

# Intermolecular interactions in binary multiblock copolymer blends

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The glass transition temperature of the soft phase has been studied in blends of multiblock polyetherester (PEE) with multiblock polyesterurethane (PUA) and poly(ether carbonate)urethane (PUC) copolymer. The  $K_1$  and  $K_2$  coefficients from the Schneider equation and the  $q$  parameter from the modified Kwei equation have been used to monitor the strength of intermolecular interaction. A suggestion for the partial miscibility of the PEE/PUC blends in the soft phase is proposed.

(Keywords: blends; copolyetherester; copolyesterurethane; copoly(ether carbonate)urethane; intermolecular interaction)

## INTRODUCTION

A miscible polymer blend, which behaves like a homogeneous phase, shows a single glass transition temperature ( $T_g$ ) generally between the  $T_{gS}$  of the initial components. The relationship between the  $T_g$  and the components in the blend with strong specific interactions shows deviation from linearity. Attempts at quantitatively characterizing these interactions have been reported by Kwei<sup>1</sup>, Chee<sup>2</sup>, Aubin and Prud'homme<sup>3</sup> and Schneider<sup>4,5</sup>. Kwei used an equation, equation (1), whose coefficients  $k$  and  $q$  account for the satisfactory approximation with experimental data:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \quad (1)$$

where  $w_1$  and  $w_2$  are the weight fractions of components 1 and 2 and  $T_{g1}$  and  $T_{g2}$  are their glass transition temperatures.

Schneider suggested another equation:

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} \times \frac{1}{w_{2c}} = (1 + K_1) - (K_1 + K_2)w_{2c} + K_2 w_{2c}^2 \quad (2)$$

where  $w_{2c} = K w_2 / (w_1 + K w_2)$ ,  $K = T_{g1} / T_{g2}$ ,  $w_1 + w_2 = 1$  and  $w_{1c} + w_{2c} = 1$ .  $K_1$  and  $K_2$  are the fitting parameters related to the intensity of the intermolecular interactions in a polymer-polymer system and the effect of the immediate surroundings on the interaction, respectively.

Block copolymers are composed of oligomer segments with different chemical structures and physical properties. Such copolymers are generally characterized to have an 'intrinsic' phase segregation and microphase morphology<sup>6</sup>. Nishi *et al.*<sup>7</sup> investigated blends of a multiblock copolyetherester with no plastified poly(vinyl chloride) to obtain a good correlation of the results obtained using equation (3):

$$T_g = w'_1 T_{g1} + w'_2 T_{g2} \quad (3)$$

where  $w'_1 = w_1 / (w_1 + \alpha w_2)$  and  $w'_2 = \alpha w_2 / (w_1 + \alpha w_2)$ . Here  $\alpha$  is the soft segment content in the copolyetherester.

The intermolecular interaction was taken into account when blends of multiblock copolymers with other polymers were estimated<sup>8-13</sup>.

This paper reports an attempt, by studying the  $T_g$ , to estimate and interpret the intermolecular interactions in a system of two multiblock copolymers.

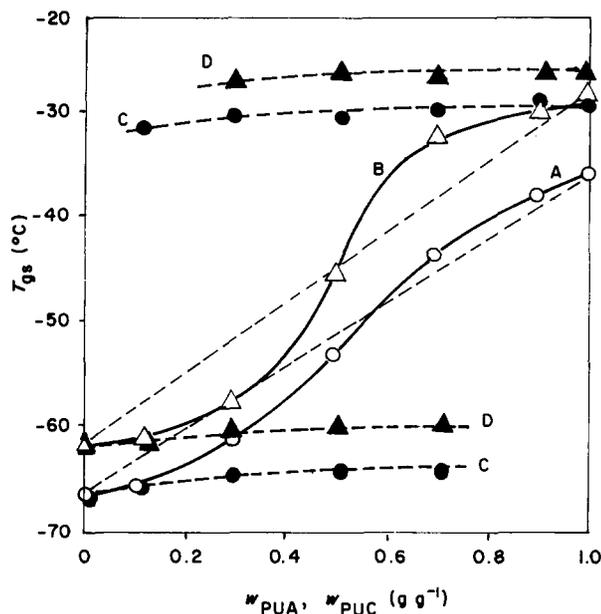
## EXPERIMENTAL

The experiments used blends in the melt of multiblock polyetherester (PEE) and polyesterurethane (PUA) or poly(ether carbonate)urethane (PUC). Elitel 4450 (Elana, Poland) containing 50/50 wt% poly(oxytetramethylene) segments and poly(butylene terephthalate) segments was used as the PEE. Desmopan 786 (Bayer AG, Germany) was used as the PUC. PUA containing 72/28 wt% poly(ethylene adipate) segments and diisocyanate-butanediol adduct segments (Jelur E-172 grade) was obtained from Jelchem Company, Poland. Polymers were mixed in a Brabender Plasticorder (at 60 rev min<sup>-1</sup>) and homogenized in a laboratory extruder (length = 25 × diameter; screw speed 60–80 rev min<sup>-1</sup>).

The glass transition temperature of the soft phase ( $T_{gs}$ ) in copolymers and copolymer blends has been determined from the d.s.c. plot (Perkin Elmer DSC-2, 10°C min<sup>-1</sup>) at half the total heat capacity change and from the dynamic mechanical diagram (Rheovibron viscoelastometer, DDV-IIc, Toyo Baldwin, 35 Hz) as the temperature of the loss modulus ( $E''$ ) maximum.

## RESULTS AND DISCUSSION

$T_{gs}$  versus weight fraction of the urethane copolymers in the blends is shown in Figure 1. The PEE/PUA blends are characterized by two glass transition temperatures



**Figure 1** Glass transition temperature of the soft phase ( $T_{gs}$ ) of PEE/PUC blends (A and B) and PEE/PUA blends (C and D) versus weight fraction of PUA and PUC: (A, C) data from d.s.c.; (B, D) data from  $E'$

near the  $T_{gs}$  of the initial components ( $T_{gsPEE}$  and  $T_{gsPUA}$ ), which confirms their immiscibility.

The PEE and PUC blends in the low temperature region show a single  $T_g$  between the glass transition temperatures of the initial components ( $T_{gsPEE}$  and  $T_{gsPUC}$ ). The relationship between the  $T_g$  and the composition of the blend is non-linear, which indicates soft segment (soft phase) interaction. However, it should be noted that the glass transition observed for the initial block copolymers exclusively affects the soft phase. The soft phase composition comes from the microphase equilibrium and depends, amongst other factors, on the fraction of soft segments and the degree of phase segregation<sup>14</sup>:

$$SR_S = \frac{w_{SS}\Delta C_P^{obs}/w_S}{w_{SS}\Delta C_P^S + w_{SH}\Delta C_P^H} \quad (4)$$

where  $SR_S$  is the degree of soft segment segregation, defined as the weight fraction of soft segment in the soft phase versus the total weight of soft segment in a copolymer,  $\Delta C_P^{obs}/w_S$  represents the observed change in heat capacity per weight fraction of soft segment in a copolymer,  $\Delta C_P^S$  and  $\Delta C_P^H$  are the changes in the heat capacity of the ideally microphase separated soft and hard segments, respectively, and  $w_{SS}$  and  $w_{SH}$  are the weight fractions of soft and hard segments in a soft phase, respectively ( $w_{SH} = 1 - w_{SS}$ ).

If it is assumed that  $\Delta C_P^H \ll \Delta C_P^S$  (in  $T_{gs}$ ), then<sup>15</sup>:

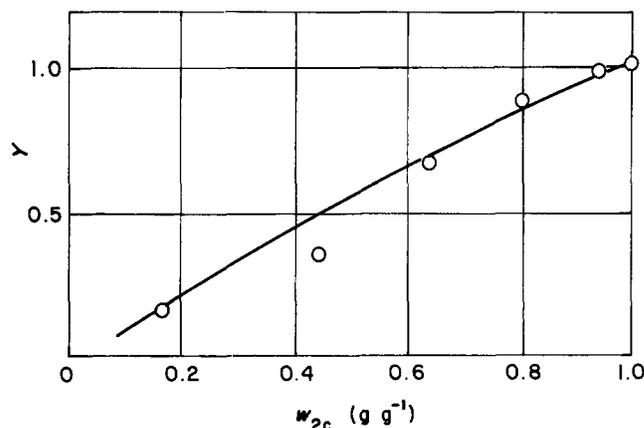
$$SR_S = \frac{\Delta C_P^{obs}}{w_S} \times \frac{1}{\Delta C_P^S} \quad (5)$$

Hence, the partial miscibility shown by single  $T_{gs}$  in this temperature range is related exclusively to the soft phases occurring in each initial copolymer.

The Schneider equation, equation (2), has been used to estimate the intermolecular interaction in PEE/PUC blends within the soft phases. The relation  $K = \Delta C_{P2}/\Delta C_{P1}$  has been applied to the theoretical and experimental assumptions made previously<sup>3,5,16</sup>. Table 1 and Figure 2

**Table 1** Schneider's correlation for PEE/PUC blends

$w_1$	$w_{2c}$	$T_g$ (°C)	
0.1	0.94	-31	$\Delta C_{P1} = 0.262 \text{ J g}^{-1} \text{ K}^{-1}$
0.3	0.81	-44	
0.5	0.65	-53	$\Delta C_{P2} = 0.484 \text{ J g}^{-1} \text{ K}^{-1}$
0.7	0.44	-62	$T_{g1} = T_{gsPEE} = -67^\circ\text{C}$
0.9	0.16	-66	$T_{g2} = T_{gsPUC} = -35^\circ\text{C}$
			$K_1 = -1.01$
			$K_2 = 0.11$



**Figure 2** Schneider's function for PEE/PUC blends:  $Y = [(T_g - T_{g1}) / (T_{g2} - T_{g1})] (1/w_{2c})$ , where  $w_{2c} = Kw_2 / (w_1 + Kw_2)$  and  $K = \Delta C_{P2} / \Delta C_{P1}$  ( $T_{g1}$ ,  $w_1$ ,  $\Delta C_{P1}$ , data for PEE)

show the data and calculated results. The  $K_1$  coefficient is less than zero due to negative deviation from linearity. The  $K_2$  constant is small. The  $K_1$  and  $K_2$  coefficients determined provide first-hand information on the interaction strength in the system, but they are of little importance in refining the intermolecular interaction.

Couchman<sup>17</sup> gave a general dependence of  $T_g$  on composition for miscible systems, based on a thermodynamic model of the glass transition:

$$\ln T_g = \frac{w_1 \Delta C_{P1} \ln T_{g1} + w_2 \Delta C_{P2} \ln T_{g2}}{w_1 \Delta C_{P1} + w_2 \Delta C_{P2}} \quad (6)$$

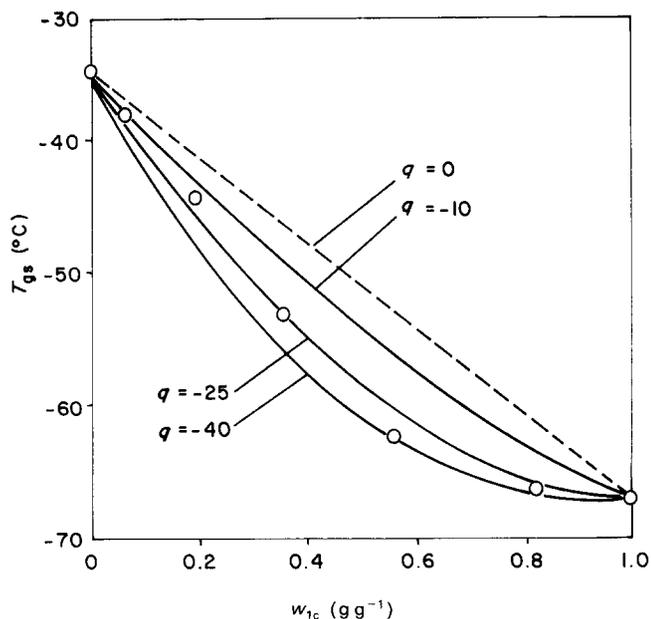
where  $T_g$  is the glass transition temperature of the blends,  $w_i$  is the weight fraction of component  $i$ , and  $\Delta C_{Pi}$  is the difference in specific heat between the liquid and glassy states at  $T_{gi}$ .

Equation (6) does not include the intermolecular interaction, but it comprises factors ( $w_1$ ,  $w_2$ ,  $\Delta C_{P1}$ ,  $\Delta C_{P2}$ ) that can be defined according to the phase model applied<sup>16</sup>. If  $T_{g2}/T_{g1}$  is equal to unity, then the logarithmic expansion of equation (6) can be limited to the first term, and  $K = \Delta C_{P2}/\Delta C_{P1}$ , one returns to equation (1) for  $q = 0$ . One interesting point is when equations (1) and (2) can be transformed to equation (7), because better correlation with experimental data is obtained (Figure 3):

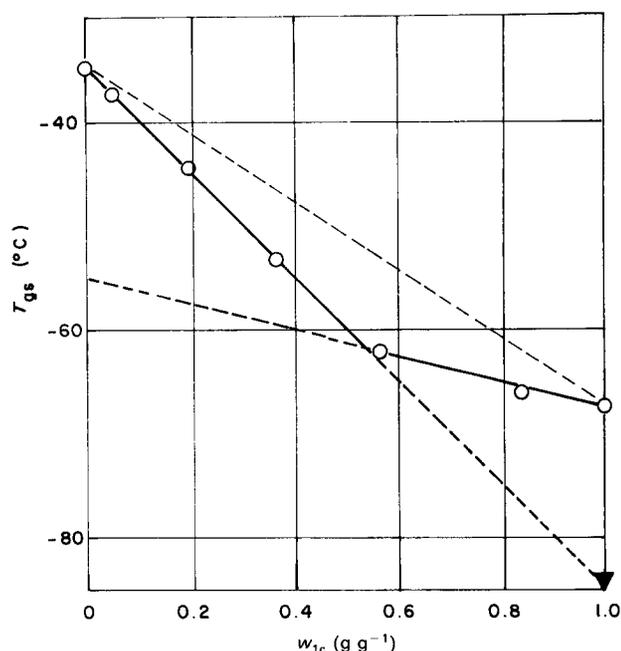
$$T_g = w_{1c} T_{g1} + w_{2c} T_{g2} + qw_{1c} w_{2c} \quad (7)$$

where  $w_{2c} = Kw_2 / (w_1 + Kw_2)$ ,  $K = \Delta C_{P2}/\Delta C_{P1}$ ,  $w_1 + w_2 = 1$  and  $w_{1c} + w_{2c} = 1$ . Agreement between the calculated and experimental  $T_g$  values (by d.s.c.) using equation (7) (for  $q = -25$ ) is within 3 K.

Figure 4 shows the relationship between  $T_{gs}$  and the corrected fraction of PEE ( $w_{1c}$ ) in the blend. The relationship can be correlated by two intersecting straight lines. Agreement between the calculated and experi-

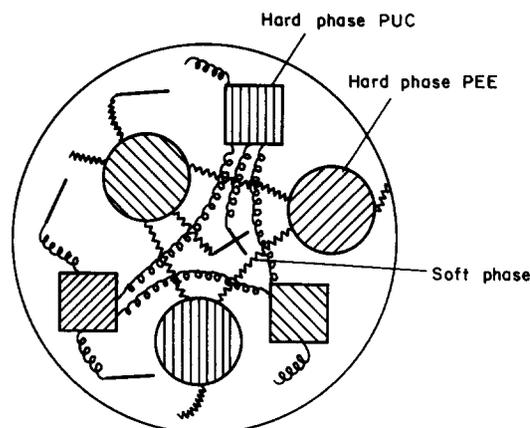


**Figure 3** Glass transition temperature of the soft phase ( $T_{gs}$ ) of PEE/PUC blends versus the corrected weight fraction of PUC ( $w_{1c}$ ): (○) experimental; (—) calculated from equation (7). Data from d.s.c.



**Figure 4** Glass transition temperature of the soft phase ( $T_{gs}$ ) of PEE/PUC blends versus the corrected weight fraction of PEE ( $w_{1c}$ ): (▼)  $T_{gsPO4}$

mental data is within 1 K. The  $T_{gsPUC}$  decreases in proportion to the soft polyether segment content from PEE, but exclusively in the range of the predominant PUC content in the blend. When plotted, the glass transition temperature of pure poly(oxytetramethylene) ( $T_{gsPO4} = -84^{\circ}\text{C}$ ) appeared to lie on the continuation of the straight line<sup>18</sup>. A similar straight line can be drawn through points corresponding to high PEE content in the blend, the point of intersection with the y axis being taken as the glass transition temperature of the polyethercarbonate being a soft PUC segment ( $\sim -55^{\circ}\text{C}$ ). Unfortunately, this temperature was not known to the author. Such a  $T_{gs}$  dependence of the PEE/PUC blends



**Figure 5** Schematic diagram of the interpenetrating polymer physical networks

implies that with an increase in PEE content the soft PUC phase is enriched with a soft polyether segment. This may follow from the mutual effect of copolymers on the phase segregation of their soft phases, which can give rise to a new phase equilibrium. A new multi-component soft phase (enriched with flexible segments of the other copolymer) is formed, the change in its composition versus that of the initial copolymer manifesting itself by the change in hard phases or by formation of an interphase with a different  $T_g$ . The strength stabilizing the system, to which the coefficients  $K_1$  and  $K_2$  refer, is due to the so-called physical network points (hard segment domains) among which chains of flexible segments composing a soft phase are 'fastened'. Such a system may be defined as an interpenetrating polymer physical network (Figure 5). At the intersection point ( $w_{1c} \sim 0.52$  corresponding to  $w_1 \sim 0.67$ ) inversion occurs leading to lower stability of the system.

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