Miscibility studies of high T_g polyester and polycarbonate blends

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Differential scanning calorimetry (d.s.c.) has been applied to characterize the miscibility of blends of a high T_g polyester, synthesized by condensation polymerization from 4,4′-(2-norbornylidene)diphenol and terephthalic acid/azelaic acid in a 60/40 molar ratio (this polyester will be denoted T(40)C-GJ), with bisphenol-A polycarbonate. The theoretical development to determine the Flory–Huggins interaction parameter (χ) of phase-separated polymer blends from their phase compositions is described. The glass transition temperature (T_g) of a miscible blend of T(40)C-GJ and a low molecular weight polycarbonate (Lexan) can be accurately described by both the Gordon–Taylor equation with $k=1.7$ and the Couchman equation. These equations were used to determine the phase compositions of a phase-separated blend of T(40)C-GJ and a high molecular weight polycarbonate (Makrolon) from the T_g data. The χ values for these blends are in the range $(8.4\text{–}9.9)\times10^{-3}$ and are slightly composition dependent. The miscibility of these blends can be quantitatively understood in terms of the χ results from the d.s.c. measurements. The morphology observed by transmission electron microscopy for 50/50 wt% blends of T(40)C-GJ and polycarbonate is consistent with the d.s.c. results.

(Keywords: polymer blends; miscibility; interaction parameter)

INTRODUCTION

There has been considerable commercial interest in blends of various polyesters with bisphenol-A polycarbonate (PC) for high performance plastics[1]. PC is a widely used engineering thermoplastic with a high heat distortion temperature and an excellent balance of toughness and rigidity, but it has poor stress crack resistance to certain chemicals, such as gasoline. Such poor solvent resistance can be improved by blending with polyesters.

The miscibility of polymer blends is related to their physical properties[2,3] and has usually been understood in terms of the Flory interaction parameter (χ) between component polymers. The method for determining the χ value in miscible blends has been studied widely. Several techniques have been applied such as small-angle neutron (SANS) and X-ray (SAXS) scattering[4–8], inverse gas chromatography[9–11] and melting point depression[12–14]. Only a few methods have been developed to determine the χ value for immiscible polymer blend systems, and most of these are ternary solution methods[15,16]. Differential scanning calorimetry (d.s.c.) may be the most convenient and inexpensive method to determine the χ value of immiscible blends. This technique has been used extensively for blends such as polystyrene/bisphenol-A polycarbonate (PS/PC)[17], PC/poly(methyl methacrylate) (PMMA)[18], PS/PMMA[19] and PC/poly(ethylene terephthalate)[20] by Burns and Kim and PS/poly(α-methylstyrene) by Yang *et al.*[21]. The χ value can be calculated using d.s.c. data from the experimental value of the glass transition temperature (T_g) and/or the heat capacity increment (ΔC_p).

In this study, we have mainly applied the d.s.c. technique to understand quantitatively the miscibility behaviour without transesterification[22–24] (which especially occurs between polyesters and polycarbonates at high temperatures) of high T_g amorphous polyester (poly[4,4′-(2-norbornylidene)diphenol-*co*-(60%)terephthalic acid/(40%)azelaic acid], which will be denoted T(40)C-GJ) and PC blends in terms of their χ values. The theoretical development to determine the χ value of phase-separated polymer blends from their phase compositions is also described.

THEORY

Sanchez[25,26] applied the Flory-Huggins theory[27,28] of polymer solutions[29–31] to describe the free energy of mixing per unit volume (Δg) of polymer blends, which can be expressed as

$$\Delta g=\Delta G/V=(-T\Delta S+\Delta H)/V=\Delta g_{\mathrm{comb}}+\Delta g_{\mathrm{ex}} \tag{1}$$

where Δg_{comb} is the combinatorial entropy of mixing

$$\Delta g_{\mathrm{comb}}/kT=(\phi_1/y_1v_1)\ln\phi_1+(\phi_2/y_2v_2)\ln\phi_2 \tag{2}$$

and Δg_{ex} is the excess free energy or enthalpy of mixing

$$\Delta g_{\mathrm{ex}}/kT=\tilde{\chi}\phi_1\phi_2=(\chi/v_0)\phi_1\phi_2 \tag{3}$$

where V is the total system volume, ϕ_i and y_i are the volume fraction and degree of polymerization of component polymer i, respectively, v_i is the molar volume of monomer i, v_0 is the reference volume of a lattice, kT has its usual significance and χ is assumed here to be composition independent for convenient discussion. It

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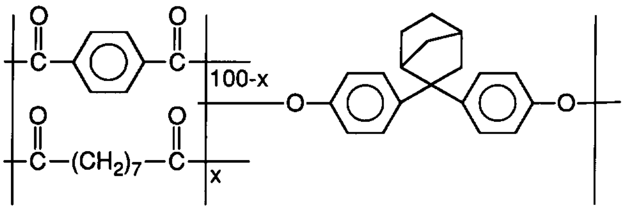
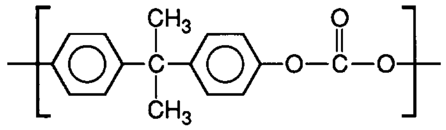


T(x)C - GJ



bisphenol-A polycarbonate

Figure 1 The structures of the polymers used in this study

is worth mentioning here that χ is usually found to be composition dependent. The detailed physical significance of the χ value obtained from different methods and its composition dependence have been discussed by Sanchez[25,26].

The chemical potential ($\Delta\mu_i$) can be obtained[27–31] by taking the first derivative of Δg with respect to n_i, which is the number of molecules of component i

$$\Delta\mu_1/kT = \ln\phi_1 + [1-(y_1v_1/y_2v_2)]\phi_2 + y_1v_1\chi\phi_2^2 \quad (4)$$

$$\Delta\mu_2/kT = \ln\phi_2 + [1-(y_2v_2/y_1v_1)]\phi_1 + y_2v_2\chi\phi_1^2 \quad (5)$$

At equilibrium the chemical potential of each component must be the same in both phases (denoted a and b)

$$\Delta\mu_1^{\mathrm{a}} = \Delta\mu_1^{\mathrm{b}}$$

$$\Delta\mu_2^{\mathrm{a}} = \Delta\mu_2^{\mathrm{b}} \quad (6)$$

then χ can be obtained from equations (4) and (6)[27–31]

$$\tilde{\chi} = \chi/v_0 = \frac{\ln(\phi_1^{\mathrm{b}}/\phi_1^{\mathrm{a}}) + [1-(y_1v_1/y_2v_2)](\phi_2^{\mathrm{b}}-\phi_2^{\mathrm{a}})}{y_1v_1[(\phi_2^{\mathrm{a}})^2-(\phi_2^{\mathrm{b}})^2]} \quad (7)$$

or from equations (5) and (6)[27–31]

$$\tilde{\chi} = \chi/v_0 = \frac{\ln(\phi_2^{\mathrm{b}}/\phi_2^{\mathrm{a}}) + [1-(y_2v_2/y_1v_1)](\phi_1^{\mathrm{b}}-\phi_1^{\mathrm{a}})}{y_2v_2[(\phi_1^{\mathrm{a}})^2-(\phi_1^{\mathrm{b}})^2]} \quad (8)$$

Therefore, χ can be calculated according to equation (7) or (8) if the phase compositions $\phi_{i,j}^{\mathrm{a}}$ and $\phi_{i,j}^{b}$ are known. The latter values can be determined from the T_g data of blends, as described in the text that follows.

The condition for phase stability of the blend at the spinodal point is

$$\partial^2\Delta g/\partial\phi^2 = 0 \quad (9)$$

then the interaction parameter at the spinodal point χ_s is given by

$$\tilde{\chi}_s = \chi_s/v_0 = \frac{1}{2}\left(\frac{1}{y_1v_1\phi_1} + \frac{1}{y_2v_2\phi_2}\right) \quad (10)$$

At the critical point, the conditions are

$$\partial^2\Delta g/\partial\phi^2 = \partial^3\Delta g/\partial\phi^3 = 0 \quad (11)$$

then the interaction parameter at that point χ_c is given by

$$\tilde{\chi}_c = \chi_c/v_0 = \frac{1}{2}\left(\frac{1}{\sqrt{y_1v_1}} + \frac{1}{\sqrt{y_2v_2}}\right)^2 \quad (12)$$

As shown in equation (12), χ_c can be derived easily from the degree of polymerization and the monomer volumes of the components. This value can serve as a criterion for predicting phase stability or phase separation of a blend if the χ value is determined. In other words, the blend can form a single and stable phase if $\chi < \chi_c$, or it will be phase separated if $\chi > \chi_c$.

EXPERIMENTAL

The structures of the polymers used in this study are shown in *Figure 1* and their physical characteristics are listed in *Table 1*. The molecular weights of the polymer samples were determined by the universal calibration method[32] based on the hydrodynamic volume or on viscosity detection. The high T_g amorphous polyester T(40)C-GJ was synthesized by condensation polymerization from 4,4′-(2-norbornylidene)diphenol and terephthalic acid/azelaic acid in a 60/40 molar ratio. The lower molecular weight PC Lexan was obtained from General Electric and the higher molecular weight PC Makrolon (MK) was obtained from Mobay. The desired weight ratios of the polymer blends were dissolved in dichloromethane (CH_2Cl_2) at 5 wt%. The polymer solutions were poured into Petri dishes and allowed to evaporate to give thin films. These films were dried in a vacuum oven at 70°C for two or three days.

The T_g and ΔC_p values of the polymers and blends were measured using a Perkin–Elmer DSC-7. A sample weight of 7–15 mg and a heating rate of 10°C min^{-1} were used. The samples were all scanned from 0 to 230°C and then fast quenched to 0°C for the second scan. The T_g is defined as the midpoint of the glass transition from the second run of the d.s.c. measurement.

Transmision electron microscopy (TEM) was used to examine the phase morphology of 50/50 wt% blends of T(40)C-GJ/Lexan and T(40)C-GJ/MK films which had been thermally treated at 230°C for 5 min in order to reach the equilibrium state but avoid transesterification. In the TEM differential mass loss causes the polycarbonate-rich areas of the thin section to appear lighter than the polyester-rich domains.

RESULTS AND DISCUSSION

Figures 2 and *3* show the second run d.s.c. curves for the T(40)C-GJ/Lexan and T(40)C-GJ/MK blends, respectively. Their T_g values are listed in *Table 2*. It can be seen that all of the T(40)C-GJ/Lexan blends show a single T_g, indicating that they are miscible. The T(40)C-GJ/MK blends, on the other hand, show two T_g values for most compositions, indicating that these two polymers are not miscible.

Table 1 The physical characteristics of the polymers used in this study

Polymer	M_w (g mol^{-1})	M_w/M_n	T_g (°C)	ΔC_p (J g^{-1} °C^{-1})
T(40)C-GJ	65 700	2.75	193.6	0.16
Makrolon	73 200	3.57	155.8	0.21
Lexan	28 100	3.02	145.2	0.19

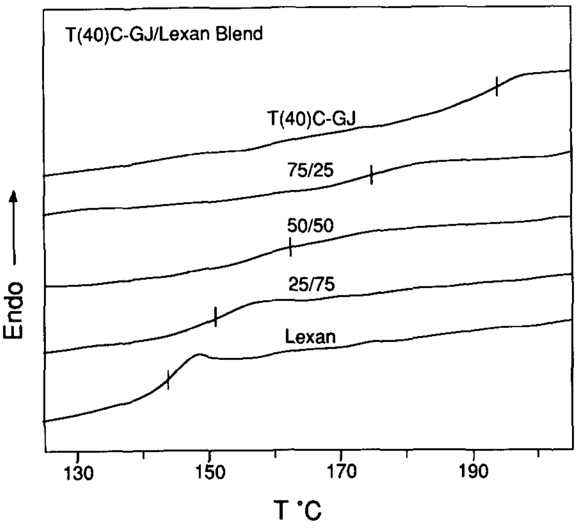


Figure 2 The second run d.s.c. curves for T(40)C-GJ/Lexan blends

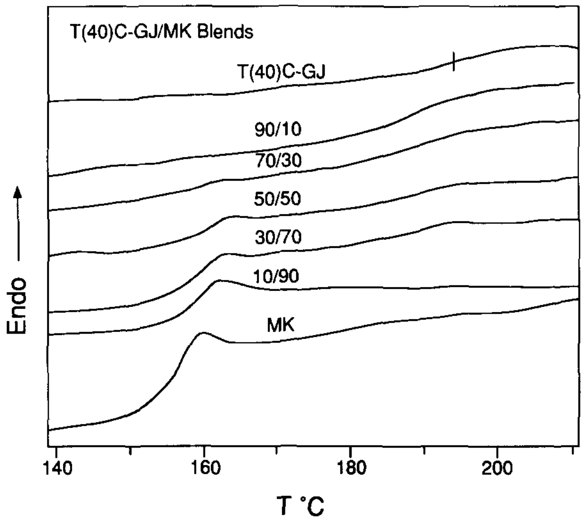


Figure 3 The second run d.s.c. curves for T(40)C-GJ/MK blends

Table 2 T_g results for the T(40)C-GJ/Lexan and T(40)C-GJ/MK blends

T(40)C-GJ/Lexan blends		T(40)C-GJ/MK blends	
Composition	T_g (°C)	Composition	T_g (°C)
25/75	152.4	10/90	157.4, -
50/50	162.9	30/70	159.1, 188.2
75/25	177.2	50/50	158.1, 187.9
		70/30	159.8, 186.7
		90/10	-, 185.2

The T_g behaviour of miscible polymer blends is usually described by the following equations.

1. The Gordon–Taylor (G–T) equation[33]

$$T_{gB}=\frac{W_1T_{g1}+kW_2T_{g2}}{W_1+kW_2} \tag{13}$$

where $k=\Delta\alpha_2/\Delta\alpha_1$.

2. The Fox equation[34]

$$\frac{1}{T_{gB}}=\frac{W_1}{T_{g1}}+\frac{W_2}{T_{g2}} \tag{14}$$

3. The Couchman equation[35]

$$\ln T_{gB}=\frac{W_1\Delta C_{p1}\ln T_{g1}+W_2\Delta C_{p2}\ln T_{g2}}{W_1\Delta C_{p1}+W_2\Delta C_{p2}} \tag{15}$$

T_{gi} and W_i are the T_g and weight ratio of the component polymer i, respectively, T_{gB} is the T_g of the polymer blend and $\Delta\alpha_i$ is the thermal expansion coefficient of the component polymer i. *Figure 4* demonstrates the fit of the T_g data of the miscible blend T(40)C-GJ/Lexan with the above three equations. It is observed that both the G–T equation with $k=1.7$ and the Couchman equation can accurately describe the T_g behaviour of T(40)C-GJ/Lexan blends. These equations were then used to determine the phase compositions for the phase-separated T(40)C-GJ/MK blends.

It is reasonable to assume that each of these two phases, e.g. phase 'a' (the high T_g T(40)C-GJ-rich phase) and phase 'b' (the low T_g MK-rich phase), can be described by either the G–T equation with $k=1.7$ or the Couchman equation. Therefore, the T_{gB} of phase 'a' can be written with the G–T equation as

$$T^{a}_{gB}=\frac{\phi^{a}_1T_{g1}+k\phi^{a}_2T_{g2}}{\phi^{a}_1+k\phi^{a}_2} \tag{16}$$

Equation (8) may be rearranged to

$$\phi^{a}_1=\frac{-k(T^{a}_{gB}-T_{g2})}{(T^{a}_{gB}-T_{g1})-k(T^{a}_{gB}-T_{g2})} \tag{17}$$

From a rearrangement of the Couchman equation, ϕ^{a}_1 can also be given as

$$\phi^{a}_1=\frac{\Delta C_{p2}(\ln T^{a}_{gB}-\ln T_{g2})}{\Delta C_{p1}(\ln T_{g1}-\ln T^{a}_{gB})+\Delta C_{p2}(\ln T^{a}_{gB}-\ln T_{g2})} \tag{18}$$

and $\phi^{a}_2=1-\phi^{a}_1$. It has to be mentioned here that ϕ_i has replaced W_i since the density of T(40)C-GJ is assumed to be equal to that of MK ($1.20\,\mathrm{g\,cm^{-3}}$). A similar calculation for phase 'b' can be made. Therefore, the phase compositions of T(40)C-GJ/MK blends can be determined by either equation (17) or (18). The calculated phase compositions are listed in *Table 3*. We can then estimate χ in terms of equation (7) or (8), provided that the system is at equilibrium or nearly so. The average χ values are listed in *Table 3*. The χ values for the T(40)C-GJ and polycarbonate blends are in the range $(8.4\text{–}9.9)\times10^{-3}$ and are slightly composition dependent.

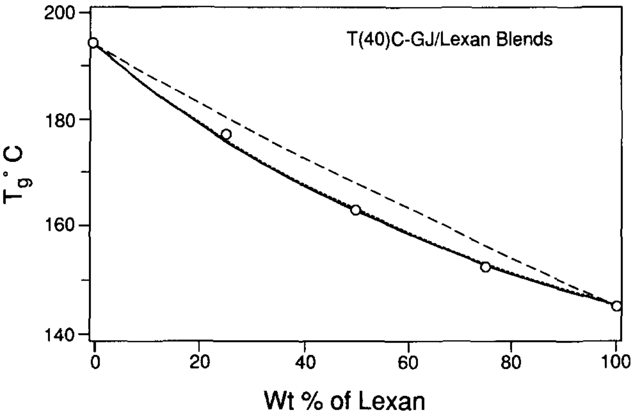


Figure 4 The fitted curves for the T_g data of T(40)C-GJ/Lexan blends: (— — —) Fox equation; (- - -) G–T equation, $k=1.7$; (——) Couchman equation

Table 3 The χ results for T(40)C-GJ/PC blends from d.s.c. measurements

T(40)C-GJ/PC	ϕ_1^a	ϕ_1^b	$10^5\tilde{\chi}$	$10^3\chi$
G–T equation, $k=1.7$				
30/70	0.911	0.140	4.62	8.88
50/50	0.905	0.061	5.13	9.86
70/30	0.884	0.180	4.45	9.25
Couchman equation				
30/70	0.898	0.123	4.46	8.58
50/50	0.892	0.087	4.57	8.79
70/30	0.867	0.148	4.36	8.38

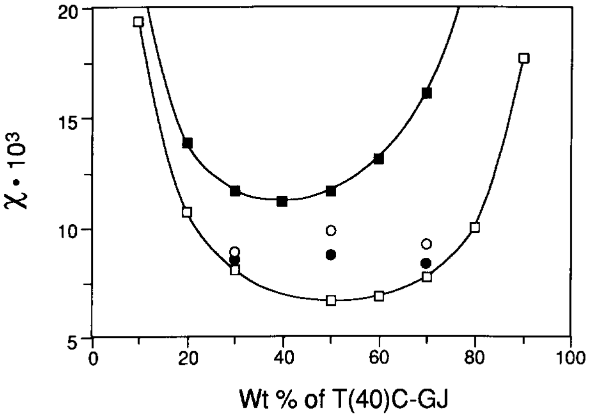


Figure 5 Plots of χ results for T(40)C-GJ/PC blends *versus* T(40)C-GJ composition: (○) experimental χ data from the G–T equation; (●) experimental χ data from the Couchman equation; (■) calculated χ_s data for T(40)C-GJ/Lexan blends; (□) calculated χ_s data for T(40)C-GJ/MK blends

The χ values in *Table 3* were calculated by assuming that $v_0 = \sqrt{v_1 v_2}$, where $v_1 = v_{T(40)C\text{-}GJ} = 174.5\ \mathrm{cm^3\,mol^{-1}}$ and $v_2 = v_{PC} = 212\ \mathrm{cm^3\,mol^{-1}}$.

The χ_c is 11.2×10^{-3} for the T(40)C-GJ/Lexan blends and 6.65×10^{-3} for the T(40)C-GJ/MK blends, as calculated according to equation (12). All χ, χ_s and χ_c data are plotted *versus* T(40)C-GJ composition in *Figure 5*. This plot clearly shows that $\chi < \chi_c$ or χ_s for the T(40)C-GJ/Lexan blend, implying a homogeneous phase, and that $\chi > \chi_c$ or χ_s for the T(40)C-GJ/MK blend, indicating that phase separation should occur. The critical composition for T(40)C-GJ/MK is about 50 wt% of T(40)C-GJ and that for T(40)C-GJ/Lexan is 40 wt% of T(40)C-GJ. The spinodal curve of T(40)C-GJ/MK is more symmetrical than that of T(40)C-GJ/Lexan owing to the fact that $\sqrt{y_1 v_1} \approx \sqrt{y_2 v_2}$ for the former blend. These results are consistent with the d.s.c. observations. TEM micrographs for 50/50 wt% T(40)C-GJ/MK and T(40)C-GJ/Lexan blends are shown in *Figures 6a* and *6b*, respectively. The first blend clearly phase separates, indicating an immiscible system, while the second blend appears to be homogeneous, indicating a miscible system. The phase morphology observed by TEM is consistent with the χ results obtained by d.s.c. measurements.

CONCLUSIONS

Differential scanning calorimetry (d.s.c.) has been successfully applied to characterize the miscibility of blends of a high T_g polyester (T(40)C-GJ), synthesized by condensation polymerization from 4,4′-(2-norbornylidene)diphenol and terephthalic acid/azelaic acid in a 60/40 molar ratio, with bisphenol-A polycarbonate (PC). For T(40)C-GJ/Lexan (the lower molecular weight PC) blends, d.s.c. shows a single T_g for all compositions studied. Their T_g behaviour as a function of composition can be accurately described by the Gordon–Taylor equation with $k = 1.7$ or the Couchman equation. For T(40)C-GJ/MK (the higher molecular weight PC) blends, d.s.c. shows two T_g values for most compositions, indicating that this system is phase separated. Theoretical expressions using the measured T_g data to obtain χ for the phase-separated polymer blend were derived, based on the Flory–Huggins theory[25–29] and the Sanchez equation[30,31]. The χ values of the blends have been determined in terms of equation (7) or (8) from the phase compositions of phase-separated T(40)C-GJ/MK blends, and the phase compositions of this blend have been calculated in terms of equation (17) or (18) from the experimental T_g equation for single-phase T(40)C-GJ/Lexan blends. The χ values of the T(40)C-GJ/PC blends are in the range $(8.4\text{–}9.9) \times 10^{-3}$ and are slightly composition dependent.

The χ values have provided a quantitative understanding of the miscibility of these blends. In other words, $\chi > \chi_c$ or χ_s for T(40)C-GJ/MK results in phase separation, while $\chi < \chi_c$ or χ_s for T(40)C-GJ/Lexan should result in a homogeneous phase. TEM micrographs of 50/50 wt% blends are consistent with the d.s.c. results and χ data.

It is concluded that the miscibility of T(40)C-GJ/PC blends is understood in terms of the χ values derived from T_g data measured by d.s.c. The miscibility is sensitive

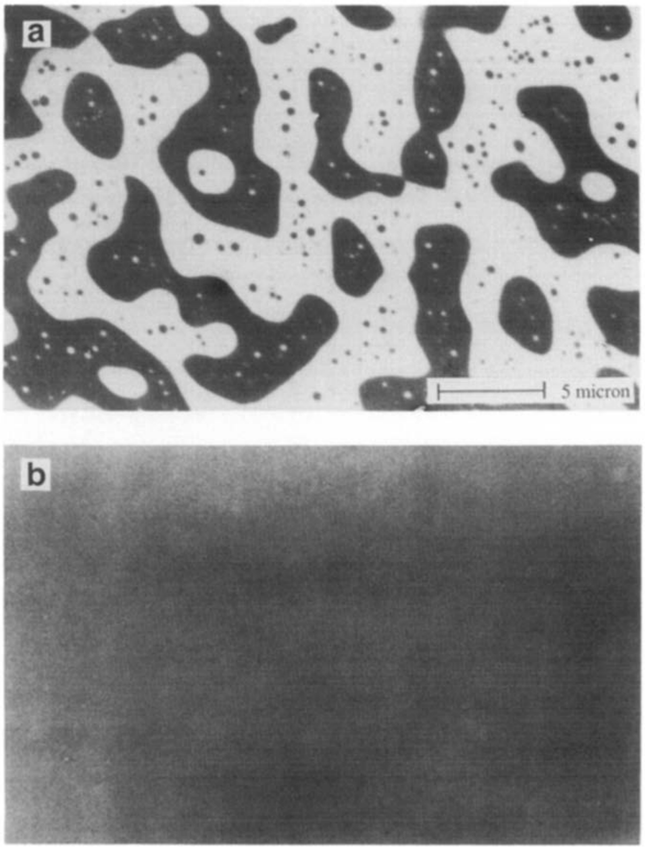


Figure 6 Transmission electron micrographs of (a) T(40)C-GJ/MK and (b) T(40)C-GJ/Lexan 50/50 wt% blends

to the molecular weights of the component polymers since the χ values are close to χ_c.

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REFERENCES

1 Freitag, D., Fengler, G. and Morbiter, L. *Angew. Chem., Int. Edn Engl.* 1991, **30**, 1598

2 Paul, D. R. and Newman, S. (Eds) 'Polymer Blends', Vols 1 and 2, Academic Press, New York, 1978

3 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1980

4 Kirste, R. G., Kruse, W. A. and Ibel, K. *Polymer* 1975, **16**, 20

5 Walsh, D. J., Higgins, J. S., Doube, C. P. and McKeown, J. G. *Polymer* 1981, **22**, 168

6 Russell, T. P. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 1593

7 Jelenic, J., Kirste, R. G., Oberthur, R. C., Schmitt-Strucher, S. and Schmitt, B. *Makromol. Chem.* 1984, **185**, 129

8 Shibayama, M., Yang, H., Stein, R. S. and Han, C. C. *Macromolecules* 1985, **18**, 2179

9 Lipson, J. E. G. and Guillet, J. E. 'Developments in Polymer Characterizations' (Ed. J. V. Dawkins), Vol. 3, Applied Science, London, 1982, Ch. 2

10 Su, A. C. and Fried, J. R. *J. Polym. Sci., Polym. Lett. Edn* 1986, **24**, 343

11 Olabisi, O. *Macromolecules* 1975, **8**, 316

12 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909

13 Aubin, M. and Prud'homme, R. E. *Macromolecules* 1980, **13**, 365

14 Harris, J. E., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1983, **23**, 676

15 Berek, D., Lath, D. and Durdovic, V. *J. Polym. Sci.* (*C*) 1967, **16**, 659

16 Shultz, A. R. and McCullough, C. R. *J. Polym. Sci.* (*A-2*) 1972, **10**, 307

17 Kim, W. N. and Burns, C. M. *J. Appl. Polym. Sci.* 1986, **32**, 3863

18 Kim, W. N. and Burns, C. M. *Macromolecules* 1987, **20** (8), 1876

19 Burns, C. M. and Kim, W. N. *Polym. Eng. Sci.* 1988, **28** (21), 1362

20 Kim, W. N. and Burns, C. M. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 1409

21 Yang, H., Ricci, S. and Collins, M. *Macromolecules* 1991, **24**, 5218

22 Godard, P., Dekoninck, J. M., Dexlesaver, V. and Devaux, J. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 3301

23 Huang, Z. H. and Wang, L. H. *Makromol. Chem., Rapid Commun.* 1986, **7**, 255

24 Suzuki, T., Tanaka, H. and Nishi, T. *Polymer* 1989, **30**, 1287

25 Sanchez, I. C. in 'Encyclopedia of Physical Science and Technology' (Ed. R. A. Meyers), Vol. 13, 2nd Edn, Academic Press, New York, 1992, p. 153

26 Sanchez, I. C. *Polymer* 1989, **30**, 471

27 Huggins, M. L. *Ann. N. Y. Acad. Sci.* 1942, **43**, 9

28 Flory, P. J. *Proc. R. Soc. London, Ser. A* 1942, **234**, 60

29 Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279

30 Tompa, H. *Trans. Faraday Soc.* 1949, **45**, 1142

31 Tompa, H. 'Polymer Solutions', Butterworth, London, 1956, Chs 4 and 7

32 Bailly, C., Daoust, D., Legras, R., Mercier, J. P., Strazielle, C. and Lapp, A. *Polymer* 1986, **27**, 1410

33 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2**, 493

34 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123

35 Couchman, P. R. *Macromolecules* 1978, **11**, 1156