Macromol. Symp. **2003**, *198,* 323-333

Blends of an Epoxy Thermosetting Polymer with Aromatic Liquid-Crystalline Polyesters

Wojciech Jasinski,[1] *Véronique Carlier,*[2] *Roger Legras,*[2] *Werner Mormann*[1,]*

[1] Universität Siegen, Fachbereich 8, Laboratorium für Makromolekulare Chemie, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany
[2] Université Catholique de Louvain, Unité de Chimie et de Physique des Hauts Polymères, place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

Summary: A series of aromatic liquid-crystalline polyesters with different composition have been synthesized to adjust transition temperatures and molecular weight. Miscibility of polyesters with bisphenol-A-diglycidyl ether (DEGBA), 4,4'-methylene-bis(3-chloro-2,6-dimethylaniline) (MCDEA) and the influence on transition temperatures has been studied. Miscibility of binary and ternary mixtures was found over the whole range of composition depending on the temperature. Thermoset formation by curing of LC-polyester / DEGBA / MCDEA mixtures containing different amounts of polyester resulted in reaction-induced phase separation with polyester content from 30 to 50 wt.%. Cloud point techniques, scanning electron microscopy (SEM) and dynamic mechanical thermal analysis (DMTA) have been applied.

Keywords: blends, epoxy resins, liquid-crystalline polyesters (LCP), reaction-induced phase separation

Introduction

Epoxy resins are important thermosetting polymers used in numerous applications because of their outstanding properties like chemical resistance, low creep, and low shrinkage on cure. These properties require a high level of crosslinking, which makes the materials brittle and results in poor resistance to crack propagation.[1] Various attempts have been made to overcome these inherent drawbacks by modification with thermoplastics or reactive rubbers. Most of these were synthesized from an initially homogenous mixture of modifier and thermoset precursors; phase separation occurs as the crosslinking reaction proceeds.[2] Kim at al. used reactive and non-reactive poly(ether sulfone) and tried to control morphology of the blends.[1] Swier et al. using the same thermoplastic polymer have investigated the reaction-induced phase separation with

DOI: 10.1002/masy.200350827

modulated different scanning calorimetery.[3] Butadiene-acrylonitrile rubber as modifier increases the fracture toughness at the expense of modulus.[4] Other polymers like polystyrene, poly(methyl methacrylate), polycarbonate, polyetherimide or poly(ε-caprolactone) have also been used as modifiers for epoxy resins.[4-7] Liquid crystalline polymers, to our knowledge, have not been described in combination with thermosetting polymers; only low molar mass liquid crystalline compounds have been used as polymer dispersed liquid crystals which however, serve other purposes.[8,9]

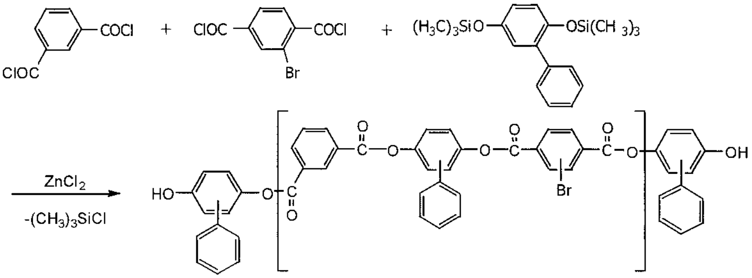
The influence of liquid-crystalline polyesters in cured epoxies has not been investigated. The reason can be their high transition temperatures and poor solubility, which makes blending rather difficult. The goal of our studies of blends from tractable LC polyesters and epoxy resins is to find out whether they can have advantages over non-LC polyester based modifiers.

In the present communication we report on the synthesis of aromatic LC polyesters with properties suitable for use as modifiers in thermosetting epoxy resins and on first results of heterogeneous blends obtained by reaction driven phase separation.

Results and Discussion

Synthesis of Polyesters

Suitable LC-polyesters were synthesized from dicarboxylic acid chlorides and trimethylsilylated bisphenols as described previously in the literature.[10]



Scheme 1

2-bromoterephthaloyl chloride together with small amounts of isophthaloyl chloride (0-10mol%) and 1,4-bis(trimethylsiloxy)-2-phenylbenzene (silylated phenylhydrquinone) were used as monomers. Molecular weight was adjusted with a slight excess of silylated phenol, which also ensured that only hydroxy terminated polyesters were obtained (Scheme 1). Isophthaloyl chloride was incorporated to interrupt the rigid chain by introduction of kinks, thus decreasing transition temperatures and improving solubility.

Polycondensation reactions were carried out either in *o*-dichlorobezene or in bulk with zinc chloride as a catalyst.[11,12] Polyesters were diluted or dissolved in *o*-dichlorobezene and precipitated in methanol. LC-properties were studied by polarized light microscopy and thermal analysis. Decrease of molecular weight alone was not sufficient to obtain polyesters with clearing temperatures below 300 °C nor did it improve solubility (Figure 1, Table 1). Modification of the polyesters by incorporation of isophthaloyl chloride helped to decrease transition temperatures (Figure 2).

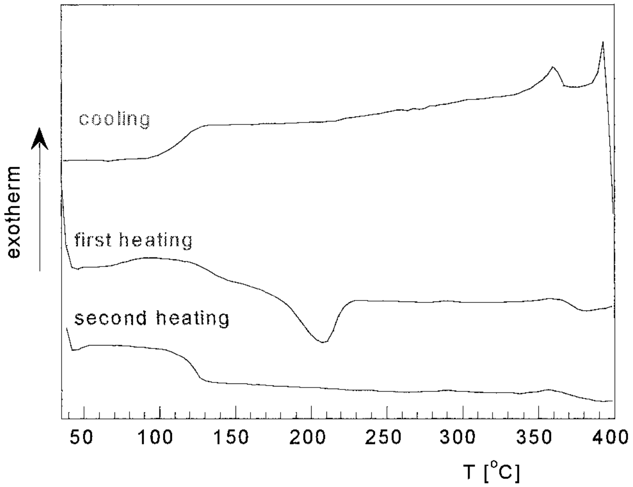


Fig. 1. DSC curves of the linear LC polyester 1 (heating rate 20 K/min).

The solubility of polyesters in common solvents was improved as well. The polyester with 2.5mol% of isophthaloyl chloride was chosen for modification of epoxy resins because of the low clearing temperature and a broad liquid-crystalline range. The results of polycondensation reactions are summarized in Table 1.

Table 1. Composition and properties of LC polyesters.

No.	Polyester	Mole ratio	GPC$^{a)}$		T_g [°C]	T_m [°C]	T_{iso} [°C]
			Mn	Mw			
1	Linear	10:11	37190	88150	121	207	386
2	Linear	9:10	28870	51580	121	192	344
3	Kinked 2.5%	9:10	1361	11220	118	130	250
4	Kinked 5%	9:10	2968	16220	112	135*	230*
5	Kinked 10%	9:10	6803	44010	112	123	210*

* temperatures obtained from polarized light microscopy

a) GPC eluent: DMAc (No. 1, 2); THF (No. 3-5)

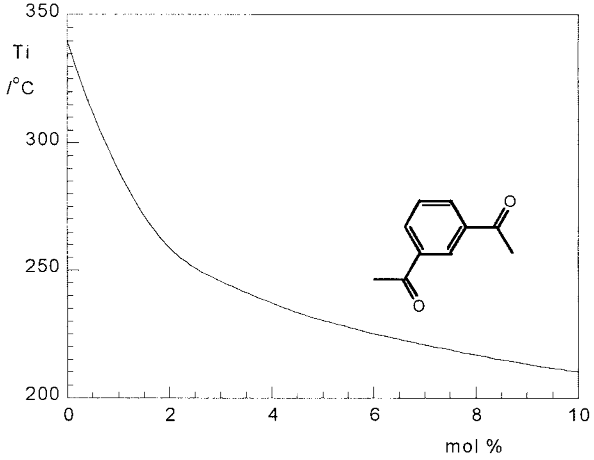


Fig. 2. Influence of isophthaloyl moieties on the clearing temperature of polyesters.

Polarized light microscopy in some cases gave the nematic schlieren texture with a biphasic region typical of step growth polymers. As annealing did not improve textures, the LC phase was identified from mixtures with a monomeric nematic substance (1,4-bis-(4-methoxybenzoyl-oxy)benzene).[13]

Epoxy/LC-Polyester Blends

Miscibility of the LC polyester with DEGBA and with the diamine MCDEA was studied with binary systems. MCDEA and the polyester after homogenization at 150 °C were miscible in any ratio. Mixtures of the polyester with DEGBA prepared in a similar manner were miscible at higher temperature in the composition range from 50 to 100 wt.% polyester, but formed two phases upon cooling. Figure 3 shows the temperature of phase separation or isotropization and the glass transition temperature versus composition of the polyester/DEGBA system. Data were obtained from DSC and optical microscopy. In the microscope two phases are visible, a macroscopic sample is transparent, which is probably due to refractive index matching.

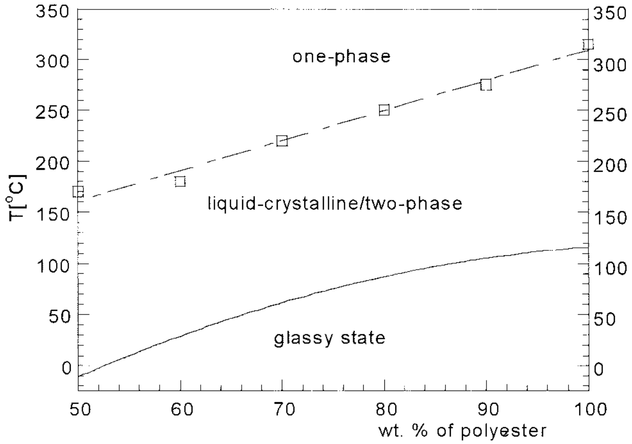


Fig. 3. Phase separation and glass transition temperature of DEGBA/polyester (2) mixtures.

Blends were prepared in a two-stage process: first, a homogeneous mixture of polyester and epoxy resin was made at 160 °C and the diamine was added to this mixture (Figure 4).

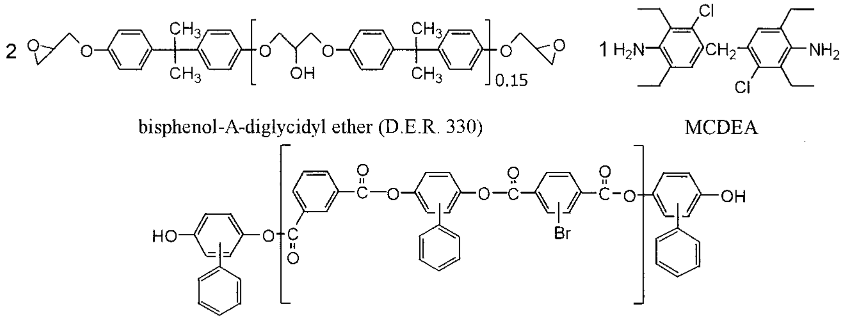


Fig. 4. Composition of polymer blends.

Side Reaction between Epoxide and Polyester

Polymerisation of epoxy groups or reaction with hydroxy terminal groups in the polyester chain can occur during preparation of samples. This was checked with DSC and GPC for a mixture of 60 wt.% polyester and 40 wt.% epoxide, which were mixed as powders in a mortar, heated to 140 °C for 5min, transferred into aluminium pans and isothermally heated to 160, 200, 220, and 250 °C for 45 minutes in the DSC cell. The results from isothermal DSC (Table 2) and GPC (Figure 5) confirm that no significant conversion of epoxy groups occurs up to 200 °C.[14]

Table 2. Enthalpies of reaction between polyester and DEGBA from DSC.

Isothermal process [°C]	$\Delta H^{a)}$ [kJ/mol of epoxy group]
160	0.54
200	2.13
220	41.3
250	$75.2^{b)}$

a)ΔH± 5kJ/mol [14], b) insoluble in THF

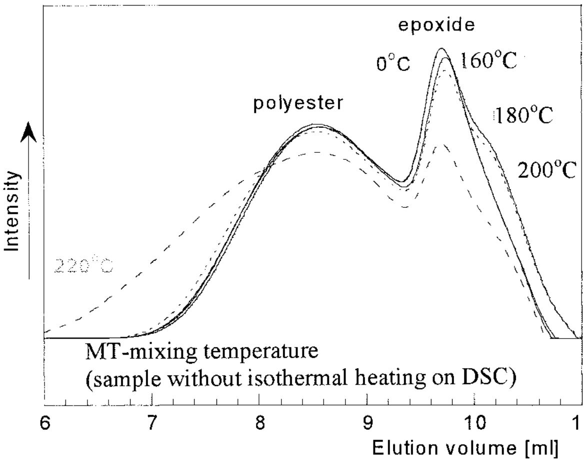


Fig. 5. GPC-elution volume curves of polyester/epoxide mixtures after heating.

Cloud Point Measurements

Phase separation in an epoxy resin/LC polyester mixture was detected by cloud point measurements, i.e. change of intensity of light transmitted and scattered through the sample. This method detects phase separation when dispersed particles have a diameter of at least 0.1μm.[15]

Table 3. Cloud point for different amount of polyester and curing temperatures.

Polyester [wt.%]	Curing temp. [°C]	t_{CP} [min]	Conv.$_{CP}$ [%]
20	160	-	-
30		50	89
40		35	69
50	160	30	59
	180	20	69
	200	-	-
	220	-	-

Samples with 20, 30, 40 and 50 wt.% of polyester reacted at 160 °C. The dependence of the phase separation on the curing temperature was investigated with a mixture with 50% of polyester at 160, 180, 200 and 220 °C.

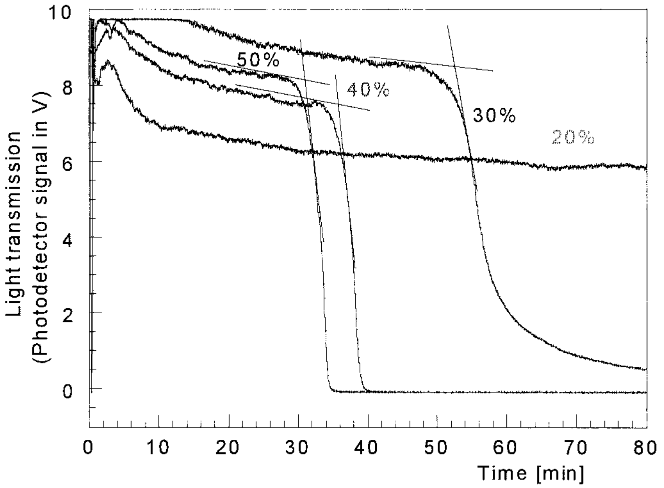


Fig. 6. Cloud point for different amount of LC-polyester in epoxy blends (curing at 160 °C).

The results obtained in these experiments show that phase separation occurred for sample with 30, 40 and 50% of LC-polyester when cured at 160 °C, the sample with 20% of polyester remained homogeneous (Figure 6). Phase separation occurs after shorter times with increasing amount of polyester. The sample with 50 wt.% polyester was also cured at 180, 200, and 220 °C. Phase separation was observed 10 minutes earlier for the sample cured at 180 °C, conversion was 10% higher than at 160 °C which is not in agreement with results from other groups that phase separation starts at given extent of reaction.[15] Further studies will be necessary to clarify this. For samples cured at 200 and 220 °C, however, no phase separation was observed (Table 3). At 220 °C this can be due to reaction of terminal groups with epoxy moieties as described above. Another explanation could be the domain size of the dispersed phase which is to small to be detected by the cloud point method.

Morphology

The existence of a phase-separated structure of the cured epoxy LC-polyester blends was proven by dynamic mechanical thermal analysis and scanning electron microscopy. Samples for DMTA were prepared as described above and cured in a mould at elevated temperatures. Curing conditions and DMTA-results are given in Table 4.

Table 4. Curing regime and viscoelastic analysis.

Curing regime[a]	% polyester	T_g [°C]		tan (δ)	
		polyester	epoxy	$h^{b)}_{\alpha\ \mathrm{polyester}}$	$h_{\alpha\ \mathrm{epoxy}}$
1	50	105	125	0.25	1.25
2		105	135	0.2	1.1
1	40	105	143	0.12	1.07
2		105	148	0.12	0.96
1	30	105	148	0.7	1.05
2		105	155	0.7	0.95
1	0	-	125	-	1.25
2		-	160	-	0.95
-	100	95	-	2.3	-

a) curing regime: **1** – 2h at 150 °C, next 2h at 190 °C; curing regime **2** – plus 30min. at 240 °C
b) peak-height of α-transitions

Dynamic viscoelastic properties can be used to yield information on relaxations and thermal transitions of individual phases in multiphase polymers, hence also on the microstructure of thermosetting resins.[16] The glass transition temperature of the neat polyester is 95 °C, that of the neat epoxy resin 160 °C.

Figure 7 shows the temperature dependence of the loss factor of modified epoxy networks between 40 and 180 °C at a frequency of 1Hz. A strong maximum between 125 and 155 °C and a weak maximum around 105 °C are visible in each curve. Peak temperatures and peak height of the maxima are included in Table 4. The low α–relaxation peak corresponds to the glass transition temperature of polyester, it is 10 °C above T_g of the pure polyester. The peak at higher temperature is the glass transition temperature of the epoxy resin. Tg of the epoxy network decreases with the increasing polymer content. Hence we deal with a polyester rich and an epoxy rich phase and the amount of polyester in the epoxy phase increases with increasing polyester content in the mixture.

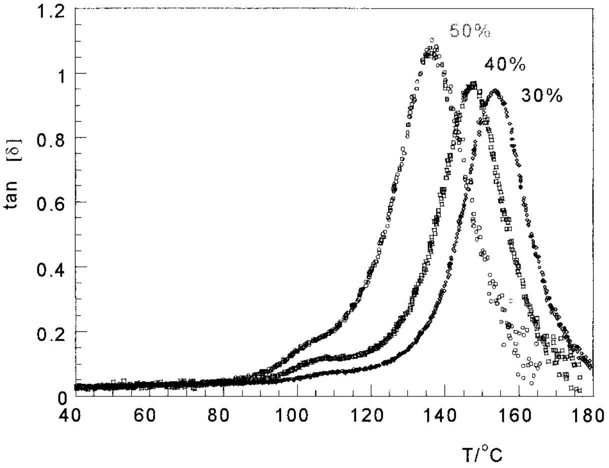


Fig. 7. DMTA of samples with different concentration of polyester (curing regime 2).

For SEM investigation cured samples were fractured in liquid nitrogen, the fracture surface was coated with gold in a sputter coater and observed in the microscope (SEM – Philips XL20, tungsten filament, 20kV acceleration voltage).

The SEM pictures (Figure 8) show nodules and holes. The sample with 20% polyester looks quite homogeneous with only few spots that could indicate the presence of a second phase (Figure 8). With increasing amounts of modifier phase separation can easily be distinguished. The finest structure is observed with 50 wt.% of polyester.

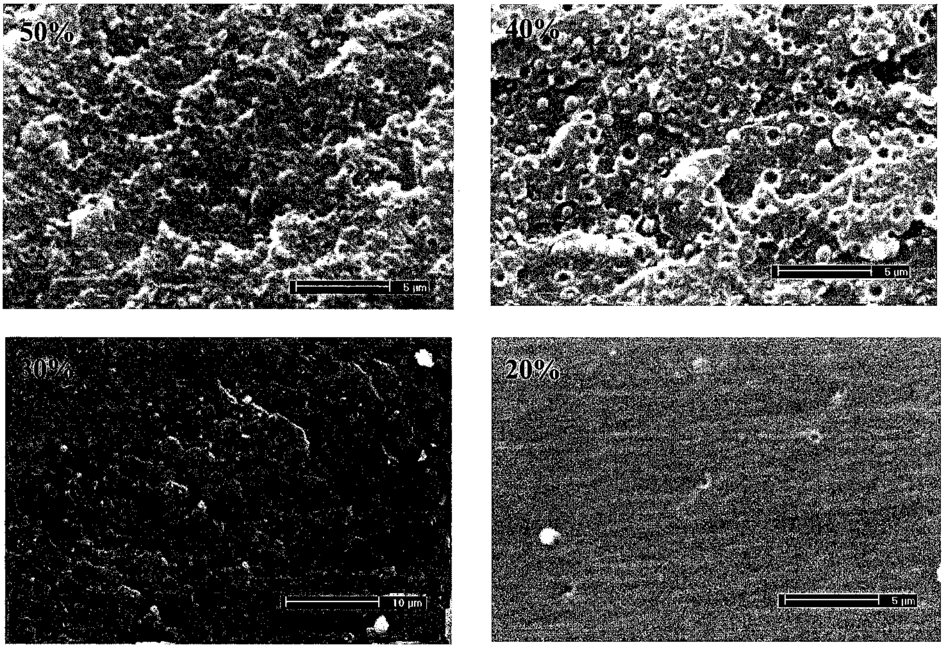


Fig. 8. SEM pictures for 50, 40, 30 and 20%.

Conclusions

Liquid-crystalline precursors for the modification of epoxy resins have been synthesized by step polycondensation. The products have lower transition temperatures and higher solubility than commercially available LC-polyesters. The polyesters were miscible with epoxy resin and diamine used in experiments. The initially homogenous reaction mixture of epoxy-amine and LC-polyester transformed to a two-phase system by reaction driven phase separation. DMTA-measurements indicated that the epoxy rich phase contained significant amounts of polyester and the polyester rich phase significant amounts of epoxy resin. Scanning electron microscopy proved the existence of a two phase system above a polyester content of more than 20 wt.%. The smallest particles of the dispersed phase were observed with 50 % polyester.

Acknowledgments

Financial support from the European Commission in the framework of the Research Training Network (contract no. HPRN-CT-2000-00146) is gratefully acknowledged.

[1] B. S. Kim, T. Chiba, I. Takashi, *Polymer*, **1995**, *36 (1)*, 43-47
[2] R. J.J. Williams, B. A. Rozenberg, J. P. Pascault, *Adv. Polym. Sci.*, **1997**, *128*, 95-156
[3] S. Swier, B. Van Mele, *Termochimica Acta*, **1999**, *330*, 175-187
[4] D. Hao, X. Tang, X. Wang, Y. Luo, *J. Appl. Polym. Sci.*, **2001**, *82 (4)*, 833-838
[5] M. J. Galante, J. Borrajo, J. J. Williams, E. Girard-Reydet, J. P. Pascault, *Macromolecules*, **2001**, *34*, 2686-2694
[6] A. Bonnet, J. P. Pascault, H. Sautereau, *Macromolecules*, **1999**, *32*, 8524-8530
[7] J. L. Chen, F, Ch. Chang, *Macromolecules*, **1999**, *32*, 5348-5356
[8] J. W. Doane, J. L. West, *US Patent 4994204*, **1991**
[9] C. C. Riccardi, J. Borrajo, J. J. Williams, M. Dumon, J. P. Pascault, *Macromolecules*, **1998**, *31*, 1124-1132
[10] H. R. Kricheldorf, *Silicon in Polym. Synth.*, **1996**, 323-324
[11] W. Heitz, N. Nießner, *Makromol. Chem.*, **1990**, *191*, 225-235
[12] H. R. Kricheldorf, G. Schwarz, *Makromol. Chem.*, **1983**, *184*, 475-496
[13] H. Han, P. K. Bhowmik, *Prog. Polym. Sci.*, **1997**, *22*, 1431-1502
[14] J. Goins, G. P. Simon, W. D. Cook, *J. Appl. Polym. Sci.*, **1999**, *72* 1479-1488
[15] C. Hedruel, J. Galy, J. Dupluy, M. Delmotte, C. More, *J. Appl. Polym. Sci.*, **2001**, *82 (5)*, 1118-1128
[16] I. Mondragon, P. M. Remiro, M. D. Martin, A. Valea, M. Franco, V. Bellenguer, *Polym. Int.*, **1998**, *47*, 152-158