제 4 강의

DSC on Polymers

4. Immiscible Polymer Blends

4.1. **Phase Behavior of Blends**

- Estimation of the Apparent Weight Fraction Dissolved in Each Phase

- Fox equation (ref. 6)

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

$$w_1' = \frac{T_{g1}(T_{g1,b} - T_{g2})}{T_{g1,b}(T_{g1} - T_{g2})} \tag{2}$$

- Couchman equation (ref. 7)

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{3}$$

$$w_1' = \frac{\Delta C_{p2}(\ln T_{g1,b} - \ln T_{g2})}{\Delta C_{p1}(\ln T_{g1} - \ln T_{g1,b}) + \Delta C_{p2}(\ln T_{g1,b} - \ln T_{g2})} \tag{4}$$

where $w_1'+w_2'=1.0$

4.2. **Polymer-Polymer Interaction Parameter**

- Flory-Huggins Model

- At equilibrium condition, the Gibbs' free energy of mixing

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} \phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \tag{5}$$

- The chemical potential of mixing is obtained from Eq. (5)

$$\Delta\mu_1/RT = \ln\phi_1 + (1 - m_1/m_2)\phi_2 + m_1\chi_{12}\phi_2^2 \quad (6)$$

$$\Delta\mu_2/RT = \ln\phi_2 + (1 - m_2/m_1)\phi_1 + m_2\chi_{12}\phi_1^2 \quad (7)$$

- At equilibrium,

$$\Delta\mu_1' = \Delta\mu_1'', \quad \Delta\mu_2' = \Delta\mu_2'' \quad (8)$$

- Polymer-Polymer Interaction Parameter (χ_{12}) (ref. 8-10)

$$\chi_{12} = \frac{(\phi_1'^2 - \phi_1''^2)[m_2\ln(\phi_1''/\phi_1') + (m_1 - m_2)(\phi_2' - \phi_2'')] + (\phi_2''^2 - \phi_2'^2)[m_1\ln(\phi_2''/\phi_2') + (m_2 - m_1)(\phi_1' - \phi_1'')]}{2m_1m_2(\phi_1'^2 - \phi_1''^2)(\phi_2''^2 - \phi_2'^2)} \quad (9)$$

● Effect of interaction parameter on physical properties of blends

- Surface tension (γ) ~ $\chi^{1/2}$
  [Chuck et al., *Macromolecules*, **27**, 55 (1994)]

- Strength of polymer interface (G) ~ $1/\chi$
  [Julious and Richard, *Macromolecules*, **26**, 5336 (1993)]

- Equilibrium thickness (d) ~ $\chi^{-1/2}$
  [Helfand and Spase, *J. Chem. Phys*., **62**, 1327(1975)]

- Relation between η_0 and χ
  [Han and Kim, *Macromolecules*, **22**, 1914 (1989)]

4. 3. **Amorphous-Amorphous Polymer Blends**

- **PEI-PC Blends** (ref. 11)

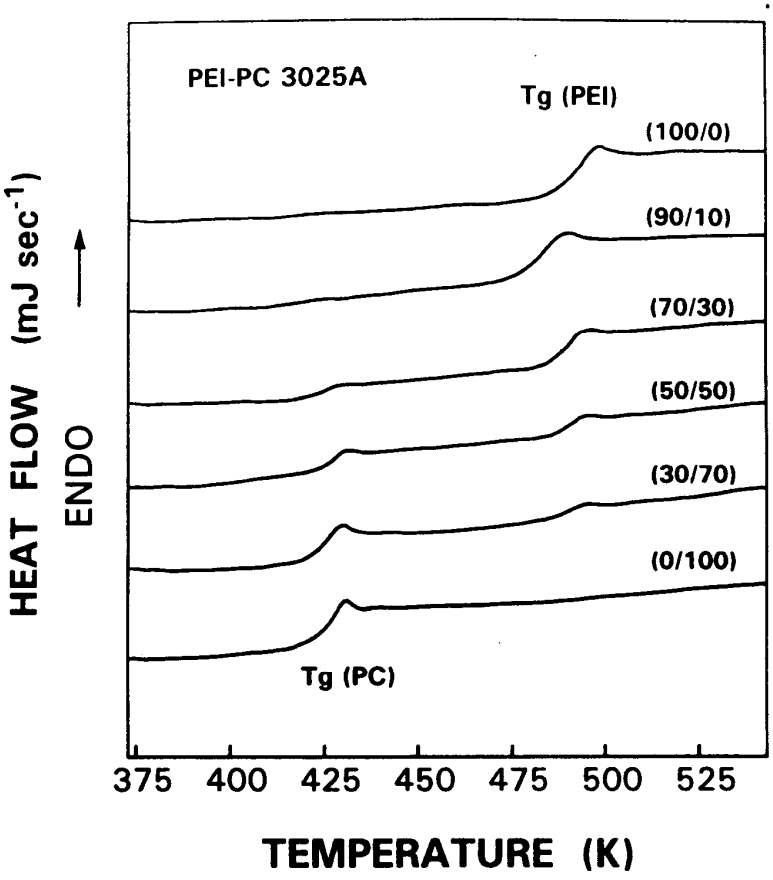


Fig. 1. Thermograms showing the glass transition temperature (T_g) of the PEI and PC of various composition for PEI-PC 3025A blends.

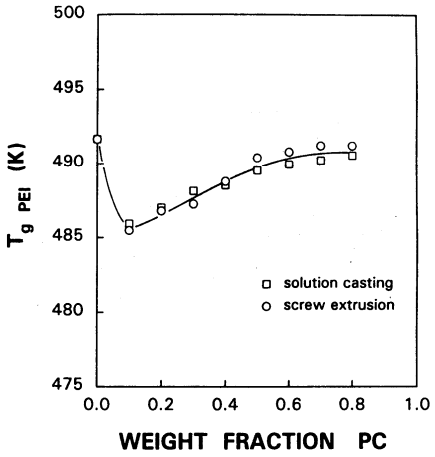


Fig. 2. Effect of blend composition on the T_g(PEI) for PEI-PC 3025A blends: (□) solution casting; (○) screw extrusion.

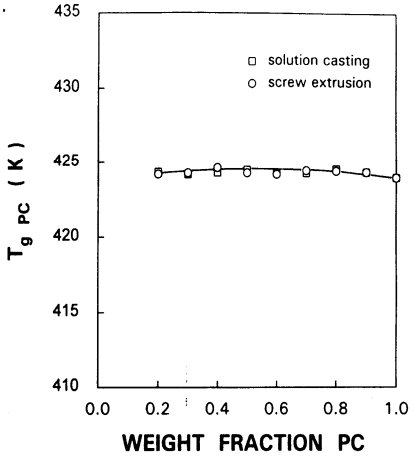


Fig. 3. Effect of blend composition on the T_g(PC) for PEI-PC 3025A blends: (□) solution casting; (○) screw extrusion.

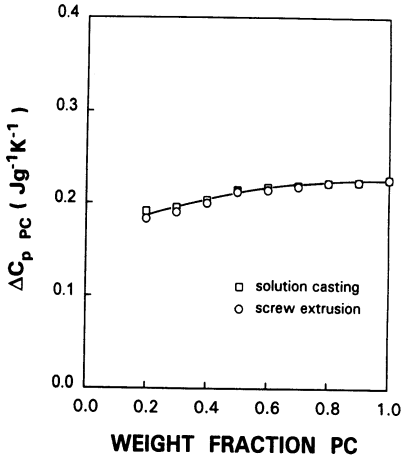


Fig. 7. Specific heat increment (ΔC_p) at the T_g of PC for PEI-PC 3025A blends: (□) solution casting; (○) screw extrusion.

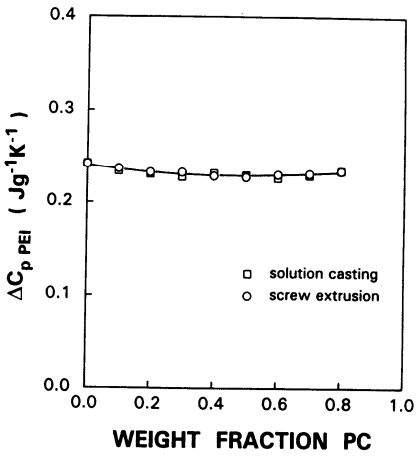


Fig. 6. Specific heat increment (ΔC_p) at the T_g of PEI for PEI-PC 3025A blends: (□) solution casting; (○) screw extrusion.

Table 2. Apparent Weight Fraction (w) of PEI and PC Components in the PEI-rich Phase and the PC-rich Phase of PEI-PC 3025A Extruded Blends.

Blend[a]	$T_{g1,b}$[b]	$T_{g2,b}$[b]	$w_2'^c$	$w_1'^c$	$w_2'^d$	$w_1'^d$
0.8	486.8	424.2	0.0630	0.0034	0.0721	0.0030
0.7	487.3	424.3	0.0566	0.0051	0.0647	0.0045
0.6	488.8	424.7	0.0372	0.0120	0.0426	0.0104
0.5	490.4	424.3	0.0166	0.0051	0.0191	0.0045
0.4	490.8	424.2	0.0115	0.0034	0.0132	0.0030
0.3	491.2	424.5	0.0064	0.0086	0.0074	0.0074
0.2	491.2	424.4	0.0064	0.0068	0.0074	0.0059

[a] Blend composition given as overall weight fraction PEI in the PEI-PC blend.
[b] Subscripts 1 and 2 denote PEI and PC components, respectively. T_gs are in K.
[c] Single prime denotes PEI-rich phase; double prime denotes PC-rich phase. w_2' is calculated from *Eq* 2. $w_1' + w_2' = 1$.
[d] w_2' is calculated from *Eq* 4.

- **PC with Partially Miscible Polymer Blends** (ref. 12)

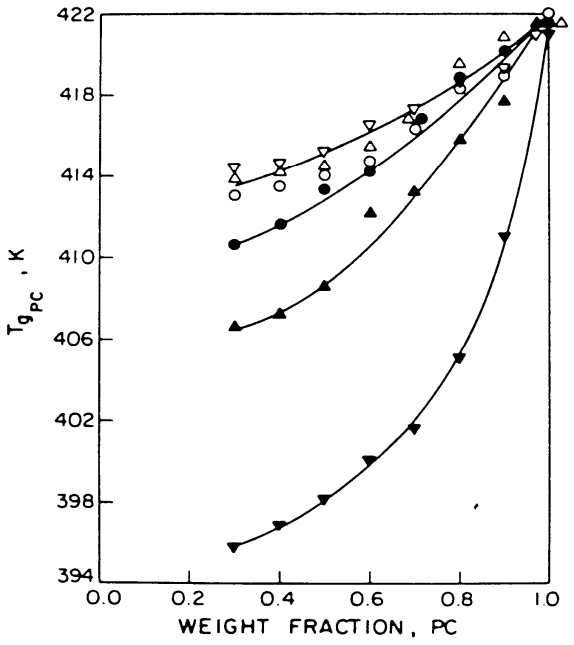


Fig. 1. Effect of blend composition on the T_g(PC) for the blends from screw extrusion: (○) PC-PS; (△) PC-PMMA; (▽) PC-SAN; (●) PC-ABS; (▲) PC-PET; (▼) PC-PBT.

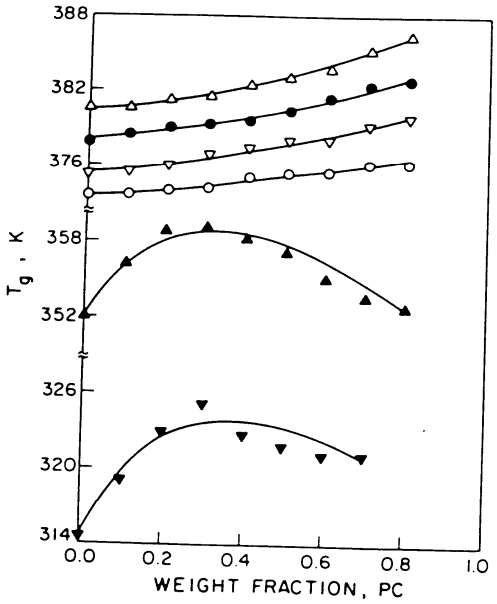


Fig. 3. Effect of blend composition on the other T_gs for the blends from screw extrusion: (○) T_g(PS); (△) T_g(PMMA); (▽) T_g(SAN); (●) T_g(ABS); (▲) T_g(PET); (▼) T_g(PBT).

TABLE II
Apparent Weight Fraction (ω) and Apparent Volume Fraction (ϕ) of the PC-Rich Phase and the PS-, SAN-, ABS-, and PMMA-Rich Phase and the Polymer–Polymer Interaction Parameter (g_{12}) of the 0.5 weight fraction PC Blends

Blend	$T_{g1,b}$[a]	$T_{g2,b}$[a]	ω_1'[b]	ω_1''[b]	ϕ_1	ϕ_1	g_{12}[c]	χ_{12}[d]
				Extruder blending				
PC–PS	414.0	375.3	0.8591	0.0421	0.8420	0.0370	0.036	0.041
PC–SAN	415.3	378.0	0.8778	0.0583	0.8658	0.0527	0.037	0.039
PC–ABS	413.3	380.4	0.8285	0.0659	0.8127	0.0596	0.034	0.038
PC–PMMA	414.5	383.1	0.8437	0.0723	0.8403	0.0706	0.037	0.040
				Solution casting				
PC–PS	419.7	374.0	0.9666	0.0117	0.9620	0.0103	0.053	0.051
PC–SAN	414.6	378.4	0.8638	0.0680	0.8507	0.0614	0.035	0.038
PC–ABS	413.6	380.2	0.8349	0.0609	0.8194	0.0550	0.035	0.039
PC–PMMA	418.3	382.6	0.9292	0.0623	0.9275	0.0519	0.043	0.044

[a] Subscript 1 denotes PC component. T_gs are in K.

[b] Single prime denotes PC-rich phase;$\omega_2' = 1 - \omega_1'$ and $\omega_2'' = 1 - \omega_1''$. ω_1' and ω_1'' are calculated from eqs. (2) and (3), respectively.

[c] All g_{12}s are calculated from eqs. (14) and (15).

[d] All χ_{12}s are calculated from eq. (16) in Ref. 7.

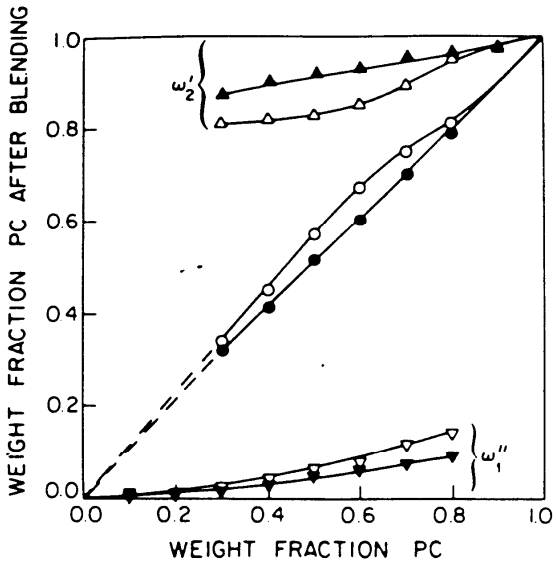


Fig. 8. Phase diagram of PC–PMMA blends from screw extrusion (○, △, ▽) and solution casting (●, ▲, ▼): weight fraction of PC in the PC-rich phase (△); weight fraction of PC in the PMMA-rich phase (▽); overall weight fraction of PC-rich phase after blending (○). For overall compositions of 0.9–0.4 PC, the extruder temperature was 250°C; for 0.3–0.1, 230°C.

4.4. **Amorphous-Crystalline Polymer Blends**

- **PC-PP Blends** (ref. 13)

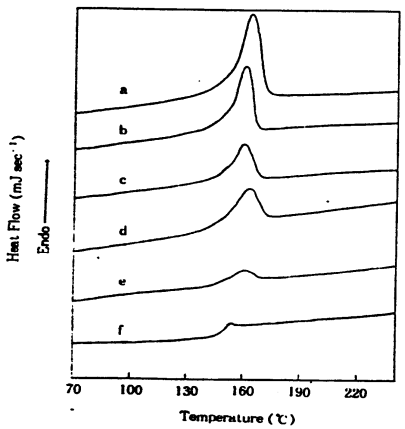


Figure 1. DSC thermograms showing the melting peak of the PP in the PC-PP blends: (a) 0/10, (b) 3/7, (c) 6/4, (d) 7/3, (e) 8/2, and (f) 10/0.

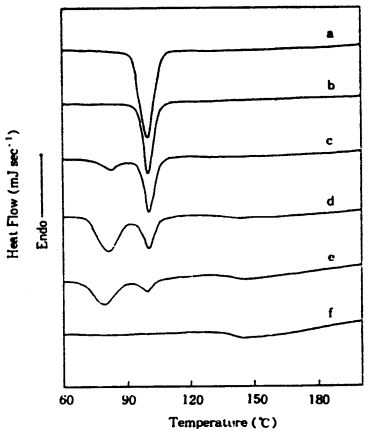


Figure 2. DSC thermograms showing the crystallization peak of the PP in the PC-PP blends: (a) 0/10, (b) 3/7, (c) 6/4, (d) 7/3, (e) 8/2, and (f) 10/0.

- **PP-PC-SEBS Blends**

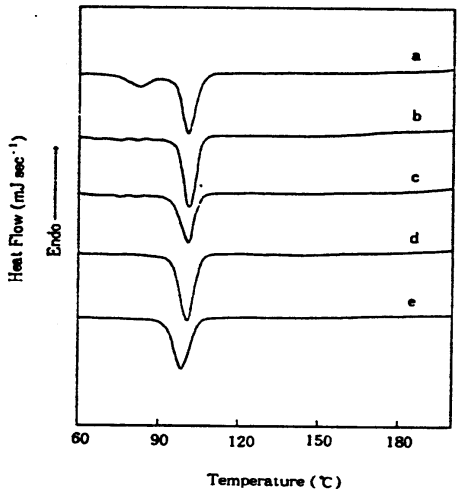


Figure 3. Effect of SEBS contents on the crystallization peak of the PC-PP 6/4 blends: (a) 0 phr, (b) 5 phr, (c) 10 phr, (d) 15 phr, and (e) 20 phr.

4. 5. **Crystalline-Crystalline Polymer Blends**

- **PP-HDPE Blends** (ref. 14)

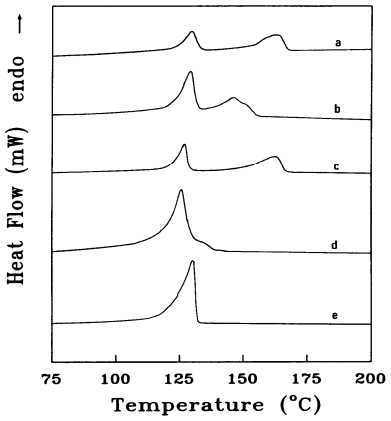


Figure 7 Thermograms showing the melting point of the PP homopolymer and PP copolymers blended with HDPE: (a) PP homopolymer; (b) EP random polymer; (c) EP block copolymer; (d) EPB terpolymer; (e) HDPE homopolymer.

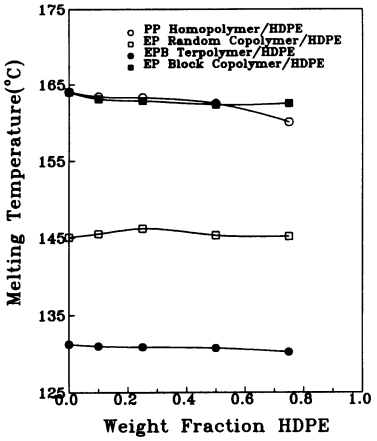


Figure 8 Effect of blend composition on the melting point of the PP homopolymer and PP copolymers blended with HDPE.

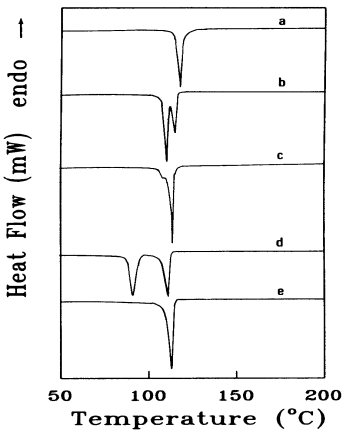
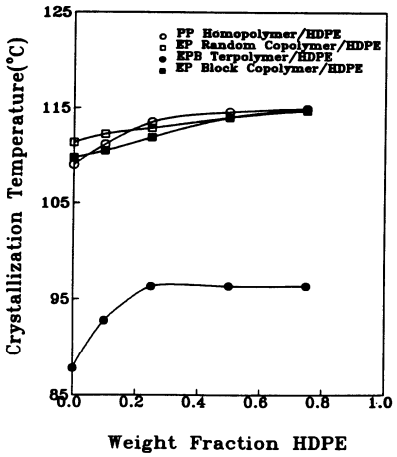


Figure 9 Thermograms showing the crystallization temperature of the PP homopolymer and PP copolymers blended with HDPE: (a) PP homopolymer; (b) EP random polymer; (c) EP block copolymer; (d) EPB terpolymer; (e) HDPE homopolymer.



'igure 10 Effect of blend composition on the crystalzation temperature of the PP homopolymer and PP coolymers blended with HDPE.

4.6. Miscible Polymer Blends

- **PEEK-PEI Blends** (ref. 15)

1. T_g of Blend

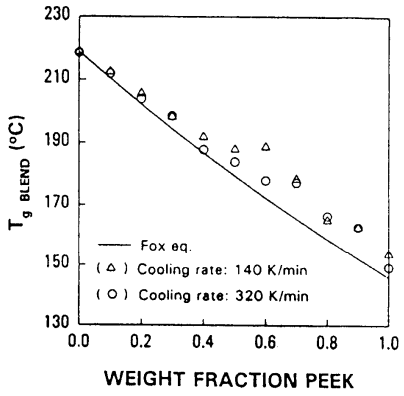


Figure 1 Effect of blend composition on the T_g of the semi-crystalline PEEK–PEI blends obtained (△) by 140 K min^{-1} cooling, (○) by 320 K min^{-1} cooling. The curve represents the mathematical model of the Fox equation[10]

2. Crystallinity

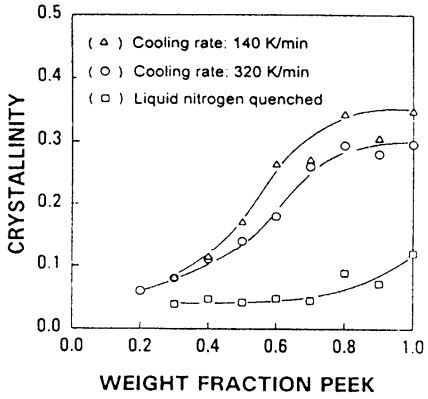


Figure 3 Effect of blend composition on the crystallinity of PEEK in the PEEK–PEI blends obtained (△) by 140 K min^{-1} cooling, (○) by 320 K min^{-1} cooling, (□) by quenching in liquid nitrogen

-Rigid Amorphous Fraction (X_r)

overall rigid fraction (X_f) of PEEK in the blends

$$X_f = 1 - \frac{\Delta C_p}{\Delta C_p^a} \qquad (11)$$

ΔC_p is the specific heat increment at T_g of the semicrystalline PEEK-PEI blends and ΔC_p^a is the specific heat increment at Tg of the fully amorphous PEEK-PEI blends

$$\Delta C_p^a = [\frac{\Delta C_p}{1 - W_1 X_c}] \qquad (12)$$

W_1 is the weight fraction of PEEK in the blends and X_c is the crystallinity of PEEK in the blends

Rigid amorphous fraction (X_r) of PEEK in the blends

$$X_r = \frac{X_f}{W_1} - X_c \qquad (13)$$

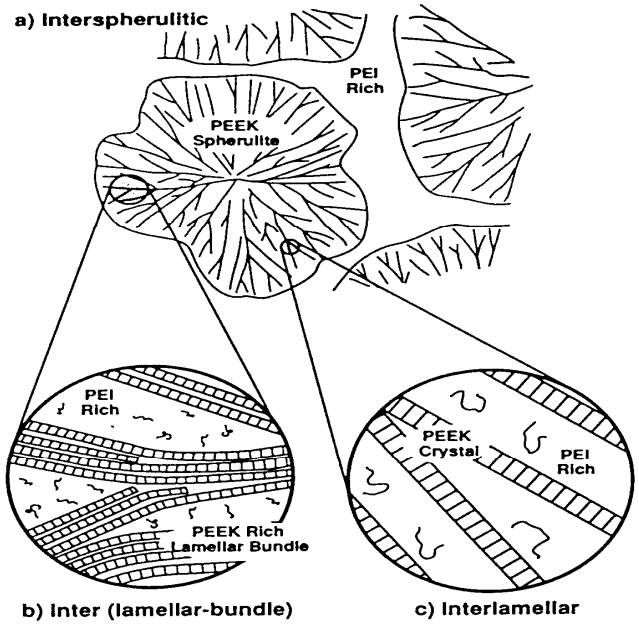


Figure 1. Schematic diagram of possible PEI segregation modes during crystallization of a compatible PEEK/PEI blend.

Table 3 Thermal properties of the semicrystalline PEEK–PEI blends

Blend[a]	X_c[b]		X_f[c]		X_f[d]	
	140 K min^{-1}[e]	320 K min^{-1}[f]	140 K min^{-1}[e]	320 K min^{-1}[f]	140 K min^{-1}[e]	320 K min^{-1}[f]
10/0	0..347	0.296	0.634	0.611	0.287	0.315
9/1	0.304	0.280	0.592	0.574	0.354	0.358
8/2	0.342	0.294	0.519	0.513	0.307	0.347
7/3	0.270	0.260	0.415	0.411	0.323	0.327
6/4	0.263	0.180	0.277	0.281	0.199	0.288
5/5	0.170	0.140	0.181	0.170	0.192	0.200
4/6	0.113	0.110	0.117	0.117	0.180	0.183
3/7	0.080	0.080	0.059	0.059	0.117	0.117
2/8	—	—	0.024	0.024	—	—
1/9	—	—	0.029	0.012	—	—
0/10	0.000	0.000	0.000	0.000	0.000	0.000

[a] Blend compositions given as the overall weight fraction PEEK in the PEEK–PEI blend
[b] Crystallinity of PEEK in the PEEK–PEI blend: data from *Figure 3*
[c] The overall rigid fraction of the PEEK–PEI blend: $X_f = 1 - \Delta C_p/\Delta C_p^a$
[d] The rigid amorphous fraction of PEEK in the PEEK–PEI blend: $X_r = X_f/w_1 - X_c$
[e] All data were obtained at heating rate of 20 K min^{-1} after the blend's being cooled at cooling rate of 140 K min^{-1}
[f] All data were obtained at heating rate of 20 K min^{-1} after the blend's being cooled at cooling rate of 320 K min^{-1}

Table 2 Thermal properties of the amorphous PEEK–PEI blends (liquid nitrogen quenched)

Blend[a]	X_c[b]	ΔC_p[c] (J g^{-1} K^{-1})	ΔC_p^a[d] (J g^{-1} K^{-1})	X_f[e]	X_r[f]
10/0	0.120	0.308	0.350	0.120	0.000
9/1	0.072	0.298	0.319	0.072	0.000
8/2	0.089	0.295	0.318	0.089	0.000
7/3	0.045	0.289	0.299	0.045	0.000
6/4	0.048	0.284	0.292	0.048	0.000
5/5	0.042	0.270	0.276	0.042	0.000
4/6	0.047	0.260	0.265	0.047	0.000
3/7	0.039	0.252	0.255	0.039	0.000
2/8	—	0.246	—	—	—
1/9	—	0.244	—	—	—
0/10	0.000	0.241	0.241	0.000	0.000

[a] Blend composition given as the overall weight fraction PEEK in the PEEK–PEI blend
[b] Crystallinity of PEEK in the PEEK–PEI blend: data from *Figure 3*
[c] Specific heat increment at T_g of the liquid nitrogen quenched PEEK–PEI blend: data from *Figure 6*
[d] Specific heat increment at T_g of fully amorphous PEEK–PEI blend: $\Delta C_p^a = \Delta C_p/(1 - X_c w_1)$, where w_1 is weight fraction of PEEK in the PEEK–PEI blend
[e] The overall rigid fraction of the PEEK–PEI blend: $X_f = 1 - \Delta C_p/\Delta C_p^a$
[f] The rigid amorphous fraction of PEEK in the PEEK–PEI blend:

-Double T_gs

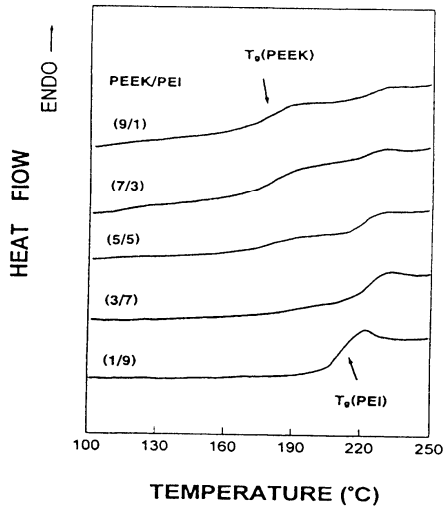


Figure 6 Thermogram showing the double T_gs behavior in the semicrystalline PEEK–PEI blends obtained by slow cooling (5 K min^{-1})

-Effect of cooling rate on T_g of blend

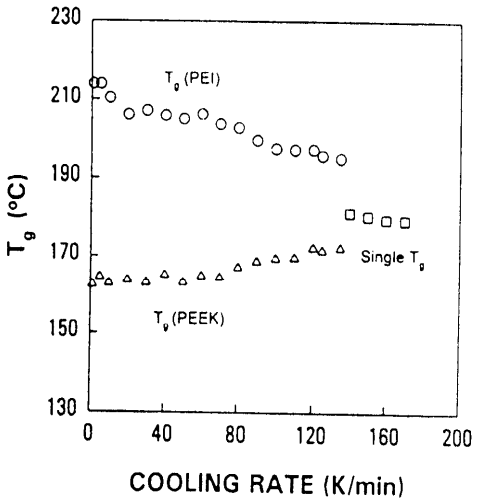
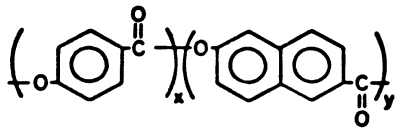


Figure 9 Effect of cooling rates on the double T_gs of the semicrystalline 7/3 PEEK–PEI blend

4. 6. LCP Based Polymer Blends

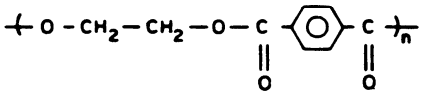
- **Vectra-PET Blends** (ref. 16)

LCP: Hoechst-Celanese Vectra A900
(73 mol% HBA and 27 mol% HNA)



Poly(HBA/HNA)

x = 73, y = 27
DP ≈ 110
M_n ≈ 15,000



PET

DP = 110
M_n = 21,000

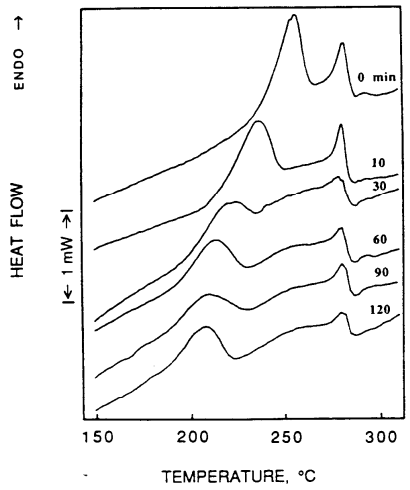


FIG. 6. Effect of annealing time in the DSC at 310 °C on the melting peak of PET and Vectra in a 9/1 Vectra/PET blend.

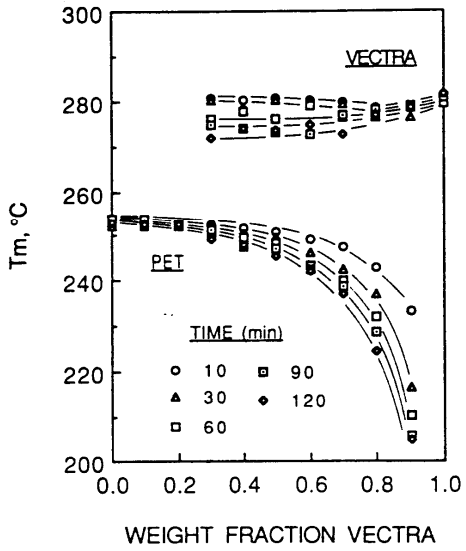


FIG. 7. Effect of blend composition and annealing time at 310 °C on the melting points of PET and Vectra for Vectra/PET blends.

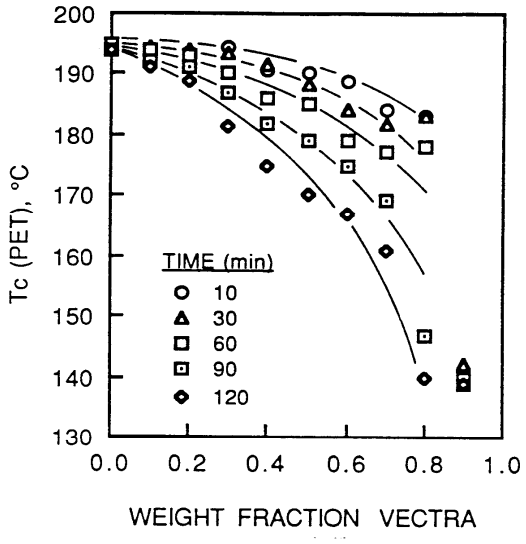


FIG. 9. Effect of blend composition and annealing time on the crystallization temperature of PET for Vectra/PET blends annealed at 310 °C in the DSC.

- **Blends of LCP and Engineering Polymers** (ref. 17)

  - Polymer Samples

LCP: Unitika Rodrun 5000
(80 mol% HBA and 20 mol% PET)

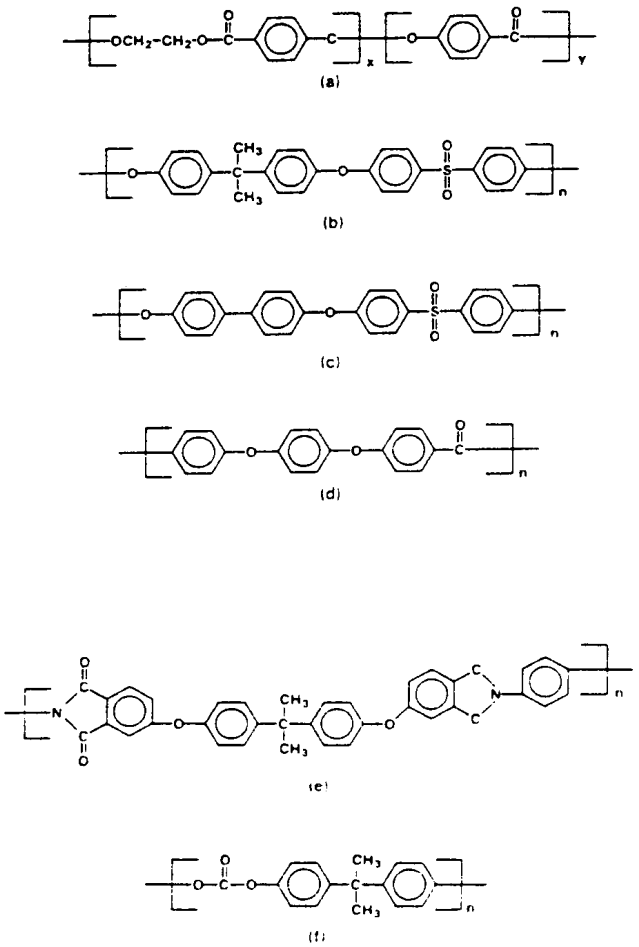


Fig. 1. Structural repeating unit of polymer samples used in this study: (a) liquid crystalline polymer, R5000 x:y=2:8, R3000 x:y=4:6; (b) polysulfone; (c) polyarylsulfone; (d) poly(ether ether ketone); (e) poly(ether imide); (f) polycarbonate.

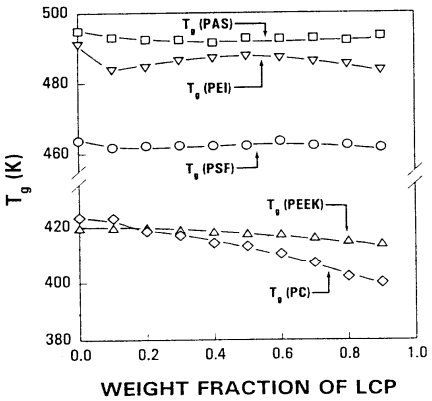


Fig. 2. Effect of blend composition on the T_gs for the blends: (○) T_g(PSF) of the LCP-PSF blend; (□) T_g (PAS) of the LCP-PAS blend; (△) T_g(PEEK) of the LCP-PEEK blend; (▽) T_g(PEI) of the LCP-PEI blend; (◇) T_g(PC) of the LCP-PC blend.

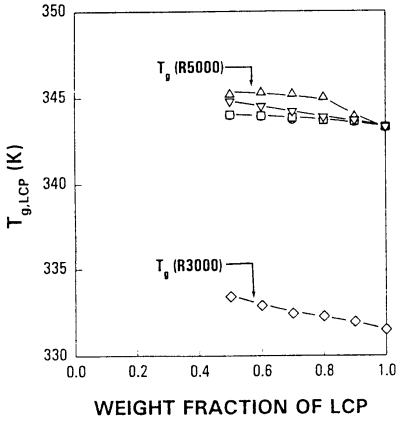


Fig. 3. Effect of blend composition on the T_g(LCP) for the blends: (○) LCP-PSF; (□) LCP-PAS; (△) LCP-PEEK ; (▽) LCP-PEI; (◇) LCP-PC.

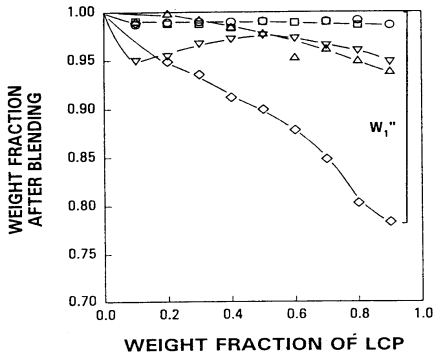


Fig. 6. Phase composition diagram of LCP-containing blends by Fox eq.: (○) weight fraction of PSF in the PSF-rich phase of the LCP-PSF blend; (□) weight fraction of PAS in the PAS-rich phase of the LCP-PAS blend; (△) weight fraction of PEEK in the PEEK-rich phase of the LCP-PEEK blend; (▽) weight fraction of PEI in the PEI-rich phase of the LCP-PEI blend; (◇) weight fraction of PC in the PC-rich phase of the LCP-PC blend.

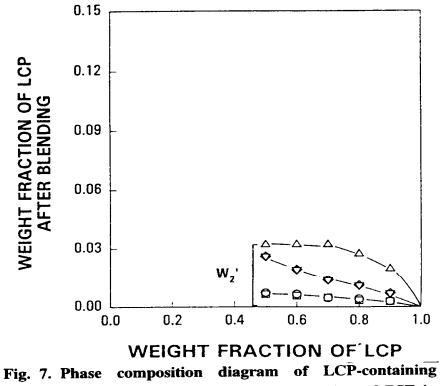


Fig. 7. Phase composition diagram of LCP-containing blends by Fox eq.: (○) weight fraction of PSF in the LCP-rich phase of the LCP-PSF blend; (□) weight fraction of PAS in the LCP-rich phase of the LCP-PAS blend; (△) weight fraction of PEEK in the LCP-rich phase of the LCP-PEEK blend; (▽) weight fraction of PEI in the LCP-rich phase of the LCP-PEI blend; (◇) weight fraction of PC in the LCP-rich phase of the LCP-PC blend.

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