

Thermal Characteristics of IPNs Composed of Polyallylamine and Chitosan

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels composed of polyallylamine and chitosan were synthesized by radical polymerization using 2,2-dimethyl-2-phenylacetophenone (DMPAP) and methylene bisacrylamide (MBAAm) as initiator and crosslinker, respectively. The IPNs thus obtained were characterized by using Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA). The melting temperatures of IPNs were observed with increasing chitosan content by DSC. 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 by TGA and appeared at near 270 °C. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1956–1960, 2002

Key words: chitosan; polyallylamine; interpenetrating polymer network (IPN); thermal properties

INTRODUCTION

Polymer hydrogels are three-dimensional, hydrophilic, polymeric networks capable of imbibing large amounts of water or biological fluids. The networks are composed of homopolymers or copolymers and are insoluble because of the presence of chemical or physical crosslinks, such as entanglements or crystallites.¹ Polymer gels have been studied for applications in a variety of fields, such as in chemical engineering, medicine, pharmaceuticals, and food and agriculture.^{2–4} On the other hand, the use of natural polymers, such as proteins and polysaccharides, for the biomedical

application has also attracted many investigations. However, these naturally abundant materials also exhibit a limitation in their reactivity and processability. Many studies have attempted to overcome these shortcomings by chemical and physical alteration of natural polymers. Among these investigations, hydrogel types and interpenetrating polymer network (IPN) structures have been noted by several researchers.^{5–11}

Yao et al.^{12, 13} reported chitosan/polyether semi-IPN hydrogels crosslinked by glutaraldehyde and their swelling kinetics. Ramarai and Radhakrishnan¹⁴ studied the swelling and release of bromothymol blue using an IPN based on gelatin and polyacrylamide. Lee et al. reported semi-IPN composed of β -chitin and poly(ethylene glycol) macromer (PEGM),^{15, 16} and IPN hydrogels based on PEGM and chitosan.¹⁷ Sun et al.^{18,19} reported hydrogel fiber composed of chitosan

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and poly(propylene glycol). Park et al.²⁰ reported poly(vinyl alcohol)/methylcellulose blend hydrogels crosslinked by glutaraldehyde in the presence of HCl.

Chitosan is a deacetylated derivative of chitin that is poly((1,4)-2-acetamido-2-deoxy- β -D-glucose). Chitin has been known as a potentially useful biopolymer produced in a huge amount in nature. Although chitin is naturally abundant, it has a limited application because of its poor solubility and reactivity. On the other hand, chitosan appears to be more useful for biomedical applications and dehydrations of aqueous solutions than chitin because it has both hydroxyl and amino groups that can be modified easily. Chitosan has been widely studied and applied in the biomedical field because of its good biocompatibility, biodegradability, nontoxicity, and easy availability.

In the present paper, we prepared chitosan/polyallylamine IPN hydrogels by chemical crosslinking with methylene bisacrylamide (MBAAm). The polyallylamine is a cationic polymer. The thermal properties of the IPNs were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA).

EXPERIMENTAL

Materials

The chitosan was purchased from Jakwang Company, Korea. Polyallylamine, 2,2-dimethyl-2-phenylacetophenone (DMPAP) and MBAAm were purchased from Sigma Co., USA and Aldrich Co., USA, respectively, and were used for hydrogels preparation without further purification. All other chemical reagents used were of extra pure grade.

Preparation of the IPNs

Polyallylamine was mixed with 1 wt % DMPAP and 0.5 mol % MBAAm in tetrahydrofuran (THF). Herein, DMPAP and MBAAm were used as initiator and crosslinker, respectively. Chitosan was dissolved in 1 wt % acetic acid aqueous solution to prepare 2 wt % chitosan solution. Later, 2 wt % chitosan solution was added to the polyallylamine reaction mixture. This mixture was heated at 65 °C for 3 h. The weight ratios of the chitosan-to-polyallylamine mixture were adjusted to 1:1, 3:1,

Table I Sample Composition and Designation

Sample Designation ^a	Chitosan (wt %)	Polyallylamine (wt %)
CPAA-1	50	50
CPAA-2	75	25
CPAA-3	83	17

^a The polyallylamine used has an average molecular weight of 6.5×10^4 .

and 5:1, respectively. The designation of each sample is listed in Table I. The solutions were poured into a Petri dish, and dried at 50 °C for 12 h. After 12 h, the dry film was obtained and washed with deionized water to remove any unreacted materials that were not incorporated into the network.

Characterization

Fourier transform infrared (FT-IR) spectroscopy (Bruker Model EQUINOX 55) was used to confirm the structure of IPNs. 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 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. To determine the crystallization temperature, the samples were heated to 250 °C, kept at this temperature for 5 min, and then cooled at a rate of 10 °C/min. 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 constant, ϵ' , and dielectric loss factor, ϵ'' , were carried out with a dielectric analyzer (TA Instruments DEA 2970) with a parallel plate ceramic sensor. The experiment was done from -60 to 200 °C at a rate of 3 °C/min with dry nitrogen adjusted to a flow rate of 50 mL/min. Applied frequencies were 100 Hz, 500 Hz, and 1 kHz.

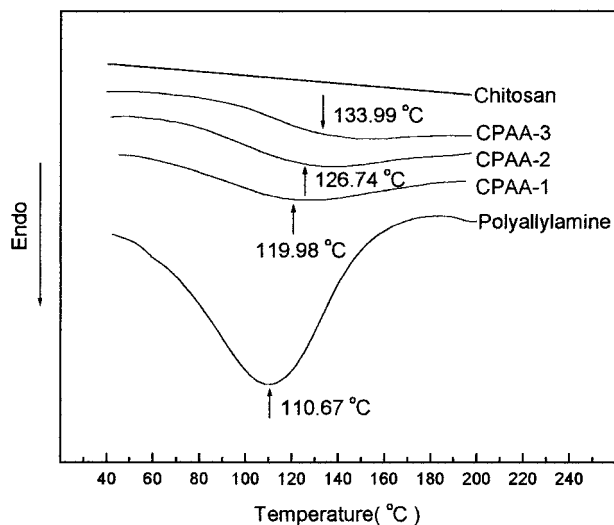


Figure 1 DSC melting endotherms of polyallylamine, chitosan, and IPNs.

RESULT AND DISCUSSION

The IPNs composed of chitosan and polyallylamine were synthesized by radical polymerization using DMPAP and MBAAm as initiator and crosslinker. In FT-IR spectra, characteristic peaks of chitosan/polyallylamine IPNs were located at $3500\text{--}3450\text{ cm}^{-1}$ for the stretching peaks of the —NH_2 and hydroxyl groups, 1700 cm^{-1} for the carbonyl group, and 1650 and 1550 cm^{-1} for amides I and II, respectively.

The DSC melting thermograms of polyallylamine, chitosan, and IPN hydrogels are shown in Figure 1. Polyallylamine reveals a relatively large and sharp melting endothermic peak at $110\text{ }^\circ\text{C}$, whereas chitosan had no endothermic curve. On the other hand, weak and broad melting endothermic peaks of polyallylamine segments in the IPN, caused by crosslinking reaction and IPN formation, appeared between 120 and $134\text{ }^\circ\text{C}$. As the content of chitosan increased, the endothermic curve of polyallylamine became broader and its peak shifted to higher temperatures. In the chitosan and the IPNs it becomes difficult to detect the peaks clearly in the DSC curve. It could be thought that a rigid chitosan chain prevents detection of peaks by DSC. The peak broadening indicates that the ordered association of the polyallylamine molecules was decreased by the presence of chitosan.

We also carried out a cooling process to obtain the peak of the crystallization temperature, but the peaks of the chitosan and the IPNs were not

observed. On the other hand, the melting temperature (T_m) of chitosan network cannot be determined by DSC analysis. Although chitosan has crystalline regions, its T_m is not found because of its rigid-rod polymer backbone and strong inter- and/or intramolecular hydrogen bonding.²¹ This behavior is frequently detected in many polysaccharides, such as cellulose and chitin derivatives.²² In general, the T_g of crosslinked polymer is difficult to detect using the ordinary DSC technique. Therefore, in this study, the more sensitive dielectric analysis (DEA) was employed to determine the T_g of each component in the IPNs. The $\log(\tan \delta)$ -to-loss factors ($\log \epsilon''$) of the IPNs, depending on temperature at 100 Hz , 500 Hz , and 1 kHz , are shown in Figure 2. Three relaxation peaks appeared at ~ 50 , 120 , and $180\text{ }^\circ\text{C}$ in the IPN. The T_g of chitosan appears at $>150\text{ }^\circ\text{C}$.²³ Accordingly, the temperature of the maximum $\tan \delta$, around $180\text{ }^\circ\text{C}$ is considered to be the T_g of chitosan. Another maximum $\tan \delta$ temperature at $120\text{ }^\circ\text{C}$ was thought to be the T_m of polyallylamine segments in IPN, as seen from DSC analysis. The lower maximum $\tan \delta$ temperature was taken to be the T_g of polyallylamine segments in IPN hydrogels. In fact, the T_g of polyallylamine itself was $-26\text{ }^\circ\text{C}$, as determined by DSC analysis in this work. DEA showed that the T_g in IPNs was much higher than that of polyallylamine and shifted up to nearly $50\text{ }^\circ\text{C}$. The maximum $\tan \delta$ temperature of polyallylamine in CPAA-1 is lower than that in CPAA-3. 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 chitosan, polyallylamine, and IPNs were investigated by TGA and are given in Figure 3. Polyallylamine and chitosan exhibited a single large peak, indicating a single degradation mechanism, whereas the IPNs exhibited two peaks, whose shapes and positions were dependent on composition. Polyallylamine was more thermally stable than chitosan, as indicated by the appearance of peaks of polyallylamine at a higher temperature than those of chitosan. As the content of chitosan increased, the peak of polyallylamine in IPN decreased rapidly and disappeared for CPAA-3. Also, the peak temperature decreased as the content of chitosan increased.

CONCLUSIONS

IPNs based on chitosan and polyallylamine were synthesized by radical polymerization using

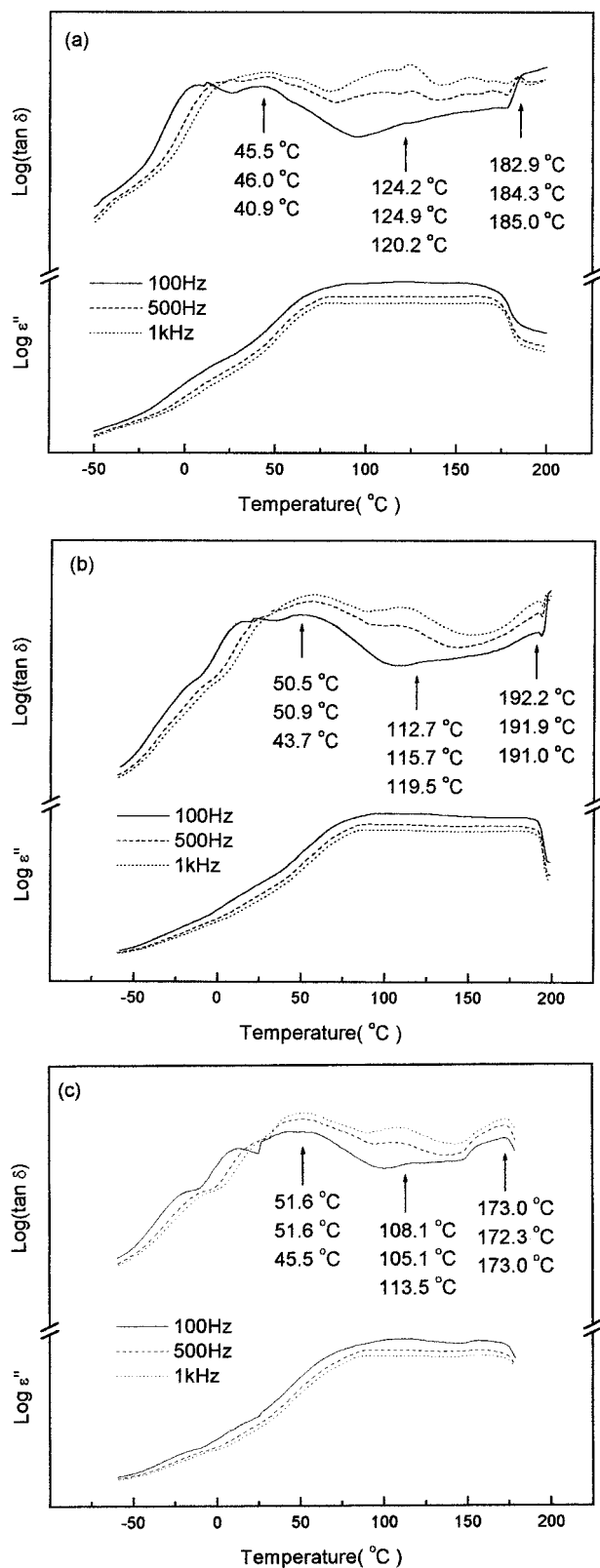


Figure 2 Dielectric analysis of the IPN hydrogels: (a) CPAA-1; (b) CPAA-2; and (c) CPAA-3.

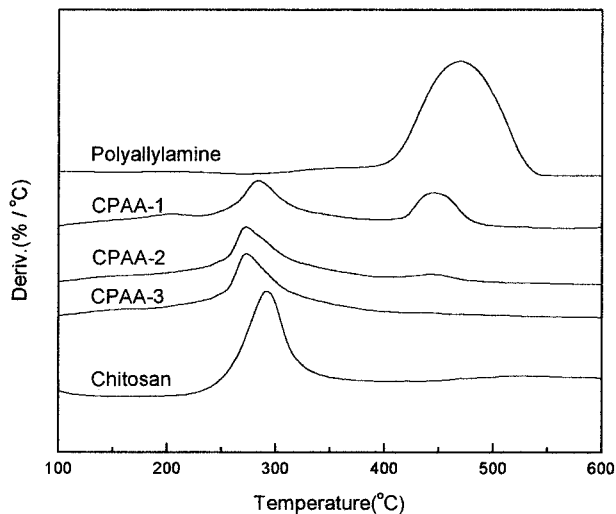


Figure 3 Derivative of the TGA thermograms of the IPN hydrogels.

DMPAP and MBAAm as initiator and crosslinker, respectively. The thermal properties of the IPNs were investigated by DSC, DEA, and TGA. The results of DSC indicate a relatively large melting endothermic peak at 110 °C for polyallylamine, but no endothermic curve for chitosan. On the other hand, weak and broad melting endothermic peaks of polyallylamine segments in the IPNs appeared between 120 and 134 °C. We also carried out a cooling process to obtain the peak of the crystallization temperature, but the peaks of the chitosan and the IPNs were not observed. DEA results revealed three relaxation peaks at ~50, 120, and 180 °C in the IPNs, and the IPNs exhibited two T_g s indicating the presence of phase separation in the IPN. TGA revealed that polyallylamine and chitosan showed 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 ~270 °C.

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