

Thermal Characteristics of Poly(vinyl alcohol) and Poly(vinylpyrrolidone) IPNs

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels based on poly(vinyl alcohol) (PVA) and 1-vinyl-2-pyrrolidone (VP) were prepared by radical polymerization using 2,2-dimethyl-2-phenylacetophenone (DMPAP) and methylene bisacrylamide (MBAAm) as initiator and crosslinker, respectively. The thermal characterization of the IPNs was investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA). Depressions of the melting temperatures of PVA segments in IPNs were observed with increasing VP

content via the DSC. The DEA was employed to ascertain the glass transition temperature (T_g) of IPNs. From the result of DEA, IPNs exhibited two T_g s indicating the presence of phase separation in the IPN. The thermal decomposition of IPNs was investigated using TGA and appeared at near 270°C. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1844–1847, 2002

Key words: thermal properties; poly(vinyl alcohol); poly(vinyl pyrrolidone); IPN

INTRODUCTION

Numerous applications of polymer hydrogels have been described recently.^{1–3} Studies of such hydrogels are interesting not only from chemical point of view, but they are also carried out in chemical engineering, pharmaceuticals, food, biochemistry, biology, and medicine. On the other hand, the interpenetrating polymer networks (IPNs) for hydrogels have also attracted many investigations. The IPNs, by their original definition,⁴ are composed of two (or more) chemically distinct components held together ideally and solely by their permanent mutual entanglements. There are two basic synthetic routes for IPNs; sequential and simultaneous IPNs.⁵ Poly(vinyl alcohol) (PVA)/poly(vinylpyrrolidone) (PVP) hydrogels in the present study are prepared by the simultaneous IPN method.

PVA is a water-soluble polyhydroxy polymer, employed in practical applications because of its easy preparation, excellent chemical resistance, and physical properties, and because it is completely biodegradable.⁶ The chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications, because of their permeability, biocompatibility, and biodegradability.^{7–10}

PVP has been used in a very large number of various applications due to its remarkable properties (hydrophilicity/polarity, complexing ability, biocompatibility, etc.).^{11,12} The PVP is one of the most frequently investigated classes of materials for use in medicine and in other applications interfacing with biological systems.^{13–16}

On the other hand, over the last decades the miscibility of blends of PVA and PVP has been intensively investigated.^{17–20} Cassu and Felisberti²¹ studied the secondary relaxations of the PVA/PVP blends by dynamic mechanical analysis (DMA). The characterization of PVA and PVP polymers, as well as PVA/PVP hydrogel prepared by irradiation, were reported by Razzak et al.²²

In our previous study²³ we synthesized novel polyallylamine/chitosan IPN hydrogels by UV irradiation and reported the thermal characteristics of IPNs composed of polyallylamine and chitosan. In the present article, we prepared PVA/PVP IPN hydrogels by chemical crosslinking with methylene bisacrylamide (MBAAm). The thermal properties of the IPNs were investigated via differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA).

EXPERIMENTAL

Materials

PVA with average of molecular weight of 124,000–186,000 and degree of saponification of 99 mol % was supplied by Aldrich Chemical Co. Inc. Also, 1-vinyl-

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TABLE I
Sample Composition and Designation

Sample designation ^a	PVA ^a (wt %)	VP (wt %)
PV11	50	50
PV31	75	25
PV51	83	17

^a The PVA used has an average molecular weight of 1.24×10^5 – 1.86×10^5 .

2-pyrrolidone (VP), 2,2-dimethyl-2-phenylacetophenone (DMPAP) and MBAAm were purchased from Sigma Aldrich, USA, and were used for hydrogels preparation without further purification. All other chemical reagents used were of extra pure grade.

Preparation of the IPNs

PVA was added to deionized water and heated at 80°C for 1 h to make a solution containing 10 wt % PVA by weight. VP was mixed with 1 wt % of DMPAP and 0.5 mol % of MBAAm in tetrahydrofuran (THF)/isopropyl alcohol (IPA) (10 : 1 v/v). Herein, DMPAP, and MBAAm were used as initiator and crosslinker, respectively. This mixture was added to PVA aqueous solution, and after completely mixing for 30 min, the mixed solutions were poured into Petri dishes, stored in a box, and exposed to a 450 W UV lamp (Ace Glass Co. USA) placed above the mold at a height of 20 cm for 1 h under N₂ atmosphere. The irradiated samples were dried in the oven at 50°C for 12 h. Three hydrogels were prepared from 1 : 1, 3 : 1, and 5 : 1 weight ratios of PVA/VP, denoted as PV11, PV31, and PV51, respectively. The designation of each sample is listed in Table I. After 12 h, dry film was obtained and washed with distilled water to remove any unreacted materials that were not incorporated into the network.

Characterization

The DSC was performed with a DSC 2010 instrument (TA Instruments) in a nitrogen atmosphere. The thermal properties of the IPNs were determined using two scans. The first heating scan, which was conducted to eliminate the residual water and solvent, was carried out at a heating rate of 20°C/min from room temperature up to 150°C and kept at the latter temperature for 5 min. The second scan was carried out at a heating rate of 10°C/min from 0 to 250°C. The thermal decomposition was carried out with a thermogravimetric analyzer (TA Instruments SDT 2960 Simultaneous DTA-TGA), by heating from room temperature to 700°C, at a heating rate of 20°C/min under a nitrogen flow. Dielectric measurements were conducted to observe the glass transition temperature (T_g) and relaxation behavior of IPN. Measurements of dielectric con-

stant, ϵ' , and dielectric loss factor, ϵ'' , were carried out using the dielectric analysis (TA Instruments DEA 2970) with a parallel plate ceramic sensor. The experiment was done from 0 to 250°C at a rate of 3°C/min with dry nitrogen adjusted to a flow rate of 50 mL/min. Applied frequencies were 100, 500, and 1 kHz.

RESULTS AND DISCUSSION

Figure 1 shows the DSC melting thermograms of PVA, PVP, and IPNs. PVA reveals a relatively large and sharp melting endothermic peak at 227°C, while a very weak and broad melting endothermic peak of PVP (not shown here) observed at around 250°C in this work. On the other hand, weak and broad melting endothermic peaks of PVA segments in the IPNs, caused by crosslinking reaction and IPN formation, appeared between 200 and 220°C. As the content of PVP increased, the endothermic curve of PVA segments became broader, and its peak shifted to lower temperatures. The endothermic peak of PVA segments decreased rapidly and disappeared for the samples containing over 50 wt % PVP. The depression of the melting temperature and the peak broadening indicates that the ordered association of the PVA molecules was decreased by the presence of PVP. In the PVP and the IPNs, it becomes difficult to detect the peaks clearly in the DSC curve. A glass transition temperature (T_g) of PVP and IPNs could not be determined from DSC analysis in this work. In general, the T_g of crosslinked polymer is difficult to detect using the ordinary DSC technique, while the dielectric study of such complex systems can reveal details of the phase structure and provide information about modes of motion in the IPN.^{24,25} Dielectric measurements often reveal more details of the various relaxation processes than the relatively broader features observed in dynamic mechanical spectroscopy, volume dilatometry, and DSC.^{26,27} Therefore, in this study, the more sensitive dielectric analysis (DEA) was employed to determine the T_g of each component in the IPNs.

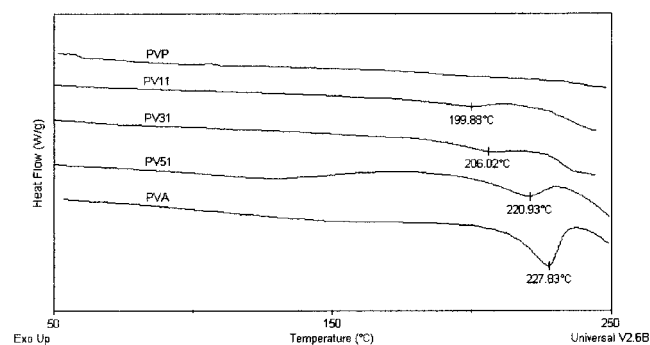


Figure 1 DSC melting endotherms of PVA, PVP, and IPNs.

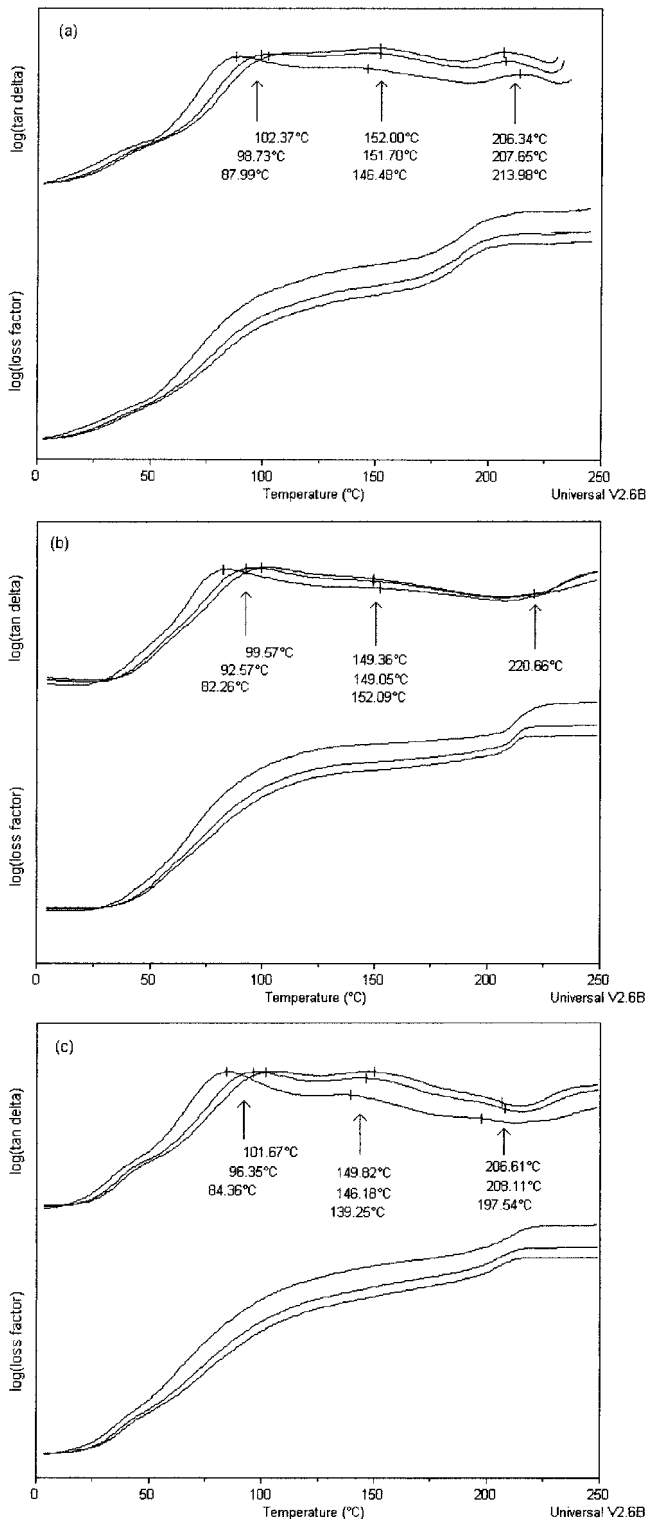


Figure 2 Dielectric analysis of the IPNs; (a) PV11, (b) PV31, and (c) PV51.

Figure 2 exhibits the $\log(\tan \delta)$ to $\log(\text{loss factor})$ ($\log \epsilon''$) of the IPNs, depending on temperature at 100, 500, and 1 kHz. Three relaxation peaks appeared at around 90, 150, and 210°C in the IPN. Abraham et al.²⁸ reported that the T_g of PVP appeared at 177°C. Ac-

cordingly, the temperature of the maximum $\tan \delta$, around 150°C, is considered to be the T_g of PVP segments in IPNs. Another maximum $\tan \delta$ temperature at 210°C was thought to be the T_m of PVA segments in IPN, as was seen from DSC analysis. The lowest maximum $\tan \delta$ temperature was taken to be the T_g of PVA segments in IPNs. In fact, the T_g of PVA itself was 80°C from DSC analysis by Razzak et al.²² DEA showed that the T_g in IPNs was higher than that of PVA and nearly shifted up to 90°C. In Figure 2(a), the peak in each of the $\tan \delta$ curves between 87 and 102°C, is assigned to a T_g of PVA in PV11 IPN. The T_g of PVA segment becomes higher as the DEA measurement frequency is increased. This is a general consequence attributed to a decrease in the steric effects hindering the micro-Brownian motion of the main chain.²⁹ A slight decrease in T_g of PV31 [Fig. 2(b)] and PV51 [Fig. 2(c)] compared to PV11 may be due to the lower degree of crosslinking. From the result of DEA, the IPN exhibited two T_g s, indicating the presence of phase separation in the IPN.

The thermal stability and thermal decomposition of PVA, PVP, and IPNs were investigated using TGA, and are given in Figure 3. PVA and PVP exhibited a single large peak, indicating a single degradation mechanism, while the IPNs exhibited two peaks, whose shapes and positions were dependent on composition. PVP was more thermal stable than PVA, because the peaks of PVP appeared at a higher temperature than those of PVA. As the content of PVA increased, the peak of PVP in IPN decreased rapidly and disappeared for PV51.

CONCLUSIONS

To prepare a polymeric biomedical material, IPN hydrogels composed of PVA and PVP were synthesized by UV irradiation and their properties were studied. The thermal properties of the IPNs were investigated via DSC, DEA, and TGA. From the result of DSC, PVA revealed a relatively large and sharp melting endothermic peak at 227°C, while a very weak and broad

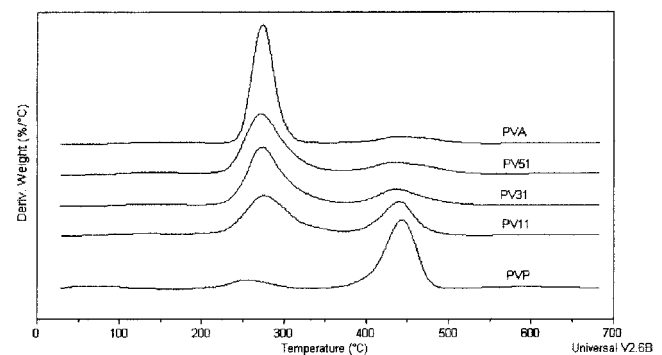


Figure 3 Derivative of the thermogravimetric thermograms of PVA, PVP, and IPNs.

melting endothermic peak of PVP was observed at 250°C. On the other hand, weak and broad melting endothermic peaks of PVA segments in the IPNs appeared between 200 and 220°C. From the result of DEA, three relaxation peaks appeared at around 90, 150, and 210°C in the IPNs, and the IPNs exhibited two T_g s, indicating the presence of phase separation in the IPN. From the result of TGA, PVA and PVP exhibited a single large peak, indicating a single degradation mechanism, while the IPNs exhibited two peaks, whose shapes and positions were dependent on composition. The thermal decomposition of IPNs appeared at near 270°C.

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