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Reaction-induced phase separation in poly(butylene terephthalate)–epoxy systems: 1. Conversion-temperature transformation diagrams

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Poly(butylene terephthalate) (PBT) was used as a semicrystalline modifier of epoxy-aromatic diamine formulations. The epoxy monomer was based on diglycidylether of bisphenol A (DGEBA) and the diamines were either 4,4′-methylenebis [3-chloro 2,6-diethylaniline] (MCDEA) or 4,4′-diaminodiphenylsulfone (DDS). PBT was more miscible in DGEBA–MCDEA than in DGEBA–DDS formulations, as revealed by the melting point depression observed in binary mixtures. Melting temperatures as a function of conversion were obtained for both systems using differential scanning calorimetry together with size exclusion chromatography. In the case of the PBT–DGEBA–DDS system, a cloud-point curve was also obtained, showing an upper-critical-solution-temperature behaviour. On the basis of melting, cloud-point, vitrification and gelation curves, conversion–temperature transformation diagrams were generated for both systems. These diagrams can be used to design particular cure cycles to generate different morphologies in the phase separation process. In the case of PBT–DGEBA–MCDEA systems, PBT could be either kept in solution in the matrix or separated by crystallization (initially or in the course of polymerization). For PBT–DGEBA–DDS systems, PBT was always segregated from the matrix, either initially through crystallization or by attainment of the cloud-point curve in the course of reaction. Morphologies generated and resulting mechanical properties will be discussed in the second part of the series. Copyright ©Elsevier Science Ltd.

(Keywords: poly(butylene terephthalate); epoxy; modified-epoxies)

INTRODUCTION

Epoxies constitute one of the most important classes of thermosetting polymers in use, including adhesives, matrices for fibre-reinforced composites and coatings. They exhibit excellent mechanical and thermal properties derived from the chemical nature of the starting monomers and the high crosslink density of the final materials. However, this kind of structure also leads to a low resistance to crack initiation and propagation making it necessary to introduce modifiers to increase toughness.

Rubber modifiers lead to toughened epoxies that are widely used as engineering adhesives. The presence of a rubber phase increases the fracture resistance but decreases the elastic modulus, yield strength and thermal stability of the material. An alternative approach to toughening epoxies is to use thermoplastics exhibiting high thermal stability and low propensity to absorb moisture. Among the thermoplastics used in the toughening of epoxies are amorphous polymers with high glass transition temperatures (T_g), such as poly(ether sulfones), poly(ether imides) and polysulfones. Also, the use of semicrystalline polymers with high melting temperatures, such as poly(butylene terephthalate) and polyamides, has been reported. A review of the developments in the area of thermoplastic-modified epoxies is available[1].

There are two main procedures to generating the dispersion of thermoplastic particles: a) phase separation during polymerization of an initial homogeneous solution (reaction-induced phase separation); and b) generation of a dispersion of the thermoplastic particles in the initial mixture of monomers.

In the case of semicrystalline modifiers, the few studies reported in the literature use the second method to generate the dispersion[2–6]. In this situation, the epoxy-hardener reaction takes place in the presence of preformed semicrystalline particles.

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The reaction-induced phase separation of poly(butylene terephthalate) (PBT), from an epoxy matrix, will be reported in this study. The use of this approach requires the reaction to be started at temperatures higher than the melting temperature (T_m) of PBT in the initial mixture of monomers. Phase separation during reaction may proceed due to: i) a decrease of the PBT solubility in the partially reacted epoxy mixture (attainment of the cloud-point curve); ii) crystallization of PBT because of the increase of T_m with conversion (in this case, the polymerization temperature must be lower than the melting temperature of pure PBT). By using two different hardeners (aromatic diamines), both situations will be explored.

In part 1, conversion–temperature transformation diagrams (CTTs) for two PBT-modified epoxy-amine formulations will be generated. The use of these diagrams to produce different morphologies and associated mechanical properties, will be reported in part 2.

EXPERIMENTAL

Materials

Chemical structures and some properties of the epoxy monomer, aromatic diamines used as hardeners and poly(butylene terephthalate), are shown in *Figure 1* and *Table 1*.

Two epoxy monomers based on diglycidylether of bisphenol A (DGEBA), were indistinguishably used. They were dehydrated under vacuum at 90°C before use. The selected hardener was either 4,4′-diaminodiphenylsulfone (DDS) or 4,4′-methylenebis (3-chloro 2,6-diethylaniline) (MCDEA). They were used in stoichiometric proportions with respect to the epoxy monomer.

Pellets of poly(butylene terephthalate) (PBT), were ground to facilitate melting. The number-average molar mass, $\bar{M}_n$, was obtained from the melt viscosity at 250°C and a correlation available in the literature[7]. Rheological characterization was performed with a Rheometrics mechanical spectrometer at 250°C, using parallel-plates geometry, a strain rate of $10\,s^{-1}$ and a maximum deformation of 25%. These conditions placed the rheological behaviour in the newtonian range. Due to the thermal degradation experienced by PBT when heated at 250°C[8,9], viscosity values had to be extrapolated to time zero. This gave a melt viscosity of 626 MPa s which, in turn, led to a number-average molar mass $\bar{M}_n$ of $33\,000\,g\,mol^{-1}$ (*Table 1*).

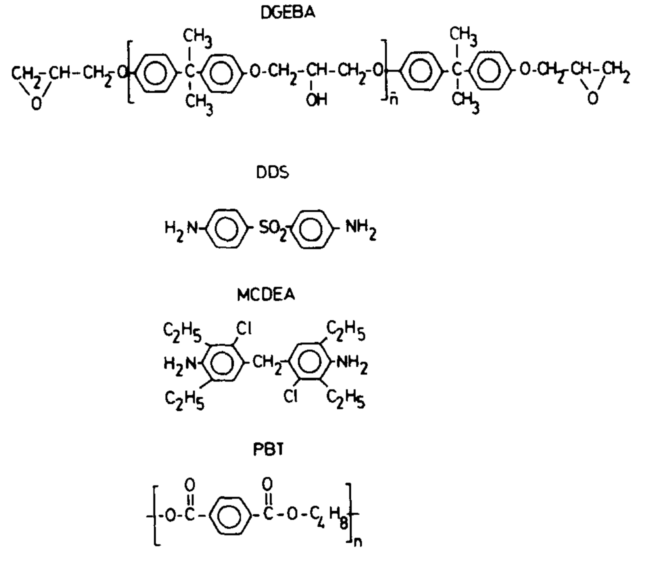

Figure 1 Chemical structures of the epoxy monomer (DGEBA), aromatic diamines (DDS and MCDEA) and poly(butylene terephthalate) (PBT)

Table 1 Characteristics of different monomers and modifiers

Compound	Supplier	Molar mass ($g\,mol^{-1}$)	Density ($g\,cm^{-3}$)
DGEBA	Dow (DER 332)	348.5 ($\bar{n}$ = 0.03)	1.17
	Ciba-Geigy (MY790)	344 ($\bar{n}$ = 0.014)	
DDS	Ciba-Geigy (HT 976)	248	1.38
	Fluka		
MCDEA	Lonza	379	1.14
PBT	GE (Valox 325)	$\bar{M}_n$ = 33000	1.30

Preparation of samples

First, PBT was dissolved in the epoxy monomer by heating the PBT–epoxy mixture at $T = 230°C$ for 30 min. Then the solution was cooled to 135°C, in the case of DDS, or 90°C, in the case of MCDEA, and a stoichiometric amount of aromatic diamine was added by heating for about 5 min. In the cooling period crystallization of PBT produced a stable dispersion of crystals with sizes in the 10 μm range. When the modified epoxy–amine dispersion was heated again above the melting temperature of PBT, a homogeneous solution was obtained. Depending on the diamine used and the selected temperature, phase separation could take place in the course of the epoxy-amine reaction (reaction-induced phase separation).

Binary mixtures of PBT with either DDS or MCDEA were prepared by heating appropriate compositions above the melting temperature of PBT while stirring.

Mass fractions of PBT in any formulation are expressed on the basis of the total mass, i.e. including PBT.

Thermal analysis

Melting temperatures (T_m), T_g and conversions were determined by differential scanning calorimetry (d.s.c.). Three different devices, calibrated by standard procedures, were used: a Mettler TA 3000, a DuPont TA 990 and a Shimadzu TA 501. Runs were carried out under argon or nitrogen atmospheres. Either isothermal and dynamic runs at a heating rate of $10°C\,min^{-1}$ were used. T_m was defined at the maximum of the melting peak, T_g was taken as the onset value of the baseline deflection, and conversion (x) was determined by

$$x = 1 - \Delta H_r/\Delta H_T \qquad (1)$$

where ΔH_r is the residual reaction heat and ΔH_T is the total reaction heat.

Size exclusion chromatography (s.e.c.)

A Waters chromatograph was used, provided with a double detection system (u.v. at $\lambda = 254$ nm and differential refractometry). The separation was carried out on four μ-styragel columns (10^3 Å, 500 Å, 100 Å, 100 Å), using tetrahydrofuran (THF) as eluent, with a flow rate of $1\,ml\,min^{-1}$. From the height of the DGEBA

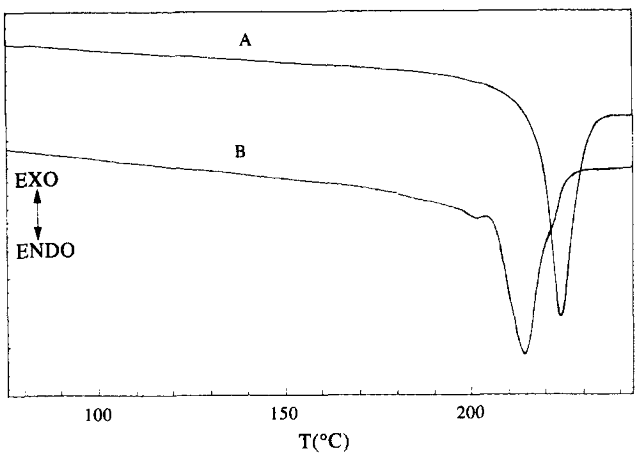

Figure 2 D.s.c. thermograms showing the melting peak of PBT: (A) initial sample; (B) after heating at 250°C during 2 h

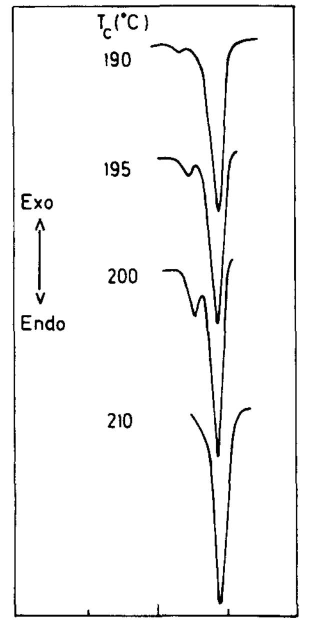

Figure 3 D.s.c. thermograms showing the effect of annealing PBT at a constant temperature during 15 min

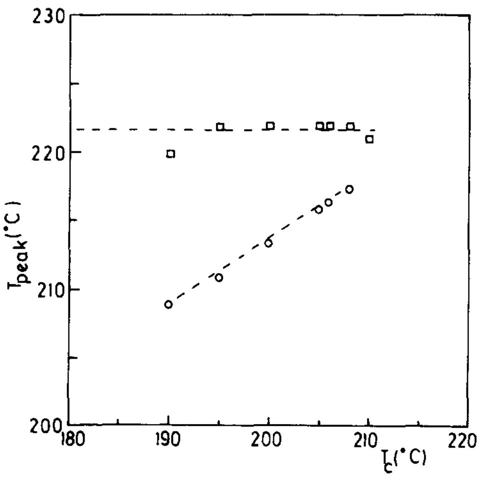

Figure 4 Temperatures of both melting peaks of PBT as a function of the annealing temperature

peak (structure with $n = 0$ in *Figure 1*), the conversion could be obtained as[10]:

$$x = 1 - (h/h_0)^{1/2} \qquad (2)$$

where h is the height of the peak at any conversion and h_0 is its initial value in the unreacted mixture.

Values arising from equations (1) and (2) were close to each other within experimental error. SEC was mainly used in the pregel stage while d.s.c. was also used after gelation.

Cloud-point curves

Polycondensation of the PBT-modified epoxy-amine mixtures at $T > T_m$, was carried out in a light transmission device, described elsewhere[11]. At the cloud point (onset of the light transmission decrease), the tube containing the sample was taken out of the device and chilled in ice. The cloud-point conversion, x_{cp}, was determined using either d.s.c. (equation (1)) or s.e.c. (equation (2)).

Kinetics

Conversion vs time curves at 160°C and 200°C, for pure and PBT-modified DGEBA-DDS and DGEBA-MCDEA formulations, were obtained by heating a set of tubes in an oil bath, removing one at a time at selected intervals, quenching in ice and determining conversion by either d.s.c. or s.e.c.

RESULTS AND DISCUSSION

Melting of pure PBT

Figure 2 shows d.s.c. thermograms of the initial PBT sample (A) and that resulting from heating at 250°C during 2 h (B). T_m was reduced from about 224°C to 214°C, showing the presence of thermal degradation. This proceeds via cyclic oligomers which react further producing linear oligomers with vinylic and acid end groups[8,9]. The constancy of T_m after thermal cycles used in the study of phase separation, constitutes an indication of the fact that thermal degradation of PBT was not significant during such cycles.

Comparing the experimental value of the heat of fusion with that of 100% crystalline PBT, i.e. 142 J g^{-1} as reported in the literature[12,13], a crystallinity of 42% for pure PBT was obtained. This value is close to crystallinities reported in the literature for unannealed PBTs, i.e. 44–46%[4].

When PBT was annealed during 15 min at different temperatures in the 190–205°C range, a second melting peak at lower temperatures was present, as shown in *Figure 3*. The temperature of both peaks is plotted as a function of the annealing temperature in *Figure 4*. This phenomenon was explained by the transformation of higher-melting to lower-melting crystals coupled to the crystallization of formerly amorphous material[14]. This behaviour is reversible and may be erased by melting and quenching from the melt. In any case, even in the presence of multiple melting peaks, the main peak (at about 222°C for pure PBT) will be taken as the T_m of PBT in a binary mixture or in an epoxy-amine formulation.

Melting of PBT in binary mixtures

The melting temperature of PBT is lowered in the presence of a solvent. *Figure 5* shows that the melting

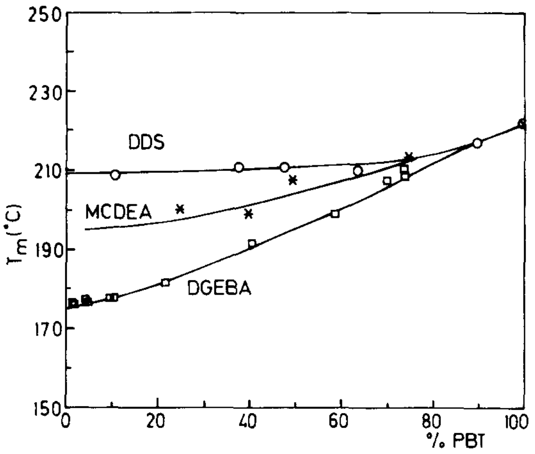

Figure 5 Melting point depression of PBT in binary mixtures with DGEBA (□), MCDEA (∗) and DDS (○), as a function of the mass fraction of PBT

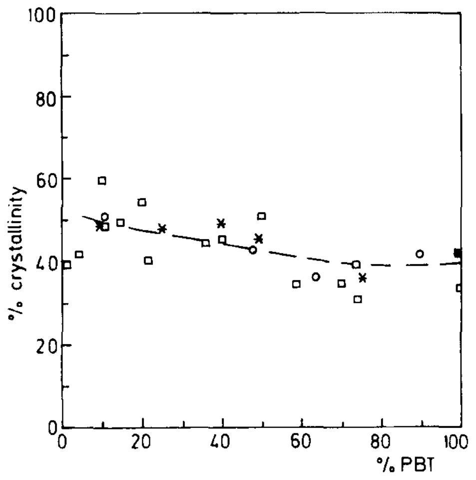

Figure 6 Crystalline fraction of PBT segregated from binary solutions with DGEBA (□), MCDEA (∗) and DDS (○), as a function of the mass fraction of PBT

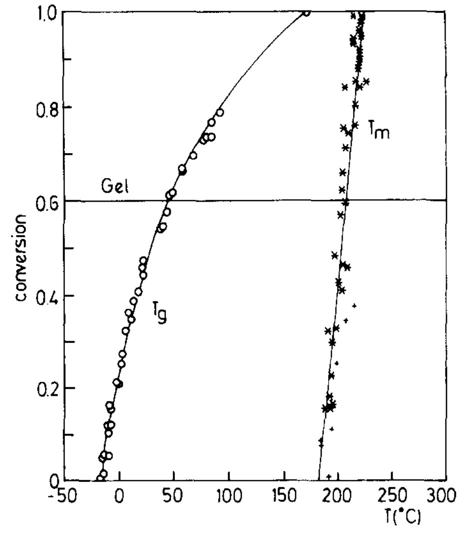

Figure 7 Conversion–temperature transformation diagram (CTT) for a PBT–DGEBA–MCDEA system: ∗, 3.3 wt% PBT; +, 6.6 wt% PBT

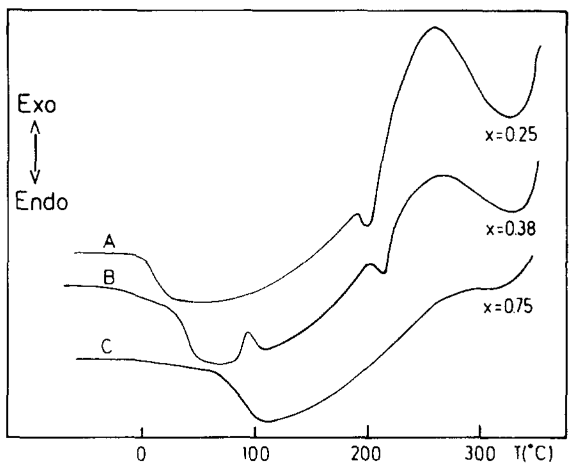

Figure 8 D.s.c. thermograms for DGEBA–MCDEA samples containing 6.6 wt% PBT that were previously reacted at $T > T_m$ to reach a particular conversion x and cooled at 5°C min^{-1}

point depression decreases in the order DGEBA > MCDEA > DDS. Taking into account that the depression is more pronounced for lower values of the interaction parameter between polymer and solvent, as predicted from Flory's equation[15] when applied to the equilibrium melting temperature (which can be obtained using extrapolative methods[16–18]), it may be inferred that PBT is more soluble in DGEBA–MCDEA than in DGEBA–DDS. It will be shown that this fact has a significant influence on the possibility of producing phase separation in the course of the epoxy–amine reaction. It has also been reported that DGEBA–MCDEA is a better solvent than DGEBA–DDS for high-T_g amorphous thermoplastics like poly(etherimide)[19].

The crystalline fraction of PBT segregated from binary solutions with DGEBA, MCDEA and DDS, when cooling below T_m, is comprised between 30–60% (*Figure 6*). Higher values are obtained in the low concentration range.

Melting and phase separation of PBT in reactive mixtures

The high viscosity of PBT-epoxy-amine mixtures made it impossible to introduce more than 7–8% mass fraction of PBT for processing purposes (i.e. casting of the initial formulation in a heated mould). The following mass fractions were selected: 3.3% and 6.6% PBT for DGEBA–MCDEA mixtures and 3.75% or 7.5% PBT for DGEBA–DDS formulations. (Notice that the PBT–DGEBA ratio is the same for both systems, at each one of the PBT levels.) Both epoxy-amine systems will be analysed separately.

PBT–DGEBA–MCDEA. When the reaction was carried out in the light transmission device to full conversion, the sample remained transparent without any sign of phase separation, at the size scale revealed by scanning electron microscopy (SEM). This is an indication of the good solubility of PBT in DGEBA–MCDEA mixtures, as was inferred from *Figure 5*. Then, the only possibility of segregating PBT from the reactive mixture is through crystallization under appropriate conditions.

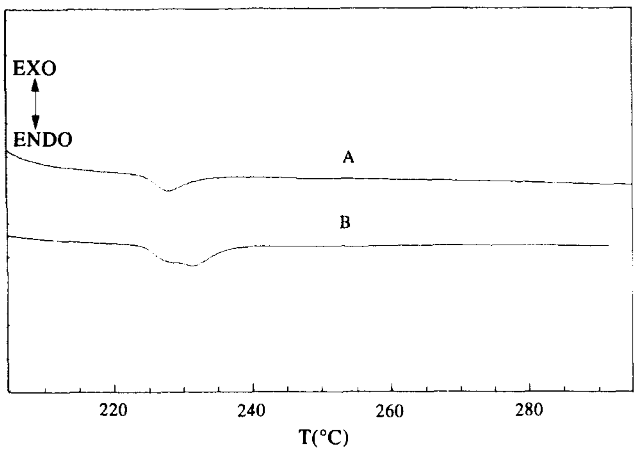

Figure 9 D.s.c. scans for DGEBA–MCDEA samples modified by 3.3 wt% PBT, previously cured at 200°C (A) and 190°C (B), to an almost complete conversion

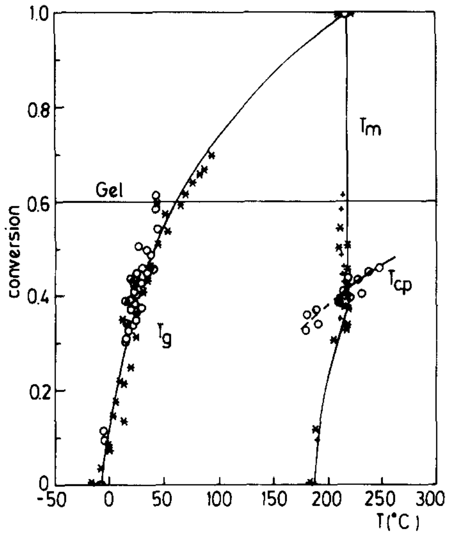

Figure 10 CTT for PBT–DGEBA–DDS systems. 3.75 wt% PBT: *, T_m; O, T_g, T_{cp}. 7.5 wt% PBT: +, T_m; O, T_g, T_{cp}. Neat system: *, T_g

Figure 7 shows the CTT[20], for a PBT–DGEBA–MCDEA system. Gelation and vitrification curves for the neat matrix[21], are used here to discuss the boundaries of the crystallization region. Melting temperatures were obtained from d.s.c. thermograms of partially reacted mixtures. Most of the T_m values were the result of advancing the reaction at a particular temperature $T_i < T_m$, i.e. in the presence of PBT crystals, cooling and rescanning in the d.s.c. to obtain both T_m and the residual reaction heat. Some of the T_m values located in the pregel region were also obtained by advancing the reaction $T_i > T_m$, cooling to produce PBT crystallization and scanning in the d.s.c. However, this was not possible at high extents of reaction because no crystallization of PBT was produced. It was observed that T_m increases with conversion reaching the value of pure PBT at full conversion. The temperature at which the melting line intercepts the gel conversion ($T_{m,gel}$) = 210°C.

Figure 8 shows d.s.c. thermograms for formulations containing 6.6% PBT, previously reacted at $T_i > T_m$ to reach a particular conversion level, and cooled at 5°C min^{-1}. For $x = 0.25$, crystallization had taken place in the cooling step as revealed by the melting peak appearing during the heating step, at the beginning of the residual exotherm. For $x = 0.38$, at least part of the crystallization took place in the heating step after devitrification of the matrix. However, for $x = 0.75$ crystallization did not take place either in the cooling or heating steps.

Therefore, for conversions located below the gel conversion, x_{gel}, in the CTT diagram (*Figure 7*), cooling from $T_i > T_m$ leads to PBT crystallization in the temperature range comprised between T_g and T_m. However, for $x > x_{gel}$ crystallization is severely restricted (it was not observed using cooling or heating rates in the range of 5–10°C min^{-1}). Conversely, when the reaction was carried out to high extents of reaction at $T_i < T_m$, in the presence of PBT crystals, followed by a temperature stage at $T_i > T_m$ during 30 min before cooling, an opalescent material was always obtained, meaning that PBT could not be completely dissolved in the highly crosslinked gel.

If the cure of a PBT-modified DGEBA–MCDEA formulation is carried out at a temperature located between T_m ($x = 0$) (about 180°C) and $T_{m,gel}$ (about 210°C), crystallization may take place in the course of the isothermal reaction. To prove this hypothesis, DGEBA–MCDEA formulations modified by 3.3 wt% PBT were polymerized at 190°C and 200°C in the isothermal mode of the d.s.c. device, to reach an almost complete conversion. Dynamic d.s.c. scans were then carried out, starting from the isothermal cure temperature. *Figure 9* shows that reaction-induced crystallization took place at both temperatures, as revealed by the appearance of a melting peak in the d.s.c. scans. Heats of fusion were 62.3 J gPBT^{-1} (run at 190°C) and 38.3 J gPBT^{-1} (run at 200°C). In the former case, the crystalline fraction is 43.9%, i.e. a typical value for PBT crystals. The low value obtained at 200°C (27% crystalline fraction) may be due to the fact that a fraction of the amorphous PBT remained dissolved in the epoxy–amine matrix, reflecting the competition between reaction rate and crystallization rate. When the epoxy–amine reaction was carried out at 210°C, no crystallization was observed. The PBT remained dissolved in the matrix giving a transparent material.

PBT–DGEBA–DDS. When the epoxy–amine reaction was carried out in the light transmission device starting at $T_i > T_m$ ($x = 0$), a cloud-point was always obtained. This means that PBT could be segregated from DGEBA–DDS matrices by a typical reaction-induced phase separation process, a fact that corroborates the lower solubility of PBT in DGEBA–DDS than in DGEBA–MCDEA.

Figure 10 shows the CTT diagram for PBT–DGEBA–DDS systems at PBT wt% = 3.75 and 7.5 (no difference in location of curves was found in this concentration range). Now, T_m increases with conversion up to the cloud-point curve where it reaches a value close to that of pure PBT. This arises from the fact that as PBT becomes phase-separated, its melting behaviour resembles that of pure PBT. The cloud-point curve is extrapolated with a dotted line in the $T < T_m$ region because crystallization is superimposed on phase separation in this temperature range (the cloud point obtained in the light transmission device could not be distinguished from crystallization, for $T < T_m$).

The positive slope of the cloud-point curve means that PBT exhibits an upper-critical-solution-temperature behaviour (UCST), in the DGEBA–DDS matrix. This means that as solubility increases with temperature, it is necessary to increase the extent of reaction to produce phase separation at higher temperatures. UCST is the typical situation for rubber and amorphous thermoplastic modifiers of epoxy systems[19]. Poly(ether sulfone) that shows a lower-critical-solution-temperature behaviour (LCST)[19,22], constitutes an exception.

The CTT diagram may be used for selecting cure cycles to obtain different morphologies. This will be discussed in the second part of the series.

Figure 11 shows d.s.c. thermograms for a DGEBA–DDS formulation containing 7.5wt% PBT. The initial scan, starting from room temperature, shows the endothermic melting peak of PBT superimposed over the exotherm of the epoxy–amine reaction. Melting of PBT occurs when the trajectory of the cure at constant heating rate intercepts the T_m curve in the CTT diagram (*Figure 10*). Phase separation occurs afterwards, when the trajectory goes through the cloud-point curve. The cooling scan shows crystallization of the previously phase separated PBT, at 196°C. A second heating scan shows T_g of the cured matrix at 195°C and the melting peak of PBT at 220°C. Although no residual exotherm is observable in the d.s.c. thermogram, the epoxy–amine matrix did not reach complete conversion during the first d.s.c. scan. A prolonged heating at 230°C increased T_g to a maximum value of 214°C.

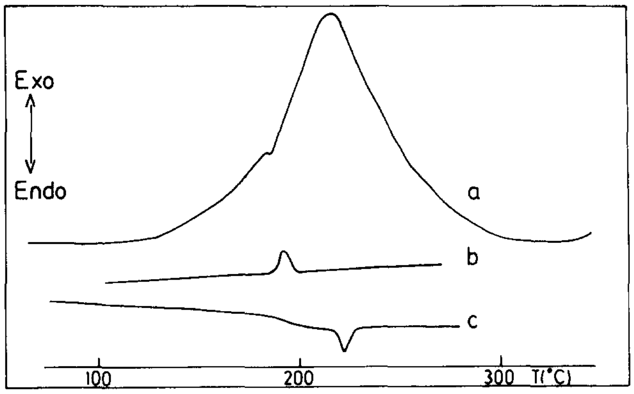

Figure 11 D.s.c. thermograms for a DGEBA–DDS formulation containing 7.5wt% PBT. (a) Initial scan from room temperature; (b) cooling after the first scan; (c) second scan after cooling

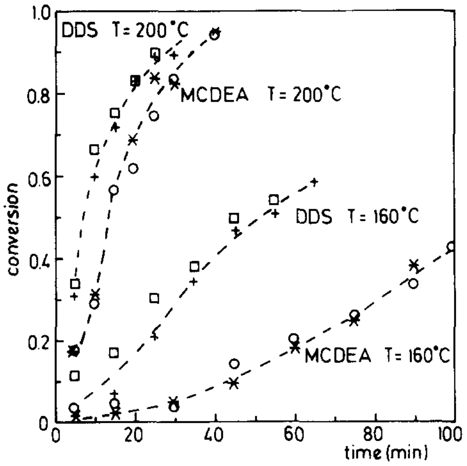

Figure 12 Conversion vs time at 160°C and 200°C showing that PBT addition has no effect on kinetics: +, DGEBA–DDS; *, DGEBA–MCDEA; □, PBT (3.75wt%)–DGEBA–DDS; ○, PBT (3.3wt%)–DGEBA–MCDEA

Table 2 Thermal properties of PBT, DGEBA–DDS and PBT–DGEBA–DDS materials after a heating cycle in the d.s.c. (c: crystallization, m: melting, g: glass transition)

Material	wt% PBT	T_c (°C)	T_m (°C)	T_g (°C)
PBT	100	193	222	40
DGEBA–DDS	0	–	–	195
PBT–DGEBA–DDS	3.75	195	221	195
PBT–DGEBA–DDS	7.5	196	220	195

Table 2 shows thermal properties of pure PBT, the neat DGEBA–DDS matrix and PBT–DGEBA–DDS materials after a heating cycle in the d.s.c. From the constancy of T_g values it may be inferred that most of the PBT gets phase-separated, i.e. there is no plasticization effect. Besides, thermal properties of PBT are practically the same when it is pure or when it has been segregated from an epoxy–amine matrix.

Kinetics of PBT-modified epoxy–amine systems

Figure 12 shows conversion vs time curves for both PBT-modified systems. At $T_i = 160$°C, the reaction is carried out in the presence of PBT crystals, at $T_i = 200$°C, segregation of PBT from the epoxy–amine matrix takes place in the course of polymerization. In both cases, the presence of PBT does not affect the cure kinetics. A similar behaviour was observed by doubling the PBT concentration in the initial formulations.

CONCLUSIONS

The solubility of PBT in a DGEBA–aromatic diamine mixture, as revealed by the melting point depression, is very sensitive to the nature of the diamine. PBT is much more compatible with MCDEA than with DDS. This means that in PBT-modified DGEBA–MCDEA formulations, the reaction can proceed to full conversion without phase separation of PBT, provided that the cure takes place at temperatures higher than T_m (at least in the pregel stage). For PBT-modified DGEBA–DDS formulations, phase separation at $T > T_m$ always takes place in the course of reaction.

For both systems, PBT crystallization may be produced either initially or in the course of the cure. Therefore, different ways of segregating PBT from the matrix are available. The implications on morphologies and mechanical properties of the resulting materials, will be discussed in the second part of the series.

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