Reaction and Miscibility of Two Diepoxides with Poly(ethylene terephthalate)

Françoise Fenouillot,[1] Claire Hedreul,[1] John Forsythe,[2] Jean-Pierre Pascault[1]

[1]Laboratoire des Matériaux Macromoléculaires, Unité Mixte de Recherche-Centre National de la Recherche Scientifique 5627, Institut National des Sciences Appliquées de Lyon, 69621 Villeurbanne Cedex, France
[2]Department of Material Engineering, Cooperative Research Center (CRC) for Polymers, Monash University, Clayton, Victoria 3168, Australia

ABSTRACT: Poly(ethylene terephthalate) (PET) was melt-blended at 270°C with two epoxy monomers, diglycidyl ether of bisphenol A (DGEBA) and 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexyl carboxylate (ECY). Intermediate proportions of the epoxy in the range of 20–0.5 wt % were used. If the epoxy monomers were added in a high proportion (10–20%), a large fraction did not react with PET. Calorimetric experiments showed that the unreacted fractions of both epoxies were miscible with the amorphous phase of the polyester. Only one glass-transition temperature was detected. It was depressed as the epoxy content was increased. The transition was broad when the PET component was crystalline, and it was narrow when the PET component was made amorphous by quenching of the blend. These features were confirmed by dynamic thermal mechanical analysis. As is often the case for crystalline blends, the crystallization and melting temperatures decreased when the proportion of the epoxy was increased. Concerning the reactivity of the epoxy with PET, the behavior differed according to the nature of the epoxy. The DGEBA monomer showed a low reactivity. It was not effective for the chain extension of PET, and no increase in the intrinsic viscosity was observed under the experimental conditions. However, some functionalization of the chain ends may be possible at a high concentration of the epoxy. ECY was more reactive, and the molecular weight of the processed PET increased, although the value of the commercial untreated polyester was not attained. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1995–2003, 2003

Key words: blends; miscibility; transitions

INTRODUCTION

Miscibility, crystallization, and chemical reactions in polyester/epoxy blends have been studied extensively, mainly at the extremities of the composition range, that is, with very high polyester contents (>99 wt %) and with low polyester contents (<10 wt %).

The first situation is encountered with poly(ethylene terephthalate) (PET) recycling. PET is used in packaging for soft drink and mineral water bottles. Its recycling is difficult because reprocessing at high temperatures causes degradation, and the decrease in the molecular weight is even more pronounced if the scrapped bottles are not carefully dried. One solution is the addition of a chain extender to recycled PET that is able to react with the chain ends created during processing. Many studies are reported in the literature in which diepoxides have been employed for this purpose with greater or less efficiency according to the chemical structure of the modifier and its solubility in PET. When the diepoxide is added for chain extension, a small proportion is needed (<1%). The studies are focused on a judicious choice of the epoxy coupler and on the quantification of the chemical reaction leading to an increase in the molecular weight of the thermoplastic.[1–7]

However, other authors have studied the second situation in which the diepoxide is the major component. In this case, PET (or poly(butylene terephthalate (PBT)) is added to improve the toughness of the blend, and generally the epoxy is crosslinked with a diamine comonomer. The concentration of the polyester is less than 10 wt %. The epoxy is miscible with the polyester at temperatures above its melting temperature (T_m). When the temperature decreases and no hardener is present, phase separation occurs, the polyester crystallizes, and different morphologies are obtained according to the thermal history of the blend.[8] When a hardener is present, the situation is complicated by the curing kinetics of the epoxy/diamine system.[9–12]

The intermediate compositions have not been studied much, except by Huang et al.,[13] who studied the miscibility of a PET/diglycidyl ether of bisphenol A (DGEBA) blend over the whole range of concentrations, but they did not quantify the extent of reaction between PET and DGEBA.

Correspondence to: F. Fenouillot (francoise.fenouillot@insa-lyon.fr).
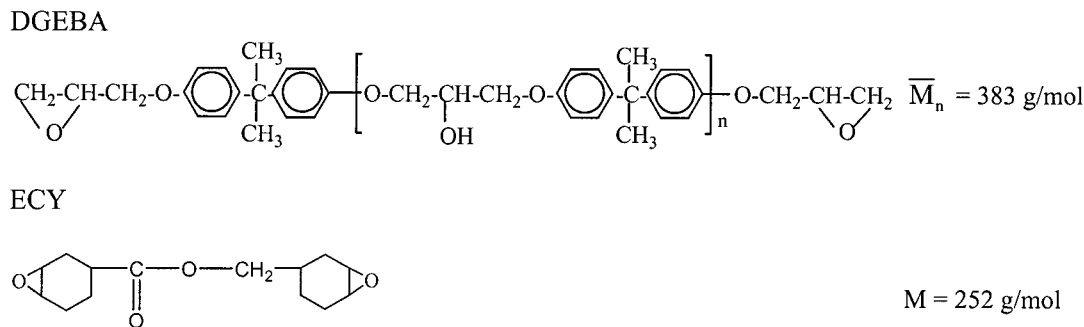
DGEBA

ECY

$M = 252$ g/mol

Figure 1 Epoxy monomers.

In this study, we used proportions of epoxy between 0.5 and 20 wt % because the aim was mainly to investigate the miscibility of large amounts of diepoxides with PET, a second condition being that PET remained the matrix so that the blend was still thermoplastic.

EXPERIMENTAL

Materials

The PET was a bottle-grade polymer. The intrinsic viscosity measured in a 1% solution in dichloroacetic acid was 0.79 dL/g. It contained 1.6 mol % isophthalic acid as a comonomer. PET was dried *in vacuo* at 120°C for 3 h before use.

The diepoxides were standard DGEBA ($n = 0.15$) and 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexyl carboxylate (ECY; Fig. 1). ECY was chosen on the basis of the work of Haralabakopoulos et al.,[1] who observed that cyclic diepoxides were more reactive with PET than diglycidyl ethers.

Both were used after drying at 40°C for 20 h.

Compositions of the blends

PET was processed alone and then blended with variable proportions of epoxy. The proportions were 10 and 20 wt % diepoxide in PET because we were interested in a high epoxy content.

However, we also tested a low blending ratio that was determined in the following way. The carboxyl end-group content of PET was 20 μmol/g (supplier data). To evaluate the theoretical amount of epoxy needed to promote chain extension, we assumed that only the carboxyl groups reacted and that a molecule of diepoxide might have reacted with two carboxyl end groups. The thermal degradation caused a decrease in the molecular weight of the polymer and produced additional carboxyl end groups. Bikiaris et al.[2] noticed that when double the theoretical amount was added, the chain extension was faster and more effective. We decided to multiply this amount by a factor of 2.

Epoxide weight percent

$$= 2 \times \frac{[\text{Carboxyl}] \times \text{MM}}{2} \times 100 \quad (1)$$

where MM is the molecular weight of the diepoxide. The theoretical amounts were 0.8 wt % for DGEBA and 0.5 wt % for ECY. In this calculation, only the reaction of the epoxy cycle with the chain ends of PET was considered.

Blending methods

Reactive blending at high temperatures under shear was carried out in a Rheocord RC300p Haake (Karlsruhe, Germany) internal mixer equipped with a 540 P mixing chamber. The temperature was set at 270°C, and the mixing speed was 60 rpm. The PET and epoxy monomer were introduced simultaneously to the mixing chamber at time $t = 0$ and were mixed for 5 min. No specific precaution was taken to preserve the melt from the oxygen atmosphere.

Determination of the residual monomer content by size exclusion chromatography (SEC)

SEC was used to determine the residual epoxy monomer content.

The blends were finely ground at a low temperature. The powder was put under agitation into a large volume of tetrahydrofuran (THF) for the extraction of the unreacted epoxy. The solution of the epoxy in THF was recovered after 2 days of agitation and was analyzed by SEC.

The measurements were performed on a Waters (Milford, MA) SEC instrument equipped with two Microstyragel HR 5 E columns. The calibration was made with DGEBA and ECY solutions of known concentrations. The height of the $n = 0$ peak was used to calculate the concentration of DGEBA.

Another method was employed to extract the unreacted epoxy because THF is not a solvent of PET. The blends were dissolved in 60/40 (w/w) phenol/tetra-
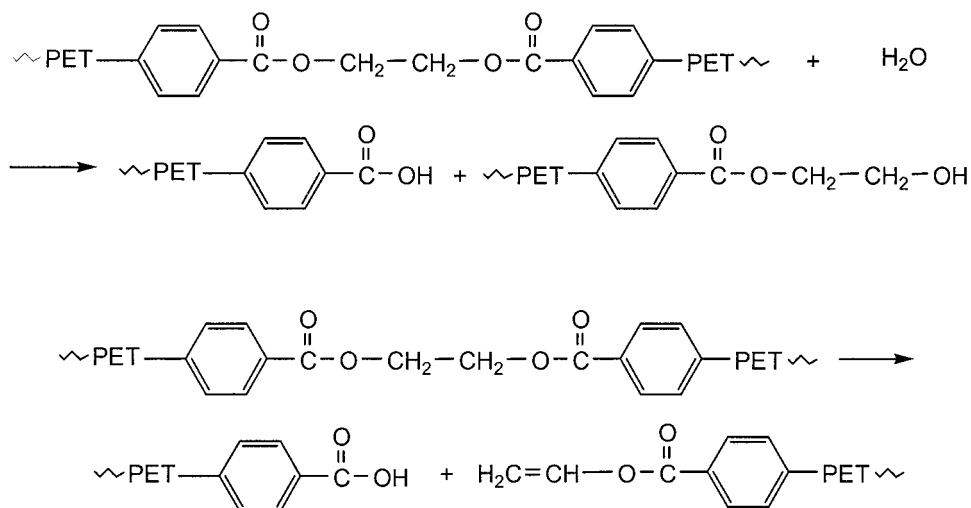
Figure 2 Hydrolysis and thermal degradation reactions of PET.

chloroethane (PTCE) at 110°C for the epoxy blends and in hexafluoroisopropanol at room temperature for the ECY blends. Then, PET was precipitated in THF, and the filtered solution was analyzed by SEC.

Determination of the molecular weight by SEC

The blends were dissolved in a mixture of dichloromethane and hexafluoroisopropanol. The molecular weight was calculated with a correction equation that took into account that the calibration was made with polystyrene standards instead of PET.

¹H-NMR spectroscopy

NMR spectra were recorded at 27°C with a Brucker DRX 400 spectrometer operating at 400 MHz for ^{1}H NMR. Chemical shifts are given with reference to tetramethylsilane. PET and blend samples were dissolved in hexafluoroisopropanol/CDCl$_3$ (1/2 v/v).

Calorimetric study

In this case, the samples were not washed with a solvent, as we wished to determine the influence of the presence of the epoxy on the thermal properties of PET.

The glass-transition temperature (T_g) and T_m were determined on a Mettler DSC 30 differential scanning calorimeter under an argon atmosphere. The calorimeter was calibrated with indium. The scanning rate was 10°C/min. T_g was taken as the onset of the heat-flow variation. The values of T_m and the cold-crystallization temperature (T_{cc}) were taken at the maxima of the endothermic and exothermic peaks, respectively.

The degree of crystallinity (X_c) was calculated as follows:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_0} \quad (2)$$

where ΔH_m and ΔH_c are the enthalpies of melting and crystallization, respectively, and ΔH_0 is the enthalpy of melting of 100% crystalline PET and is equal to 144 J/g.[14] The enthalpies of the blends were normalized to 100% PET.

The scanning procedure was as follows. A first scan was run from −100 to 270°C at 10°C/min and was then held isothermally at 270°C for 2 min. The differential scanning calorimetry (DSC) sample was quenched into liquid nitrogen to limit the crystallization of the polyester. Finally, the second scan was run under the same conditions used for the first one.

Dynamic mechanical thermal analysis (DMTA)

The samples were compression-molded and were either cooled rapidly to obtain an amorphous blend or annealed for 15 min at 140°C. Their crystallinity was measured by DSC after the compression molding.

The thermomechanical dynamic analysis was performed on a Rheometrics Solid Analyzer II spectrometer at a frequency of 1 Hz. The temperature range was −100 to 200°C.

RESULTS AND DISCUSSION

PET/epoxy reactivity

In a preliminary step, we checked that the epoxy monomers did not polymerize when heated alone at high temperatures. They were subjected to a temperature scan from −100 to 270°C at 10°C/min in the DSC oven, and then the temperature was maintained at 270°C for 30 min. The T_g values of the samples were

TABLE I
Molecular Weight of the PET Component as Measured by SEC

PET and blends	Composition	M_n of the PET (SEC; g/mol)	M_w/M_n of the PET (SEC)
PET as received	100	21,100	2.13
PET processed for 5 min at 270°C	100	14,000	1.99
PET/DGEBA	99.2/0.8		
	90/10		
	80/20	12,400	2.03
PET/ECY	99.5/0.5	18,300	2.05
	90/10	18,100	2.12
	80/20	16,400	2.20

measured before and after the thermal treatment. A negligible exotherm was detected for ECY, and its T_g was 3°C higher after the treatment; DGEBA showed no exotherm and no change in T_g. During the melt-blending step, the monomers spent only 5 min at 270°C.

PET was processed alone under the same conditions used for the melt-blending step. The hydrolysis of the PET chain yielded carboxylic acid end groups and hydroxyl ester end groups (Fig. 2). The resultant chain scission induced a reduction in the average molecular weight of the polymer.

Even though the PET granules were carefully dried, this was clearly observed for the processed PET. Its intrinsic viscosity and molecular weight were greatly reduced in comparison with the untreated initial polymer (Table I).

When an epoxy monomer was added to PET, the epoxy ring could react with the carboxylic acid end groups and, to a lesser extent, with the hydroxyl end groups (Fig. 3).

For the lowest blending ratios (0.8 and 0.5 wt % epoxy), the reaction of the two epoxy rings with the carboxyl end groups should result in the chain extension of the polyester and, therefore, an increase in its intrinsic viscosity. However, this was not the case in this study (Table I). This is not so surprising for DGEBA, which other authors found to be not very reactive.[1,6] Nevertheless, ECY is known to promote chain extension,[1] and we observed an increase in the number-average molecular weight ($M_n = = 18,000$ g/mol) in comparison with that of the processed PET ($M_n = 14,000$ g/mol), although the improvement was not as high as Haralabakopoulos et al.[1] observed.

The blends containing 10 and 20% epoxy behaved differently according to the nature of the epoxy. DGEBA did not extend the PET chains, whereas ECY did when it was used at growing concentrations.

To determine what fraction of the epoxy monomer really reacted, we extracted the residual epoxy and analyzed it by SEC. In addition, ^{1}H-NMR spectroscopy was used to confirm the results (Table II). The advantage of using ^{1}H-NMR was that no extraction step was needed. However, to interpret the data collected from the ^{1}H-NMR spectra, we were obliged to suppose that no diepoxide molecules had reacted on their two epoxy functions. This hypothesis was probably valid for DGEBA, as the absence of chain extension indicated that only one function had reacted. Nevertheless, for the ECY chain, coupling occurred, and the hypothesis could lead to an overestimation of the fraction having reacted.

Table II gives some insight into some contradictory features. Although DGEBA did not increase the molecular weight of the polyester, a measurable fraction of it was not extracted from the blends. We may think that this fraction reacted with PET in some manner other than chain extension. The epoxy was in excess in comparison with the PET chain ends, and the reaction of only one epoxy function per DGEBA molecule could lead to epoxy-functionalized polyester chains rather than chain coupling (Fig. 3). If we make the hypothesis that every chain end group of PET is a potential reaction site for a molecule of DGEBA, the quantity of DGEBA involved would be approximately 6 g/100 g of PET. This indicates that only a fraction of the end groups were functionalized, most likely the carboxyls.
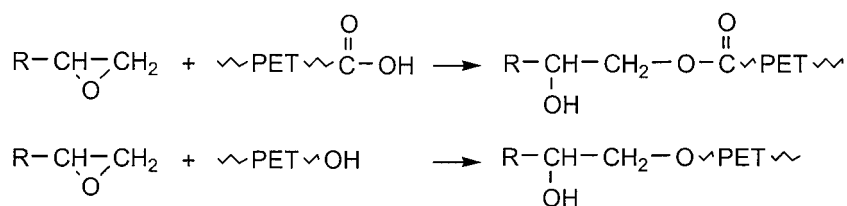

Figure 3 Reaction of the epoxy with the end groups of PET.

TABLE II
Fraction of Epoxy Having Reacted with PET as Estimated by SEC and ^{1}H-NMR

Blend	Diepoxide initial content (%)	Fraction of diepoxide having reacted		
		SEC (g/100 g of epoxy)	^{1}H-NMR	SEC (g/100 g of PET)
	0.8	5	9.5	0.04
PET/DGEBA	10	16	14	1.8
	20	15	31	3.8
	0.5	100		0.5
PET/ECY	10	57		6.3
	20	18	43	5.5

A second possible reaction is the etherification of the hydroxyl groups by the epoxy ring (Fig. 4). This case is a little more intriguing with ECY because a maximum of 0.5–1 g/100 g of PET may be involved in chain extension and potentially 2.8 g/100 g of PET may have functionalized the PET chains. If we only consider the chain extension and the functionalization reactions, only 2.8 g/100 g of PET should have reacted instead of the 6.3 and 4.5 g/100 g measured by extraction. To explain, at least partly, this deviation, we suspect that a fraction of ECY was lost by evaporation at the end of the blending operation, as discussed later. However, this difference might have come from the potential transesterification reactions between the ester group of the ECY and the hydroxyl and carboxyl chain ends of PET (Fig. 5).

The estimation of the fraction of the epoxy that reacted with PET is important for two reasons. First, this miscibility study requires us to know the actual free epoxy content to interpret the calorimetric experiments. Furthermore, if we intend to crosslink the epoxy, the stoichiometry will need to be adjusted to the amount of epoxy functions truly available in the blend.

PET/epoxy miscibility

Above T_m of PET, both epoxies were miscible with PET. A perfectly transparent melt was obtained. When the blend was quenched in liquid nitrogen, a transparent material was also obtained, indicating that the epoxies could be miscible with the amorphous phase of PET even at room temperature. This was confirmed by SEM observations of the fractured surface of an 80/20 PET/DGEBA blend. The blend surface showed the same type of topography before and after treatment with THF as a solvent. No trace of an epoxy separated phase was detected.

A calorimetric study was made to confirm these qualitative observations. T_g of the PET/epoxy blends depended on the miscibility of the components, on the state of crystallization of PET, and on the composition of the amorphous phase. For comparison, it is important that samples be subjected to similar thermal histories. In this study, the treatment consisted of one temperature scan at 10°C/min followed by the quenching of the sample into liquid nitrogen. The second scan was run at 10°C/min.

After a sample has been quenched from the melt, it is very difficult to obtain a completely amorphous sample, and we have simplified the denomination of the samples, using the term *amorphous* for a blend that was quenched and had an X_c value of less than 10%. The term *crystalline* is used when the sample had an X_c value greater than 20%.

For PET alone, the T_g value of a crystalline sample was broad and difficult to detect, whereas for an amorphous sample, the transition was narrow and sharp. In addition, a decrease of 4°C in the T_g value was revealed from the crystalline sample to the amorphous sample (Table III). The same trend was noticed with the blends.

An example of the thermograms obtained for the two scans is shown in Figure 6 for an 80/20 PET/DGEBA blend. The glass transition of the crystalline sample (first scan) was so broad and indistinct that the
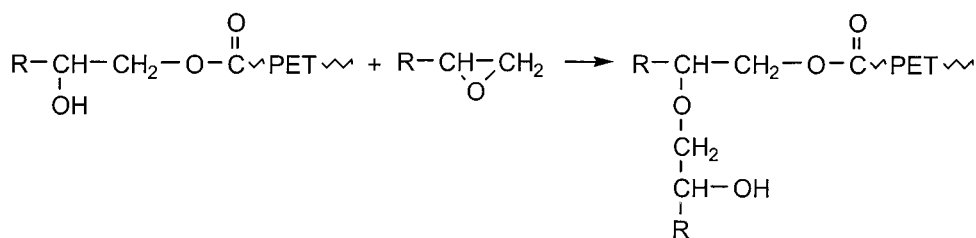

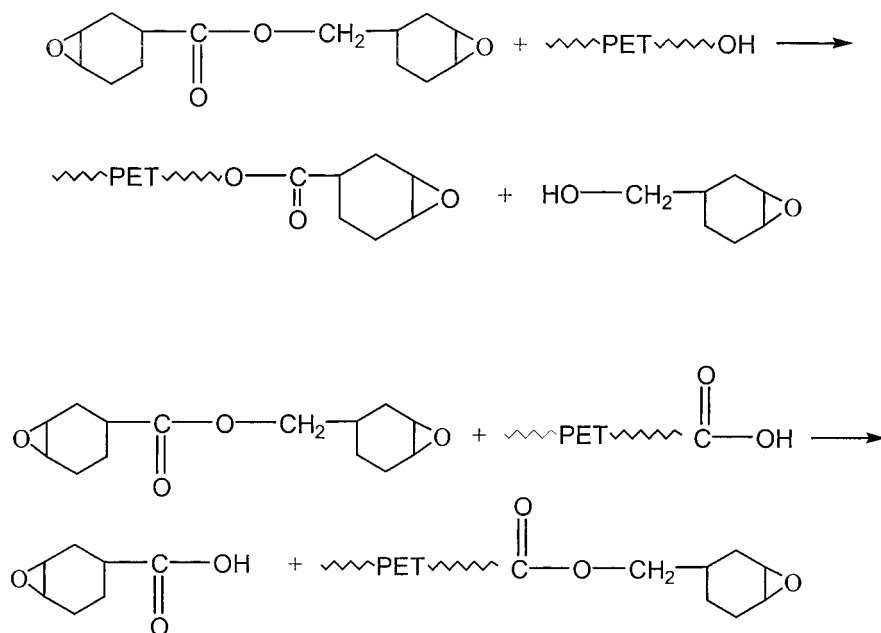**Figure 4** Etherification of the hydroxyl functions by the epoxy.

Figure 5 Reaction of ECY with the end groups of PET.

determination of its onset was difficult. The endothermic melting peak was found around 248°C. For the amorphous sample (second scan), the exothermic crystallization peak was observed around 110°C, and T_g was narrow.

The broadening of the transition is not surprising: it is often observed for miscible polymer blends[15,16] and is sometimes attributed to local fluctuations of the concentration. Another reason may be the inhomogeneity of the chain mobility caused by the crystalline domains. We confirmed it by DMTA on the same blend (Fig. 7). The data present the loss factor tan δ versus the temperature. A sharp relaxation peak was detected for the amorphous blend, with a shoulder

TABLE III
Thermal Properties of the Blends and Their Components

Polymer and quenched blends	T_g onset (°C)	T_{cc} (°C)	ΔH_c (J g^{-1} K^{-1})/PET	T_m (°C)	ΔH_m (J g^{-1} K^{-1})/PET	X_c (%)
DGEBA	−19	—	—	—	—	—
ECY	−69	—	—	—	—	—
PET processed 5 min at 270°C	72	—	—	256	39	27
PET processed 5 min at 270°C and then quenched	68	130	34	254	44	7
PET/DGEBA 99.2/0.8						
First scan				256	41	28
Second scan	70	130	32	253	45	9
PET/DGEBA 90/10						
First scan				250	45	31
Second scan	55	119	36	248	49	10
PET/DGEBA 80/20						
First scan				248	51	35
Second scan	42	113	36	245	57	14
PET/ECY 99.5/05						
First scan				254	38	26
Second scan	73	133	32	253	41	6
PET/ECY 90/10						
First scan				250	44	30
Second scan	58	123	33	249	45	8
PET/ECY 80/20						
First scan				247	51	35
Second scan	48	117	38	246	51	9

The second scan was recorded after quenching of the sample, so a less crystalline blend was obtained.
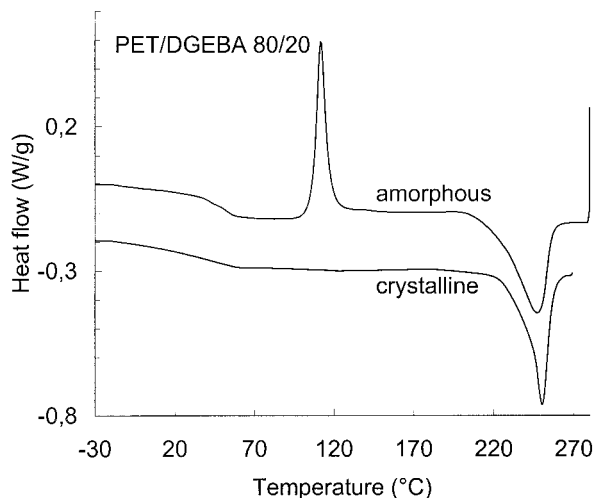
Figure 6 DSC thermograms of 80/20 PET/DGEBA blends with different crystallinities. The trace recorded during the first scan was crystalline. The second run after quenching from the melt was amorphous.

starting at 82°C when the crystallization began. For the crystalline blend, the mechanical transition was broad, almost 110°C, and smooth.

The broadening of the α relaxation is clearly observable in the mechanical spectra (Fig. 8). The more epoxy the blend contained, the larger the tan δ peak was.

The DSC and DMTA measurements showed that the samples had a single T_g or a broad α relaxation intermediate between those of pure epoxy and pure PET, regardless of the blending ratio and X_c. They confirmed that the epoxies were fully miscible with the amorphous fraction of PET. The evolution of the thermograms with the blend composition is shown in Figures 9 and 10, and a summary of the results is given in Table III. The data are given for the amorphous and crystalline samples. It was not possible to determine T_g objectively for the latter.

The theoretical value of T_g of the blends was calculated with the Fox equation:
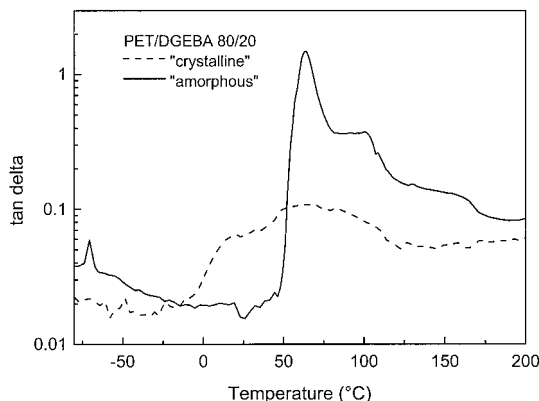

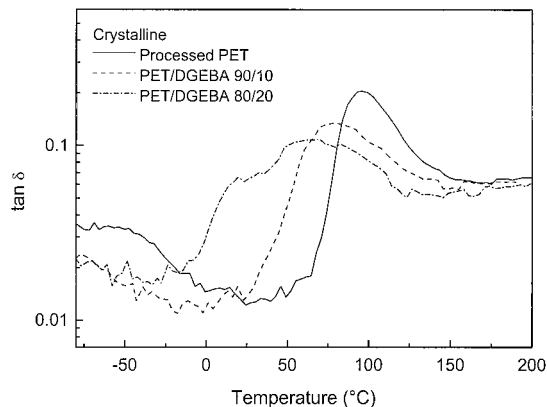**Figure 7** Tan δ versus temperature for 80/20 PET/DGEBA blends with different crystallinities.

Figure 8 Tan δ versus temperature for crystalline PET and PET/DGEBA blends.

$$\frac{1}{T_g} = \frac{W_{EP}}{T_{gEP}} + \frac{W_{PET}}{T_{gPET}} \qquad (3)$$

where W_{EP} and W_{PET} are the weight fractions of the epoxy and PET in the amorphous part of the blend, respectively, and T_{gEP} and T_{gPET} are the glass-transition temperatures of the epoxy and PET, respectively. A result of PET crystallization was an increase in the epoxy concentration in the amorphous phase. To calculate W_{EP} and W_{PET}, we took into account the crystallinity of the blend and subtracted the quantity of the epoxy assumed to have reacted with PET.

The measured T_g's were higher than those calculated for PET/ECY blends (Fig. 11). The interpretation for the high value of T_g of PET/ECY blends is that some ECY was lost during the blending procedure, so the true ECY fraction was lower than the expected one. ECY was quite volatile at 270°C, as some vapor was observed when the operator opened the mixer. A
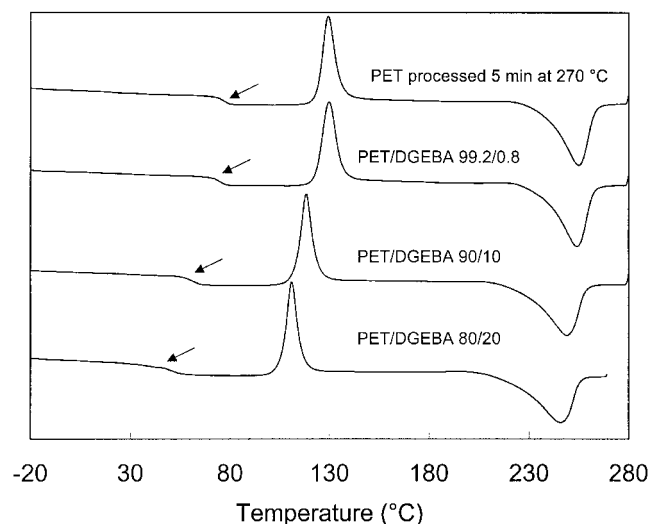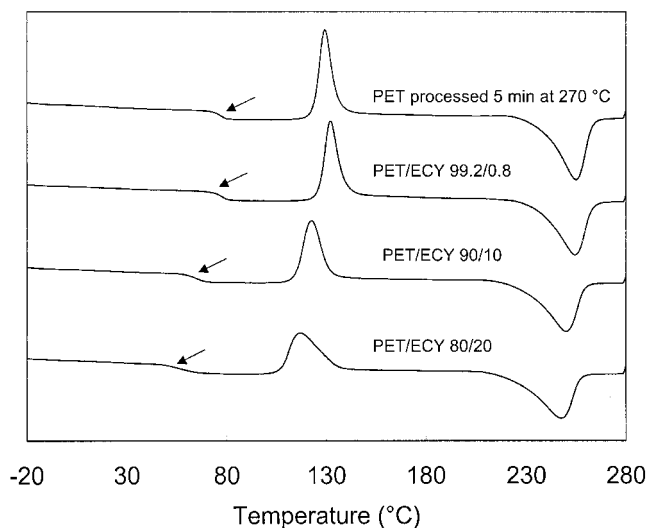

Figure 9 DSC thermograms of quenched PET/DGEBA blends.

Figure 10 DSC thermograms of quenched PET/ECY blends.

thermogravimetric measurement demonstrated that ECY began to evaporate at 120°C.

T_{cc} and T_m were depressed by the presence of the epoxies (Figs. 12 and 13). This is typically the case for a miscible blend with a crystallizable component.[15–17] The analysis of the melting-point depression may be used to estimate the Flory interaction parameter (χ), which determines the strength of the intermolecular forces between the components of a blend. However, no such attempt was made in this study because the equilibrium T_m of the blend is needed to calculate reliable values of χ.

CONCLUSIONS

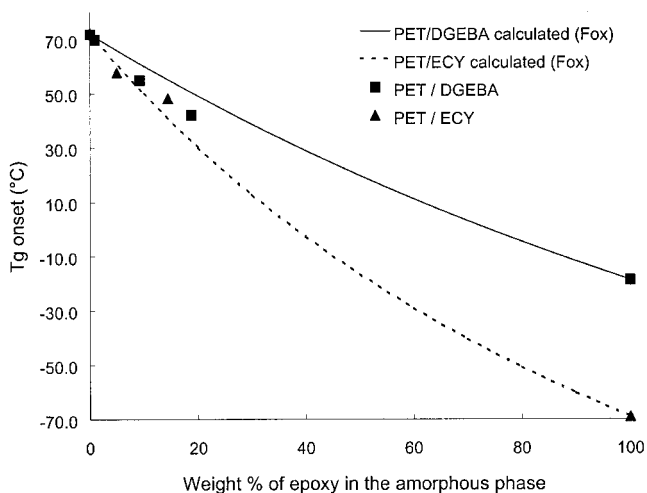The objectives of this work were to determine whether high proportions of two epoxy monomers (DGEBA

Figure 11 T_g of PET/epoxy blends as a function of the weight percentage of the epoxy in the amorphous phase of the quenched blends.
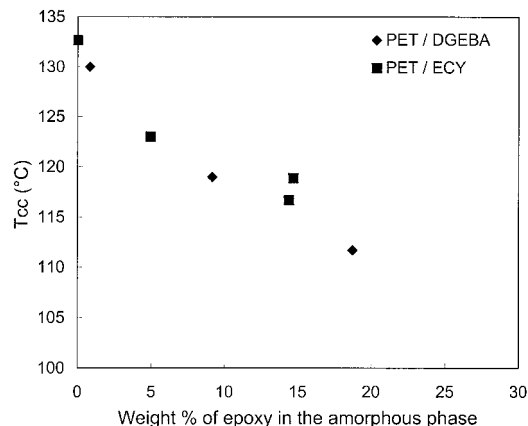

Figure 12 Evolution of T_{cc} of PET as a function of the weight percentage of the epoxy in the amorphous phase of the quenched blends.

and ECY) were miscible with PET and what the effect was of the presence of these monomers on the thermal and thermomechanical relaxation properties of the blends.

The miscibility of DGEBA and ECY was demonstrated. The blends were transparent above T_m of PET and also at room temperature when the molten polymer was quenched. Only one T_g was observed that could be approximated by a calculation with the Fox equation. T_g of the crystalline blends was broad and difficult to detect by calorimetric measurements. The DMTA analysis turned out to be more effective for detecting the relaxation peak. T_{cc} and T_m decreased with an increasing fraction of the epoxy, as is often noticed for polymer blends and for blends of a semi-crystalline polymer with a small molecule (epoxy in our case).

The epoxies are potentially reactive with PET, and we have shown that it is important to evaluate the amount of the monomer that has reacted with the thermoplastic polymer. Although we managed to do
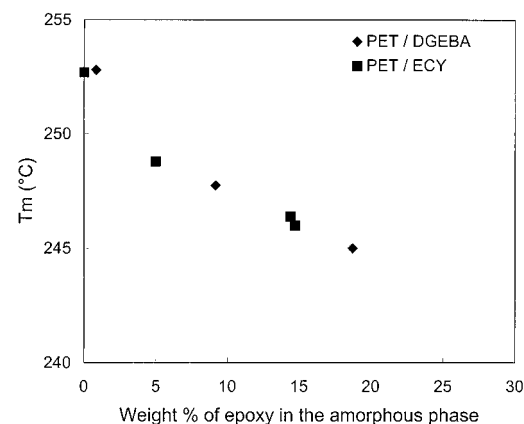

Figure 13 Evolution of T_m of PET as a function of the fraction of the epoxy in the amorphous phase of the quenched blends.

so by an extraction technique and by ^{1}H-NMR spectroscopy, the type of chemical reaction involved between the epoxy and PET was not clear. We know that a significant fraction of the epoxy functions reacted. For DGEBA, the intrinsic viscosity measurement, coupled with the extraction of the unreacted monomer, demonstrated that if DGEBA did not promote chain extension, some reaction occurred between PET and the diglycidyl ether epoxy. The functionalization of the PET chains and the etherification of the hydroxyl groups are the reactions that we propose. For ECY, we have some indirect indications that functionalization of the chain ends occurred as well as chain coupling and transesterification reactions, but more analytical work is needed to confirm this hypothesis.

References

1. Haralabakopoulos, A. A.; Tsiourvas, D.; Paleos, C. M. J Appl Polym Sci 1999, 71, 2121.
2. Bikiaris, D. N.; Karayannidis, G. P. J Polym Sci Part A: Polym Chem 1995, 33, 1705.
3. Cardi, N.; Po, R.; Giannotta, G.; Occhiello, E.; Garbassi, F.; Messina, G. J Appl Polym Sci 1993, 50, 1501.
4. Incarnato, L.; Scarfato, P.; Di Maio, L.; Acierno, D. Polymer 2000, 41, 6825.
5. Japon, S.; Boogh, L.; Leterrier, Y.; Manson, J. A. E. Polymer 2000, 41, 5809.
6. Torres, N.; Robin, J. J.; Boutevin, B. J Appl Polym Sci 2001, 79, 1816.
7. Xanthos, M.; Young, M. W.; Karayannidis, G. P.; Bikiaris, D. N. Polym Eng Sci 2001, 41, 643.
8. Nichols, M. E.; Robertson, R. E. J Polym Sci Part B: Polym Phys 1994, 36, 1607.
9. Oyanguren, P. A.; Frontini, P. M.; Williams, R. J. J.; Girard-Reydet, E.; Pascault, J. P. Polymer 1996, 37, 3079.
10. Oyanguren, P. A.; Frontini, P. M.; Williams, R. J. J.; Vigier, G.; Pascault, J. P. Polymer 1996, 37, 3087.
11. Kim, S.; Jo, W. H.; Kim, J.; Lim, S. H.; Choe, C. R. J Mater Sci 1999, 34, 161.
12. Wang, X.; Li, Y.; Yu, Y. J Mater Sci 1997, 32, 111.
13. Huang, P.; Zhong, Z.; Zheng, S.; Zhu, W.; Guo, Q. J Appl Polym Sci 1999, 73, 639.
14. Van Krevelen, D. W. Properties of Polymers; Elsevier: Amsterdam, 1976.
15. Hsiao, B. S.; Sauer, B. B. J Polym Sci Part B: Polym Phys 1993, 31, 901.
16. Paul, D. R.; Bucknall, C. B. Polymer Blends; Wiley: New York, 1999; Vol. 1.
17. Sperling, L. H. Introduction to Physical Polymer Science; Wiley: New York, 1992.