Cloud-point curves and interaction parameters of unsaturated polyester–styrene solutions

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Experimental cloud-point curves of unsaturated polyester (UP) prepolymers with styrene have been determined in this work. The UP prepolymers are copolymers based on maleic anhydride and two types of glycols: diethylene glycol (DEG) and neopentyl glycol (NPG). For UP prepolymers with the same number-average molecular weight ($\bar{M}_n$) and the same hydroxyl functionality ($\bar{f}_{OH}$), the miscibility with styrene increases when the NPG content increases. For the different chemical structures, the calculated solubility (δ) and interaction (χ) parameters of the prepolymers decrease when the NPG content increases. A linear correlation between the theoretical critical temperatures (T_c) and the interaction parameters (χ) is observed.

(Keywords: cloud-point curves; interaction parameter; unsaturated polyester resin; miscibility)

INTRODUCTION

Unsaturated polyester (UP) resins are some of the most important resins for composites applications. They are particularly used in sheet moulding compounds (SMC) or bulk moulding compounds (BMC) for manufacturing automotive parts. Many researchers[1–9] have studied the curing kinetics of the bulk copolymerization of styrene–unsaturated polyester resins. Like most thermosetting matrices, unsaturated polyester resins have been blended with several additives to improve their properties[10]. For example, the impact properties of UP resins blended with elastomer additives were examined to improve the product's brittleness[11]. During curing, the high shrinkage of the UP resin may cause several moulding problems such as poor surface quality, warpage, sink marks, internal cracks, blisters and dimension changes[12,13]. To date, these problems have been mostly eliminated by the use of low-profile additives (LPA) such as poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVA) for compensating the resin shrinkage[14–18].

Recently, a mechanism of phase separation of these ternary systems has been proposed[19]. It demonstrates that the morphologies are correlated to the ternary system miscibility, i.e. the ternary phase diagram. It has also been shown that the miscibility of the unsaturated polyester prepolymer with styrene is a key factor for morphology control. Moreover, the miscibility of this binary system influences the network formation in terms of copolymerization kinetics[20].

The solubility of polyester prepolymers has not been widely studied in the literature. Rosso *et al.*[21–24] in the 1970s reported the influence of polyester molecular structure on the miscibility and crystallization of polyesters in various solvents. Unfortunately, their studies were performed with saturated polyester prepolymers instead of UP prepolymers. More recently, Thoinon[25] studied the influence of the diacid nature on the miscibility of diethylene glycol-based polyester oligomers with styrene. The results reported in *Figure 1* provided the following classification in order of increasing miscibility: fumaric acid < terephthalic acid < isophthalic acid.

The relative influences of molecular weight and chain-end nature have also been investigated[26]. In general, the miscibility of a polymer solution can be increased by lowering the molecular weight of the added polymer[19,27]. The UP prepolymer chain ends consist of hydroxyl and carboxyl groups. However, they are very polar and are expected to be unfavourable for system miscibility. Consequently, a decrease in the UP molecular weight enhances the chain-end effect and therefore the system miscibility decreases.

Nevertheless, the hydroxyl and/or carboxyl end-groups of the UP resins are not practically avoidable in the synthesis of UP resins. Therefore, one can modify the resin miscibility by controlling the molecular structure and the molecular weight of UP prepolymers.

In this work, the miscibilities of systems containing styrene and various unsaturated polyester prepolymers were determined. The system miscibility has been expressed in terms of cloud-point curves (*CPC*). The

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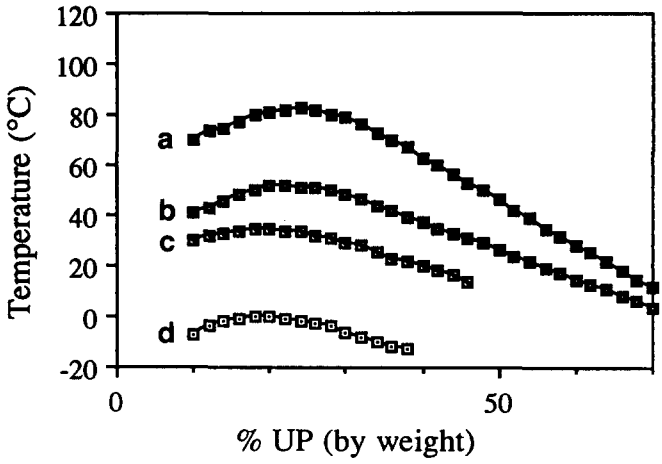

Figure 1 Experimental cloud-point curves of polyester oligomers: a, fumaric acid; b, isophthalic–fumaric acid; c, terephthalic acid; d, isophthalic acid[25]

polyester prepolymer chemical structure was changed by using two different glycols: diethylene glycol (DEG) and/or neopentyl glycol (NPG). For the different chemical structures, the critical temperatures (T_c) were correlated to the calculated solubility (δ) and interaction (χ) parameters.

EXPERIMENTAL

Materials

The unsaturated polyester resins used in this study were supplied by Cray Valley. They are 1:1 copolymers of maleic anhydride (MA) with diols in a styrene solution. The diols were diethylene glycol (DEG) and neopentyl glycol (NPG). The molar ratio of DEG to NPG in the resin was in the range of 100/0 to 60/40. The notation and the molecular characteristics of these UP resins are summarized in *Tables 1, 2* and *3*.

A polyurethane-extended polyester resin was also used in this study. It is obtained by reacting the unsaturated polyester prepolymer F90-1 (90/10 of DEG/NPG) with a pure 4,4'-diphenylmethane diisocyanate (MDI; from Bayer, reference 44M). The stoichiometry ratio was chosen to be [NCO]/[OH] = 0.5 and the reaction was carried out in styrene at room temperature. The extent of reaction was monitored by *FT*i.r. by following the NCO peak at 2270 cm^{-1}.

^1H n.m.r.

Samples were examined by ^1H n.m.r. with a Brucker 1M360. The proton spectra show the resonances that demonstrate the isomerization of maleate (6.2–6.3 ppm) to fumarate (6.9–7.1 ppm) and the double-bond saturation by glycols (Ordelt reaction) (2.8–3.1 ppm).

Cloud point

A liquid mixture could be transparent or opaque (cloudy) depending on the system composition and the system temperature. Theoretically, if the refractive indices of the mixture components are sufficiently different, a transparent mixture represents a miscible single-phase system; while a cloudy mixture always represents an immiscible two-phase system. The cloud point is the point at which the system changes from transparent to cloudy or changes from cloudy to transparent on changing the composition or the temperature.

In this work, the cloud points of styrene–UP prepolymers were determined by observing the change of transparency of the systems by increasing the mixture temperature under moderate agitation.

Chromatography

Gel permeation chromatography (g.p.c.) was used to measure the polymer molecular weight (MW) at room temperature with the following column combination: 10^5, 10^4, 10^3 and 500 Å. All the g.p.c. curves were analysed by using the calibration curve obtained with standard samples of monodisperse polystyrene to estimate the molecular weight.

I_{OH} and I_A

The concentration of hydroxy or carboxy chain ends was determined by titration. I_{OH} was determined using potassium hydroxide (KOH) and acetic acid, and I_A was determined using potassium hydroxide (KOH). From these results it is possible to calculate the functionalities and the number-average molecular weight of our UP prepolymers, assuming that there is no Ordelt reaction occurring:

$$\bar{f}_{OH} = \frac{2I_{OH}}{I_{OH} + I_A} \qquad \bar{f}_{COOH} = \frac{2I_A}{I_A + I_{OH}}$$

$$\bar{M}_n = \frac{2 \times 56.1 \times 10^3}{I_A + I_{OH}}$$

Calorimetry

Differential scanning calorimetry (Mettler TA3000) was used to determine the glass transition temperature (T_g) of the UP prepolymers. The scanning rate was set at 7.5°C min^{-1}. The results of T_g are listed in *Table 3*. In some cases, the melting temperatures (T_m) of the prepolymers were also measured by d.s.c.

RESULTS AND DISCUSSION

Characterization of UP prepolymer

The structure of the UP prepolymers was confirmed by n.m.r.

During the synthesis of polyester prepolymers, two major side reactions may occur. The first one is double-bond isomerization from a *cis* conformation to a *trans* conformation, i.e. from maleate to fumarate. This reaction is necessary to provide the fumarate double bonds in the polyester backbone, which are more suitable for copolymerization with styrene than the corresponding maleate[28]. In our case, the isomerizations were kept

Table 1 Formulations and notations used in this work

Nomenclature[a]	DEG (%)	NPG (%)
M0	0	100
F60	60	40
F80	80	20
F90-1, F90-2, F90-3	90	10
F95	95	5
F100; M100	100	0

[a]F, fumarate; M, maleate; F90-*X*, same formulation, different molecular weight

Table 2 Characteristics of unsaturated polyester prepolymers

Ref.	Isomerization (%)	Ordelt[a] (%)	I_{OH}	I_A	$\bar{f}_{OH}$[b]	$\bar{f}_{COOH}$[b]	$\bar{M}_{n,calc}$[b]
M0	55	1.5	74.3	20.3	1.57	0.43	1190
F60	94	2.5	73.0	17.1	1.62	0.38	1245
F80	95	4.0	71.8	17.5	1.61	0.39	1260
F90-1	95	3.8	72.4	17.7	1.61	0.39	1245
F90-2	95	4.0	51.4	15.9	1.53	0.47	1670
F90-3	97	3.2	42.5	7.8	1.69	0.31	2230
F95	97	3.8	72.6	19.8	1.57	0.43	1210
F100	93	4.0	72.3	17.7	1.61	0.39	1250
M100	57	2.4	72.8	15.2	1.65	0.35	1275

[a]See text
[b]Calculated with Ordelt ratio equal to zero

Table 3 G.p.c. characterization and glass transition temperature (T_g) of UP prepolymers

Ref.	G.p.c. characterization			T_g (°C)
	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$	
M0	2020	1.84	1.64	−9.0
F60	2510	2.00	1.88	−18.7
F80	2470	2.01	2.01	−21.7
F90-1	2450	1.91	1.83	−23.9
F90-2	3190	2.56	2.89	−19.6
F90-3	4370	8.02	8.51	−17.5
F95	2590	1.95	1.91	−24.1
F100	2380	1.93	1.71	−24.2
M100	2200	1.92	1.86	−27.1

constant at a value higher than 95% except for the prepolymers referenced as M (*Table 2*).

The second important side reaction is double-bond saturation by glycols[29]. This reaction is sometimes called the 'Ordelt reaction'. The use of primary glycols (e.g. diethylene glycol) rather than secondary glycols (e.g. propylene glycol) reduces the amount of double-bond saturation[30]. This is the reason why the double-bond saturation in this work was kept constant at a very low level less than or equal to 4% (*Table 2*).

All the UP prepolymers have $\bar{f}_{OH}$ in the range 1.5–1.7. We would like to have $\bar{f}_{OH} = 2$, but this is impossible to achieve without an increase in the percentage of the Ordelt reaction.

All the UP prepolymers have $\bar{M}_n$ in the range 1200–1275 except F90-2 and F90-3, which were prepared to study the molecular-weight effect on mixture miscibility.

The g.p.c. curves are not given here, but the $\bar{M}_n$ expressed in PS standards and the polydispersity indices are given in *Table 3*. All the polydispersity indices are around 2 except for the UP with the highest molecular weight whose polydispersity index $\bar{M}_w/\bar{M}_n$ increases up to 8. This increase in $\bar{M}_w/\bar{M}_n$ is due to a queue of high molecular weight. Its $\bar{M}_z/\bar{M}_w$ is equal to 8.5. Note that the percentage of Ordelt reaction stays constant.

The polyester prepolymers referred to as M0 and F60 crystallize at room temperature after a few days of storage. The crystallization is due to the presence of a high amount of the rigid symmetric NPG molecules in the polyester backbone. M0 and F60 exhibited two melting points at 35°C and −30°C corresponding to the polyester and prepolymer and to the styrene, respectively.

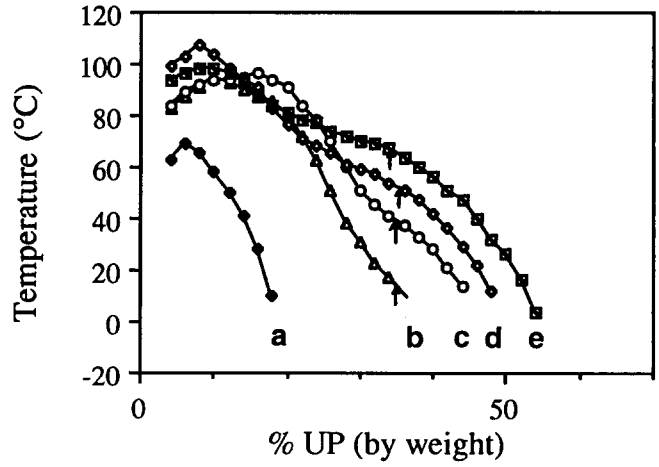

Figure 2 Experimental cloud-point curves of unsaturated polyester prepolymers–styrene: a, F60; b, F80; c, F90-1; d, F95; e, F100. The prepolymer M0 is entirely miscible. The arrows indicate the critical points

Because NPG is more rigid than DEG, the glass transition temperatures of the prepolymers increase quasi-linearly with the NPG content (*Table 3*). The *MW* increase induces an increase in the T_g of the polyester prepolymers. This classical trend can be expressed by a Fox–Flory analysis[31]:

$$T_g = T_{g\infty} - K/M$$

in which $T_{g\infty}$ is the glass transition temperature of the corresponding infinite *MW* polymer; T_g is the glass transition temperature of the polymer having a *MW* equal to M; and K is a constant. In our case, the best-fitting result shows $T_{g\infty} = -9$°C and $K = 1.82 \times 10^4$ mol K g^{-1}.

Cloud-point curves (CPC)

Figure 2 shows the *CPCs* of the systems containing styrene and the UP prepolymers F100, F95, F90-1, F80 and F60, respectively. Below the *CPC* is the two-phase region. The curves are similar to the *UCST* (upper critical solution temperature) curves for most of the binary polymer solutions[26]. This means that, from an application point of view, for a given NPG amount one needs either to increase the temperature or to increase the UP content to obtain a miscible resin.

The cloud-point curves show a very familiar shape for

Table 4 Determination of the critical weight fraction (Ψ_c) and critical temperature (T_c). T_c was determined from the cloud-point curve knowing Ψ_c

Ref.	ρ (g cm^{-3})[a]	$\bar{V}_w$ (cm^3 mol^{-1})[b]	$\bar{V}_z$ (cm^3 mol^{-1})[b]	ϕ_c[c]	Ψ_c[d]	T_c (°C)[e]
M0	1.269	1275	2830	0.247	0.314	
F60	1.346	1850	3475	0.253	0.334	
F80	1.374	1843	3705	0.260	0.347	13
F90-1	1.388	1713	3135	0.258	0.347	40
F90-2	1.388	3080	8902	0.246	0.332	40
F90-3	1.388	12885	109651	0.215	0.295	41
F95	1.395	1691	3231	0.264	0.355	52
F100	1.403	1718	2938	0.251	0.341	66
M100	1.403	1745	3246	0.258	0.349	79

[a]Specific volume of UP prepolymer calculated with Fedors' tables[33]
[b]Weight- and *z*-average molecular volume calculated with equations (2) and (3)
[c]Critical volume fraction of UP prepolymer calculated with equation (1)
[d]Critical weight fraction of UP prepolymer
[e]Critical temperature determined from the *CPC* knowing Ψ_c

quasi-binary systems, i.e. systems containing polydisperse species. For quasi-binary polymer solutions, the critical point is the intercept of the *CPC*, the spinodal curve and the shadow curve, where the two separate phases become identical and form one phase. The polymer volume fraction at the critical point, denoted as the critical volume fraction ϕ_c, is expressed by[32]:

$$\phi_c = \frac{1}{1 + \bar{V}_w/(V_s\bar{V}_z)^{1/2}} \quad (1)$$

where $\bar{V}_w$ and $\bar{V}_z$ are the weight-average and *z*-average polymer molar volumes, respectively, and V_s is the solvent molar volume. In our case, V_s is 113.4 cm^3 mol^{-1} for the styrene, and $\bar{V}_w$ and $\bar{V}_z$ may be obtained through the following expressions:

$$\bar{V}_w = \frac{\bar{M}_{w,gpc}}{\bar{M}_{n,gpc}} \frac{\bar{M}_{n,calc}}{\rho_{calc}} \quad (2)$$

$$\bar{V}_z = \frac{\bar{M}_{z,gpc}}{\bar{M}_{w,gpc}} \bar{V}_w \quad (3)$$

where $\bar{M}_{z,gpc}$, $\bar{M}_{w,gpc}$ and $\bar{M}_{n,gpc}$ are the *z*-average, the weight-average and the number-average molecular weights of the UP prepolymers determined by gel permeation chromatography; $\bar{M}_{n,calc}$ is the calculated number-average molecular weight using a titration method and assuming the polymer density from Fedors' table[33] (see Appendix). Since the concentrations are plotted in weight fractions (Ψ), the weight fractions are calculated by assuming no volume change during mixing and using 0.91 for the density of styrene.

The results of Ψ_c calculations for the different UP prepolymers are presented in *Table 4*. The corresponding critical points for the resins with different amounts of NPG are shown in *Figure 2* by the arrows. From these critical points, one can easily obtain the critical temperatures, T_c. It is clearly shown that T_c is influenced by the NPG content of the UP prepolymer. *Figure 3* shows the relationship between T_c and NPG content. The result indicates that T_c decreases linearly when the NPG content of the UP prepolymer increases. The equation of the resulting straight line is:

$$T_c\,(\mathrm{K}) = 349 - 2.63 \times (\%\mathrm{NPG}) \quad (4)$$

This equation shows that T_c is very sensitive to the percentage of NPG. An increase of 5% of NPG decreases T_c by about 13°C.

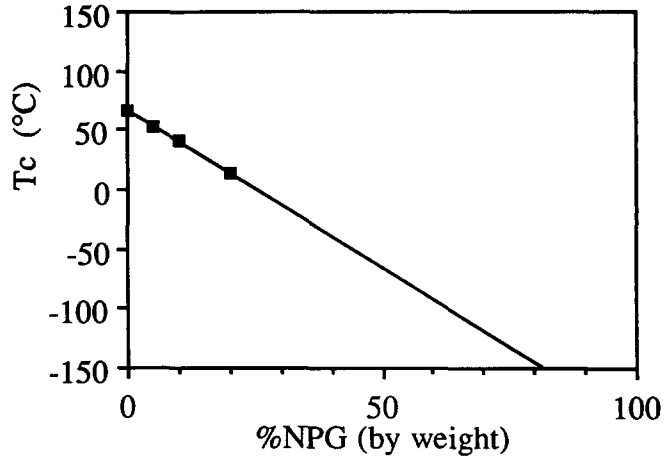

Figure 3 Critical temperature (T_c) *versus* NPG content of unsaturated polyester prepolymers

For a polydisperse polymer solution, the critical point may be affected by the molecular weight, the polydispersity and the molecular structure of the polymer. Since the *MW* and the polydispersities of the UP prepolymers used in *Figures 2* and *3* are similar, the resulting T_c can be a good indicator of system miscibility. The lower the T_c of the system, the higher is the miscibility. Consequently, from *Figure 2* and equation (4), one obtains that an increase in NPG content results in better miscibility of UP prepolymer in styrene. A pure NPG resin should have an extrapolated T_c value of 86 K. This miscibility trend can also be observed in *Figure 2* on the *CPC*s. The M0 prepolymer containing 100% NPG is totally miscible with styrene at room temperature. Decreasing the NPG content leads to an upward movement of the corresponding *CPC* to a higher-temperature region, indicating a decrease in system miscibility.

In *Figure 2* it is found that the critical points are not located on the maximum points of the *CPC*s. For the *UCST* curve of a real binary polymer solution (with monodisperse polymer solute), it is true that the critical point is the maximum of the *CPC*. For a quasi-binary

polymer solution like UP resin, the maximum of the *CPC*, called the precipitation threshold by Tompa[34], shifts from the critical point towards lower polymer concentrations. The shift of the maximum is caused by the polydispersity of the polymer[35]. A more highly polydisperse polymer leads to a larger shift of the maximum from its critical point. It should also be noted that the precipitation threshold temperature, T_p, is always higher than the critical temperature, T_c.

The *CPC*s of the systems containing F90-1, F90-2 and F90-3 are presented in *Figure 4*. These prepolymers have similar molecular compositions but different molecular weights, and unfortunately also different polydispersity indices. Their characteristics are shown in *Tables 2* and *3*. The critical points are indicated by the arrows in *Figure 4*. Their critical fractions, ϕ_c and Ψ_c, and critical temperatures, T_c, are listed in *Table 4*. Among these systems, F90-1 shows the highest Ψ_c and for the most part the highest *CPC*, although it has a similar T_c to the others. One may conclude that F90-1 has the worst miscibility because it has the lowest molecular weight, which enhances the chain-end polarity effect mentioned in the 'Introduction'.

However, it is difficult to draw any conclusion for the F90-2 and F90-3 systems. As shown in *Table 3*, a large increase in polydispersity accompanies a molecular-weight increase for F90-3 as compared with F90-2. This leads to a compensation effect. On the one hand, the increase in molecular weight for F90-3 can result in better miscibility according to the chain-end effect. On the other hand, the large increase in polydispersity, from 2.56 for F90-2 to 8.02 for F90-3, tends to decrease the system miscibility. Consequently, the combination of these two opposing effects results in quite similar *CPC*s shown in *Figure 4* for F90-2 and F90-3.

The CPC of the resin PU/F90-1, i.e. polyurethane-extended F90-1 prepolymer, is also shown in *Figure 4*. The extension of the polyester chain by urethane groups increases the $\bar{M}_n$ from 2450 (F90-1) to 4220 (PU/F90-1). The polydispersity, however, does not change too much, from 1.9 for F90-1 to 2.2 for PU/F90-1. Note that the number-average molecular weight $\bar{M}_{n,gpc}$ of PU/F90-1 measured by g.p.c. is in the same range as that of F90-3 without urethane chain extension. In *Figure 4* it is clearly shown that the miscibility of PU/F90-1 is much lower

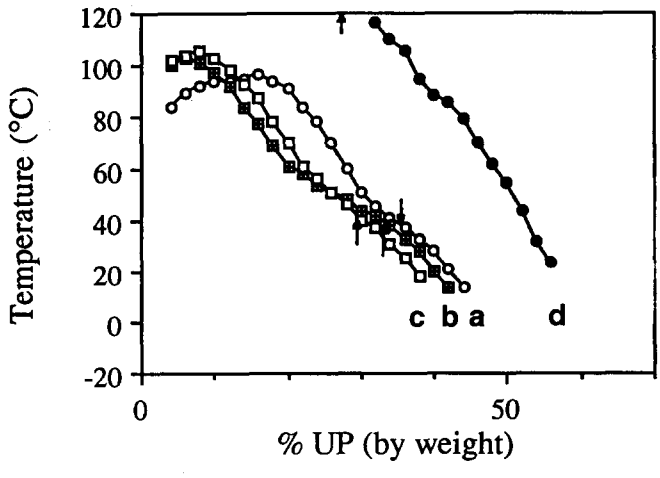

Figure 4 Experimental *CPC* of F90 prepolymers and PU/F90-1: a, F90-1; b, F90-2; c, F90-3; d, PU/F90-1. The arrows indicate the critical points. The critical temperature of PU/F90-1 is higher than 120°C

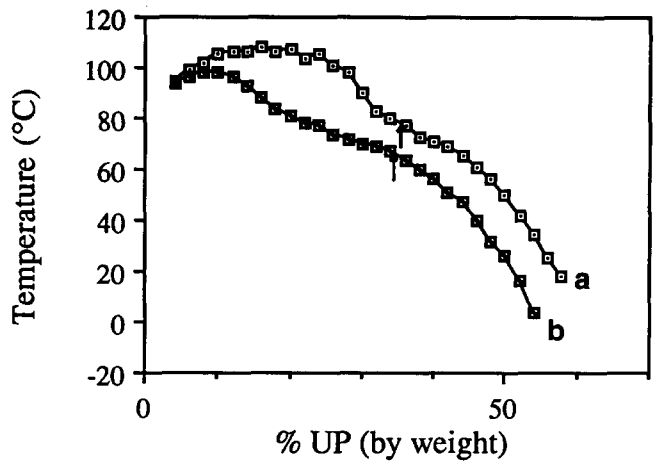

Figure 5 Experimental *CPC* of F100 and M100: a, M100; b, F100. The arrows indicate the critical points

than that of F90-1 because the *CPC* of the former is much higher than that of the latter. The miscibility of PU/F90-1 is also much lower than that of F90-3. The result is very complicated to explain in simple terms because there are several effects contributing to the system miscibility.

First of all, since the molecular weight of PU/F90-1 is higher than that of F90-1, the molecular-weight effect may cause a lower miscibility for PU/F90-1 as indicated by the classical theory[26]. While, as mentioned, the increase in molecular weight decreases the number of hydroxyl and carboxyl end-groups, and thus may increase the system miscibility. This chain-end effect may compensate for some of the molecular-weight effect.

The addition of isocyanates to produce urethane extensions of the polyester chains also results in two opposing effects. Wang *et al.*[36] revealed that there is a specific interaction between the –NH– groups of urethane bonds and the π electrons of styrene. This electron interaction may increase the system miscibility. In addition, the benzene rings from the MDI used in this work can also enhance the miscibility of PU/F90-1 with styrene. However, according to the urethane reaction, most of the hydroxyl end-groups of the polyester chains are consumed by isocyanate groups. That leaves almost only the carboxyl groups on the polyester chain ends. The hydrogen bonding between the carboxyl groups is strong enough to create an artificial molecular-weight increase that may decrease the system miscibility.

In short, there are several effects that either enhance or reduce the miscibility of PU/F90-1, compared with F90-1 or with F90-3, in styrene. Observing the *CPC* results in *Figure 4*, one may say that the molecular-weight effect is greater for PU/F90-1 than for F90-3 as compared with F90-1. Consequently PU/F90-1 is less miscible in styrene. This effect will be very useful for understanding the mechanism of UP thickening by isocyanate[25].

The effect of isomerization of the UP prepolymer on the *CPC* is presented in *Figure 5*. The isomerized UP prepolymer, F100, is more miscible in styrene than the non-isomerized one, M100. Their isomerization degrees are given in *Table 2*. The critical temperature and the critical fraction increase with the isomerization degree. In other words, isomerization improves the UP prepolymer miscibility with styrene.

Solubility and interaction parameters

The Flory–Huggins binary interaction parameter, χ, may be expressed in terms of the Hildebrand solubility parameter, δ, by[37,38]:

$$\chi = \frac{V_S}{RT}(\delta_S - \delta_{UP})^2 \quad (5)$$

where V_S is the styrene molar volume, and δ_S and δ_{UP} are the styrene and UP prepolymer solubility parameters, respectively. The Hildebrand solubility parameters, δ, of model organic compounds are calculated from vapour pressure data, i.e. $\delta = (\rho \Delta E_{vap}/M)^{0.5}$. Coleman *et al.*[39] note that this is not correct for compounds containing strongly self-associating groups such as alcoholic and phenolic hydroxyl, amide, urethane and carboxylic acid groups. In these cases a significant fraction of the molecule remains associated at the boiling point. The determination of the solubility parameter is ambiguous as M (molecular weight) is no longer just the molecular weight of the monomer but some larger value reflecting an average molecular weight of the associated species. According to Coleman *et al.*[39] in our calculations, the molar attraction constant of the –OH unit is false. For a polymer, δ is defined to be the same as that of a solvent in which the polymer will mix in all proportions without heat effects and without volume changes. Then, δ could be estimated from the structural formula of the polymer.

For a non-polar and non-associated polymer, the solubility parameter can be calculated by the following equation:

$$\delta = \sum F_i / \sum V_i \quad (6)$$

where F_i and V_i are the molar attraction constant[40] and the molar volume[33], respectively, of a constitutive unit i on the polymer chain. With the assumption that the UP prepolymer is non-polar and non-associated, one can estimate the solubility parameter for each UP prepolymer of different molecular structures. One example of a calculation of δ is given in the Appendix (for UP prepolymers with the same $\bar{M}_n$ and the same functionalities $\bar{f}_{OH}$ and $\bar{f}_{COOH}$, the polar effect of the chain ends will be the same). With the estimation of δ, one can then estimate the Flory–Huggins binary interaction parameter, χ, by equation (5).

The estimated δ and χ are shown in *Figure 6* for the DEG/NPG composed UP prepolymers at room temperature. The results show that both δ and χ decrease with the increase of NPG content in the UP prepolymer. As mentioned before, increasing the NPG content may increase the system miscibility. Thus, it may be concluded that the increase in system miscibility is caused by the decrease in χ. Nevertheless, one must note that the miscibility should be estimated by the difference between χ and the corresponding critical interaction parameter, χ_c. In practice, χ_c can be calculated by the following expression[41]:

$$\chi_c = \frac{1}{2}\left(1 + \frac{1}{\overline{DP}_w^{1/2}}\right)^2 - \frac{\overline{DP}_z^{1/2} - \overline{DP}_w^{1/2}}{2\overline{DP}_z\overline{DP}_w} \quad (7)$$

where $\overline{DP}_w$ and $\overline{DP}_z$ are the weight-average and z-average degrees of polymerization, respectively. The χ_c and χ results for all the systems used in this work are listed in *Table 5*.

Theoretically, if χ of a polymer solution or a polymer blend is smaller than its χ_c, the system should be miscible;

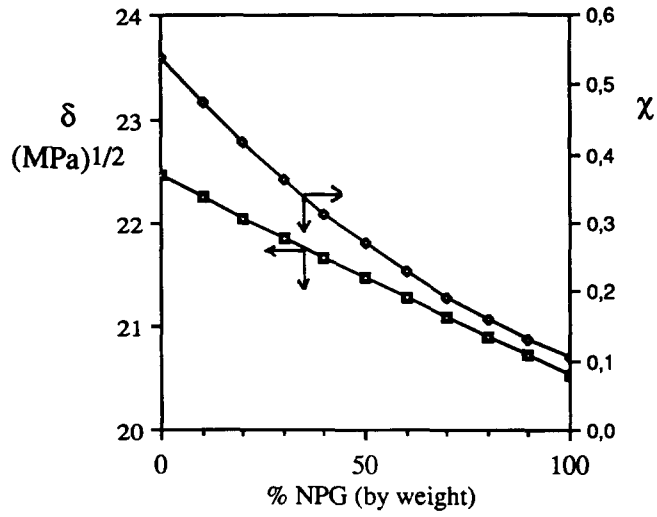

Figure 6 Solubility parameter (δ) and interaction parameter (χ) *versus* percentage of NPG

Table 5 Estimated interaction parameters (χ) and critical interaction parameters (χ_c) of unsaturated polyester prepolymers

Ref.	χ	χ_c
M0	0.105	0.831
F60	0.315	0.808
F80	0.417	0.805
F90-1	0.475	0.816
F90-2	0.475	0.729
F90-3	0.475	0.607
F95	0.506	0.817
F100	0.539	0.813
M100	0.539	0.811

otherwise it is immisicible. In order to increase the system miscibility, χ must be decreased. By equation (7), χ_c is only dependent on the distribution of the degree of polymerization, but χ is temperature-dependent and composition-dependent, as shown in equation (5). Therefore, there are two ways to increase the miscibility of a UP prepolymer in styrene: either heat up the system or decrease the solubility parameter, δ, of the UP prepolymer, for example, by increasing the NPG content (for UP prepolymers with the same $\bar{M}_n$ and the same $\bar{f}_{OH}$). Both results are clearly shown in *Figure 2*. Increasing system temperature can move the system higher than its *CPC*; then it can become miscible. With the other method, increasing the NPG content moves the *CPC* towards the lower-temperature region; then the system becomes miscible.

This work shows that one may easily estimate the system miscibility at a desired temperature by calculating χ and χ_c by the polymer characteristics. However, when applying this method to miscibility estimations, it must be noted that, for certain systems, χ is not only temperature-dependent but also concentration-dependent[26]. Neglecting the concentration effect sometimes may underestimate χ.

As mentioned previously, the critical temperature T_c may be a good indicator of system miscibility, i.e. lower T_c, higher miscibility. This is true for the UP prepolymers of constant molecular weight but having different NPG contents as shown in *Figure 2* and *Table 4*. *Figure 7* shows the correlation of T_c with χ at room temperature for the systems F80, F90-1, F95 and F100, which have similar

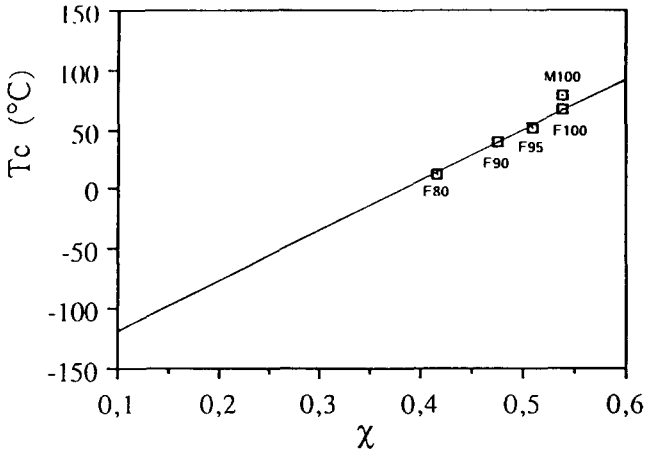

Figure 7 Critical temperature (T_c) *versus* interaction parameter (χ) of unsaturated polyester–styrene solutions

molecular weights. A linear correlation is observed, which indicates that one may estimate the critical temperature from the calculation of interaction parameter χ for the UP prepolymer–styrene solution. The T_c–χ point of M100 is also shown in *Figure 7*. This point is not located on the straight line of the F series system, owing to the low isomerization degree of M100. The best-fitting result of the straight line is:

$$T_c\ (\mathrm{K}) = 424.6\chi - 167.1$$

CONCLUSIONS

The miscibility of UP prepolymers with styrene depends on the structure of the UP prepolymers: the introduction of NPG ameliorates the miscibility. The calculation of the solubility and interaction parameters from the structural formulae show that both δ and χ decrease with the increase in NPG content in the UP prepolymers. A linear correlation between the critical temperature (T_c) and the interaction parameter (χ) for the UP prepolymers with the same $\bar{M}_n$ and the same $\bar{f}_{OH}$ was found.

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APPENDIX

Example calculation of the solubility and interaction parameters

Theoretical formula of unsaturated polyester prepolymers:

$$\mathrm{HO\text{-}R\text{-}O(CO\text{-}CH{=}CH\text{-}COO\text{-}R\text{-}O)_n\text{-}H}$$

with -R- : $\mathrm{-CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2-}$ (72 g mol^{-1})

or $\mathrm{-CH_2\text{-}C(CH_3)\text{-}CH_2-}$ (70 g mol^{-1})

Table 6 Values for example calculation

Atoms or groups of atoms	Number	Molar volume[33] ($\mathrm{cm^3\ mol^{-1}}$)	F(small)[38] ($\mathrm{J^{1/2}\,cm^{3/2}\,mol^{-1}}$)
-OH	2	10	348
-COO-	2×9=18	18	634
-CH=CH-	1×9=9	27	454
$-CH_2-$	8×4+2×2=36	16.1	272
-O-	8×1=8	3.8	143
$-CH_3$	2×2=4	33.5	438
-C-	2×1=2	−19.2	−190

Because $M_{DEG} \approx M_{NPG}$, the molar percentage of NPG constitutional units is approximately equal to the weight percentage of NPG in the formulation.

For 20% NPG, 80% DEG and $n = 9$ ($n + 1 = 10$), $M_{prepolymer} = 1776\ \mathrm{g\ mol^{-1}}$.

Numerical values for V_i and F_i are listed in *Table 6*. From these:

$$\sum V_i = 1292.6\ \mathrm{cm^3\ mol^{-1}}$$

$$\sum F_i = 28\,502\ \mathrm{J^{1/2}\ cm^{3/2} mol^{-1}}$$

$$\rho = \frac{\sum V_i}{M} = 1.2\ \mathrm{cm^3\ g^{-1}} \qquad \delta_{UP} = \frac{\sum F_i}{\sum V_i} = 22.05\ \mathrm{MPa^{1/2}}$$

where $\delta_S = 19.03\ \mathrm{MPa^{1/2}}$ (ref. 42), $V_S = 113.4\ \mathrm{cm^3\ mol^{-1}}$ (ref. 42) and $T = 298$ K, from equation (5) one obtains $\chi = 0.417$.

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