (20 °C)	0.6545	0.0143
12 (20 °C)	0.6508	0.0137
15 (20 °C)	0.6314	0.0140
0 (37 °C)	0.4567	0.0627
3 (37 °C)	0.4733	0.0540
6 (37 °C)	0.5034	0.0438
9 (37 °C)	0.5421	0.034
12 (37 °C)	0.5534	0.0311
15 (37 °C)	0.5818	0.0238
0 (55 °C)	0.2712	0.1955
3 (55 °C)	0.2920	0.1671
6 (55 °C)	0.3203	0.1395
9 (55 °C)	0.3311	0.1275
12 (55 °C)	0.3830	0.0929
15 (55 °C)	0.4262	0.0686

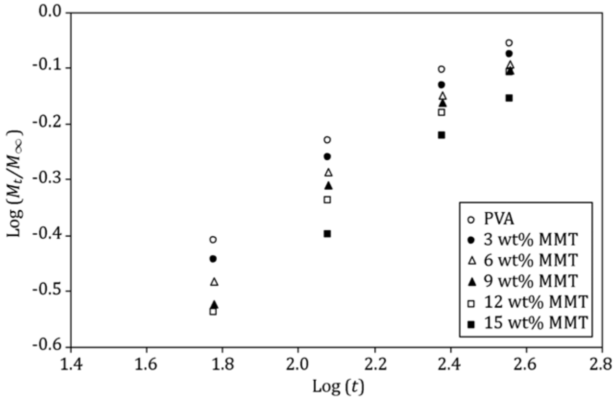

Figure 7: Plots of $\log(M_t/M_\infty)$ against $\log(t)$ for nanocomposite hydrogels at 37 °C.

4. Conclusions

The nanocomposite hydrogels exhibited partially exfoliated morphology with desirable dispersion of silicate layers in the PVA hydrogel matrix. The gel fraction test indicated that the addition of MMT hydrophilic layers increased the gel fraction value of PVA hydrogel. It was deduced that MMT acts as a crosslinker during the crosslinking process of PVA nanocomposite hydrogel. The dehydration investigation showed that the presence of MMT nanoclay inside the PVA hydrogel decreased the rate of water removal from the hydrogel and prolonged its dehydration process. A direct dependency between dehydration rate and drying temperature was also observed for all the prepared nanocomposite hydrogels. It was concluded that the dehydration process of PVA–MMT nanocomposite hydrogels was affected mainly by the dehydration temperature. Further, at constant temperature, all nanocomposite hydrogels exhibited nearly similar dehydration mechanisms.

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