

Thermal Analysis of Poly(Acrylic Acid)/Poly(Oxyethylene) Blends

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SYNOPSIS

Blends between poly(acrylic acid) and two different poly(oxyethylenes), (1) polyethylene glycol (PEG-1000) and (2) poly(oxyethylene) (20) sorbitan monooleate (Tween-80), were studied by differential scanning calorimetry. The glass transition temperatures, T_g , of the various compositions of these blends were found to follow Fox's equation. At room temperature, blends containing no more than 60% PEG-1000 were amorphous and exhibited only a single glass transition. For these blends with PEG-1000, the glass transition temperatures for the annealed samples were higher than for the quenched samples due to the formation of a PEG crystalline phase. It was also found that addition of an amorphous polymer such as poly(acrylic acid) significantly reduced the degree of crystallinity of a semicrystalline polymer such as poly(oxyethylene). The Tween-80 systems did not show phase separation at room temperature. The compatibility between this poly(acrylic acid) and this poly(oxyethylene) was attributed to hydrogen bonding and to the lower crystalline lattice energy of this poly(oxyethylene) through its effect on its ideal solution solubility.

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INTRODUCTION

Poly(carboxylic acids) such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) form in solution hydrogen-bonding interpolymer complexes¹⁻⁴ with poly(oxyethylenes) (POEs) such as poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO). Blends formed from solvent evaporation of the precipitated complexes have been reported to be thermally sensitive⁵ as well as pH sensitive⁶ due to their hydrogen bonding. Such behavior may have interesting applications for controlled release drug delivery because the swelling of the polymer could be modulated.⁷ Previous studies of this subject, however, have been limited to polybases with long oxyethylene chains. Recently, Lee⁸ reported the formation of polymeric association complexes between PAA and some POEs with low molecular weights. In this study, blends of PAA with

the low-molecular-weight nonionic surfactants PEG-1000 and Tween-80 were investigated. Thermal analysis was used to characterize these blends because the glass transition temperature, T_g , may influence the transport and mechanical properties.

EXPERIMENTAL

Materials

A lightly crosslinked pharmaceutical grade PAA with a molecular weight of 3.0×10^6 (Carbopol-934P, B. F. Goodrich, Cleveland, OH) was used as obtained. PEG with an average molecular weight of 1000 (Carbowax PEG-1000, Union Carbide, Danbury, CT) and the nonionic surfactant, POE (20) sorbitan monooleate (Tween-80, ICI America Inc., Wilmington, DE), with an average molecular weight of 1310 were also used as received.

Preparation of Blends

Blends of varying compositions were prepared by adding PEG-1000 or Tween-80 into the aqueous so-

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lutions of Carbopol-934P. The overall concentrations were 5–10% (w/w) in the white aqueous dispersion. Films were prepared by solvent casting, followed by drying the films in a 60°C oven for 2 days. All samples were placed in a desiccator with anhydrous CaSO₄ for at least 3 days to remove the residual moisture. The final hydrogel was transparent with the physical properties dependent upon the composition. The annealed samples were allowed to crystallize at room temperature for an additional 3 months. The quenched sample was maintained at 65°C for 20 min before being quenched to -100°C by liquid nitrogen contained in the differential scanning calorimetry (DSC). The glass transition temperature was measured immediately.

DSC

Thermal analysis was conducted with a DSC (TA4000/DSC-30, Mettler, Hightstown, NJ) calibrated for temperature by the melting points of indium, lead, and zinc and for heat flow with indium. The heating rate was 10°C/min, and the heating scans were from -100 to 150°C. Liquid nitrogen was used to cool the sample cell. Five- to 25-mg samples were placed in the aluminum crucible sample pan. For the glass transition temperature measurements,

the midpoint temperatures of the transition region were reported.

RESULTS AND DISCUSSION

DSC thermograms for Carbopol-934P/Tween-80 and Carbopol-934P/PEG-1000 systems are presented in Figures 1 and 2, respectively. A single glass transition temperature, an indication of a compatible polymer blend, was observed. The compatibility between PAA and POE was presumably due in part to the hydrogen bonding between the carboxylic acids in the PAA and the ether units in the POE.^{1-4,8} POE behaved as a plasticizer as exhibited by the decrease with POE composition of the glass transition temperature of the PAA. Moreover, the glass transition temperatures of compatible polymer blends can be predicted from the T_g of its pure components by the well-known Fox⁹ equation:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

where W_1 is the mass fraction composition of the blend for species 1 and T_{g1} is the glass transition

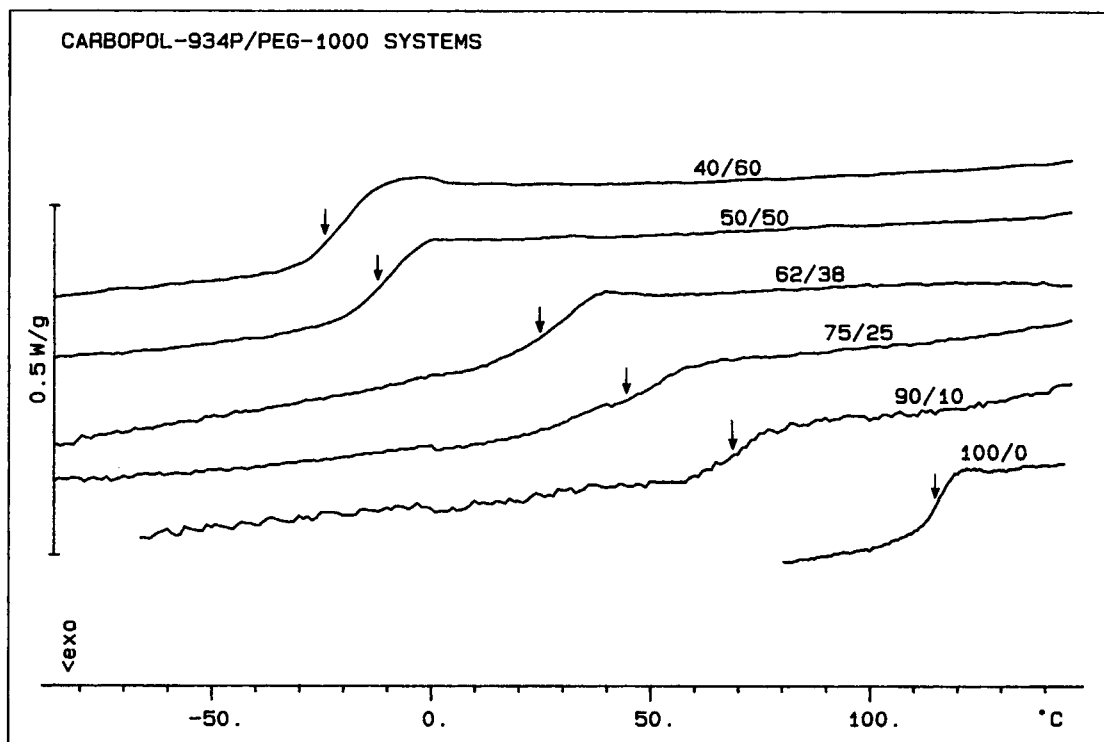


Figure 1 DSC thermograms for various Carbopol-934P/PEG-1000 compositions (w/w).

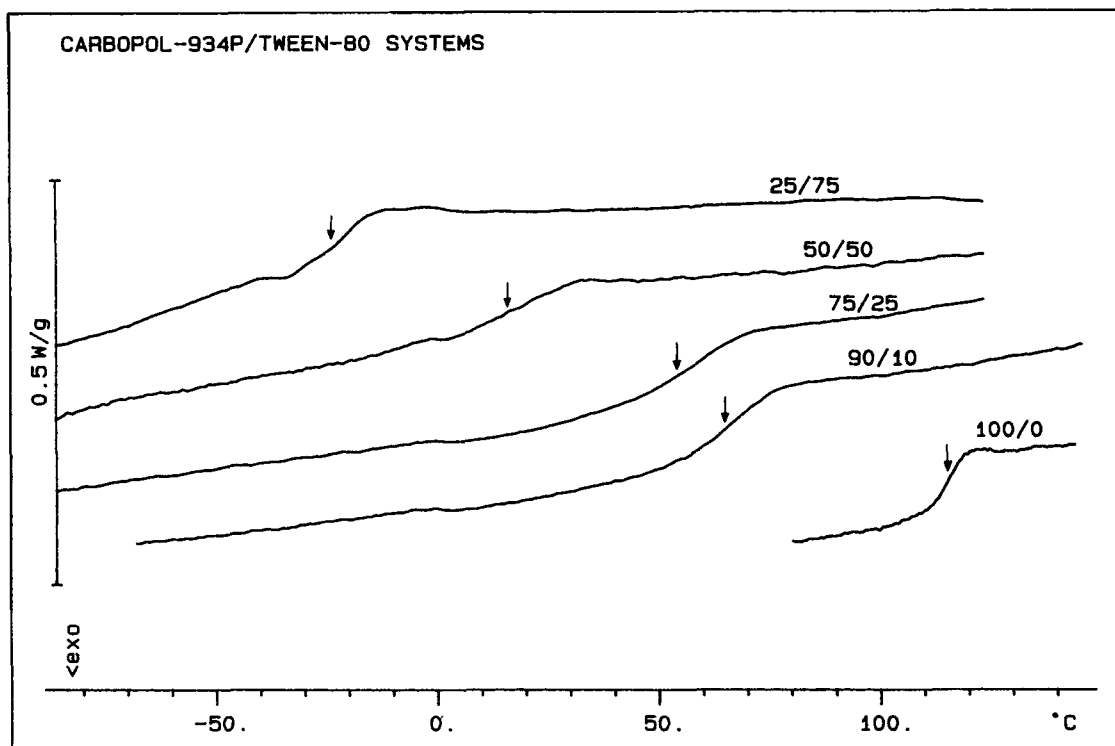


Figure 2 DSC thermograms for various Carbopol-934P/Tween-80 compositions (w/w).

temperature of the pure component 1. Figure 3 shows comparisons of the measured glass transition temperatures with those calculated from Fox's equation. For the 25/75 and 10/90 Carbopol-934P/PEG-1000 samples, the data for the quenched samples are presented in these figures. It was observed that the glass transition temperatures of these blends agreed quite well with the predictions of the Fox equation.

Smith et al.¹ reported a maximum glass transition temperature at 10% PEO composition for a PAA/PEO system. The T_g for PAA at 75°C reported in their study was significantly lower than other literature data (103°C,⁹ 106°C.¹¹) Moisture content may have affected their glass transition temperature measurement of PAA. Sorption of moisture up to 15% weight of PAA at 30°C and 70% relative humidity has been reported.¹² The effect of water on the T_g of hydrophilic polymers is significant due to the low glass transition temperature of water ($T_g = -138^\circ\text{C}$.¹³)

Figure 4 compares thermograms of a quenched (curve A) and an annealed sample (curve B) of 25/75 Carbopol-934P/PEG-1000. Recrystallization of PEG was observed in the quenched sample during the heating scan, and the glass transition temperature at -46°C was consistent with the T_g of a com-

pletely amorphous polymer blend with a composition of 25/75 Carbopol-934P/PEG-1000. However, for the sample that had been annealed at room temperature for 3 months crystallization of the excess PEG-1000 was apparent, and the melting point was consistent with that of neat PEG-1000. Recrystallization was not observed in the DSC heating scans, and the glass transition temperature at -19°C was significantly higher than that measured for the quenched sample of the same composition. It was speculated that two phases were present in the Carbopol-934P/PEG-1000 system: One was a domain formed primarily by the compatible blend and the other was the excess semicrystalline PEG-1000. Similar behavior was found by Smith et al.¹ for PAA blended with a high-molecular-weight PEO. The extent of the additional POE phase can be calculated from the heat of fusion in the DSC thermogram. The fraction of free semicrystalline PEG was estimated from the following equation:

$$X = \frac{\Delta H}{W_2 \Delta H_2} \quad (2)$$

where ΔH is the heat of fusion (J/g) for the blend,

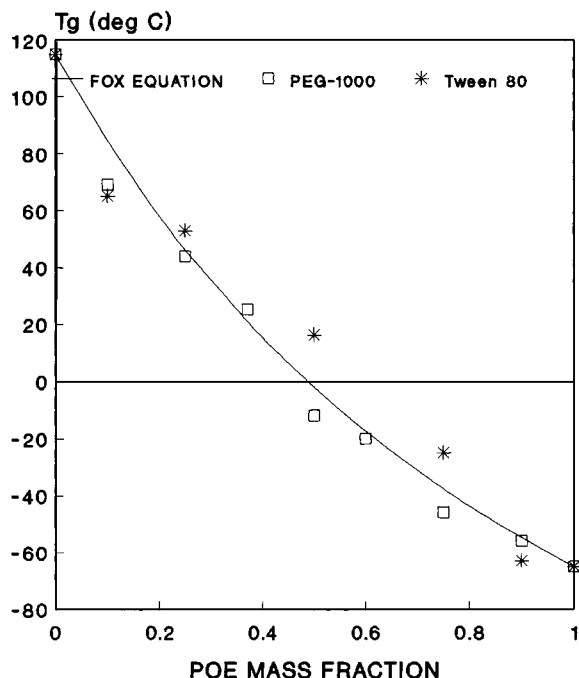


Figure 3 T_g vs. composition for Carbopol-934P/PEG-1000 and Carbopol-934P/Tween-80 systems.

ΔH_2 is the heat of fusion (J/g) measured for pure PEG-1000 at its melting point, and W_2 is the mass fraction for the PEG-1000 in the blend. The cal-

culated value X represents the fraction of free semicrystalline PEG relative to neat PEG-1000. It was observed (Fig. 5) that addition of Carbopol-934P into the PEG-1000 sharply reduced the fraction of semicrystalline PEG in the polymer blend. Similar behavior has been found for other amorphous-crystalline polymer blends.¹⁴ It is believed that amorphous-crystalline polymer blends could be compatible in the molten state. Incompatibility normally occurred when one component begins to crystallize.

Aubin et al.¹⁵ reported the T_g to be approximately 16°C for samples of 75/25, 50/50, and 25/75 mol ratio PAA/PEO. This was attributed to an equimolar PAA/PEO complex in these samples. However, they did not observe an additional glass transition or melt for a separate phase. The results for the present Carbopol-934P/PEG-1000 systems behaved differently. If an equimolar association between PAA and PEG with a composition of 62/38 (w/w) obtained, T_g should have remained constant; however, the glass transition temperatures were found to decrease continuously even beyond the equimolar composition. The compatible blends in the present study are adequately described by Fox's equation. While Aubin et al.¹⁵ used a lower-molecular-weight PAA (2.5×10^5) and a higher-molecular-weight PEO (3.0×10^5), these differences do not account for this complex formation alone. Spe-

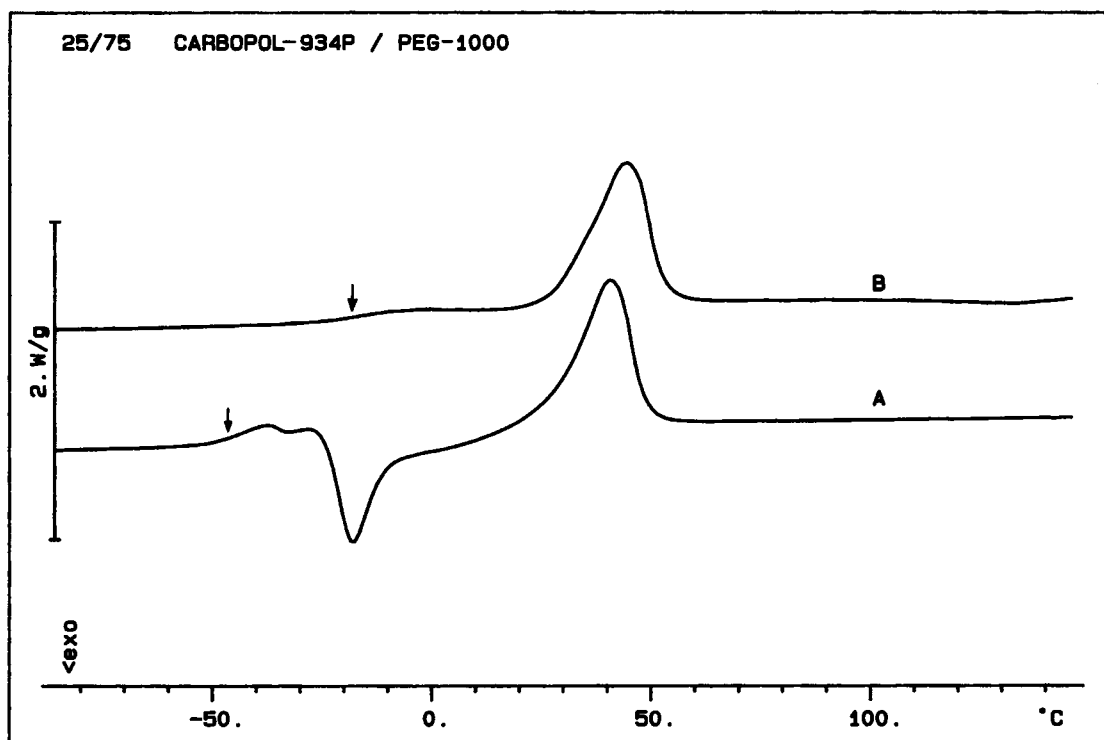


Figure 4 Thermograms for 25/75 Carbopol-934P/PEG-1000. Curve A: quenched from 65°C; curve B: annealed for 3 months.

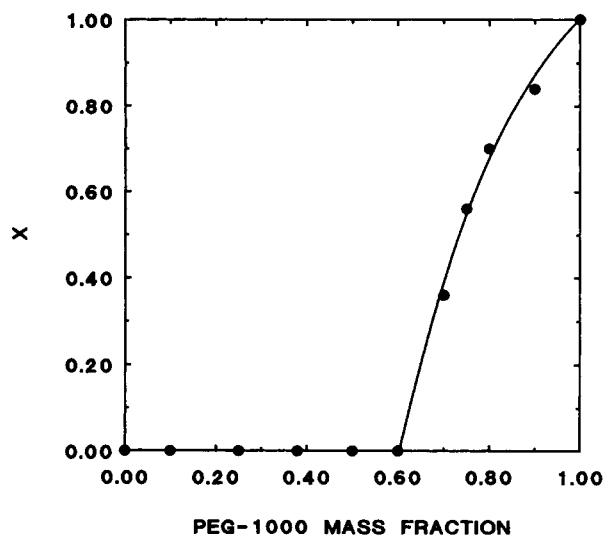


Figure 5 Fraction of crystalline PEG vs. total PEG composition in Carbopol-934P/PEG-1000.

cifically, Smith et al.¹ also used high-molecular-weight PEO and observed behavior similar to that in the current study.

The DSC thermograms of Carbopol-934P/Tween-80 blends were quite different. Crystallinity was not observed for any blends and no difference can be found in the glass transition temperature between the quenched and annealed samples even at very high Tween-80 composition. It is noted that Tween-80 (-12°C), as compared to PEG-1000 (38°C), has a lower crystalline lattice energy, as reflected by the melting point and similar heats of fusion. The lower crystalline lattice energy should increase its solubility, i.e., compatibility, in PAA as predicted by ideal solution theory. Such an increased compatibility of the blends was observed at the high POE concentrations of Tween-80.

In summary, while association complexes between PAA and POE are well established in the literature^{1-4,8} the present systems behave as classical

polymer blends and the behavior of T_g obeys Fox's equation. For the higher-molecular-weight POE with its resulting higher crystalline lattice energy, the compatibility of the blend was limited and a second semicrystalline phase was observed in annealed samples.

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