Thermal Characteristics of Interpenetrating Polymer Networks Composed of Poly(vinyl alcohol) and Poly(N-isopropylacrylamide)

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ABSTRACT: Interpenetrating polymer networks (IPNs) composed of poly(vinyl alcohol) (PVA) and poly(N-isopropylacrylamide) (PNIPAAm) were prepared by the sequential-IPN method. The thermal characterization of the IPNs was investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA). Depression of the melting temperature (T_m) of the PVA segment in IPNs was observed with increasing PNIPAAm content using DSC. DEA was employed to ascertain the glass-transition temperature (T_g) of IPNs. From the result of DEA, IPNs exhibited two T_g values, indicating the presence of phase separation in the IPNs. The thermal decomposition of IPNs was investigated using TGA and appeared at near 200°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 881–885, 2003

Key words: poly(vinyl alcohol) (PVA); poly(N-isopropylacrylamide); interpenetrating networks (IPN); thermal properties; glass transition

INTRODUCTION

Polymer hydrogel transitions (volume changes) occur in response to changing environmental conditions such as temperature,[1] pH,[2] solvent composition,[3] and electrical stimuli.[4] Polymer hydrogels are three-dimensional, hydrophilic, elastic crosslinked networks capable of imbibing large amounts of water or biological fluids. Studies of such polymer hydrogels are not only found in chemistry, but are also found in chemical engineering, pharmaceuticals, food processing, biochemistry, biology, and medicine.[5–7] Meanwhile, the interpenetrating polymer networks (IPNs) for hydrogels have also been the subject of many investigations. The IPNs, by their original definition,[8] are composed of two or more chemically distinct components held together ideally and solely by their permanent mutual entanglements.

Poly(vinyl alcohol) (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.[5] Chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biocompatibility, and biodegradability.[9–12]

Poly(N-isopropylacrylamide) (PNIPAAm) is noteworthy for exhibiting a lower critical solution temperature (LCST) at around 32°C in aqueous solution; that is, it dissolves in water below the LCST and precipitates from solution above the LCST. PNIPAAm hydrogels with a crosslinked structure are characterized by a temperature-responsive nature in which they swell in water below the LCST and shrink in water above the LCST.[13]

Many researchers have reported on polymer hydrogel types. Gudeman and Peppas[14,15] reported innovative pH- and temperature-responsive IPN hydrogels composed of PVA and poly(acrylic acid) (PAAc). Kim et al.[16,17] reported on drug release behaviors of electrically responsive PVA/PAAc IPN hydrogels under an electric stimulus. Nishi et al.[18] and Yao et al.[19] studied pH as another external signal to stimuli-sensitive hydrogels. Hoffman et al.[20] synthesized fast temperature responsive, macroporous PNIPAAm gels. Okano et al.[21,22] prepared thermosensitive PNIPAAm hydrogels having PNIPAAm chains grafted on the backbone of the PNIPAAm network.

In previous studies,[23,24] polyallylamine/chitosan IPNs and PVA/poly(vinyl-pyrrolidone) IPNs were

synthesized and their thermal properties were studied. In the present study, IPNs composed of PVA and PNIPAAm were prepared by the sequential-IPN method. The thermal properties of the IPNs were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA).

EXPERIMENTAL

Materials

PVA with an average molecular weight of 1.24–1.86 $\times$ 10^5 and a degree of saponification of 99 mol %, N-isopropylacrylamide (NIPAAm), N,N'-methylene-bisacrylamide (MBAAm), and ammonium peroxydisulfate (APS) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Glutaraldehyde (GA; 25 wt % solution in water), hydrochloric acid (HCl), and N,N,N',N'-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chemical Co. (Japan). These were used for IPN preparation without further purification and all other chemical reagents used were extra pure grade.

Preparation of the PVA/PNIPAAm IPNs

Crosslinked PVA (c-PVA) was prepared by dissolving PVA deionized water and heating it at 80°C for 2 h to make a 5 wt % aqueous solution. PVA was crosslinked using GA and HCl as a crosslinking agent and catalyst, respectively.

Crosslinked PNIPAAm (c-PNIPAAm) was prepared by dissolving NIPAAm in deionized water at room temperature for 30 min to make a 5 wt % aqueous solution. NIPAAm was polymerized with APS, TMEDA, and MBAAm as an initiator, accelerator, and crosslinking agent, respectively, at room temperature for 24 h under N_2 atmosphere.

IPNs were prepared by the sequential-IPN method. PVA was dissolved in deionized water and heated at 80°C for 2 h to make a 5 wt % aqueous solution. The NIPAAm monomers were then mixed. PVA was crosslinked in the presence of NIPAAm, using GA and HCl as a crosslinking agent and catalyst, respectively. Then NIPAAm was polymerized with APS, TMEDA, and MBAAm as an initiator, accelerator, and crosslinking agent, respectively, at room temperature for 24 h under N_2 atmosphere. The contents of the initiator and accelerator were 1 wt % of monomer and the contents of the crosslinking agent were 3 mol % of monomer. Three IPNs were prepared from 50 : 50, 65 : 35, and 80 : 20 weight ratios of PVA/NIPAAm, denoted as IPN1, IPN2, and IPN3, respectively. The designation of each sample is listed in Table I. The dry film was washed with distilled water to remove any

TABLE I
Sample Composition and Designation

Sample designation	PVA (wt %)	NIPAAm (wt %)
c-PNIPAAm	0	100
IPN1	50	50
IPN2	65	35
IPN3	80	20
c-PVA	100	0

nonreactive materials that were not incorporated into the network.

Characterization

DSC was performed with a DSC 2010 instrument (TA Instruments, New Castle, DE) in a nitrogen atmosphere. The TA DSC 2010 was calibrated using indium (melting point, 156.6°C; heat of fusion, $\Delta H_m/M$ = 28.51 J/g). Hermetically sealed aluminum pans were used in the measurement of thermal properties by DSC. The thermal properties of the IPNs were determined using two scans. The first heating scan, which was conducted to eliminate residual water and solvent, was carried out at a rate of 20°C/min from room temperature 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. Thermal decomposition was carried out with a thermogravimetric analyzer [TA Instruments SDT 2960 Simultaneous TGA-DSC (DTA)], by heating it from room temperature to 700°C at a heating rate of 20°C/min under a nitrogen flow. Before the themogravimetric experiment, calibrations of the TA SDT 2960, TGA weight, and temperature were carried out. The temperature calibration was carried out using zinc (m.p., 419°C). Dielectric measurements were conducted to observe the glass-transition temperature (T_g) and relaxation behavior of IPNs. Measurements of the dielectric constant ϵ' and the dielectric loss factor ϵ'' were carried out using DEA (TA Instruments DEA 2970) with a parallel plate ceramic sensor. Calibrations of DEA 2970, temperature, and instrument were carried out. The temperature calibration was performed during a sensor calibration step of the experiment. Instrument calibration was performed using the DEA calibration software program. The experiment was done from 0 to 300°C at a rate of 3°C/min with dry nitrogen adjusted to a flow rate of 50 mL/min. Applied frequencies were 100, 200, and 300 Hz.

RESULTS AND DISCUSSION

Figure 1 shows the DSC melting thermograms of c-PVA, c-PNIPAAm, and IPNs. c-PVA reveals a relatively large and sharp melting endothermic peak at
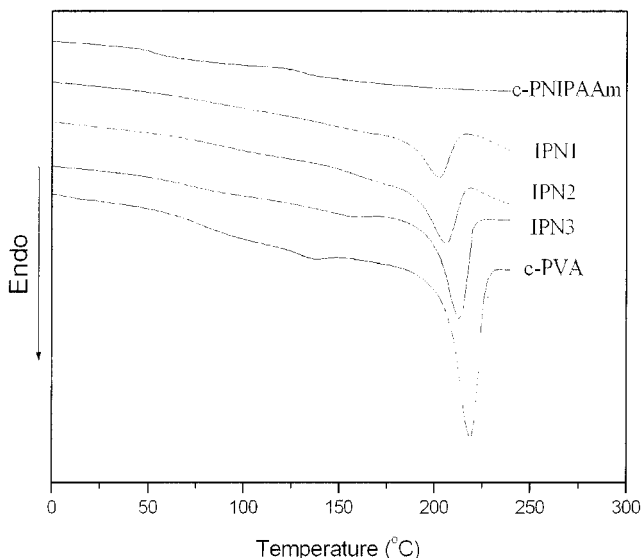
Figure 1 DSC melting endotherms of c-PVA, c-PNIPAAm, and IPNs.

219°C, whereas the melting endothermic peak of c-PNIPAAm was not observed. Meanwhile, weak and broad melting endothermic peaks of PVA segments in the IPNs, caused by crosslinking reactions and IPN formation, appeared between 202 and 213°C. As the content of PNIPAAm increased, the endothermic peak of PVA segments became broader and its peak shifted to lower temperatures and decreased rapidly. The depression of the melting temperature (T_m) and the peak broadening indicate that the ordered association of the PVA molecules was decreased by the presence of PNIPAAm. In the c-PNIPAAm and the IPNs, it becomes difficult to detect the peaks of T_g and T_m clearly in the DSC curve. A T_g of c-PNIPAAm and IPNs could not be determined from DSC analysis. In general, the T_g of crosslinked polymer is difficult to detect using the ordinary DSC technique, whereas the dielectric study of such complex systems can reveal details of the phase structure and provide information about modes of motion in the IPN. Dielectric measurements often reveal more details of the various relaxation processes than the relatively broader features observed in volume dilatometry and DSC.[25,26] Therefore, the more sensitive DEA was employed to determine the T_g of each component in the IPNs.

Figure 2 exhibits the log(tan δ) to log(loss factor) (log ϵ'') of the IPNs depending on temperature at 100, 200, and 300 Hz. Three relaxation peaks appeared at around 130, 200, and 260°C in the IPNs. In Figure 2, the maximum temperature in each of the tan δ curves between 260 and 266°C was assigned to the T_g of PNIPAAm segments in IPNs. Another maximum temperature in each tanδ curves between 192 and 217°C was thought to be the T_m of PVA segments in IPN as was seen from DSC analysis. The lowest maximum tan
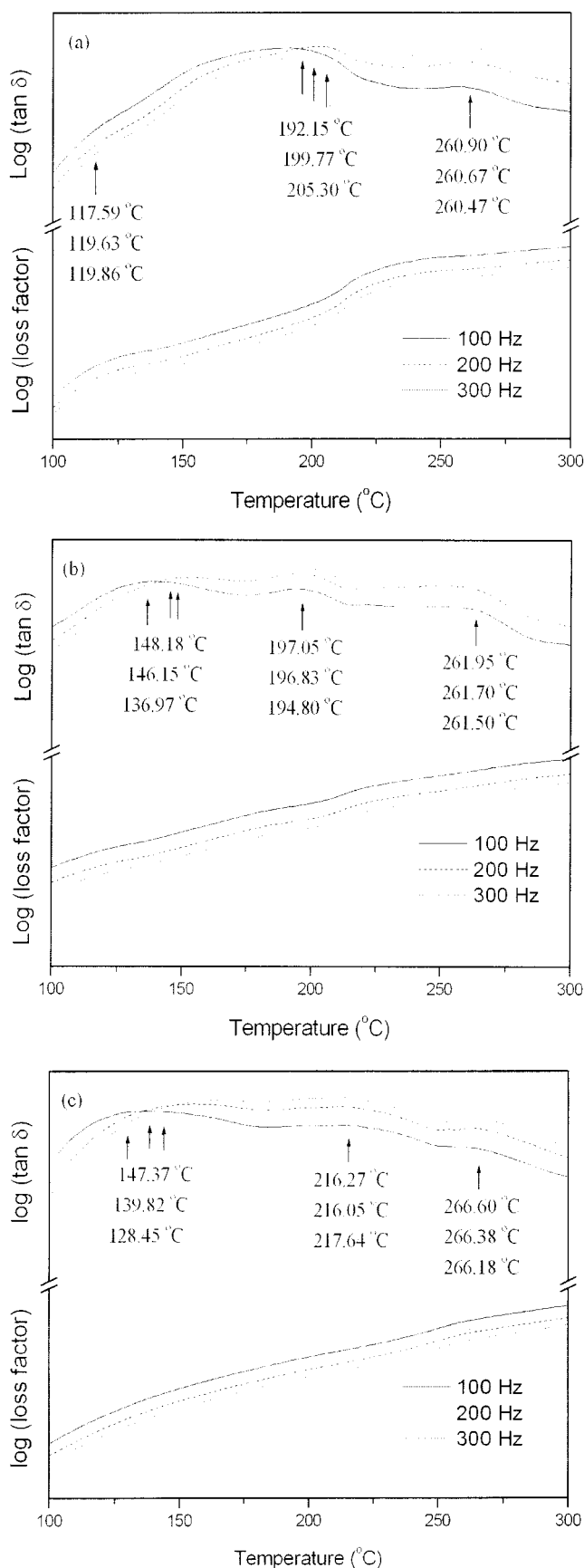

Figure 2 Dielectric analysis of the IPNs: (a) IPN1, (b) IPN2, and (c) IPN3.

δ 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 found in previous work.[24] Meanwhile, it was reported that T_g and T_m of PVA are 85°C and 232–267°C, respectively.[27] DEA showed that the T_g in IPNs was higher than that of PVA and nearly shifted up to about 130°C. In Figure 2(b), the peak in each of the tan δ curves between 137 and 148°C is assigned to a T_g of PVA segment in IPN2. The T_g of the 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.[28] A slight increase in T_g of IPN2 [Fig. 2(b)] and IPN3 [Fig. 2(c)] compared to that of IPN1 [Fig. 2(a)] may be attributed to a higher degree of crosslinking. From the results of DEA, the IPN exhibited two T_g values, indicating the presence of phase separation in the IPN.

The thermal stability and thermal decomposition of c-PVA, c-PNIPAAm, and IPNs were investigated using TGA and are given in Figure 3. c-PVA and c-PNIPAAm exhibited a single large peak, indicating a single degradation mechanism, whereas the IPNs exhibited two peaks, whose shapes and positions were dependent on composition. c-PNIPAAm was more thermally stable than c-PVA because the peak of c-PNIPAAm appeared at a higher temperature than that of c-PVA. As the content of PVA increased, the peak of c-PNIPAAm in IPN decreased rapidly. Figure 4 also shows the thermogravimetric curves of c-PVA, c-PNIPAAm, and IPNs. For c-PVA and c-PNIPAAm, it was observed that no significant degradation occurred before 200 and 250°C, respectively. The total degradation of c-PVA and c-PNIPAAm was observed in a single stage and was completed by 460 and 470°C,
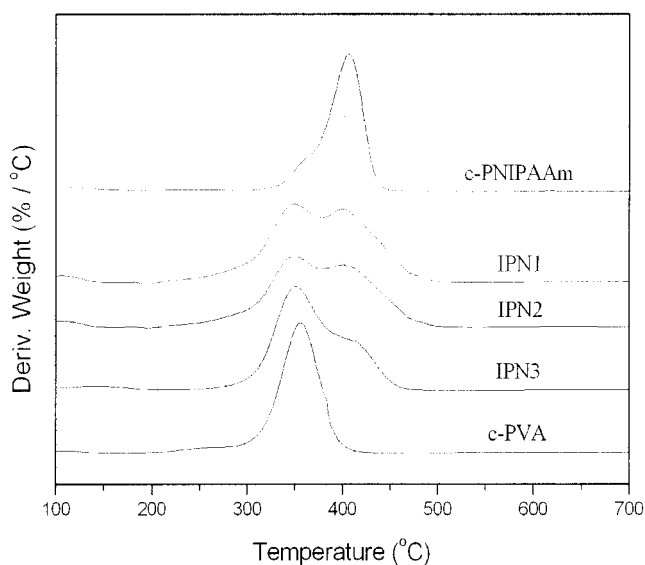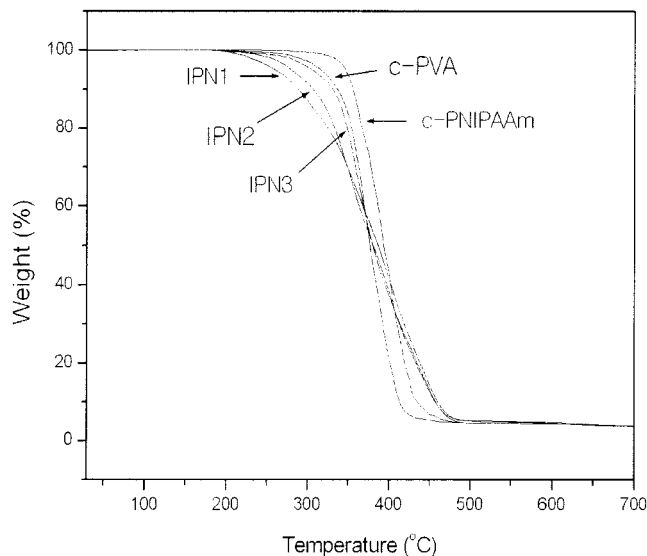

Figure 4 Weight loss of TGA thermograms of c-PVA, c-PNIPAAm, and IPNs.

respectively. For IPNs, degradation took place in two stages. The first stage began at 200°C and the second stage, up to 380°C, was completed by 490°C. The first stage and the second stage could be attributed to the PVA segments and PNIPAAm segments in the IPN, respectively.

CONCLUSIONS

The thermal properties of the PVA/PNIPAAm IPNs were investigated using DSC, DEA, and TGA. From the results of DSC, c-PVA revealed a relatively large and sharp melting endothermic peak at 219°C, whereas the melting endothermic peak of c-PNIPAAm was not observed. Meanwhile, weak and broad melting endothermic peaks of PVA segments in the IPNs appeared between 202 and 213°C. From the results of DEA, three relaxation peaks appeared at around 130, 200, and 260°C in the IPNs, and the IPNs exhibited two T_g values, indicating the presence of phase separation in the IPN. From the result of TGA, c-PVA and c-PNIPAAm exhibited a single large peak, indicating a single degradation mechanism, whereas the IPNs exhibited two peaks, whose shapes and positions were dependent on composition. The thermal decomposition of IPNs appeared at near 200°C.

Figure 3 Derivative of the thermogravimetric thermograms of c-PVA, c-PNIPAAm, and IPNs.

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