Toughening Epoxy Resins by Liquid Crystalline Polymers

C. CARFAGNA,[1,*] L. NICOLAIS,[1] E. AMENDOLA,[1] C. CARFAGNA, JR.,[1] and A. G. FILIPPOV[2]

[1]University of Naples, Department of Materials and Production Engineering, Piazzale Tecchio, 80125 Napoli, Italy, and [2]Shell Development Company, Westhollow Research Center, Houston, TX 77251-1380, USA

SYNOPSIS

Toughening epoxy resins can be achieved by blending a low percentage of Liquid Crystalline Polymer with the thermoset. The processing technique consists of the spinning of blends of a thermoplastic (Ardel) with the LCP (PET/PHB60). The bundled filaments are subsequently dissolved in the uncured epoxy resin (Epon 825). After curing, the LCP phase separates from the matrix in the form of microfibers with a very high aspect ratio, which act as crack stoppers and improve fracture toughness of the material.

INTRODUCTION

Epoxy resins are desired materials for many applications with required high modulus and strength, low creep, and good performance at elevated temperatures. However, for some applications the improvement in fracture resistance is highly desirable.

One of the methods used to improve the toughness is based on attaining a dispersion consisting of a particulate second phase in the thermosetting polymer.[1,2] According to this procedure, a filler can consist of rigid particles (e.g., alumina, silica, or glass spheres), or it can be made by reactive rubbers, or by both rigid and rubbery materials. The inclusion of a second phase of dispersed rubbery particles in a thermoset has proven to be the most effective method for toughening. However, the presence of the rubbery phase usually results in lowering the effective properties, such as T_g and elastic modulus, which are crucial performance factors under hot/wet conditions.[3-7]

Another approach for the toughening of thermosets is to incorporate tough, high performance thermoplastics into brittle thermosets, such as epoxides, cyanates, and bismaleimides, which approach is receiving increasing interest.[8,9] The important features of thermoplastics include: the chemical constitution, the T_g, the molecular weight, the mechanical and the thermal properties, and the presence of chemically reactive groups at the chain ends

or in the polymer backbone or pendant to the backbone. The results look very promising. In fact the presence of small amounts of some thermoplastics can, in some cases, increase the fracture toughness without substantially sacrificing T_g and modulus of the resulting blend. However, the use of a solvent, for dissolving the thermoplastic in the resin can create difficulties during the processing.

In our approach we used Liquid Crystalline Polymers (LCP) as fillers in the compounding of epoxy resins for improved toughness.

Independantly, LCPs have the following advantages:

1. Excellent dimensional stability,
2. High mechanical properties,
3. Low thermal expansion,
4. Good high temperature properties, and
5. Outstanding environmental resistance.

Therefore, blending LCP with epoxy resins could increase their toughness, without sacrificing T_g and mechanical properties. This article describes the preparation and physical characterization of blends of LCP and epoxy resins.

EXPERIMENTAL

Materials

Thermoplastic Filler

Polyarylates, based on bisphenols and tere/isophthalates, have been recognized as being in an im-

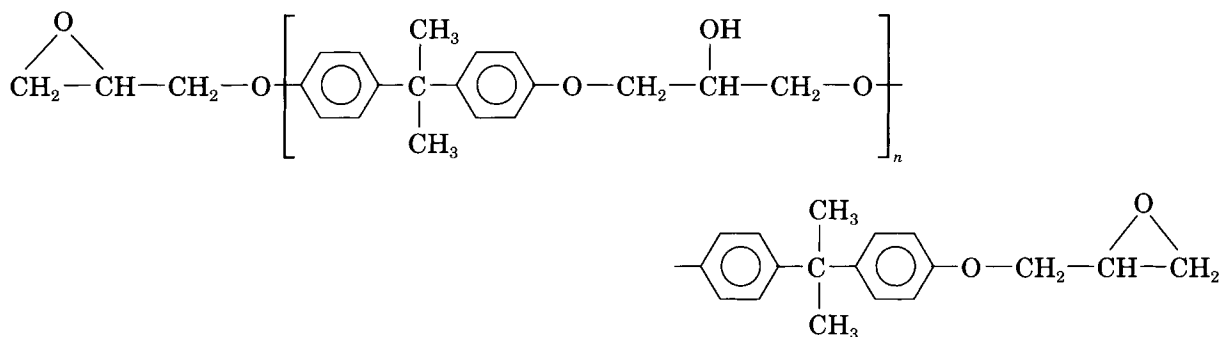portant class of polymeric materials for over two decades.[10]

Specifically, the polyarylate based on Bisphenol A and tere/isophthalates is now commercially available as ARDEL-D100 from Union Carbide, offering a high heat distortion temperature, excellent toughness, high resilience from deformation, and excellent mechanical property retention after long-term UV exposure.[11-13]

Blends of polyarylates with different polymers have been mentioned in various patents and in several references in the technical literature.

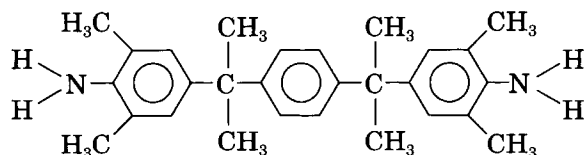Ardel is an amorphous polymer with a T_g of 196°C (Fig. 1).

Liquid Crystalline Polymer

As LCP, PET/PHB60 by Eastman Kodak was utilized. The polymer, first synthesized in 1976, is a block copolyester that is well known in the literature.[14]

Blending Procedure of LCP and Epoxy Resin

The blending procedure of LCP and epoxy resins can be summarized in the following steps:

A first processing step consists in the spinning of thermoplastic materials containing the LCP. The resulting bundled filaments will contain the LCP in the form of microfibers with a very high aspect ratio. The presence of thermoplastic is required to increase the viscosity of the Epoxy Resin during the hot lay-up.
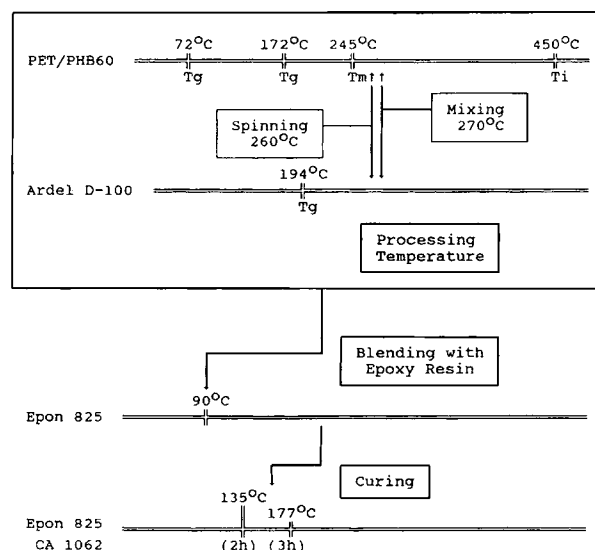
A second step consists of mixing the spun fiber blend in the uncured epoxy resin. In this step, the thermoplastic constitutes a single phase with the resin, increasing its viscosity; the LCP will be present as fibers with an high aspect ratio.
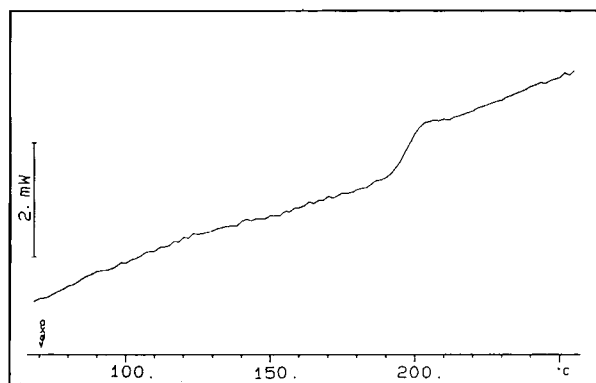
In the third step, the curing agent is added to the mixture.

Finally the system is cured according to the curing schedule.

Epoxy Resin

The Epoxy Resin is Epon 825.

with n ranging between 0 and 1 (WPE = 172–178).

The curing agent is Epon HPT Curing Agent 1062.

Curing was performed by blending the stoichiometric amount of the two components and heating the mixture at 135°C for 2 h and then at 177°C for 3 h. The cured resin exhibited a T_g of 179°C (Fig. 2). The processing schedule of the blend and the curing of the epoxy resin can be summarized as follows:

Figure 1 DSC thermogram of Ardel-D100. Rate: 10°C/min.

Preparation of the Blends of Ardel and PET/PHB60

The blends of Ardel and PET/PHB60 were obtained by means of a Brabender mixer. The two components, in the form of granules before mixing, were put in a vacuum oven at 130°C for 14 h, and then were poured in the mixer. The mixing operations were carried out at 270°C for 10 min at an angular rate of the mixer of 30 min⁻¹. Subsequently, the material was pressed at 260°C and then was chopped.

Spinning of the Blends of Ardel and LCP

Spinning was performed by means of a capillary viscometer (CEAST Rheoscope 1000), provided with a melt spinning unit using a die having a diameter of 1 mm and L/D = 10 at 260°C. The filament was extruded in air at room temperature and collected by a 8-cm diameter take-up apparatus, placed at a distance of approximately 0.3 m from the extruder die.
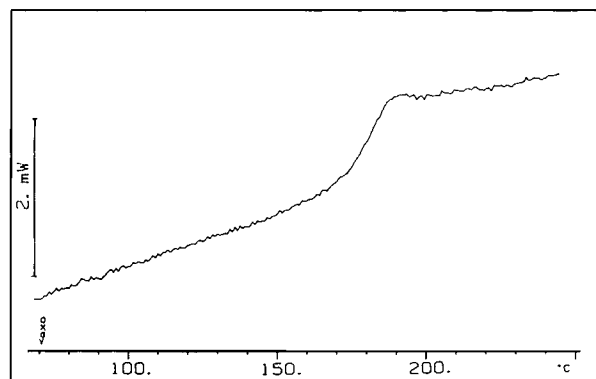
Figure 2 DSC thermogram of cured resin. Rate: 10°C/min.

Calorimetry

A differential scanning calorimeter (DSC), Mettler TA 3000 System was used to evaluate the transition temperatures of the polymers and their blends.

Microscopy

A scanning Electron Microscope (Hitachi) was utilized to analyze the transversal sections of the cured resin samples.

The morphology of the LCP in the blends was also investigated by means of an optical microscope (Polyvar by Reichert–Jung) under cross polarizers at room temperature.

Mechanical Properties

Experiments were performed to measure the fracture toughness of the resulting blends. All tests were performed in accordance with ASTM E-399 test procedure using a 1 in. × 1 in. × $\frac{1}{8}$ in. compact tension specimens.

Flexural properties of the cured resins were measured according to ASTM D790. In this test method, a bar, of rectangular cross-section, is tested in flexure as a simple beam. The bar rests on two supports and is loaded by a loading nose midway between the support. The specimen is deflected in this manner until rupture occurs or until the maximum fiber strain of 5% is reached, whichever occurs first.
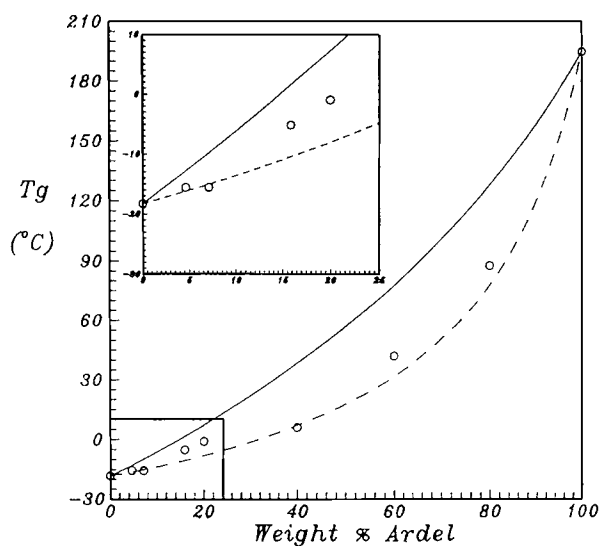

Figure 3 Glass transition temperature (T_g) vs. composition for uncured Epon 825-Ardel blends: (——) Fox equation; (O) Experimental; (– – –) Couchman equation.
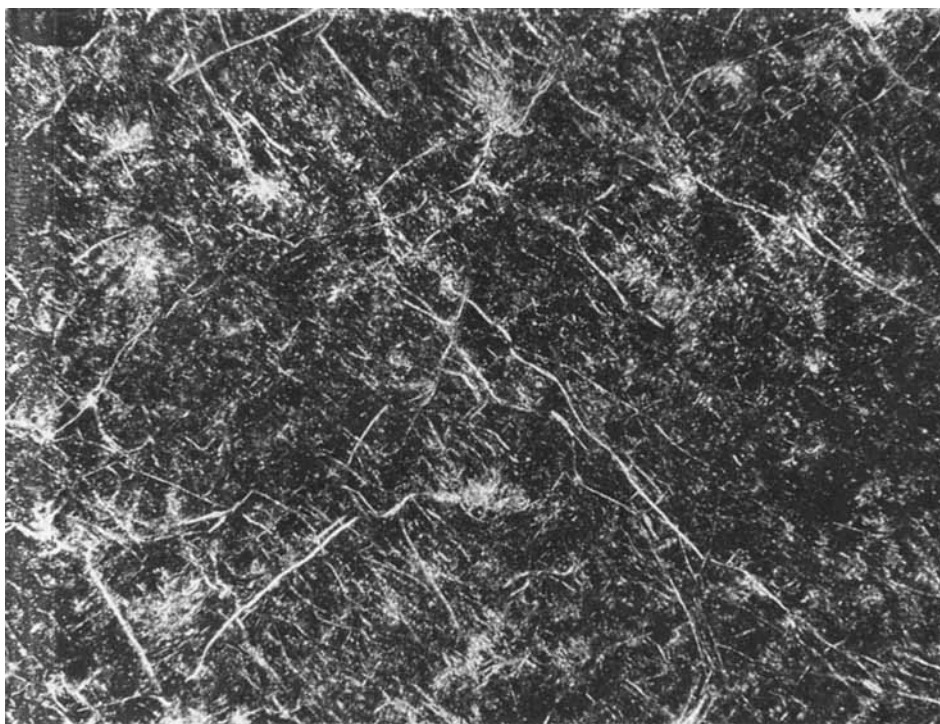
Figure 4   Optical micrograph (×100) of uncured Epon 825-Ardel-PET/PHB60 (1.7% LCP) at room temperature. The amount of LCP in Ardel is 20%, fibers draw ratio is 50.
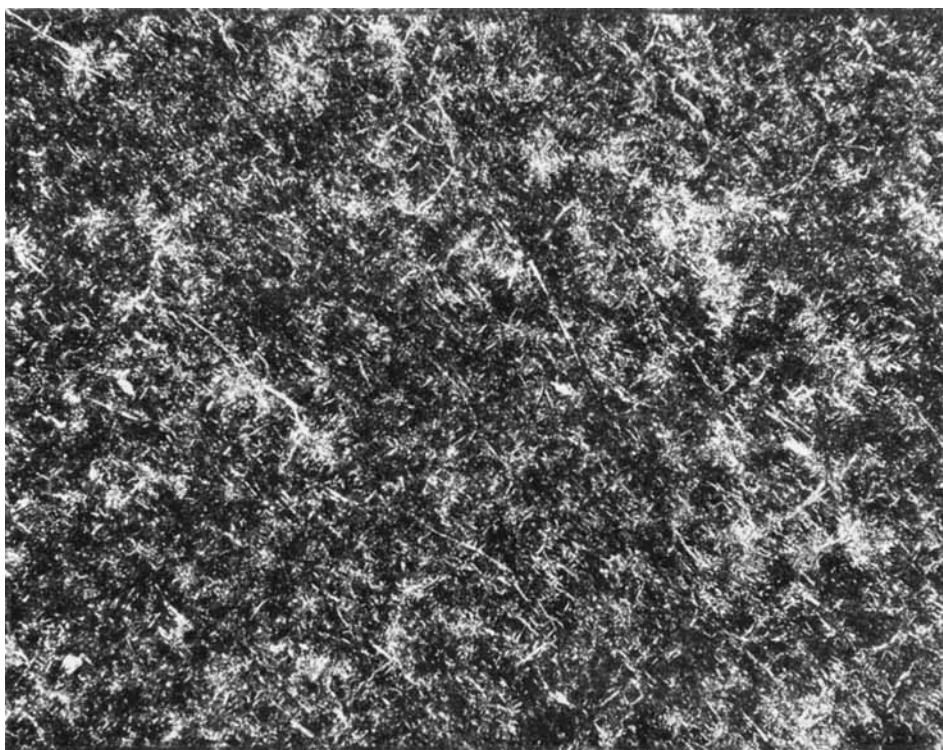
Figure 5   Optical micrograph (×100) of uncured Epon 825-Ardel-PET/PHB60 (3.1% LCP) at room temperature. The amount of LCP in Ardel is 40%, fibers draw ratio is 50.
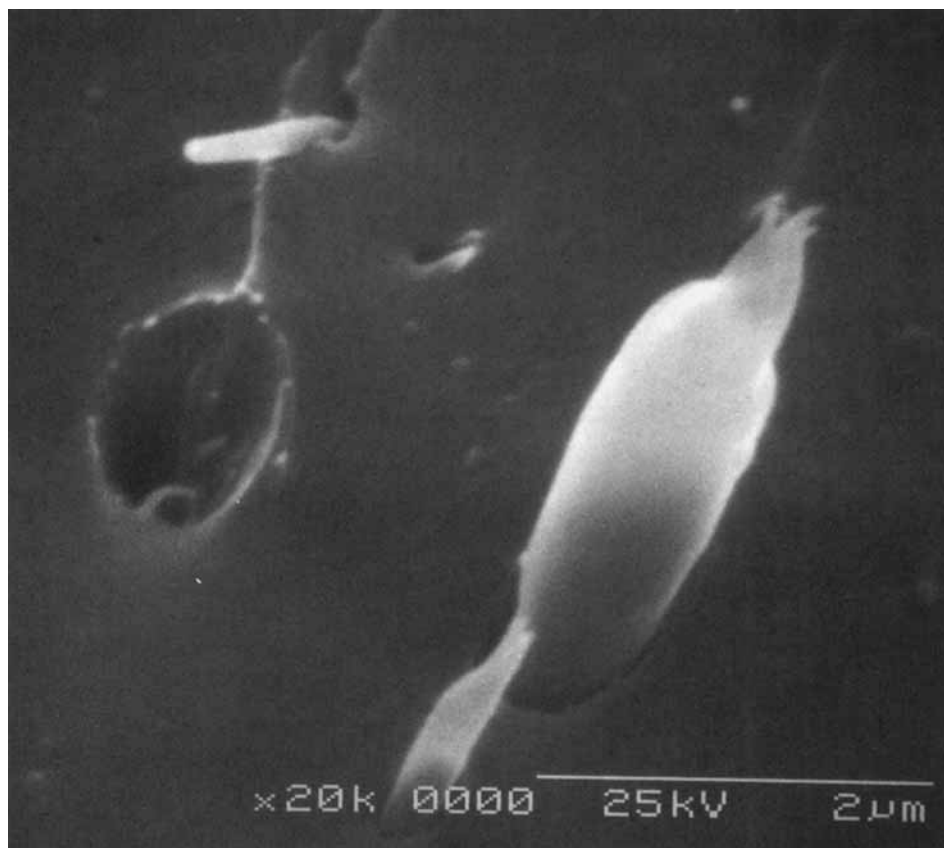
Figure 6 SEM of cured system Epon 825-CA 1062-Ardel (3.0%)-PET/PHB60 (2.0%). Fibers drawn at T = 260°C with draw ratio of 50.

RESULTS AND DISCUSSION

As referred to in the experimental section, the processing schedule for the blends of epoxy resins and LCP is based, in the first step, on the mixing of the uncured epoxy resin with the chopped bundles of Ardel and LCP. This procedure allows dispersion of the liquid crystalline fibers in the resin without solvent. Moreover, since the fibers of LCP can be dispersed in Ardel on a quasimolecular scale, their dimensions will be noticeably smaller than those of the spun fibres of the pure LCP at the exit of the die.

The first part of the work is devoted to study the compatibility between Ardel and uncured Epon 825. One of the most diffused methods to investigate the compatibility of the multiphase system is to evaluate the glass transition temperatures (T_g) of the blend and to relate it to those of the parent polymers.

Several models exist in literature to estimate the T_g of compatible blends. The most popular are the equation of Fox[15] and the equation of Couchman.[16]

Fox's equation is:

$$1/T_g = w_a/T_{g_a} + w_b/T_{g_b}$$

Couchman's equation is:

$$\ln T_g = \frac{w_a \, \mathrm{DCp}_a \ln T_{g_a} + w_b \, \mathrm{DCp}_b \ln T_{g_b}}{w_a \, \mathrm{DCp}_a + w_b \, \mathrm{DCp}_b}$$

where: w_i = weight fraction of species i, $T_{g_i} = T_g$ of component i, and DCp_i = Difference in Cp between glass end rubber states for component i.

Figure 3 reports the values of T_gs for the blends of Ardel and Epon 825, as deduced from the calorimetric analysis. The experimental values lie intermediately between the two models, revealing a fair compatibility between the two polymers.

Due to the closeness of T_gs of Ardel and of cured Epon 825, it is much more difficult to determine the compatibility between the thermoplastic polymer and the crosslinked epoxy resin. However, as it will be shown by SEM, the two systems seem to be compatible also after the curing of the thermoset.

The evaluation of the compatibility between the uncured epoxy resin and Ardel is very important. In fact, in the first step of the processing of the blends, Epon 825 must dissolve the bundles of Ardel and LCP. Before curing, the pluriphasic system will contain the fibers of LCP, isotropically dispersed in the homogeneous solution of Ardel and Epon 825 (Figs. 4 and 5). After curing, the LCP appears as a separate phase in the cured thermoset in the form of microfibers with a very high aspect ratio. No phase separation can be observed between Ardel and Epon 825 (Fig. 6).

The results of the evaluation of the fracture toughness are reported in Table I.

As can be seen, the addition of only 2.0% by weight of LCP to the epoxy resin increases the fracture toughness about 20%. This increase is not due to the presence of Ardel. In fact, for the samples prepared with the same amount of Ardel, but containing no fibers of LCP, the value of Kq is practically equal to that of the unmodified epoxy resin.

With higher content of LCP, the toughness of the material dramatically increases. However, this effect can be partially due to the larger amount of Ardel that can contribute to plasticize the blend.

As previously mentioned, in many cases toughening of brittle matrices is achieved with sacrifices in T_g and elastic properties. In our cases, however, both T_g and modulus are only slightly affected by the presence of LCP. Figure 7 reports the value of the flexural modulus measured at room temperature for the specimens containing different amounts of Ardel and LCP. The small reduction in the elastic properties could be due to the plasticizing effect of Ardel and of a small amount of LCP. The T_g of the cured resin is not affected by the presence of Ardel and LCP, as can be observed from Figure 8.

CONCLUSIONS

The processing technique proposed for toughening brittle matrices with Liquid Cristalline Polymers seems to offer promising results.

**Table I Fracture Toughness, Kq, (MPa $\times$ m$^{1/2}$)**

% LCP	% Ardel			
	0	3.0	4.7	9.4
0	0.670	0.650	0.660	
2.0		0.770	0.820	
4.0				0.960
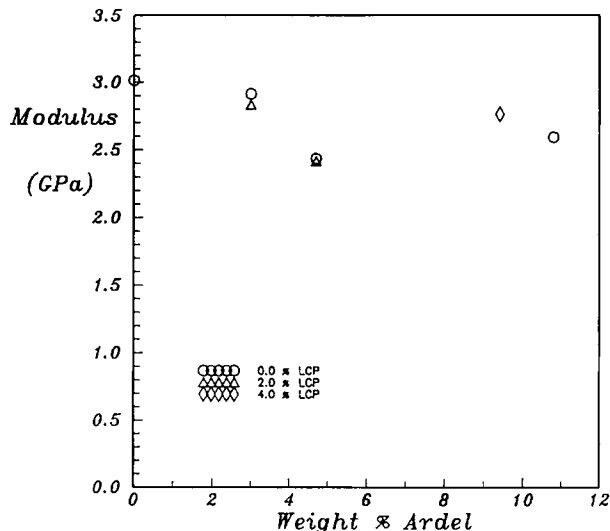
Figure 7 Flexural modulus vs. composition for cured system Epon 825-CA 1062-Ardel-PET/PHB60.

Small amounts of fibers of LCP can increase the toughness of brittle matrices, acting as crack stoppers, without reducing the T_g and elastic modulus of the thermoset.

As a comparison, the same increase of fracture toughness can be obtained with not less than 25–30% of some engineering thermoplastics, as reported in the literature.[8,9] Moreover, in many of these cases, the blending with the toughener is carried out with the use of a solvent. This procedure can dramatically affect the properties of the blend if the solvent is not completely removed from the resin.
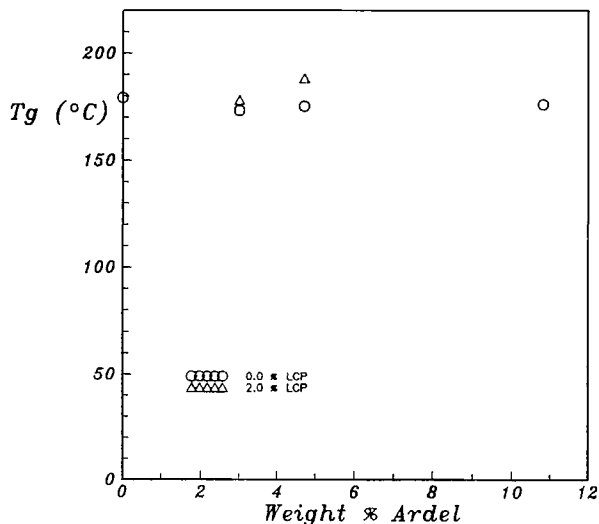
Figure 8 Glass transition temperature (T_g) vs. composition for cured system Epon 825-CA 1062-Ardel-PET/PHB60.

A further advantage derived from this blending procedure consists in the fact that the form of the fibers of LCP can be easily varied by adjusting the processing parameters (temperature, spinning rate, draw ratio) of the blends of Ardel and LCP.

REFERENCES

1. A. J. Kinlock and R. J. Young, *Fracture Behaviour of Polymers,* Applied Science, London, 1983, p. 421.
2. D. Maxwell, A. J. Kinlock, and R. J. Young, *J. Mater. Sci.,* **3,** 9 (1984).
3. C. B. Bucknall and T. Yoshii, *British Polym.,* **10,** 53 (1978).
4. S. C. Kunz, J. A. Sayre, and R. A. Assink, *Polymer,* **23,** 1987 (1982).
5. R. S. Bauer, *Proc. 18th Int. SAMPE Tech. Conf.* (1986) p. 510.
6. R. A. Pearson and A. F. Yee, *J. Mater. Sci.,* **21,** 2475 (1986).
7. J. Diamant and R. J. Moulton, *Proc. 29th Nat. SAMPE Symp.,* (1984) p. 422.
8. C. B. Bucknall and I. K. Partridge, *Polymer,* **24,** 639 (1983).
9. R. S. Bauer, *Toughened High Performance Epoxy Resins: Modification with Thermoplastics,* Fourth Annual Conference on Crosslinked Polymers, Luzern, Switzerland, 1990.
10. L. M. Robeson, *J. Appl. Polym. Sci.,* **30,** 4081 (1985).
11. J. D. Domine, *37th ANTEC of SPE,* New Orleans, 1979, p. 655.
12. D. Freitag and K. Reinking, *Kunststoffe,* **71**(1), 46 (1981).
13. H. Sakata, *32nd ANTEC of SPE,* San Francisco, 1974, p. 459.
14. W. J. Jackson, Jr. and H. F. Kuhfuss, *J. Polym. Sci.,* **14,** 2043 (1976).
15. T. G. Fox, *Bull. Amer. Phis. Soc.,* **1,** 123 (1956).
16. P. R. Couchman, *Macromolecules,* **11,** 1156 (1978).