

Hydrogen Bonding in Epoxy Resin/Poly (ϵ -caprolactone) Blends

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Synopsis

Poly(ϵ -caprolactone) (PCL) of ca. 20,000 molecular weight is shown to be partially miscible with three aromatic-amine-cured epoxy resins. This conclusion is based on the depression of the epoxy T_g , the effect on physical and mechanical properties, and the observation that a large proportion (40–55%) of the PCL ester groups are involved in hydrogen bonding. This miscibility behavior is compared to PCL blends with anhydride-cured epoxy resins, which appear to have a two-phase morphology. The different miscibilities are rationalized on the basis of the existence of functional groups (e. g., hydroxyl) in amine-cured epoxies which are capable of hydrogen bonding to the PCL ester groups. Anhydride-cured epoxy resins contain fewer potential hydrogen bonding sites.

INTRODUCTION

Epoxy resins are used widely as the matrix component of high performance composite materials because of their stiffness, chemical resistance, and high-temperature stability.^{1,2} The fracture properties (fracture energy and tensile strength) of crosslinked epoxy resins, however, are of some concern, and an extensive patent and scientific literature exists dealing with additives which modify these properties.^{3–6} For example, the fracture toughness of an amine-cured epoxy resin can be increased by a factor of 3 by the incorporation of a carboxyl-terminated rubber,³ while other additives are described^{5,6} which can increase the tensile strength of amine-cured epoxy resins by at least 50%. As part of a larger study of the effect of additives on the properties of crosslinked epoxy resins, we describe here a study of epoxy resin/poly(ϵ -caprolactone) (PCL) blends and, in particular, the role of hydrogen bonding in influencing the miscibility of PCL with crosslinked epoxies.

The majority of polymer–polymer blends are immiscible, i. e., the polymers do not mix on a molecular level.⁷ However, PCL has been shown to be miscible with a number of other polymers, particularly when an opportunity exists for hydrogen bonding or other polar interactions with the second polymer.^{7–11} The most extensive published study of epoxy resin/PCL blends is by Noshay and Robeson,¹² who examined the miscibility of a range of anhydride-cured epoxy resins with PCL of different molecular weights and with different end groups. They concluded that above a critical molecular weight of PCL, the blends had a two-phase structure and that the

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PCL end groups reacted with the anhydride curing agent to produce a type of block copolymer. The purpose of the present work is to examine PCL blends with amine-cured epoxy resins and to compare their properties with anhydride-cured systems, because of the opportunity which exists for hydrogen bonding in amine-cured epoxy resins (reaction of an amine with an epoxide produces hydroxyl groups while reaction of an anhydride with an epoxide largely produces ester groups).

EXPERIMENTAL

The epoxy resins used for this study were of commercial origin and are classified here according to their major constituents: (a) DGEBA (Epon 828, Shell), largely the diglycidylether of bisphenol-A; (b) DGEBF (XD7818, Dow), largely the diglycidyl ether of bisphenol-F; (c) PGEPF (DEN 431, Dow), a polyglycidyl ether of a phenol formaldehyde novalac. The resins were used as received other than being degassed at 100°C before use. The curing agents were diaminodiphenylmethane (DDM, Ciba-Geigy), "Nadic" methyl anhydride (NMA, Fisher, methylbicyclohept-5-ene-2,3-dicarboxylic acid anhydride) and *N,N'*-bis(2-aminoethyl)-1,2-diamoethane (known commercially as triethylenetetramine, TETA), and were used as received other than being degassed. Benzyltrimethylamine (BDMA, Ciba-Geigy) catalyst was also used in the NMA-cured system at 1 phr (parts by weight per hundred parts of resin). The PCL was of commercial origin (Aldrich Chemicals), with an intrinsic viscosity of $32.6 \text{ cm}^3 \cdot \text{g}^{-1}$ in tetrahydrofuran at 25°C corresponding to an average molecular weight of about 20,000.

Cured epoxy samples were prepared by mixing the degassed resin, curing agent, PCL, and accelerator (for NMA) and pouring into stainless steel molds. The formulations and curing conditions were as follows:

(a) DGEBA (100 parts), DDM (30 parts), PCL (0–50 parts), cured for 1 h at 100°C and 4 h at 175°C.

(b) DGEBF (100 parts), DDM (33 parts), PCL (0–50 parts) cured for 1 h at 100°C and 4 h at 150°C.

(c) DGEBA (100 parts), NMA (93 parts), BDMA (1 part), PCL (0–34 parts) cured for 3 h at 100°C and 3 h at 150°C.

(d) PGEPF (100 parts), DDM (30 parts), PCL (0–10 parts) cured for 1 h at 100°C and 4 h at 175°C.

(e) DGEBA (100 parts), TETA (10 parts), PCL (20 parts) cured for 1 h at 100°C.

Samples for tensile testing, mechanical spectroscopy, and fracture energy measurements were cut from the cured sheets using a high speed band saw and milling tool. Tensile testing was performed at 2 mm/min and 25°C according to ASTM D638 (Type II). Fracture energy measurements (G_{Ic} , critical strain energy release rate) were performed on rectangular compact tension specimens as described by Ting and Cottingham.¹³ Measurements of shear modulus, loss modulus, and loss tangent were made as a function of frequency and temperature using a Rheometrics mechanical spectrometer (RMS-605) in the forced torsion mode.⁶ A DuPont 990 Differential Scanning Calorimeter (DSC) was used to supplement the thermal transition data obtained by mechanical spectroscopy.

The extent to which the ester groups of PCL were hydrogen bonded to the crosslinked epoxy resin was determined by the infrared (IR) spectroscopic method described by Garton.¹⁴ This method involves obtaining IR spectra of thin films of the blends (cured between sodium chloride discs) at -150°C . The low temperature causes sharpening of the IR absorptions so that the carbonyl stretch absorptions of the hydrogen bonded and nonbonded ester groups can be resolved and quantified. The relative extinction coefficients (based on area) for the carbonyl stretch absorptions of the bonded and nonbonded ester groups were assumed to be identical to the ratio (1.23:1) previously measured for Phenoxy (a polyhydroxyether of bisphenol A)/PCL blends¹⁴ because of the chemical similarity between the Phenoxy and a cured epoxy resin. Methods for obtaining IR spectra and quantifying the extent of hydrogen bonding were identical to those described previously.¹⁴

RESULTS

Miscibility of Blends

Although the theoretical concept of miscibility (i. e., molecular mixing) is relatively clear, experimentally the problem remains of selecting criteria for defining miscibility.¹⁵ The most commonly used criteria are optical clarity, the observation of a single glass transition (T_g) intermediate between the T_g 's of the two blend components, and the observation of perturbations in the vibrational spectra of the component polymers.

All the PCL/epoxy blends described here were optically clear at ≤ 30 phr PCL, but this is obviously an insufficient criterion from which to infer miscibility. One may only conclude that if phase separation occurs it is on a scale of dimensions less than the wavelength of visible light.

Figure 1 shows the T_g 's as measured by mechanical spectroscopy (taken

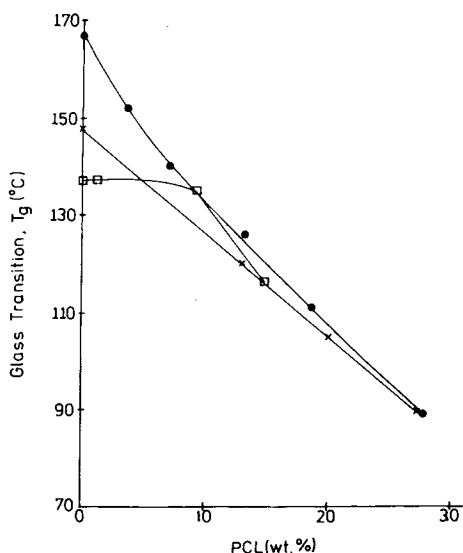


Fig. 1. T_g (by mechanical spectroscopy) of blends vs. PCL content: (●) DGEBA-DDM; (X) DGEBA-DDM; (□) DGEBA-NMA.

TABLE I
 Transition Data for Epoxy/PCL Blends

Sample	PCL (phr)	T_g (RMS) (°C)	T_g (DSC) (°C)	Sample	PCL (phr)	T_g (RMS) (°C)	T_g (DSC) (°C)
DGEBA- DDM	0	167	165	DGEBF- DDM	0	148	156
	2	—	155		20	120	113
	5	152	146		34	104	105
	10	140	136	50	89	90	
	20	126	—	DGEBA- NMA	0	139	137
	30	111	105		2	139	137
50	89	—	20		137	135	
PGEPF- DDM	0	166	164	34	116	100-120	
	10	145	130				

as the peak in the loss tangent vs. temperature curve at 10 rads/s) as a function of PCL content (wt %) for two amine-cured epoxies and one anhydride cured epoxy. The most noticeable feature is that the depression of the T_g by PCL is much more pronounced in the amine-cured systems than in the anhydride-cured system. Table I shows a comparison of T_g data obtained by mechanical spectroscopy and by DSC. While there is not precise quantitative agreement between the values, as would be expected because of the different effective frequencies of the two techniques, the DSC data support the conclusion from mechanical spectroscopy that PCL is at least partially miscible with amine-cured epoxies and is less miscible with the NMA-cured system. It should also be noted that, for the DGEBA-NMA system, the depression in T_g noted at 34 phr PCL (Table I) may result from other causes than miscibility with PCL. It has been reported that PCL end groups react with NMA,¹² and so, at high PCL concentrations, the epoxide-anhydride stoichiometry may be changed sufficiently to modify the curing (and hence T_g) of the epoxy resin. To confirm this hypothesis, additional samples were prepared with 30 phr PCL, but containing an increased amount of NMA (100 parts). On completion of the standard cure cycle the T_g (by DSC) was increased by about 5°C over samples containing 93 phr NMA.

As well as a depression of the epoxy T_g , a further criterion for miscibility is the presence or absence of a feature in the mechanical spectra or DSC data at $\sim -60^\circ\text{C}$ corresponding to the T_g of PCL. Unfortunately, because of overlap with the low temperature transitions of the epoxy resin (see later), frequently it is impossible to draw a reliable conclusion regarding the PCL T_g . However, for the DGEBA-NMA system, the PCL T_g could be distinguished by DSC at 20 and 34 phr PCL, as expected from the data of Noshay and Robeson,¹² confirming that discrete regions of "pure" PCL exist in the blend. For the amine-cured systems (DGEBA-DDM and DGEBF-DDM) the PCL T_g could only be distinguished at high PCL concentrations (> 30 phr). At lower PCL concentrations, no reliable conclusion could be drawn either from mechanical spectroscopy or DSC regarding the presence or absence of discrete regions of PCL.

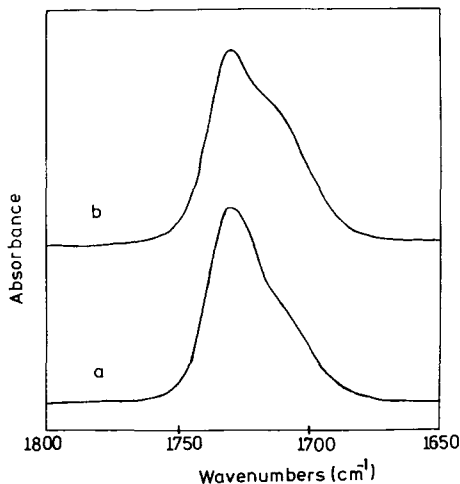


Fig. 2. IR Spectra of DGEBA-DDM/PCL blends at -150°C : (a) 30 phr PCL; (b) 5 phr PCL.

IR spectroscopy is particularly useful in describing miscibility because changes in the molecular environment of the polymer will generally result in perturbations in the IR spectra. The proportion of PCL ester groups which are hydrogen-bonded to the epoxy resin (PCL does not appreciably hydrogen bond to itself) is therefore a direct measure of how well the polymers are mixed on a molecular level. The chosen IR method obviously is inapplicable to the anhydride-cured system because the carbonyl stretch absorption of the ester groups produced by reaction of NMA with the epoxy resin obscures the carbonyl stretch absorption of PCL. However, as is shown in Figure 2, IR spectroscopy of amine-cured epoxy/PCL blends is more informative. With the aid of Fourier deconvolution and curve fitting procedures described previously,¹⁴ the complex carbonyl stretch absorptions of Figure 2 can be resolved into a non-hydrogen-bonded component at $\sim 1731\text{ cm}^{-1}$ and a hydrogen bonded component at $\sim 1714\text{ cm}^{-1}$. Qualitatively, it is clear from Figure 2 that fewer of the PCL ester groups are hydrogen-bonded at 30 phr PCL in DGEBA-DDM than at 5 phr PCL. The results of quantitative analysis of the spectra (after correction for the different ex-

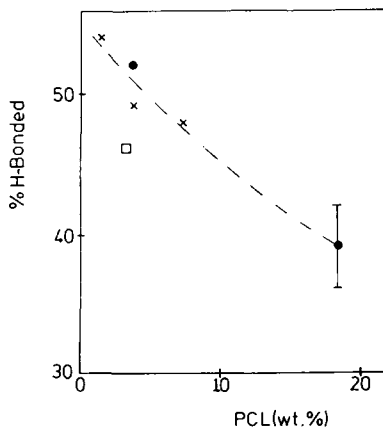


Fig. 3. Percentage of PCL ester groups which are involved in hydrogen bonding vs. PCL content: (X) DGEBA-DDM; (●) DGEBA-DDM; (□) PGEPA-DDM.

TABLE II
 Physical Properties of Epoxy/PCL Blends

Sample	PCL (phr)	Tensile modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation to break (mm)	Fracture energy (kJ · m ⁻²)
DGEBA- DDM	0	2.50 × 10 ³	—	76.9	4.5	0.40
	10	2.77 × 10 ³	—	83.5	4.5	0.34
	30	2.62 × 10 ³	—	53.8	2.2	0.38
DGEBF- DDM	0	3.05 × 10 ³	90.1	87.8	6.9	0.70
	20	2.93 × 10 ³	96.7	82.9	5.7	0.36
	34	2.75 × 10 ³	73.9	64.1	5.9	0.32
DGEBA- NMA	0	3.32 × 10 ³	—	73.8	2.3	0.20
	2	3.30 × 10 ³	—	83.3	2.8	0.12
	20	2.74 × 10 ³	71.5	66.9	5.0	0.88
	34	1.95 × 10 ³	43.8	42.2	6.0	0.91

tion coefficients of the bonded and non-bonded absorptions) are shown in Figure 3. At low PCL concentrations about 50% of the ester groups are hydrogen-bonded, a value similar to that found in Phenoxy/PCL blends, which are considered to be miscible.¹⁴ At higher PCL contents the proportion involved in hydrogen bonding diminishes, implying that some phase separation may have occurred.

In order to test the hypothesis that the PCL miscibility was influenced by thermal degradation at the high cure temperatures used, a DGEBA/DDM/20 phr PCL blend was cured for 1 h at 100°C between sodium chloride discs. Although these conditions are insufficient to fully cure the epoxy resin, the crosslinking reaction proceeded appreciably past the gel point (~20 min at 100°C). The subsequent IR spectrum was similar to those shown in Figure 2, showing extensive hydrogen bonding and so confirming that thermal degradation of the PCL (which is unlikely to occur in 1 h at 100°C) was not a factor in its miscibility with the epoxy resin.

Finally, some limited experiments were carried out using an aliphatic amine curing agent (TETA), which allows the use of lower curing temperatures. At temperatures ≤ 60°C, the PCL precipitated from a DGEBA/10 phr TETA/20 phr PCL mixture *before* it gelled. At ≥ 70°C (i.e., above the melting point of PCL) the mixture remained transparent through the gel point and the IR spectrum of the cured material at 25°C (after 1 h at 100°C) showed no sign of immediate PCL crystallisation (a relatively sharp carbonyl stretch absorption at 1724 cm⁻¹). However, the gel time of the DGEBA/TETA system is so short (≤ 2 min) at these temperatures that reliable, reproducible mixing of the reagents was impossible by conventional techniques and no conclusion was drawn concerning the miscibility of the system.

Physical Properties of Blends

Details of tensile modulus (calculated from the shear modulus at 25°C and 10 rads/s assuming Poisson's ratio = 0.30), yield strength, tensile

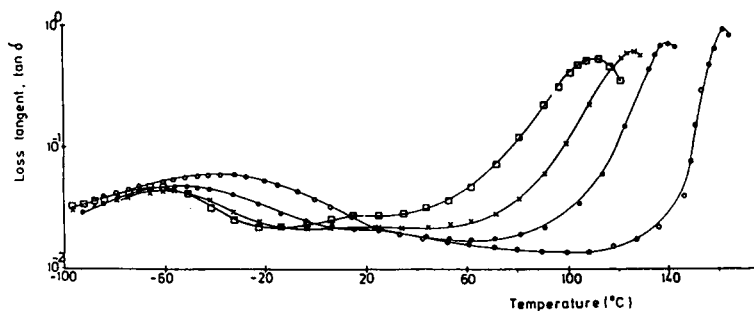


Fig. 4. Loss tangent (10 rads/s) vs. temperature for DGEBA-DDM/PCL blends: (O) DGEBA-DDM control; (●) 10 phr PCL; (X) 20 phr PCL; (□) 30 phr PCL.

strength, elongation to break, and fracture energy (G_{Ic}) for selected blend formulations are shown in Table II. It should be noted that fracture data (tensile strength, elongation to break, and fracture energy) are subject to considerably more scatter than dynamic data such as tensile or shear modulus, particularly when the mode of failure is brittle (i.e., no yield point occurs). To some degree, the uncertainty in the fracture data was compensated for by increasing the number of samples (e.g., 5 for G_{Ic}). Nevertheless, several trends are obvious on inspection of Table II. For the amine-cured systems (DGEBA-DDM and DGEBA-DDM) the addition of PCL decreased the elongation to break and fracture energy while producing only a small change in modulus. In contrast, for the anhydride-cured system (DGEBA-NMA), after initially behaving like the amine-cured systems at low PCL levels, the addition of PCL produced a marked decrease in modulus and increase in elongation and fracture energy.

The difference between anhydride-cured and amine-cured systems was also apparent by mechanical spectroscopy. Figure 4 shows that, as well as depressing the T_g , the addition of PCL to DGEBA-DDM suppresses the low temperature relaxations of the cured epoxy resin. Room temperature physical properties will therefore reflect the decrease in molecular mobility.

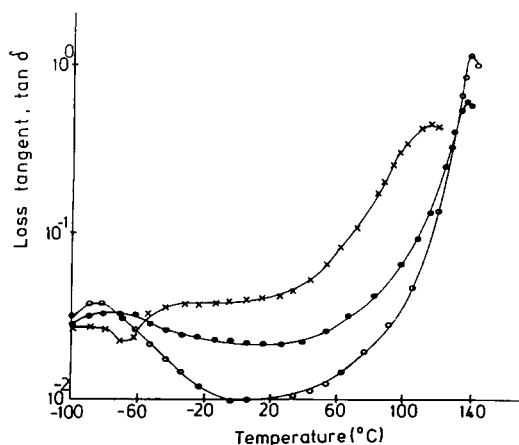


Fig. 5. Loss tangent (10 rads/s) vs. temperature for DGEBA-NMA/PCL blend: (O) DGEBA-NMA control; (●) 20 phr PCL; (X) 34 phr PCL.

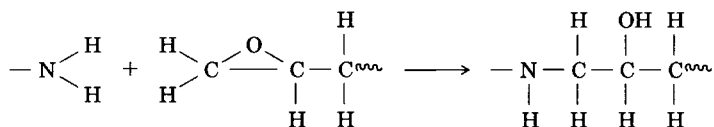
However, for the anhydride-cured system (DGEBA-NMA, Fig. 5) the ability of the sample to dissipate energy at room temperature and below was enhanced by the addition of PCL. The breadths of both the high and low temperature relaxations imply that a range of molecular environments exist within the sample, making it difficult to define the exact location of transitions.

DISCUSSION

The occurrence of even partial miscibility in a polymer blend where one component has an infinite molecular weight (i.e., is highly crosslinked) is surprising and requires comment. The conclusion that PCL is at least partially miscible with amine-cured epoxy resins is based on the depression of T_g (Fig. 1), on the observation that many PCL ester groups are involved in hydrogen bonding (Figs. 2 and 3) on the suppression of the epoxy resin low temperature relaxations (Fig. 4), and indirectly on the mechanical properties. The conclusion that PCL is not *completely* miscible with amine-cured epoxy resins is based on the observation of a PCL T_g at high PCL concentrations, and on the observation that the proportion of PCL ester groups involved in hydrogen bonding decreases as the PCL content increases (Figs. 2 and 3).

The data for the anhydride cured system (DGEBA-NMA) support the conclusion of Noshay and Robeson¹² that PCL of 20,000 average molecular weight is largely immiscible with anhydride-cured epoxy resins and that reaction occurs between the end groups of PCL and the anhydride, producing a type of block copolymer. The data supporting this conclusion include the observation of the PCL T_g by DSC, the small magnitude of the depression of the epoxy T_g (Fig. 1), the introduction of a low temperature relaxation mechanism (Fig. 5), and, indirectly, the effect on the mechanical properties. At low PCL concentrations (≤ 5 phr) the situation is less clear, since a slight increase in modulus and a decrease in fracture energy implies some degree of miscibility (see below).

The most obvious difference between amine-cured and anhydride-cured systems to explain their different miscibility with PCL is the presence of hydroxyl groups in the amine-cured system:



The reaction mechanism between an epoxy resin and an anhydride curing agent is complex,¹ but the major crosslinking product is an ester, with a low yield of hydroxyl groups. Hydrogen bonding between hydroxyl groups and ester groups in polymer blends is well documented, and such bonding is proposed as the driving force for miscibility in blends of PCL with Phenoxyl, which is chemically similar to an epoxy resin.^{8,14,16} The observation that not all the ester groups of PCL are involved in hydrogen bonding with the crosslinked epoxy resin (Fig. 3), even at low PCL concentrations, is a consequence of the mismatch of repeat unit lengths of the two polymers.

The distance between hydroxyl groups in the crosslinked epoxy is appreciably greater than the distance between ester groups in PCL. Geometric and steric factors will therefore limit the amount of hydrogen bonding even when molecular mixing occurs.¹⁴

It would be unwise to treat the partial miscibility described here in the conventional thermodynamic fashion^{7,10} (i.e., the calculation of interaction parameter and enthalpies of mixing) because of the chemical complexities of the system. The chemical and physical nature of the epoxy resin changes dramatically as the crosslinking progresses, and kinetic factors may also prevent separation of the PCL even after it becomes thermodynamically immiscible. Conceptually the system is better envisaged as a "semi-interpenetrating polymer network" (semi-IPN) according to the terminology of Sperling,¹⁷ but the chemical and physical intractability of crosslinked epoxies makes it difficult to treat the system in a quantitative fashion. Other complications arise from the fact that the PCL is undoubtedly not monodisperse in molecular weight and that the PCL end groups may become involved in the epoxy crosslinking process.

The complex interrelationship between blend morphology, molecular miscibility, and physical properties is illustrated in Table II. The small change in modulus and the decrease in elongation and fracture energy when PCL is added to amine-cured epoxies is characteristic of the decrease in free volume which occurs when two interacting polymers mix.¹⁸ The decrease in free volume inhibits the low temperature relaxations of the epoxy resin (Fig. 4), producing a stiffer, more brittle polymer than would have been predicted from simple additivity of properties. However, it should be noted that this "antiplasticisation" effect^{19,20} of PCL is very temperature-dependent because PCL also broadens and depresses the temperature of the α -transition (Fig. 4). At $\geq 50^\circ\text{C}$, therefore, molecular mobility is sufficiently enhanced by the onset of the broad α -relaxation that the PCL may be considered as behaving more in its conventional²¹ role as a "polymeric plasticizer." In the anhydride-cured system (DGEBA-NMA-PCL) the blend morphology is an additional parameter, and the increase in fracture energy can be largely attributed to the two-phase structure. From a technological viewpoint, a balance of physical properties must be considered (e.g., both a high T_g and a high fracture energy may be desired). The work reported here supports the general conclusion that, to achieve improvements in fracture properties of epoxy resins by the use of polymer blends without a large sacrifice in T_g , a two-phase morphology is preferable.

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References

1. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
2. *Epoxy Resins: Chemistry and Technology*, Y. Tanaka and C. A. May, Eds., Marcel Dekker, New York, 1973.
3. A. J. Kinloch, S. J. Shaw, D. A. Tod, and D. L. Hunston, *Polymer*, **24**, 1341 (1983).
4. R. J. Morgan and J. E. O'Neal, *Polym. Plast. Technol. Eng.*, **10**, 49 (1978).
5. P. D. McLean, R. F. Scott, and A. Garton, *Br. Polym. J.*, **15**, 66 (1983).
6. J. Daly, A. Britten, A. Garton, and P. D. McLean, *J. Appl. Polym. Sci.*, **29**, 1403 (1984).

7. S. Krause, in *Polymer Blends*, D. R. Paul and S. Newman Eds., Academic, New York, 1978, Vol. 1, Chap. 2.
8. L. Brode and Y. Koleske, *J. Macromol. Sci., Chem.*, **A6**, 1109 (1972).
9. R. S. Barnum, S. H. Goh, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **26**, 3917 (1981).
10. R. E. Prud'homme, *Polym. Eng. Sci.*, **22**, 90 (1982).
11. M. M. Coleman and J. Zarian, *J. Polym. Sci., Polym. Phys Ed.*, **17**, 837 (1979).
12. A. Noshay and L. M. Robeson, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 689 (1974).
13. R. Y. Ting and R. L. Cottingham, *J. Appl. Polym. Sci.*, **25**, 1815 (1980).
14. A. Garton, *Polym. Eng. Sci.*, **24**, 112 (1984).
15. A. Garton, *Polym. Eng. Sci.*, **22**, 124 (1982).
16. M. M. Coleman and E. J. Moskala, *Polymer*, **24**, 251 (1983).
17. L. H. Sperling, in *Recent Advances in Polymer Blends, Grafts and Blocks*, L. H. Sperling, Ed., Plenum, New York, 1974.
18. J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.*, **21**, 985 (1981).
19. N. Hata and J. Kumanotani, *J. Appl. Polym. Sci.*, **21**, 1257 (1977).
20. W. J. Jackson, Jr., and J. R. Caldwell, *J. Appl. Polym. Sci.*, **11**, 227 (1967).
21. C. F. Hammer, in *Polymer Blends*, D. R. Paul and S. Newman Eds., Academic, New York, 1978, Chap. 17.

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