Swollen Behavior of Crosslinked Network Hydrogels Based on Poly(vinyl alcohol) and Polydimethylsiloxane

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ABSTRACT: Poly(vinyl alcohol) (PVA) was dissolved in the water to make a 10 wt % aqueous solution, and polydimethylsiloxane (PDMS) was mixed with 1 wt % 2,2-dimethyl-2-phenylacetophenone (DMPAP) and 0.5 mol % methylenebisacrylamide (MBAAm) in isopropyl alcohol. This mixture was added to a PVA aqueous solution and heated at 90°C for 7 h. Various crosslinked networks were prepared at different molar ratios of PVA/PDMS (1:1, 1:3, and 3:1). The characterization of PVA/PDMS crosslinked networks was determined by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), a universal testing machine (UTM), and the equilibrium water content (EWC). The DSC melting endotherms showed, at 219.49°C, a sharp endothermic peak of PVA, and PVA/PDMS crosslinked networks had melting peaks close to this point. The value of EWC increased with the content of PVA in the crosslinked networks, simultaneously depending on the temperature. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 957–964, 2002

Key words: poly(vinyl alcohol); polydimethylsiloxane; hydrogel

INTRODUCTION

Generally, hydrogels are hydrophilic polymeric networks that absorb water from 10% (an arbitrary lower limit) to thousands of times their dry weight. The networks are held together by molecular entanglements and/or secondary forces including ionic, hydrogen-bonding, or hydrophobic interactions. Hydrogels are crosslinked macromolecular networks swollen in water or biological fluids. Wide ranges of hydrophilic polymers have been examined as potential candidates for the replacement of soft tissue or for other biomedical applications. Furthermore, hydrogels have become excellent carriers for the release of drugs and bioactive macromolecules either in their swollen equilibrium state or as dynamically swelling systems. Their major problems (i.e., their relatively low mechanical strength) can be overcome either by crosslinking, by formation of interpenetrating networks, or by crystallization that induces crystallite formation and considerable reinforcement of their structure.[1–3]

Recently, polymer hydrogels have been studied for various applications, including drug-delivery systems or for mechanical actuators. Among those, pH and thermosensitive polymers have received much attention because these are the most available environments inside the human body.[4,5]

The fundamental swelling behavior of hydrogels has been investigated since Tanaka[6] suggested the swelling theory with respect to the change in temperature. In an aqueous system, the temperature dependence of the swelling of a polymeric gel is closely related to the temperature

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dependence of polymer–water and polymer–polymer interactions. Many researchers have reported on specific polymer–water interactions. Hoffman[7] and Yoshida et al.[8] studied polymeric hydrogels, such as a crosslinked poly(*N*-isopropyl acrylamide) (PNI–PAAm) hydrogel, by which temperature-controlled on–off drug-release systems were developed. Gudeman and Peppas[9,10] reported on pH-sensitive membranes from poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc) interpenetrating networks (IPNs). In this case, the IPN was crosslinked by using glutaraldehyde. Shin et al.[11] reported on a novel pH- and temperature-responsive IPN hydrogel composed of PVA and PAAc crosslinked by ultraviolet (UV) irradiation. Kim et al.[12,13] reported on the drug-release behavior of electrical responsive PVA/PAAc IPN hydrogels under an electric stimulus. In the case of pH as another external signal to a stimuli-sensitive hydrogel, Nishi and Kotaka[14] and Yao et al.[15] studied pH-sensitive hydrogels. Charged polymeric networks have been recognized as useful matrices for drug delivery because their volume changes in repulsion between charged groups incorporated into the gel matrix. Reports of hydrogel using silicone are infrequent. Lopour et al.[16] reported on silicone rubber–hydrogel composites as polymeric biomaterials. They showed the relationship between the properties and influence of the interaction of polymeric phases on their mechanical properties in silicone rubber–hydrogel composite materials.

In this article, we report on the preparation and swelling properties of novel temperature- and pH-dependent PVA/polydimethylsiloxane (PDMS) hydrogels. In addition, differential scanning calorimetry (DSC) and universal testing machine (UTM) studies were performed to understand the state of water for the swollen gel and in drying hydrogels. Further work including the study of electrostatic interactions is under way in our laboratory.

EXPERIMENTAL

Materials

Silicone, vinyl-terminated PDMS, was obtained from the Shinetsu Co. (Japan) and its viscosity was 58 CST. PVA was purchased from the Aldrich Chemical Co. (USA) and the degree of hydrolysis was 99%. The average molecular weight was 124,000 g/mol. 2,2-Dimethyl-2-phenylacetophenone (DMPAP) as an initiator and methylenebisacrylamide (MBAAm) as a crosslinker and all other chemical reagents used were extra pure grade.

Preparation of PVA/PDMS Hydrogels

PVA/PDMS hydrogels were synthesized by the following procedure: PVA was dissolved in water to become a 10 wt % aqueous solution. PDMS was mixed with 1 wt % of DMPAP and 0.5 mol % of MBAAm and 3 mL of isopropyl alcohol (IPA). IPA was used as the solvent for DMPAP and MBAAm. This mixture was added to the PVA aqueous solution and, after completely mixing, heated at 90°C for 7 h. Three hydrogels were prepared from 1:1, 1:3, and 3:1 molar ratios of PVA/PDMS, denoted as H11, H13, and H31, respectively. Samples were poured into Petri dishes and dried at 70°C for 16 h. After 16 h, the dry films obtained were washed with distilled water to remove any unreacted materials.

Swelling Experiments of PVA/PDMS Hydrogels

Dynamic swelling studies were performed by placing the previously dried polymer films in a deionized water and distilled water bath for different times, drying it with filter paper, and then weighing it on a balance, repeating the drying procedure until no weight change was observed. This way, the water content in the gel can be calculated as a function of time:

$$W_t\ (\text{g/g hydrogel}) = \frac{W_h - W_s}{W_s} \qquad (1)$$

where W_h is the film weight at a given time, and W_s, the dry film weight;

$$\text{EWC}\ (\%) = [(W_h - W_s)/W_h] \times 100 \qquad (2)$$

where W_h and W_s represent the weight of swollen and dry-state samples, respectively. Each experiment was performed three times for every one of the polymers synthesized.

Measurement of Bound and Free Water

The bound and free water of the polymers could be determined by DSC. The empty sample pan and the sealed pan were weighed. The sealed pan was quickly frozen inside the DSC chamber to −40°C and several minutes were allowed for the system to come to equilibrium. The sample holder

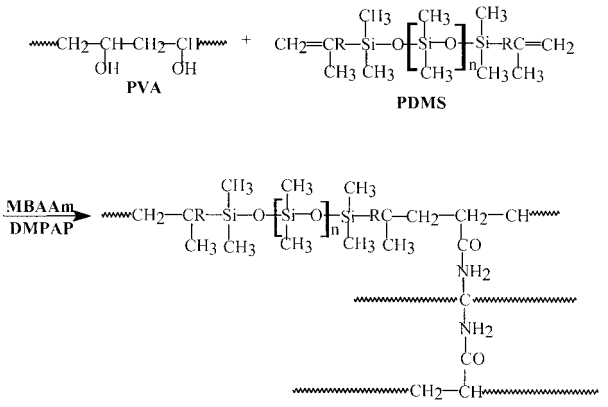

Figure 1 Scheme of the synthesis of PVA/PDMS crosslinked networks.

assembly was then heated at a rate of 5°C/min. A scanning speed of 5°C/min was found to give the optimum values of peak height and peak spread. This minimized the errors in the experimental measurements. The measurement of DSC was conducted using a TA Instruments DSC 2010 under N_2 flow.

Mechanical Strength of Hydrogels

A universal testing machine (Instron Model 4201) measured the tensile strength and elongation at break of each sample in dry and wet states with an extension rate of 10 mm/min at room temperature.

RESULTS AND DISCUSSION

The hydrogels of PVA and PDMS were synthesized by radical polymerization using DMPAP as an initiator and 0.5 mol % MBAAm as a crosslinker. Figure 1 illustrates briefly the synthesis procedure of PVA/PDMS crosslinked networks.

Swelling kinetics was determined by calculating the gel water content, W_t, each time from eq. (1), until thermodynamic equilibrium was reached, calculated by means of W_∞. The equilibrium water content (EWC) was calculated according to eq. (2). Values for EWC for the different hydrogels are shown in Table I.

It can be seen, in general, that EWC increases with the PVA content in PVA/PDMS crosslinked networks. Figures 2–4 show the swelling kinetics of all the samples with the temperature. All the swelling experiments were carried out in a pH 7 buffer solution at 30–45°C. All the hydrogels swelled rapidly and reached equilibrium within 1.5 h. The EWC values of the hydrogels are in the range of 44–55%. All the hydrogels show temperature-dependent swelling behavior. With increase of the hydrophilic part, PVA in the crosslinked networks, the EWC obtained at each temperature increased in the order of H13, H11, and H31. Based on the hydrophilicity of the polymeric network, a lower EWC would be expected when the PDMS content was increased as a consequence of the higher hydrophobicity introduced in the crosslinked networks at each temperature. Furthermore, all the hydrogels exhibited a temperature-dependent swelling behavior due to disassociation/association of the hydrogen bonding by hydroxyl groups in the PVA chain in the crosslinked networks.

To determine the nature of water diffusion into the hydrogel, the following equation was used:

$$F_t = \frac{W_t}{W_\infty} = kt^n \tag{3}$$

where W_t and W_∞ represent the amount of water absorbed by the hydrogel at time t and at equilibrium, k is a constant characteristic of the system, and n is an exponent which takes into account the mode of water transport. A value of $n = 0.5$ indicates a Fickian diffusion mechanism, while a value of $0.5 \leq n \leq 1$ indicates that diffusion is anomalous or Fickian. Equation (3) applies to initial swelling states and linearity is observed when Log F_t as a function of log t is represented by a swelling fraction equal to 0.6.[17] From the intercept and the slope of the curves, the values of the kinetic constant, k, and the diffusion exponent, n, are obtained. These results are shown in Table II.

Table I Water State of Hydrogels Calculated by Using DSC Measurement

Sample	EWC (%)	Free Water (%)	Bound Water (%)
H11	50.0	38.3	11.1
H13	48.7	36.3	12.4
H31	52.7	40.2	12.6

[a] All the samples were measured in pH 7 buffer solution at 35°C.

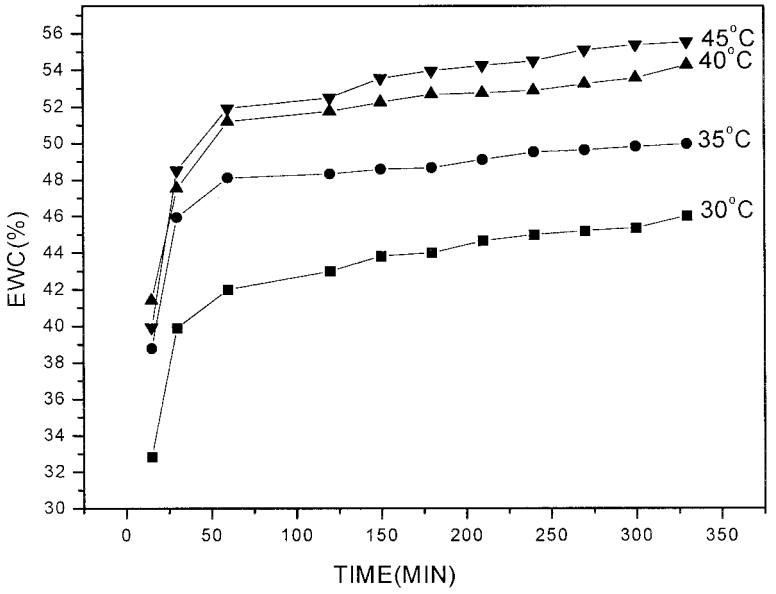

Figure 2 Swelling kinetics of H11 (PVA:PDMS = 1:1).

No variation of the diffusion exponent with PDMS content is observed, and its value higher than 0.50, indicating diffusion of water to the interior of all the hydrogels, follows an anomalous mechanism and reveals the existence of certain coupling between molecular diffusion and tension relaxation developed during swelling of the hydrogels. Changes in the rate of water admission can be attributed to a slight decrease as shown by the kinetic constant, k, as the content of hydrophobic PDMS content increases. Generally, PVA has a high affinity for water and, depending on its degree of crystallinity, may or may not be water-soluble. The highly anomalous behavior of this polymer is due to the regularity of the chain and strong interchain interactions, leading to a compact structure which would accentuate the anomalous aspects of diffusion even for a molecule as small as water. However, in this study, water diffusion through PVA/PDMS crosslinked net-

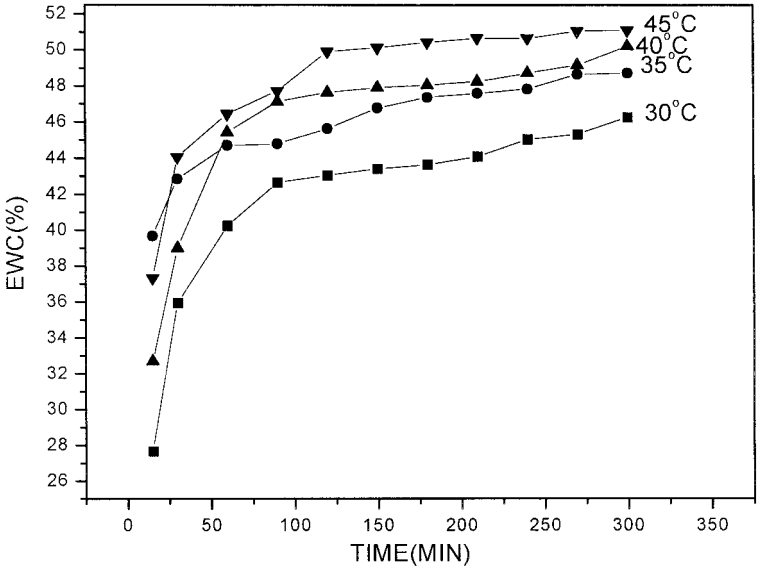

Figure 3 Swelling kinetics of H13 (PVA:PDMS = 1:3).

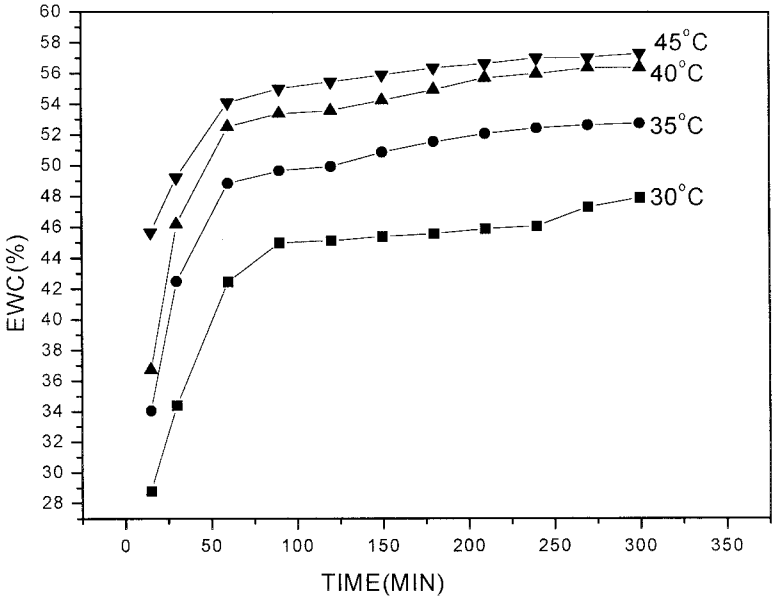

Figure 4 Swelling kinetics of H31 (PVA:PDMS = 3:1).

works is closer to Fickian diffusion, due to a more irregular chain and more open structure with the PDMS content.

pH-dependent swelling behavior was observed at 35°C, with changes in the pH 2–10 buffer solution as shown in Figure 5: The swelling ratio increases with the increase of pH until pH 7. The EWC values of all PVA/PDMS crosslinked networks at pH 2 are relatively small. The EWC values at pH 7 displayed the highest values in all the hydrogels. This result was due to the ionization of the pendent hydroxyl group in the PVA chain. Thus, hydrogels composed of PVA/PDMS showed simultaneous pH and temperature sensitivity. Since H31 possesses more hydrophilic and hydroxyl groups within its structure, the swelling ratio may be the highest among the other hydrogels, resulting in the highest EWC at all swelling experiments.

The thermal properties of PVA/PDMS crosslinked networks were investigated by DSC measurement. Figure 6 shows DSC melting endotherms of dry crosslinked networks and a pure PVA sample. PVA gives a sharp endothermic peak at 219.49°C, and crosslinked networks showed slightly right-shifted melting peaks with the PDMS content. As the molar ratio of PVA to PDMS increased from 1:3 to 3:1, the integration of the peaks of crosslinked networks became more intensive. It is evident that the crystallinity was remarkably reduced as a result of crosslinking and the decrease was affected mainly by the PDMS composition. The melting endotherms of swollen gels were investigated to measure the free water and bound water content in the hydrogels as follows:

Figure 7 shows a DSC thermogram of fully swollen hydrogels. The endothermic peak of the swollen gel appears between −5 and 10°C. The fraction of free water is approximately estimated by the ratio of the endothermic peak, integrated between these ranges, to the melting endothermic peak of the heat of fusion for pure water. The free water (or bulk water) is that portion of water not associated or not bound with the polymer, which means that it has no interaction with the polymer chains. However, the bound water (i.e., the associated water) is associated by secondary forces such as the hydrogen bonding force in the polymer matrix. The bound water is expressed as the difference between the total water and the free water. The fraction of free water in the total wa-

Table II Values of *k* and *n* for Swelling of Several PVA/PDMS Hydrogels

Hydrogel	k (h^{-n})	Power Law Diffusional Exponent, n
H11	0.584	0.55 ± 0.1
H13	0.543	0.53 ± 0.1
H31	0.601	0.56 ± 0.1

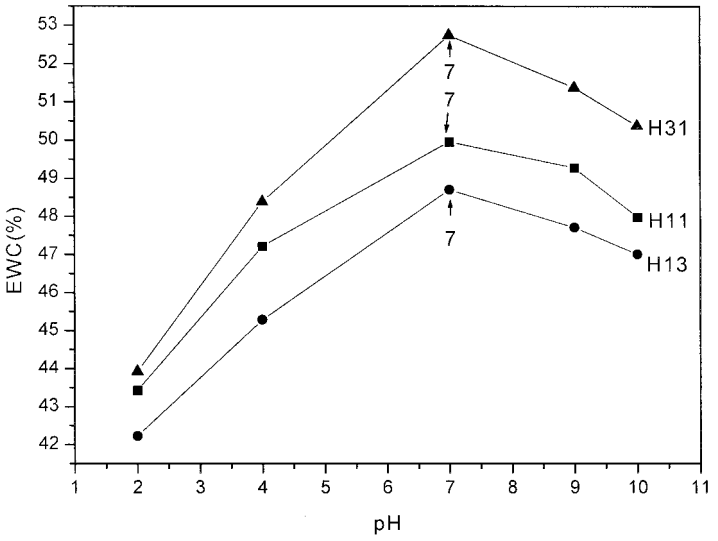

Figure 5 pH-dependent swelling behavior of PVA/PDMS crosslinked networks at 35°C; H11, H13, and H31.

ter is approximately calculated as the ratio of the endothermic peak area for a water-swollen hydrogel to a melting endothermic heat of fusion (79.9 cal/g) for pure water:

$$W_b = W_t - (W_f + W_{fb}) = W_t - Q_{\text{endo}}/Q_f \quad (4)$$

where Q_{endo} is the heat of fusion for ice (equal to 79.7 cal/g) and Q_f is the heat of fusion for the sample. EWC values, free water content, and bound water content were calculated and are listed in Table I. The free water content in the hydrogels of H11, H13, and H31 are 38.32, 36.30, and 40.17 at pH 7, respectively. The H13 sample shows the lowest EWC and free water content. This result confirms that H13 had a more compact structure than that of H11 or H31. It is clear that the increase of swelling at pH 7 and at higher temperature is attributed mainly to the free water content, and the ionic repulsion of hydroxyl ions, and thus the dissociation of hydrogen bonding, also induces the decrease of bound water in hydrogels.

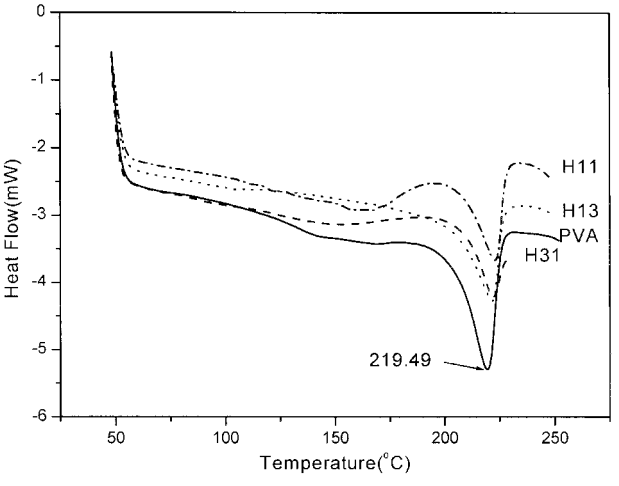

Figure 6 DSC thermograms of PVA/PDMS crosslinked networks and PVA; H11, H13, H31, and PVA.

The EWC in hydrogels is one of their basic properties. A hydrogel with a high water content is generally more advantageous in increasing permeability and biocompatibility. However, this fact adversely affects its mechanical properties; for example, hydrogels with high-equilibrium hydration degrees show poor mechanical properties at ambient temperature, showing low resistance to traction and tear. Copolymerization of different monomers, to obtain the desired properties, is a way of solving this problem. Generally, a hydrophilic monomer (which will ensure a higher water content in the network) is mixed with a more hydrophobic monomer to improve the mechanical properties in the resulting hydrogel.[18] The mechanical strength of the PVA/PDMS hydrogels is also shown in Table III. As the PDMS network region, formed by crosslinking within the copolymer matrix, increased, the tensile strength of the PVA/PDMS hydrogels at the dry state increased while their elongation at break decreased. This indicated that the degree of crosslinking in the

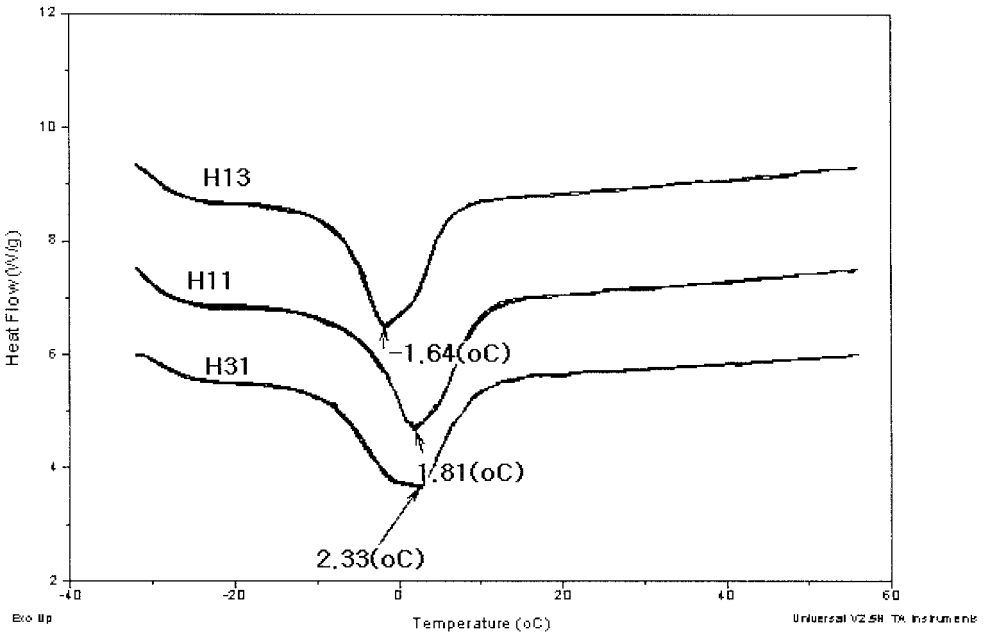

Figure 7 DSC thermograms of hydrogels fully swollen at pH 7.

network played a major role in the mechanical strength of the hydrogels in the dry state. The H13 sample showed the highest tensile strength and the lowest elongation in the swollen state. Thus, we could consider that the mechanical properties of the PVA/PDMS hydrogels are more affected by the degree of crosslinking in the swollen state. In other words, as we already mentioned, H13 had the most compact complex structure; thus, it showed a lower EWC than those of H11 and H31. Accordingly, in the swollen state, H13 exhibits the highest tensile strength value of 3.9 MPa at an EWC of 48.7%. On the other hand, the 66.8% elongation at break of H13 was lower than those of the other hydrogels.

Table III Mechanical Properties of PVA/PDMS Hydrogels

	Tensile Strength (MPa)		Elongation at Break (%)	
Sample	Dry	Wet	Dry	Wet
PVA	9.7	4.1	37.0	134.0
H11	6.5	3.7	14.0	67.7
H13	6.9	4.0	12.4	66.8
H31	7.3	3.9	11.6	90.6

CONCLUSIONS

We prepared hydrogels based on PVA/PDMS by crosslinking. Prepared networks were characterized and confirmed by DSC. The EWC values of the hydrogels were in the range of 44–55% and changed with the molar ratio of PVA/PDMS. The EWC of the networks exhibited a relatively high EWC at 45°C in a pH 7 buffer solution. The pH-sensitive characteristics of the networks were studied by a swelling test under various pH conditions at 35°C. An increase of the EWC at pH 4, 7, and 10 was noticed. The EWC values of all PVA/PDMS copolymers at pH 2 were relatively small. The swelling behavior at pH 7 was the highest in all the hydrogels. Hydrogels composed of PVA/PDMS showed simultaneous pH and temperature sensitivity. The free water contents in the hydrogels of H11, H13, and H31 were 38.32, 36.30 and 40.17 at pH7, respectively.

In the measurement of the mechanical properties of the hydrogels, the H13 sample showed the highest tensile strength and the lowest elongation in the swollen state. From these results, we consider that the mechanical properties of PDMS/PVA crosslinked networks are more affected by the degree of crosslinking in the swollen state. The PVA/PDMS crosslinked networks, prepared in this study, might be expected to be of use,

because of their hydrophilic and hydrophobic biocompatibility, in the biomedical field.

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