

# Thermal Characteristics of IPNs Composed of Poly(propylene glycol) and Poly(acrylic acid)

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**ABSTRACT:** Interpenetrating polymer networks (IPNs) based on poly(propylene glycol) (PPG) and poly(acrylic acid) (PAAc) were prepared by UV irradiation and characterized using fourier transform infrared (FTIR), differential scanning calorimetry (DSC), dielectric analysis (DEA), and thermogravimetry (TGA). The glass transition temperatures ( $T_g$ s) of these IPNs exhibited a relatively higher tem-

perature with an increased PAAc content. The decomposition temperature of PAAc is lower than that of PPG. PAAc affects the thermal stability of IPN more than PPG. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2570–2574, 2003

**Key words:** interpenetrating networks (IPN); thermal properties

## INTRODUCTION

IPNs are defined as “a combination of two or more polymers in network form, that are synthesized in juxtaposition.”<sup>1</sup> They can also be described as crosslinked polymer networks held together by permanent entanglements. The networks are held by “topological bonds,” essentially without covalent bonds between them.<sup>2–5</sup> By definition, an IPN’s structure is obtained when at least one polymer network is synthesized and/or crosslinked independently in the immediate presence of another. As long as the reacting ingredients are blended thoroughly during synthesis, thermodynamic incompatibility can be overcome due to the permanent interlocking of network segments. IPNs with limited phase separation are obtained. It has been reported that polymeric materials with improved mechanical properties can be obtained via IPN’s structures.<sup>6</sup>

PAAc has a very high charge density based on carboxyl groups, which can also be suitable as crosslinking sites; therefore, it has polyelectrolyte properties. PAAc have wide applications because of those properties. Lee et al. reported PAAc/PVA IPN hydrogels crosslinked by UV irradiation and their swelling kinetics, electric stimulus, and permeation of solutes.<sup>7–9</sup> PAAc is known to form a complex structure

with polyoxyethylene (POE) in the IPN form. PAAc/POE IPNs show that swelling-deswelling and mechanochemical reactions proceed reversibly for full IPNs, but irreversibly for the semi-IPNs upon changing pH. It was also reported that PAAc/poly(*N,N*-dimethyl acrylamide) IPN hydrogels showed upper critical solution temperature behavior due mainly to the presence of PAAc.<sup>10</sup> Poly(propylene glycol) (PPG) has more hydrophobic polyether than poly(ethylene glycol) (PEG), and has been used in various biomedical areas such as lubricious coating on absorbable sutures and as the soft segment of biocompatible polyurethanes.<sup>11</sup>

In this study, we prepared PPG/PAAc IPNs. The thermal properties of the IPNs were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dielectric analysis (DEA).

## EXPERIMENTAL

### Materials

PPG ( $M_n = 3500$ ) was purchased from Aldrich Chemical Co., Milwaukee, WI, and was dried by azeotropic distillation with benzene. Acryloyl chloride and 2,2-dimethoxy-2-phenylacetophene (DMPA), a photoinitiator, were obtained from Aldrich Chemical Co., and were used without further purification. Acrylic acid (AAc) monomer was purchased from Junsei Chemical Co., Japan, and used after purification with an inhibitor removal column. Methylenebisacrylamide (MBAAm) was used as a crosslinking agent. All other chemicals used were reagent grade and used as purchased without further purification.

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**TABLE I**  
Composition and Designation of IPNs

Sample	PPGM : PAAc (wt %)
PA04	4:0
PA31	3:1
PA22	2:2
PA13	1:3
PA04	0:4

### Synthesis of PPG macromer (PPGM)

Twelve grams (3.2 mM) of the PPG was dissolved into 150 mL of benzene and heated to 80°C. A total of 0.89 mL (3.2 mM) of triethylamine and 0.61 mL (7.5 mM) of acryloyl chloride were added and the reaction mixture was stirred for 3 h at 80°C. After filtering triethylamine · HCl, the macromer were purified by pouring the reaction mixture into a large excess of hexane. A solvent from the filtrate was removed by rotary evaporation. The resulting syrup containing viscous macromer was dried under a vacuum for 1 day.

### Preparation of PAAc/PPG IPNs

The IPNs were prepared by the simultaneous method. PPGM and AAc monomer were dissolved in ethyl alcohol. Then crosslinkers, *N*-vinylpyrrolidone and MBAAm, and initiator, DMPA, were mixed with that solution. The solutions were poured into a circular glass mold and irradiated using a 450-W UV lamp (Ace Glass Co., USA) placed above it at a height of 20 cm for 10–20 min until gelation occurred. The mold was then kept under reduced pressure to evaporate the solvent. After 1 day, a dry film was obtained and was washed to remove unreacted chemicals. The detail composition and designation of PPG/PAAc IPNs are listed in Table I.

### Characterization

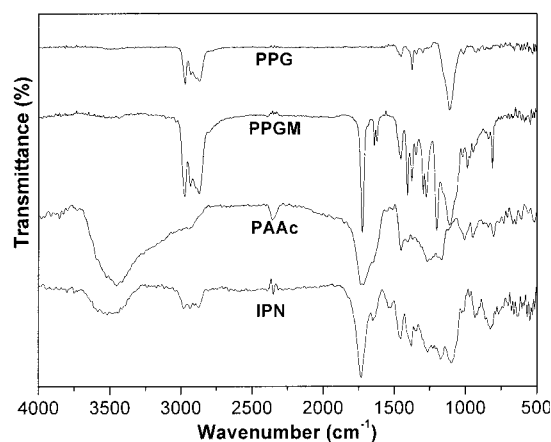
Fourier transform infrared (FTIR) spectroscopy (Nicolet Model Magma IR 550) was used to confirm the hydrogen bondings between PPGM and PAAc in the IPNs. KBr tablets are prepared by grinding the samples with KBr and compressing the samples in the mold. The DSC was performed with a DSC 2010 instrument (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 –50 to 350°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 the IPN. Measurements of the dielectric constant,  $\epsilon'$ , and the dielectric loss factor,  $\epsilon''$ , were carried out using the dielectric analysis (TA Instruments DEA 2970) with a parallel plate ceramic sensor. The experiment was done from –100 to 300°C at rate of 3°C/min with dry nitrogen adjusted to a flow rate of 50 mL/min.

## RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of the PPG, PPGM, PAAc, and PAAc/PPG IPN. A new peak appears at 1730  $\text{cm}^{-1}$  in PPGM that can be attributed to the formation of a carbonyl bond due to the reaction between acryloyl chloride and hydroxyl groups in PPG. Two more peaks at 1629 and 1430  $\text{cm}^{-1}$  indicate the presence of a C=C bond. Meanwhile, the IR spectra of crosslinked PAAc hardly varied from that of PAAc without crosslinking.<sup>12,13</sup> The IR spectrum of PAAc exhibits the characteristic absorption band at 1720  $\text{cm}^{-1}$  due to the C=O stretching vibration of the carboxylic groups. With PPG/PAAc IPN, peaks of the carboxylic acid group and aliphatic ethers appear at both 1713–1718  $\text{cm}^{-1}$  and 2840–2995  $\text{cm}^{-1}$ . This result shows that PPG/PAAc IPNs were synthesized.<sup>8,14</sup>

Figure 2 depicts DSC thermograms obtained for PPG/PAAc IPNs. In the DSC curve of the IPN samples, a single, clear baseline gap reflecting the glass transition of the IPN appears. From the midpoint of the discontinuity in heat flow, the  $T_g$ s of these IPNs were evaluated to be 32.3°C (PA31), 95.6°C (PA13), which was situated between the two  $T_g$  values of the corresponding homopolymer, i.e., –72°C (for PPG), 106°C (for PAAc) in Figure 3. The fact that a single  $T_g$  was obtained in the IPN suggested that there was



**Figure 1** FTIR spectra of PPG, PAAc, PPGM, and PPG/PAAc IPN.

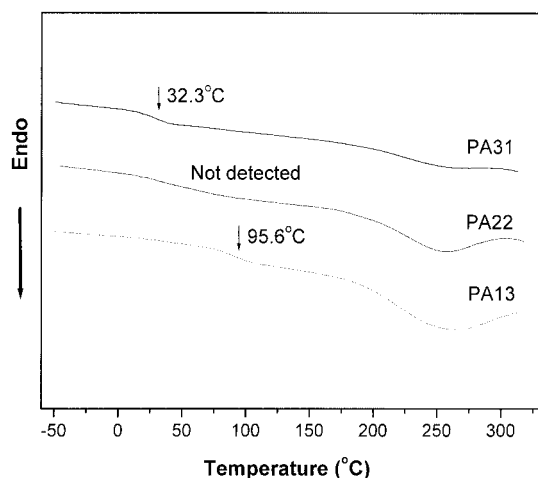


Figure 2 DSC thermogram of PPG/PAAc IPNs.

good interpenetration in IPNs. Looking over the DSC data for the IPNs, we can see a general trend of the  $T_g$  elevation with an increase in PAAc content. Glass transition temperature depends on the molecular structure of the polymer (chain stiffness, number, and bulkiness of the side groups, and the inter- and intramolecular interactions) and on the crosslink density of the polymer.<sup>15,16</sup>

We can find the  $T_g$ s of both PA31 and PA13, but cannot find that of PA22. The  $T_g$  of the 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. Dielectric measurements often reveal more detail of the various relaxation process than the relatively broader features observed in dynamic mechanical spectroscopy, volume dilatometry, and DSC. Therefore, the more sensitive DEA was employed for the  $T_g$  of PA22, which we could not find. Figure 4 exhibits the  $\log(\tan \delta)$  to loss factor ( $\log \epsilon''$ ) of the IPNs depending on temperature at 10 Hz by DEA. The peak of the  $\tan \delta$  curves is assigned to a glass transition temperature of IPNs. Each relaxation peak appeared at 42.6, 45.3, and 96.5 °C in the IPNs. They are similar to  $T_g$  values at the DSC thermogram (PA31 and PA13). We can measure the  $T_g$  of IPNs.

Thermal degradation of PPG/PAAc IPNs is best analyzed with reference to the thermal degradation of the corresponding homopolymers. To this end, the thermograms of PPG and PAAc obtained at a heating rate of 20 °C/min under nitrogen are shown in Figure 5. The thermogram of PPG exhibits only one stage. The region in the range 180–460 °C peaking at 368 °C is associated with depolymerization and decomposition units of the polymer.

The differential thermogravimetric curve of PAAc in Figure 5 shows three degradation steps. The decom-

position stages below 180 °C in the thermograms of PAAc are the result of the evolution of water associated with the polymer, as it has been shown that there is no significant degradation of PAAc at these temperatures under the present thermal treatment.<sup>17</sup>

The degradation stage in the interval 187–326 °C, peaking at 290 °C in the thermogram of PAAc has been interpreted as a result of dehydration and decarboxylation of the polymer.<sup>17,18</sup> Dehydration is the first degradation process of PAAc, and it can proceed by intra- or intermolecular reaction of carboxyl groups. The intramolecular reaction leads to the formation of cyclic structures of 2,4-dimethylglutaric anhydride in the macromolecular chains. It has been stressed that dehydration begins above 170 °C and proceeds at a maximum rate around 250 °C, whereas decarboxylation is evident at temperatures above 200 °C, and becomes increasingly important above 250 °C.<sup>13</sup> At temperatures above 350 °C, bulk decomposition of the polymer residue takes place, giving rise to highly unsaturated structures.<sup>17,18</sup>

Figure 6 is the thermogram of IPNs. Three main decomposition stages are observed. The first one at 40–150 °C, depending on the sample, is associated with loss of water, and the second one at 180–320 °C is dehydration and decarboxylation of PAAc. The third one at 350–500 °C is the region of bulk decomposition of PPG and PAAc. We cannot find a distinct peak between PPG and PAAc. It takes place simultaneously, but the height of peak is different, depending on sample. The decomposition temperature of PAAc is lower than that of PPG, and PAAc affects the thermal stability of IPN more than PPG.

## CONCLUSIONS

IPNs composed of PAAc and PPG were synthesized by UV irradiation and their thermal properties were studied. Hydrophobic PPG diacrylate macromer seg-

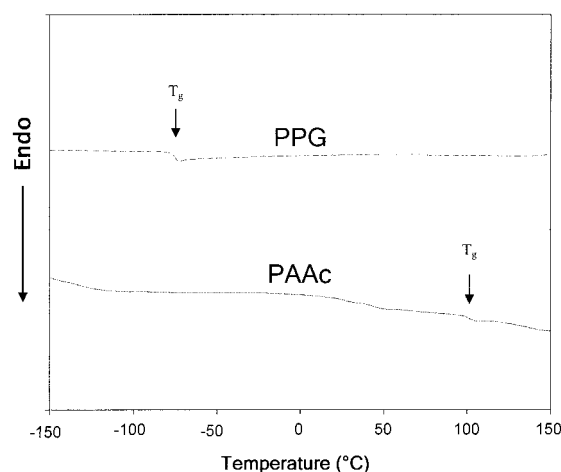


Figure 3 DSC thermogram of pure PPG and PAAc.

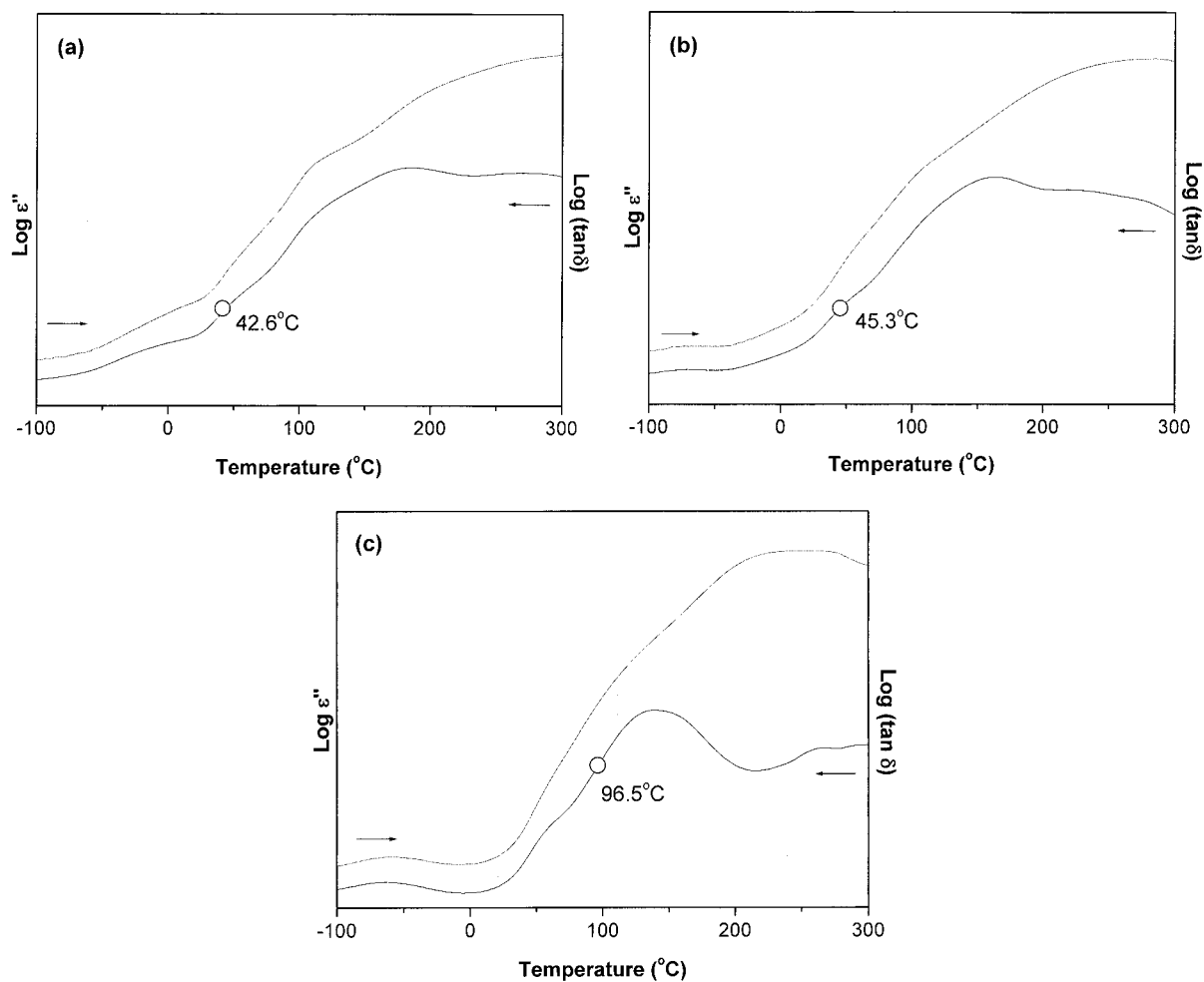


Figure 4 Dielectric analysis of the IPNs; (a) PA31, (b) PA22, (c) PA13.

ments and PAAc segments were crosslinked and formed. The thermal properties of the IPNs were investigated via DSC, DEA, and TGA. From the results of DSC, the  $T_g$ s of IPNs were observed, but the  $T_g$  of PA22 was not observed. Its  $T_g$  is measured by DEA

analysis.  $T_g$ s of these IPNs were evaluated to be about 32.3°C (PA31), 45.3°C (PA22), and 95.6°C (PA13). The  $T_g$ s of these IPNs exhibited a relatively higher temperature with an increased PAAc content. The decomposition temperature of PAAc is lower than that of PPG

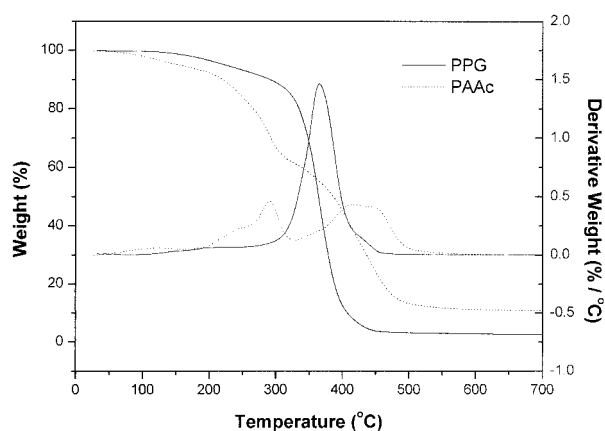


Figure 5 Thermogravimetric thermograms of the PPG and PAAc homopolymers.

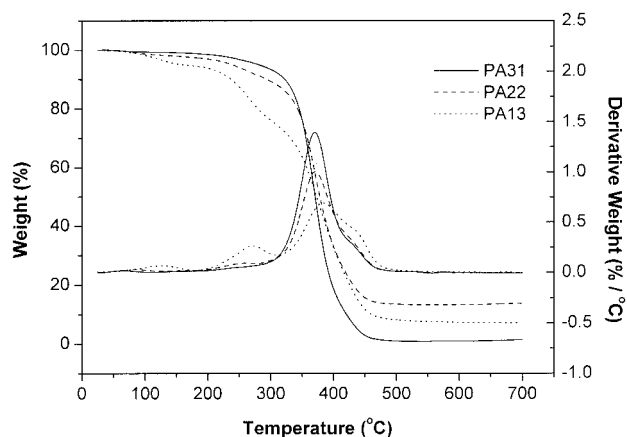


Figure 6 Thermogravimetric thermograms of PPG/PAAc IPNs.

in IPNs. Therefore, PAAc affects the thermal stability of IPNs more than PPG does. The thermal decomposition of IPNs appeared at about 200°C.

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