

# Thermal and Rheological Properties of Poly(vinyl alcohol) and Water-Soluble Chitosan Hydrogels Prepared by a Combination of $\gamma$ -Ray Irradiation and Freeze Thawing

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**ABSTRACT:** Poly(vinyl alcohol) (PVA)/water-soluble chitosan (ws-chitosan) hydrogels were prepared by a combination of  $\gamma$ -irradiation and freeze thawing. The thermal and rheological properties of these hydrogels were compared with those of hydrogels prepared by pure irradiation and pure freeze thawing. Irradiation reduced the crystallinity of PVA, whereas freeze thawing increased it. Hydrogels made by freeze thawing followed by irradiation had higher degrees of crystallinity and higher melting temperatures than those made by irradiation followed by freeze thawing. ws-Chitosan disrupted the ordered association of PVA molecules and decreased the thermal stability of both physical blends and hydro-

gels. All the hydrogels showed shear-thinning behavior in the frequency range of 0.2–100 rad/s. Hydrogels made by freeze thawing dissolved into sol solutions at about 80°C, whereas those made by irradiation showed no temperature dependence up to 100°C. The chemical crosslinking density of the hydrogels made by irradiation followed by freeze thawing was much greater than that of hydrogels made by freeze thawing followed by irradiation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3825–3830, 2008

**Key words:** hydrogels; irradiation; rheology; thermal analysis; freeze thawing

## INTRODUCTION

Hydrogels are crosslinked hydrophilic polymer networks that can absorb large amounts of water without dissolution in water. Because of their hydrophilic character and potential to be biocompatible materials, hydrogels have been of great interest to biomaterial scientists for many years.<sup>1–3</sup>

Chitosan, the partially deacetylated form of chitin, is a well-known material for wound dressing because of its excellent biocompatibility, biodegradability, hemostatic nature, and antibacterial activity.<sup>4–6</sup> However, chitosan is soluble not in water but in acid solutions. Hydrogels made from chitosan acid solutions often need a repeated cleaning process to neutralize the acid. The use of water-soluble chitosan (ws-chitosan) can simplify the hydrogel-making process and reduce the toxicity of the product. Poly(vinyl alcohol) (PVA), a water-soluble polyhydroxyl polymer, has been used widely in practical applications because of its easy preparation, excellent chemical resistance, and biocompatibility. PVA hydrogels

prepared from aqueous solutions by freeze thawing (FT) have many interesting properties. They have good mechanical strength and flexibility and are stable at room temperature. However, these hydrogels are opaque and not stable at high temperatures. Irradiation is a suitable tool for hydrogel formation. The process can be easily controlled, and there are no initiators or crosslinkers, which may be harmful and difficult to remove. In addition, the two processes of hydrogel formation and sterilization can be achieved in one technological step. However, these hydrogels often have poor mechanical strength.

Much research has focused on preparing hydrogels by irradiation<sup>7–10</sup> or FT,<sup>11–14</sup> but few studies have been conducted on the preparation of hydrogels by a combination of the two processing techniques.<sup>9,15</sup> Recently, we prepared a series of PVA/ws-chitosan hydrogels by a combination of irradiation and FT, pure irradiation, and pure FT.<sup>16</sup> The gel fraction, swelling behavior, water evaporation rate, and microstructural properties of these hydrogels were investigated. The hydrogels made by irradiation followed by FT and FT followed by irradiation showed quite different properties. The thermal and rheological properties of these hydrogels were investigated with differential scanning calorimetry (DSC), thermogravimetry (TG), and rheological techniques, and we discuss them by taking into account the micro-

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structural variation revealed by attenuated total reflection/Fourier transform infrared (ATR-FTIR) measurements.

## EXPERIMENTAL

### Materials

PVA was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The degrees of polymerization and hydrolysis of PVA were  $1750 \pm 50$  and 98%, respectively. ws-Chitosan, manufactured by the protonation of chitosan in an HCl/CH<sub>3</sub>CH<sub>2</sub>OH solution, was obtained from Jinhu Chitin Co., Ltd. (Qingdao, China). The molecular weight and deacetylation degree of the chitosan before protonation were about 200,000 and 91.7%, respectively.

### Preparation of the hydrogels

PVA was dissolved in distilled water at 96°C for 3 h under refluxing. The homogeneous solutions, containing 7 wt % PVA and various contents of ws-chitosan, were obtained through the stirring of the mixed solution at 40°C with a physical stirrer for 30 min. The aqueous solutions were poured into Petri dishes to prepare hydrogels by  $\gamma$ -irradiation (Irra.),  $\gamma$ -irradiation followed by FT (Irra.+FT), FT, and FT followed by  $\gamma$ -irradiation (FT+Irra.). Irra. was performed in an atmosphere of N<sub>2</sub> with <sup>60</sup>Co  $\gamma$ -rays to 30 kGy at a dose rate of 0.76 kGy/h. Freezing and thawing were repeated up to three times. Each cycle of FT involved the lowering of the temperature to -20°C, standing at this temperature for 1.5 h, the raising of the temperature to 25°C, and standing at this temperature for 1 h. The obtained hydrogels were directly submitted to rheological measurements without any other pretreatments. For thermal and ATR-FTIR experiments, the hydrogels were extracted by the immersion of the gels in distilled water at 45°C for 72 h, with the water being changed every 8 h, and afterward they were dried at 37°C for 48 h.

### Thermal properties

The DSC measurements were performed with a Mettler-Toledo DSC822e (Columbus, United States) in a nitrogen atmosphere. The physical blends and extracted dry hydrogel samples (ca. 9 mg) were heated from 30 to 360°C at a heating rate of 10°C/min. The physical blends were obtained by the drying of the homogeneous solutions of PVA/ws-chitosan at 37°C for 48 h. TG analysis of the extracted dry samples (ca. 20 mg) was performed with a Netzsch STA 409 PC (Selb, Germany) from 30 to 700°C at a heating rate of 10°C/min in an atmosphere of N<sub>2</sub>.

### ATR-FTIR analysis

The ATR-FTIR spectra of the samples were recorded on an Avatar 370 spectrometer (Thermo Nicolet Corporation, Madison, WI, United States). All spectra were collected in the 4500–550-cm<sup>-1</sup> region with a resolution of 4 cm<sup>-1</sup>.

### Rheological properties

The rheological properties of the hydrogels were studied on an ARES strain-controlled rheometer (TA Instruments, Twin Lakes, WI, United States) with parallel plates 25 mm in diameter with a plate-to-plate distance of 1–2 mm. All rheological measurements were carried out in the linear viscoelastic regime with a strain of 0.2%. The experiment went through frequency scanning at 25°C in the frequency range of 0.2–100 rad/s. The temperature dependence of the rheological properties was investigated in the temperature range of 25–100°C at 1 rad/s with a ramp rate of 5°C/min. To prevent dehydration during rheological measurements, a thin layer of Vaseline was placed on the peripheral surface of the hydrogel held between the plates. Each measurement was performed at least twice on two different disc specimens from the same hydrogel sample.

## RESULTS AND DISCUSSION

### Thermal analysis

The TG and differential thermogravimetry (DTG) curves of PVA and ws-chitosan are presented in Figure 1. The weight loss at about 100°C is considered to be the water evaporation from the samples. ws-Chitosan is degraded at about 238.4°C. PVA shows two degradation stages. One is at about 277.5°C, and the other is at about 433°C.

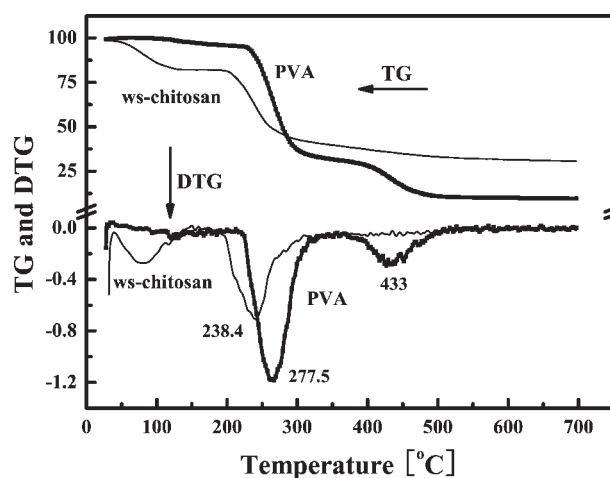
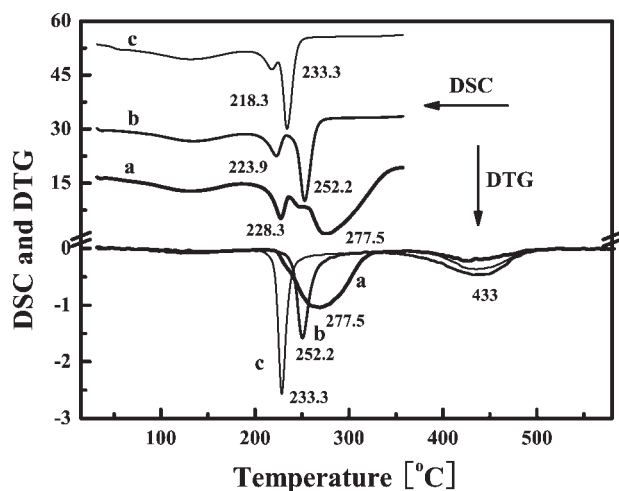


Figure 1 TG and DTG curves of PVA and ws-chitosan.

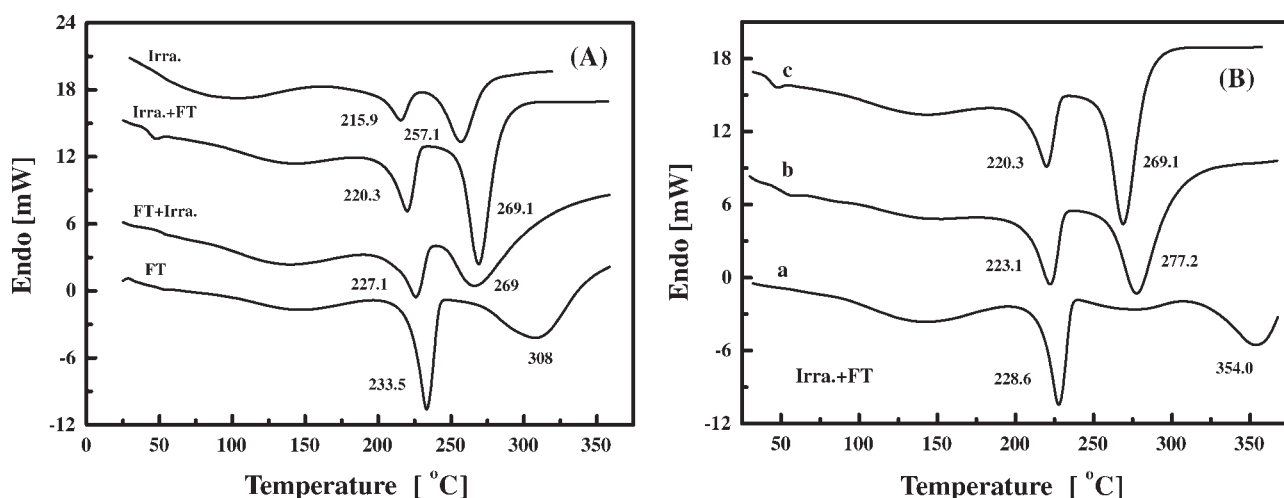


**Figure 2** DSC and DTG curves of physical PVA/ws-chitosan blends with various contents of ws-chitosan: (a) 7 wt % PVA, (b) 7 wt % PVA and 1 wt % ws-chitosan, and (c) 7 wt % PVA and 3 wt % ws-chitosan.

Figure 2 exhibits the DSC and DTG curves of PVA/ws-chitosan physical blends with ws-chitosan contents of 0, 1, and 3 wt %. For all the samples, a peak appears at about 100°C because of the water evaporation. The DTG curves indicate two degradation stages for all the samples. The first stage is in the range of 200–350°C, and the second stage is at about 433°C. From a comparison of the DTG curves of PVA and ws-chitosan shown in Figure 1, it can be concluded that the second decomposition stage is due to the decomposition of PVA. There is only one degradation peak in the range of 200–350°C for each of the physical blends, whereas the reactants degrade at two different temperatures (238.4°C for ws-chitosan and 277.5°C for PVA). This may indicate that there is an interaction between PVA and ws-chi-

tosan molecules. The first degradation temperature of the physical blends decreases gradually with increasing ws-chitosan content, and this implies that ws-chitosan can decrease the stability of the physical blends. The DSC curves in Figure 2 show two endothermic peaks in the range of 200–350°C for each blend. PVA has been reported to exhibit an endothermic peak around 230°C that corresponds to the melting temperature.<sup>17</sup> ws-Chitosan has no endothermic peak in the temperature range of 200–230°C. From a comparison with the DTG curves, it can be concluded that the endothermic peak at the lower temperature is associated with the melting of PVA, whereas the peak at the higher temperature is related to the first decomposition stage of the sample. The melting temperature decreases with increasing ws-chitosan content. This may be due to the fact that the addition of ws-chitosan disrupts the ordered association of the PVA molecules, as proposed by Park et al.<sup>17</sup>

The DSC and DTG curves of PVA/ws-chitosan hydrogels show endothermic peaks and degradation stages similar to those of the physical blends depicted in Figure 2. That is, in the DSC curves, the endothermic peak at 100°C is due to water evaporation, the peak at about 200–230°C corresponds to the melting temperature of the hydrogel, and the peak at the higher temperature is related to the decomposition of the system. As shown in Figure 3, the melting temperature of the hydrogel made by FT is the highest, whereas that of the hydrogel made by Irra. is the lowest, even lower than that of the corresponding physical blend, as shown in Figure 2. As is known, the variation in the melting temperature is caused by morphological and chemical modifications.<sup>17</sup> The morphological changes involve the thickness of the crystallites and the degree of crystallinity.

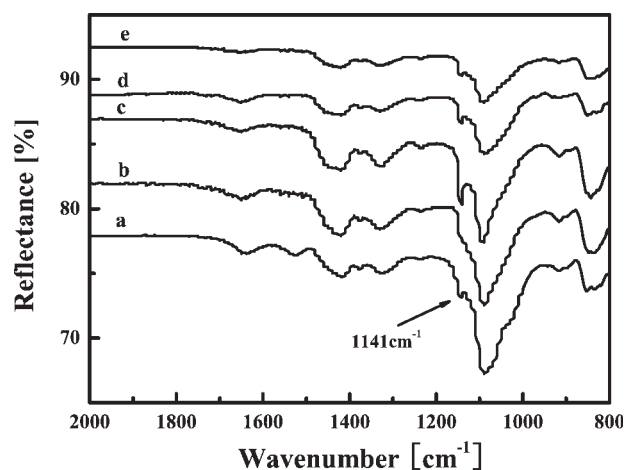


**Figure 3** (A) DSC curves of hydrogels with 7 wt % PVA and 3 wt % ws-chitosan made by Irra., Irra.+FT, FT, and FT+Irra. and (B) DSC curves of hydrogels with various ws-chitosan contents made by Irra.+FT: (a) 7 wt % PVA, (b) 7 wt % PVA and 1 wt % ws-chitosan, and (c) 7 wt % PVA and 3 wt % ws-chitosan.

**TABLE I**  
Degree of Crystallinity of Hydrogels with 7 wt % PVA and Different Contents of ws-Chitosan Made by Various Methods

ws-Chitosan (wt %)	Degree of crystallinity (%)			
	Irra.	Irra. + FT	FT + Irra.	FT
3	29.9	38	38.4	63.9
1	45.7	44.7	55.8	65.6
0	50.2	51.5	57.5	60.2

PVA hydrogels prepared by FT are crosslinked physically with polymer crystallites acting as junction points.<sup>14,18,19</sup> The formed crystallites can increase the degree of crystallinity of these hydrogels. The chemical changes formed by irradiation often involve crosslinking, grafting, and degradation, and these changes often reduce the degree of crystallinity.<sup>20</sup> Therefore, the ordered association of PVA molecule is enhanced by FT but is disrupted by irradiation, which results in the increase in the melting temperature for hydrogels made by FT and the decrease in the melting temperature for those made by irradiation. A similar phenomenon was observed in our former study<sup>21</sup> and by some other researchers.<sup>7,17</sup> The melting temperature of the hydrogel made by FT+Irra. is higher than that of the hydrogel made by Irra.+FT. This probably implies that the changes of morphological and chemical modifications are mainly affected by the first step in the hydrogel formation processes. Figure 3(B) shows that the melting temperature of the hydrogels made by Irra.+FT decreases gradually with increasing ws-chitosan content. The depression in the melting temperature suggests that the ordered association of the PVA molecular segments is altered by the presence of ws-chitosan, which is similar to that in the physi-



**Figure 4** ATR-FTIR spectra of (a) a 7 wt % PVA/3 wt % ws-chitosan physical blend and (b–e) hydrogels containing 7 wt % PVA and 3 wt % ws-chitosan and made by Irra., FT, FT+Irra., and Irra.+FT, respectively.

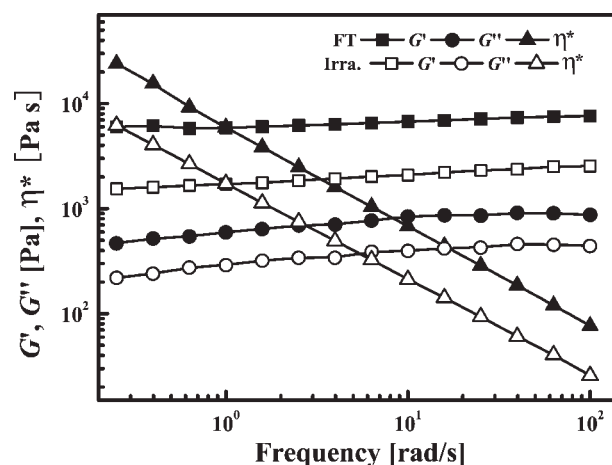
cal blends, as shown in Figure 2. The first degradation temperature of the hydrogels can also be obtained from Figure 3. The results demonstrate that hydrogels are more stable than their corresponding physical blends (see Fig. 2) and that a hydrogel with a higher melting temperature is more stable. Table I shows the degree of crystallinity of the hydrogels calculated by an analysis of the DSC thermograms with the following equation:

$$X_t = \Delta H / \Delta H_c \times 100\%$$

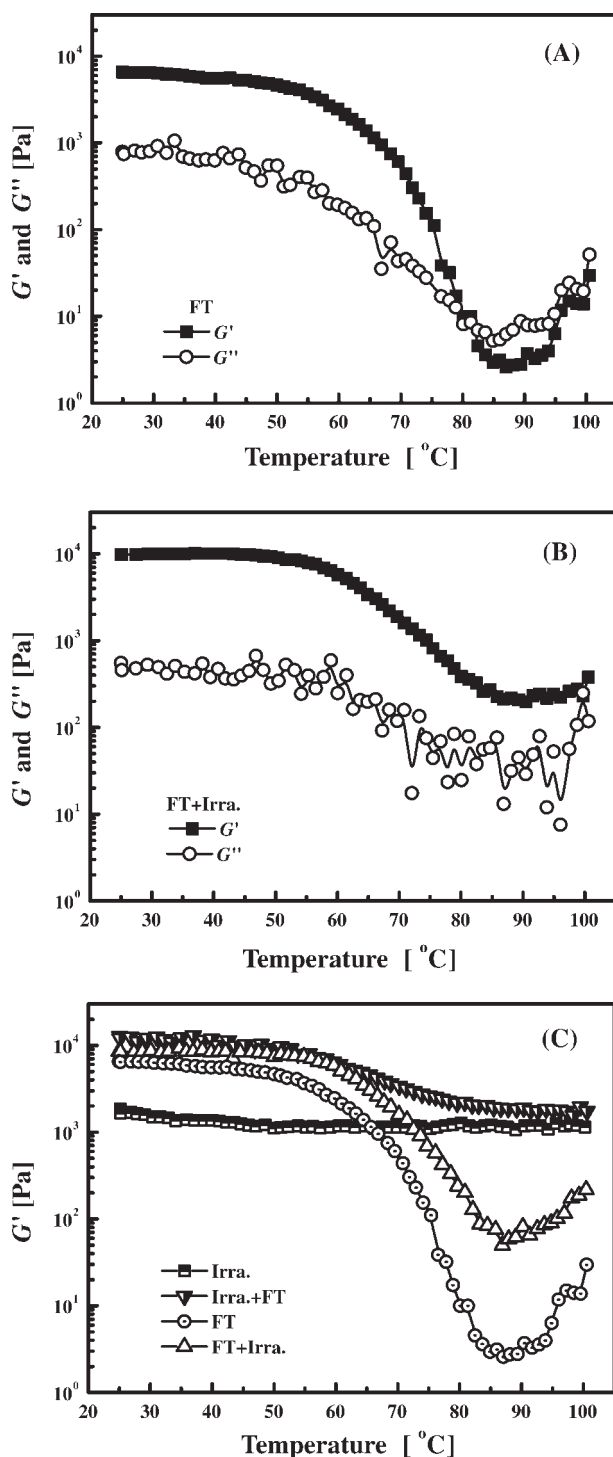
where  $X_t$  is the degree of crystallinity,  $\Delta H$  is the heat required for melting a sample, and  $\Delta H_c$  is the heat required for melting a 100% crystalline PVA sample (138.6 J/g).<sup>22</sup> The degree of crystallinity decreases in the following order: hydrogels made by FT, hydrogels made by FT+Irra., hydrogels made by Irra.+FT, and hydrogels made by Irra. Meanwhile, a gradual decrease in the crystallinity can be observed for hydrogels containing increasing contents of ws-chitosan.

#### ATR-FTIR analysis

The ATR-FTIR spectra of the PVA/ws-chitosan physical blend and hydrogels made by various methods are shown in Figure 4. The strength of the peak at 1141  $\text{cm}^{-1}$  of the hydrogel made by FT is the greatest, whereas that of the hydrogel made by Irra. is the smallest. Some researchers have reported that the absorption peak at 1141  $\text{cm}^{-1}$  of PVA hydrogels arises from a C—C stretching mode and increases with an increasing degree of crystallinity.<sup>23,24</sup> Therefore, the hydrogel made by FT has the largest degree of crystallinity, whereas that made by Irra. has the lowest degree of crystallinity, and this agrees with the DSC results.



**Figure 5**  $G'$ ,  $G''$ , and  $\eta^*$  as a function of frequency for hydrogels containing 7 wt % PVA and 3 wt % ws-chitosan and made by FT and Irra, respectively.



**Figure 6** (A,B)  $G'$  and  $G''$  at 1 rad/s as a function of temperature for hydrogels made by FT and FT+Irra., respectively, and (C)  $G'$  at 1 rad/s as a function of temperature for hydrogels made by various methods. The composition of the hydrogels was 7 wt % PVA and 3 wt % ws-chitosan.

### Rheological behavior

In Figure 5, the storage modulus ( $G'$ ), loss modulus ( $G''$ ), and viscosity ( $\eta^*$ ) of the hydrogels are charted as a function of frequency.  $G'$  and  $G''$  exhibit a pro-

nounced plateau in the investigated frequency range, and  $G'$  is considerably larger than  $G''$  for each sample. This implies that a well-developed network has been formed in the hydrogel.  $\eta^*$  of the hydrogels decreases with increasing shear frequency in the investigated frequency range, and this obviously shows shear-thinning behavior. All the other hydrogels show the same rheological behavior. The hydrogel made by FT exhibits larger  $G'$ ,  $G''$ , and  $\eta^*$  values than that made by Irra. This indicates that the former hydrogel is stiffer than the latter.

The gel-sol transition can be studied through rheological measurements.<sup>25,26</sup> The temperature dependence of  $G'$  and  $G''$  is compared for hydrogels made by FT [Fig. 6(A)] and FT+Irra. [Fig. 6(B)]. In each case,  $G'$  is larger than  $G''$  at low temperatures, and this confirms that the samples behave as solid-like gels. However, above 50 °C, an increase in temperature results in a reduction in both  $G'$  and  $G''$ . The reduction in  $G'$  is followed by a crossover with  $G''$  for the hydrogel made by FT [Fig. 6(A)], and this indicates that at high temperatures, the physical network dissolves, and the system exhibits liquid-like behavior.<sup>27,28</sup> The gel-sol transition temperature is approximately 80 °C, and this agrees with the result found by Hatakeyema et al.<sup>29</sup> However, for the hydrogel made by FT+Irra.,  $G'$  is considerably higher than  $G''$  even at high temperatures [Fig. 6(B)]. This is due to the chemical crosslinking networks formed by irradiation. Figure 6(C) shows that the thermal stability of the hydrogel made by Irra.+FT is greatly improved in comparison with those made by FT and FT+Irra.  $G'$  of the hydrogel made by Irra. changes little in the range of 25–100 °C because the chemical crosslinking networks are stable against temperature. At about 80 °C, the value of  $G'$  for the hydrogel made by Irra.+FT is similar to that for the hydrogel made by Irra. but is much larger than that for the hydrogel made by FT+Irra. This implies that hydrogels made by Irra. and Irra.+FT have similar chemical crosslinking densities which is much larger than that of the hydrogel made by FT+Irra. The lower chemical crosslinking density of the hydrogel made by FT+Irra. implies that the physical crosslinking formed during the FT process inhibits the formation of chemical crosslinking during the irradiation process, and this agrees with the conclusion of our former study.<sup>21</sup>

### CONCLUSIONS

PVA/ws-chitosan hydrogels were made by a combination of Irra. and FT. The thermal and rheological behaviors of these hydrogels were compared with the behaviors of those prepared by pure irradiation and pure FT. The thermal analysis shows that the melting and first degradation temperatures and the

degree of crystallinity of the hydrogels made by FT followed by irradiation were higher than those of the hydrogels made by irradiation followed by FT and decreased with increasing ws-chitosan content. Irradiation reduced the crystallinity of PVA, whereas FT increased it. All the hydrogels exhibited shear-thinning behavior in the frequency range of 0.2–100 rad/s. Hydrogels made by FT exhibited a gel–sol transition at about 80°C, whereas those made by irradiation showed no temperature dependence up to 100°C. The larger  $G'$  value at high temperatures for hydrogels made by irradiation followed by FT in comparison with the  $G'$  value of those made by FT followed by irradiation indicates that the FT process inhibits the formation of chemical crosslinking.

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