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PREDICTION OF THE GLASS TRANSITION TEMPERATURE FOR COMPATIBLE POLYMER BLENDS OF VARYING COMPOSITIONS

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ABSTRACT

Compatible polymer blends have been found to have widespread commercial applications. The simplest criterion for judging polymer—polymer miscibility in the solid state is the glass transition temperature (T_g), which can vary widely according to blend composition for a compatible system.

Recently, an equation which predicts the T_g of intimate mixtures of compatible polymers has been derived, based on classical thermodynamics. Only a knowledge of the T_g and heat capacity increment (ΔC_p) of each pure component is required to predict the T_g at any composition.

In this paper, the validity of this entropy-based relationship is investigated for a variety of commercial compatible polymer blends, including some based on poly(vinyl chloride), polystyrene, and poly(2,6-dimethyl-1,4-phenylene oxide). The T_g and ΔC_p of each pure component are measured with a Perkin-Elmer DSC-2 differential scanning calorimeter, and predicted glass transition temperatures are compared with those observed experimentally.

INTRODUCTION

Development of new polymeric materials by the synthesis of unique monomers is at a technological plateau in the plastics industry. Blending or alloying two or more polymers with different chemical structures and physical properties is, however, showing a dramatic commercial upswing. Blending of polymers is significant because it is often the easiest and most economical method for improving rheological, mechanical, degradative, and other performance properties.

The glass transition temperature of these polyblends is of vital importance, because it is often the single most important factor in determining many of their mechanical properties, as well as being the easiest way to assess degree of compatibility. The glass transition temperature of a compatible polyblend is a function of composition and is always located somewhere between the pure component T_g's. Rather than experimentally blending a compatible pair at various composition levels to obtain a desired T_g, it is much easier to calculate the required blend composition using physically measurable parameters of the pure components.

In order for two polymers to be compatible, their free energy of mixing must be negative

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \tag{1}$$

Mixing is always accompanied by a gain in entropy, but the heat of mixing of polymers is in most cases positive; that is, heat must be absorbed into the system for mixing to occur. Mutual compatibility depends on the rather rare situation in which ΔH_{mix} is negative.

The importance of entropy decreases as molecular size increases, while the contribution of the heat of mixing remains approximately the same. This is because entropy depends upon the number of molecules per unit volume, which decreases with an increase in molecular size. However, heat of mixing per unit volume is a function of the number of molecular unit contacts, which remains nearly constant with increase in molecular size. When the components in the mixture are polymers, the entropy change per unit volume is often so small that it can be neglected, and the heat of mixing alone will determine the homogeneity of the mixture.

It is extremely difficult to obtain ΔH or ΔS for polymer mixtures experimentally. Therefore, polymers are generally termed compatible if they exhibit a single compositionally dependent glass transition when examined by a variety of techniques. Differential scanning calorimetry (DSC) is the quickest and easiest method to determine polymer compatibility when the T_g's of the pure components are sufficiently far apart that they can be resolved if the polymers are incompatible.

In this paper, we have made us of a new relationship derived by Couchman [1]. This relationship allows the prediction of glass transition temperatures of polyblends, using only the heat capacity increments and glass transitions of the pure blend components.

EXPERIMENTAL

The mutually compatible polymer pairs examined were:

(1) polystyrene/α-methylstyrene (PS/AMS);

(2) poly(2,6-dimethyl-1,4-phenylene oxide)/α-methylstyrene (PPO/AMS);

(3) poly(vinyl chloride)/styrene-acrylonitrile-α-methylstyrene (PVC/S-AN-AMS);

(4) poly(vinyl chloride)/styrene-acrylonitrile-α-methylstyrene-butadiene (PVC/S-AMS-BD).

Blends of α-methylstyrene with polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) were prepared by co-dissolving in toluene and reprecipitating into methanol. The blends were subsequently dried in a vacuum oven below their T_g for 48 h.

The PVC/S-AN-AMS systems were melt-blended on a two-roll mill at 350° F (175° C). Stabilizer and the necessary amount of lubricant were added to the PVC to inhibit dehydrochlorination during the blend process.

Samples were compression molded into thin films and ~40 mg discs were punched from these for DSC analysis. Films were heated in a Perkin-Elmer

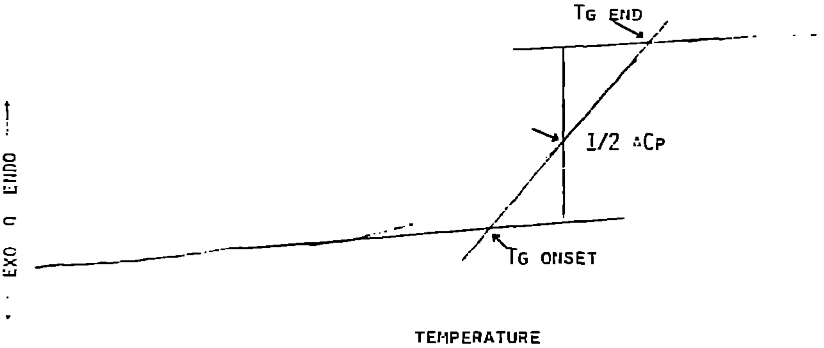


Fig. 1. Measurement of glass transition temperature and width.

DSC-2 to above their T_g to destroy any prior thermal history, cooled at 20° $\min^{-1}$ and reheated. Calorimetric response of the DSC was calibrated with 99.999% indium using a heat of fusion of 6.78 cal g^{-1}. Measurements of ΔC_p and T_g were made only on reheated samples and at least two separate determinations were run on each material. Although DSC temperature accuracy was about ±0.5°, precision of the measurement and lack of reproducibility due to physical effects led to an estimated uncertainty of ±2° in all temperature data.

Figure 1 shows a typical class transition and illustrates how the measurements were made. It was often difficult to draw a straight line through the baseline preceding the T_g. Since this was found to be a source of considerable inaccuracy in the heat capacity measurement, the technique was standardized by drawing the best straight line through the baseline beginning 50° prior to the transition onset. Transition width was defined as the difference between the extrapolated end and onset of the glass transition. The 1/2 ΔC_p temperature for the glass transition was used in all cases.

RESULTS AND DISCUSSION

The relationship below has been derived by Couchman [1] for predicting the effect of composition on glass transition temperatures in compatible mixtures

$$\ln T_g = \frac{M_1\, \Delta C_{p_1} \ln T_{g_1} + M_2\, \Delta C_{p_2} \ln T_{g_2}}{M_1\, \Delta C_{p_1} + M_2\, \Delta C_{p_2}} \tag{2}$$

where M is the mass fraction of each of the blend components. This equation requires that at the glass transition the total entropy of the glassy state is identical to that of the liquid state. If for a particular system, $T_{g_1}/T_{g_2} \approx 1$, and $\Delta C_{p_1} T_{g_1} \approx \Delta C_{p_2} T_{g_2}$, Couchman's equation reduces to the familiar Fox equation

$$\frac{1}{T_g} = \frac{M_1}{T_{g_1}} + \frac{M_2}{T_{g_2}} \tag{3}$$

This equation, the so-called inverse rule of mixtures, is probably the most commonly used model equation for compatible polymer blend T_g's.

The PS/PPO blend is a well-characterized system which is known to be homogeneous at all compositions. Previously published data [2,3] for this system were examined in order to illustrate the general utility of the two equations. Table 1 shows the observed vs. predicted T_g's for four different mass fractions of PPO. The Fox equation predicted temperatures which were in only fair agreement with experimentally observed values. This is expected since the T_g for PPO is 110° higher than that for PS and the ratio of the two T_g's does not closely approximate 1. In contrast, Couchman's equation is not influenced by large differences in either the T_g or ΔC_p of blend components. Figure 2 illustrates that the Couchman equation fits the experimentally measured T_g's better than the Fox equation.

The two equations for predicting glass transition temperatures were tested for several other compatible polymer blend systems. Predicted and experimental glass transition temperatures for the PPO/AMS polyblend system are tabulated in Table 2. Note that the Fox and Couchman-predicted temperatures agree very well with one another, probably because the component T_g's are not as widely separated as in the PS/PPO system. The comparison is illustrated graphically in Fig. 3. The curve represents T_g's predicted using the Couchman relationship. For almost all blend compositions examined, predictions fell within the experimental error of the observed values.

Transition widths for a particular polyblend system can serve as a measure of "level" of compatibility [3]. Broadening of the transition indicates a decrease in compatibility level. Transition widths as a function of composition for the PPO/AMS system are also plotted in Fig. 3. The glass transition width did not change significantly as blend composition varied. Therefore the level of compatibility in this system is not markedly influenced by composition.

The same AMS was then blended with a polystyrene of much higher molecular weight than the PPO. The width of the glass transition was found to vary to a greater extent, as shown in Fig. 4. The transition width data indicate that PS/AMS is a less compatible system than the PPO/AMS blend. Good agreement of the Couchman predicted values with experimental T_g's

TABLE 1

Observed and predicted T_g for PPO/PS blends of varying mass fractions [2]

Mass fraction PPO	Predicted T_g (K)		Observed T_g (K)	ΔC_p (cal g^{-1} $°C^{-1}$)
	Couchman	Fox		
0			378	0.0671
0.20	394	396	394	
0.40	413	416	413	
0.60	434	438	431	
0.80	460	462	458	
1.00			489	0.0528

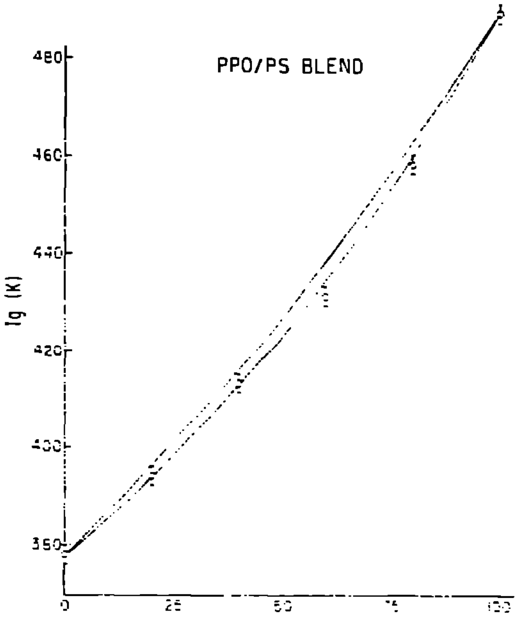


Fig. 2. Glass transition as a function of percent PPO in PPO/PS blend. Upper curve, Fox equation; lower curve, Couchman equation.

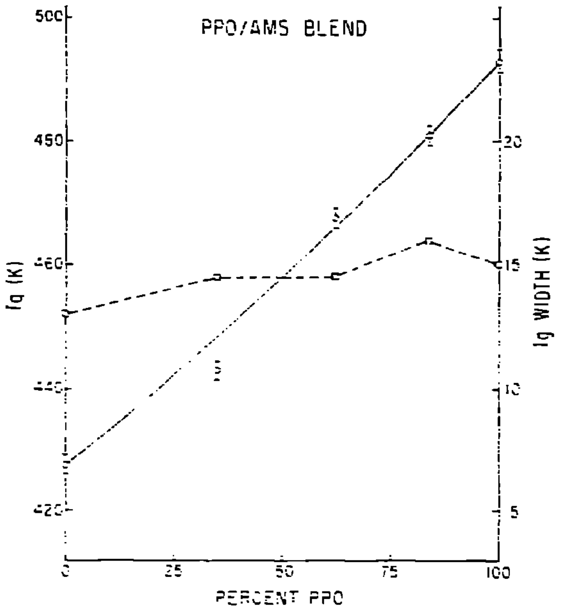
is again observed. Fox and Couchman values are very similar, as shown in Table 3. The temperatures predicted from the Fox equation fit the observed data almost as well as T_g's which Couchman's relationship predicts.

Two systems based on PVC were examined. These were PVC blended with S-AN-AMS, and an impact-modified S-AN-AMS analog, S-AN-AMS-BD. Both of these copolymers are commerically available materials which raise the heat deflection temperature of PVC. Table 4 shows the predicted vs. observed T_g data for the PVC/S-AN-AMS blend at different mass fractions of copolymer. Agreement between T_g's predicted using the Couchman and Fox equations is very good. A plot of the Couchman values vs. experimental data (Fig. 5) shows agreement at all composition levels. A pronounced variation in glass transition width implies that this blend is compatible to a lesser degree at levels where neither component predominates.

TABLE 2

Observed and predicted T_g for PPO/AMS blends of varying mass fractions

Mass fraction PPO	Predicted Tg (K)		Observed Tg (K)	ΔC_p (cal g^{-1} °C^{-1})
	Couchman	Fox		
0			428	0.062
0.35	448	448	443	
0.62	466	466	468	
0.84	481	481	481	
1.00			493	0.058



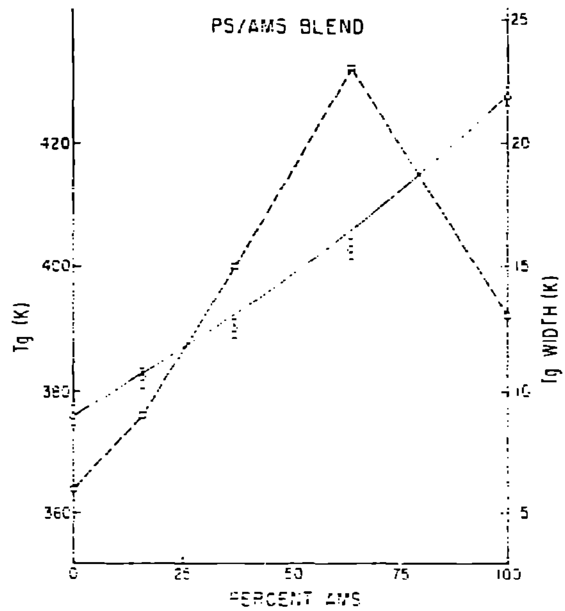


Fig. 3. Glass transition as a function of percent PPO in PPO/AMS blend. Solid curve, Couchman equation; dashed line, transition width data.

Fig. 4. Glass transition as a function of percent AMS in PS/AMS blend. Solid curve, Couchman equation; dashed line, transition width data.

TABLE 3

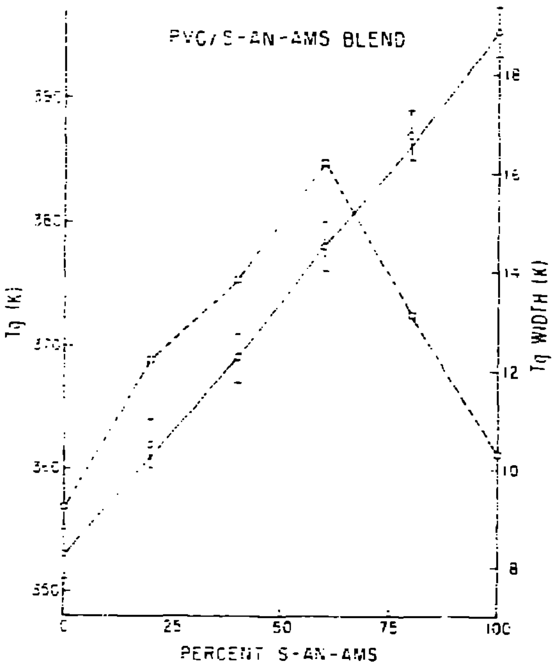
Observed and predicted T_g for PS/AMS blends of varying mass fractions

Mass fraction S-AN-AMS	Predicted T_g (K)		Observed T_g (K)	ΔC_p (cal g^{-1} $^\circ C^{-1}$)
	Couchman	Fox		
0			353	0.074
0.20	361	361	362	
0.40	369	369	369	
0.60	378	377	378	
0.80	386	386	387	
1.00			396	0.072

TABLE 4

Observed and predicted T_g for PVC/S-AN-AMS blends of varying mass fractions

Mass fraction AMS	Predicted T_g (K)		Observed T_g (K)	ΔC_p (cal g^{-1} $^\circ C^{-1}$)
	Couchman	Fox		
0			376	0.073
0.16	383	383	382	
0.37	392	394	390	
0.64	406	407	403	
1.00			428	0.062



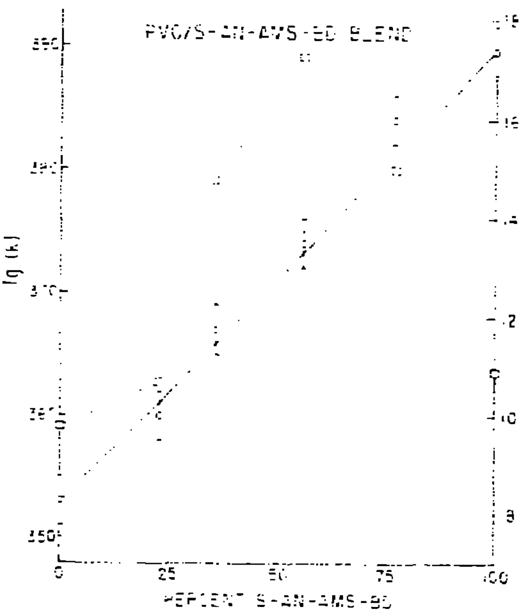


Fig. 5. Glass transition as a function of percent S-AN-AMS in PVS/S-AN-AMS blend. Solid curve, Couchman equation; dashed line, transition width data.

Fig. 6. Glass transition as a function of percent S-AN-AMS-BD in PVC/S-AN-AMS-BD blend. Solid curve, Couchman equation; dashed line, transition width data.

The last system examined was PVC blended with S-AN-AMS-BD, in which the butadiene portion serves as a heat distortion modifier (Table 5). The inclusion of butadiene results in a two-phase system and the butadiene component does not enter into the heat capacity change at the blend glass transition. Therefore, mass fraction values for S-AN-AMS-BD have been adjusted based on the percentage BD which does not contribute to the transition. It is apparent from the plot of composition vs. T_g (Fig. 6) that with this correction Couchman's relationship also holds for this two-phase system.

TABLE 5

Observed and predicted T_g for PVC/S—AN—AMS—BD blends of varying mass fractions

Mass fraction S-AN-AMS-BD [a]	Predicted T_g (K)		Observed T_g (K)	ΔC_p (cal g^{-1} $°C^{-1}$)
	Couchman	Fox		
0			353	0.074
0.23	360	361	360	
0.36	364	365	367	
0.56	371	373	374	
0.77	379	381	384	
1.00			390	0.060

[a] Corrected to subtract BD fraction.

CONCLUSION

The general applicability of the thermodynamically-based Couchman relationship has been explored and its predictions validated in several types of polymer blend systems. The T_g's for polyblends of known composition can be accurately predicted using Couchman's relationship. In addition, mass fractions of blend components can be calculated from a single experimentally observed glass transition. The Couchman approach appears to have greater potential than the traditional inverse rule of mixtures or other empirical models, in that it provides accurate T_g predictions for the widest variety of possible polymer blends regardless of the separation of the T_g's of the blend components.

REFERENCES

1 P.R. Couchman, Macromolecules, 11 (1978) 1156.
2 J.R. Fried, Ph.D. Dissertation, Polymer Science and Engineering, University of Massachusetts, 1976.
3 J.R. Fried, F.E. Karasz and W.J. MacKnight, Macromolecules, 11 (1978) 150.