

Thermal Properties of Poly(vinyl alcohol)/Poly(diallyldimethylammonium chloride) Interpenetrating Polymer Networks

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ABSTRACT: Interpenetrating polymer networks (IPNs) constructed with poly(vinyl alcohol) (PVA) and poly(diallyldimethyl ammonium chloride) (PDADMAC) using a sequential IPN method were prepared. The thermal characterization of the IPNs was investigated by differential scanning calorimetry (DSC), dielectric analysis (DEA), and thermogravimetric analysis (TGA). Decreases in the melting temperature of PVA segments in IPNs were observed with increasing PDADMAC content using DSC. DEA was employed to

ascertain glass transition temperature of IPNs. The thermal decomposition of IPNs was investigated using TGA, and thermal decomposition of IPNs could be decelerated by changing PVA content. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1346–1349, 2003

Key words: thermal properties; interpenetrating polymer network (IPN); pdy(vinyl alcohol); diallyldimethylammonium chloride

INTRODUCTION

An Interpenetrating polymer network (IPN) is defined as a combination of two polymers that has the two following characteristics: first, one of the polymers must be synthesized or crosslinked in the immediate presence of the other, and second, the combination must provide the possibility of effectively producing advanced multicomponent polymeric systems with new property profiles.^{1–4} Recently, IPNs have gained widespread acceptance in industrial applications and newer IPNs showing better applications such as medicine, pharmaceuticals and food are emerging day by day.⁵

Diallyldimethyl ammonium chloride (DADMAC) is a water-soluble quaternary ammonium compound that can be cyclopolymerized to its corresponding polymer and is used in water treatment, paper manufacturing, mining, and in biology. Crosslinked poly(diallyldimethyl ammonium chloride) (PDADMAC) is a polyelectrolyte gel that is able to absorb several hundred times its volume of water, but has the fatal

defect of poor wet strength due to the high charge density along the polymer chains.^{6,7}

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.⁸ Chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biocompatibility, and biodegradability.^{9–12}

In the present article, PVA/PDADMAC IPNs using a sequential IPN method were prepared. The thermal properties of the IPNs were investigated using differential scanning calorimetry (DSC), dielectric analysis (DEA), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

PVA, with the average molecular weight 8.50×10^4 – 1.46×10^5 , *N,N'*-methylenebisacrylamide (MBAAm), DADMAC (65 wt % solution in water), and ammonium peroxydisulfate (APS) were purchased from Aldrich Chemical Co., Milwaukee, WI. Glutaraldehyde (25 wt % solution in water) (GA), hydrochloric acid (HCl) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chemical Co., Japan. All other chemicals were reagent grade and used without further purification.

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Preparation of IPN

IPNs were prepared using a sequential-IPN method. PVA was dissolved in deionized water and heated at 80°C for 2 h to make a 5 wt % aqueous solution. Next, the DADMAC monomers were mixed. PVA was crosslinked in the presence of DADMAC using GA and HCl as a crosslinking agent and catalyst, respectively. Next, the DADMAC was polymerized with APS, TMEDA, and MBAAm as an initiator, accelerator, and crosslinking agent, respectively, at room temperature for 36 h. The contents of the initiator and the accelerator were 1 wt % of monomer and the contents of crosslinking agent were 3 mol % of monomer. The detail composition and designation of PVA/PDADMAC IPNs are listed in Table I. To remove nonreactive agents, the films were dipped into the deionized water for 2 days and dried in a 40°C vacuum oven for 1 week.

Characteristics

DSC was performed with a DSC 2010 instrument [TA Instruments with a refrigerated cooling accessory (RCS)] in a nitrogen atmosphere. The thermal properties of the IPNs were determined using two scans. The first heating scan, which was conducted to eliminate residual water, 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. 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. 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, 200, and 500 Hz. The thermal decomposition was carried out with a thermogravimetric analyzer (TA Instruments SDT 2960 Simultaneous TGA-DSC), by heating the sample from room temperature to 700°C at a rate of 20°C/min under a nitrogen flow.

TABLE I
Composition and Designation of IPNs

Sample	Feed composition PVA : PDADMAC (wt %)
IPN51	5 : 1
IPN31	3 : 1
IPN11	1 : 1

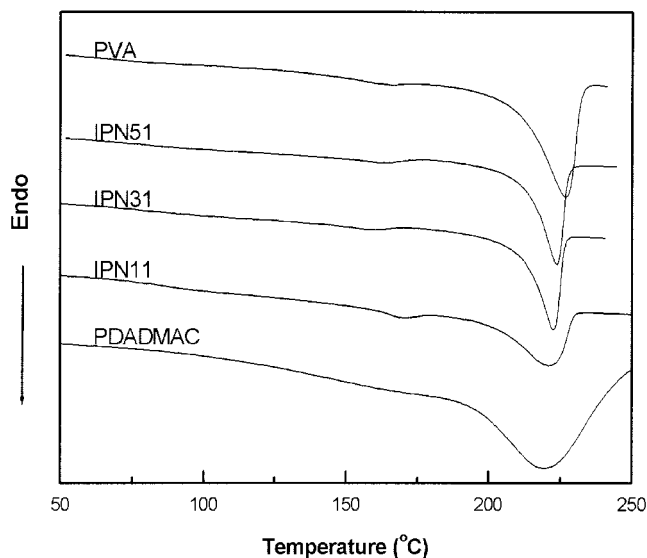


Figure 1 DSC melting endotherms of PVA, PDADMAC, and IPNs.

RESULTS AND DISCUSSION

Figure 1 shows the DSC melting thermograms of PVA, PDADMAC, and IPNs. PVA reveals a relatively large and sharp melting endothermic peak at 227°C, while a very broad melting endothermic peak of PDADMAC occurred at around 219°C. On the other hand, weak and broad melting endothermic peaks of PVA and PDADMAC segments, caused by a crosslinking reaction and IPN formation, appeared between 220 and 225°C. As the content of PDADMAC increased, the endothermic curve of PVA segments became broader and its peak shifted to a lower temperature. 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 PDADMAC.

In general, the T_g of a crosslinked polymer is difficult to detect using the ordinary DSC technique. The dielectric study of such complex systems can reveal details of the phase structure and provide information about modes of motion in the IPNs. 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.¹³ More sensitive DEA was employed to determine the T_g of PVA in the IPNs. Figure 2 exhibits the $\log(\tan \delta)$ to $\log(\text{loss factor})$ ($\log \epsilon''$) of the IPNs depending on temperature at 100, 200, and 500 Hz. Two relaxation peaks of PVA appeared at around 80 and 220°C in the IPNs. Accordingly, the temperature of the maximum $\tan \delta$, around 220°C was thought to be the T_m composed of PVA and PDADMAC segments in IPNs as seen from DSC analysis. The lowest maximum $\tan \delta$ temperature at 80°C was taken

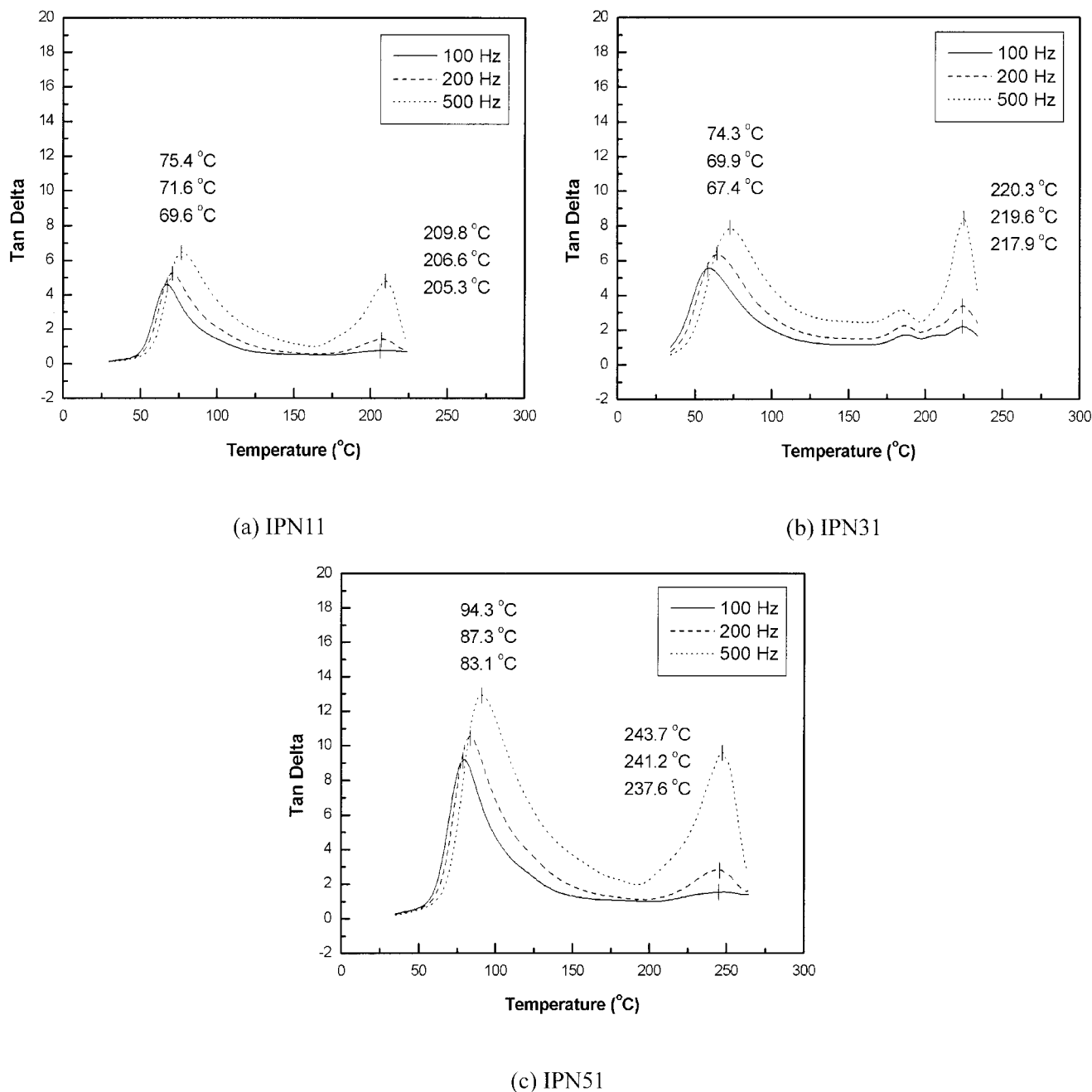


Figure 2 Dielectric analysis of the IPNs; (a) IPN11, (b) IPN31, and (c) IPN51.

to be the T_g of PVA segments in IPNs. In fact, 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.¹⁴

The thermal stability and thermal decomposition of IPNs were investigated using TGA and are shown in Figure 3. Around 5% of the weight loss in the vicinity of 100°C may be attributed to the elimination of moisture from the samples. As shown in Figure 3, it can be

said that the thermal decomposition of IPNs could be decelerated by changing PVA content.

CONCLUSIONS

IPNs composed of PVA and PDADMAC were synthesized and their thermal properties were studied. The thermal properties of the IPNs were investigated using DSC, TGA, and DEA. From the results of DSC and DEA, weak and broad melting endothermic peaks of PVA and PDADMAC segments appeared between

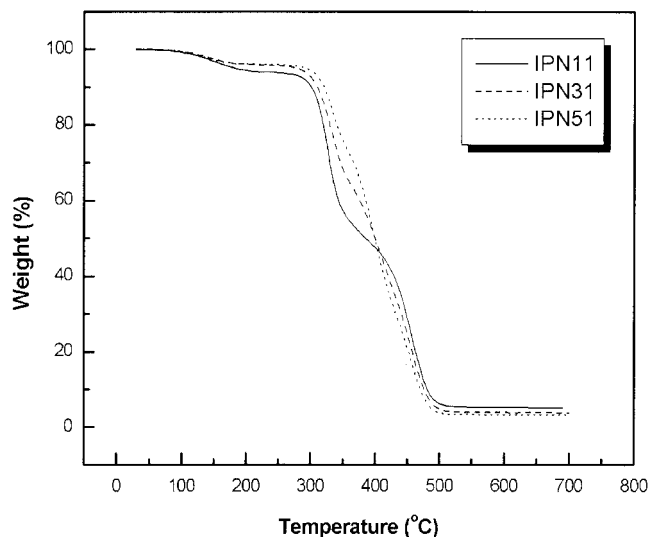


Figure 3 Thermogravimetric thermograms of IPNs.

220 and 225°C, and two relaxation peaks appeared at around 80 and 220°C, indicating the T_g of PVA and PDADMAC segments in IPNs. The thermal degrada-

tion of IPNs could be decelerated by changing PVA content in TGA.

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