CRANFIELD INSTITUTE OF TECHNOLOGY

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'Blends of Epoxy Resin with polycarbonate and CTBN Rubber'

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ABSTRACT

The study described in this thesis examines how the toughenability of a difunctional epoxy resin cured with a diamine hardener is affected by the presence of a dissolved polycarbonate in the epoxy matrix, when that matrix is modified by CTBN rubber particles.

The compatibility between the epoxy resin and four different polycarbonate types is investigated.

Influence of polycarbonate content and of the type of polycarbonate upon the mechanical properties and morphology of polycarbonate or rubber-polycarbonate modified epoxy systems is considered.

Toughenability of the epoxy matrix is found not to be improved by the presence of dissolved polycarbonate.

Study of chemical interactions between polycarbonate and epoxy resin and polycarbonate and hardener shows a degradation of the polycarbonate by the epoxy resin and also by the diamine hardener.

Failure of the polycarbonate to increase the toughenability of the epoxy matrix is considered to be related to this degradation.

Toughness properties of polyethersulfone modified epoxy systems are also considered.

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LIST OF FIGURES

NOTATION

a : Fracture specimen notch depth

B : Fracture specimen thickness

d : Average particle diameter

dy : Displacement from initial height to height at yield point

E_{100} : Isochronous modulus

E' : Storage modulus (DMTA)

ΔE_v : Energy of vaporisation

f : Calibration factor

G_{IC} : Critical strain energy release rate

ΔG_m : Isothermal free energy of mixing

ΔH_m : Enthalpy of mixing per unit volume

ΔH : Heat of reaction

$\Delta H_{100\%}$: Normalised heat of reaction

ho : Initial height of the compression test specimen

K_A, K_B : Specific rate constants

K_{IC} : Critical stress intensity factor

Mc : Molecular weight between cross-links

Mn : Number-average molecular weight

P_Q : Maximum load at crack initiation

P_y : Load at yield point

R : Molar gas constant

So : Initial loaded surface of the compression test specimen

ΔS_m : Entropy of mixing per unit volume

$\tan\delta$: Loss factor (DMTA)

T : Temperature

T_{min} : Temperature of the minimum of the exothermal peak (DSC)

T_g : Glass transition temperature

T_{gi} : Glass transition temperature of component i

ET_g : Glass transition temperature of the epoxy-rich phase

RT_g : Glass transition temperature of the rubber-rich phase

$T\beta$: β transition temperature

U_i : Indentation energy

U_Q : Elastic energy stored at crack initiation

V_A, V_B : Molar volume of component A and B respectively

V : Total volume of the blend

V_R : Reference volume of the constitutive unit

V_D : Volume fraction of the dispersed phase

W : Fracture specimen width

W_i : Weight fraction of component i

W_E^o : Initial epoxy resin weight fraction (including the hardener)

W_R^o : Initial rubber weight fraction

W_R^c : Weight fraction of rubber dissolved in the continuous phase

W_{PC}^o : Initial polycarbonate weight fraction

x : Conversion of epoxy groups

X_i : Degree of polymerisation of component i

P_E : Specific gravity of polycarbonate modified epoxy matrix or specific gravity of pure epoxy resin

P_R : Specific gravity of rubber

P_{PC} : Specific gravity of polycarbonate

ϕ : Energy calibration factor

ϕ_i : Volume fraction of component i

ϕ_E^c : Volume fraction of epoxy in the continuous phase

ϕ_E^D : Volume fraction of epoxy in the dispersed phase

ϕ_R^o : Initial rubber volume fraction

ϕ_R^c : Volume fraction of rubber dissolved in the continuous phase

ϕ_R^D : Volume fraction of rubber in the dispersed phase

σy : Yield stress

ν : Poisson's ratio

χ_{AB} : Flory's interaction parameter

δ_i : Solubility parameter of component i

wt : weight

phr : part per hundred parts of resin by weight

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INTRODUCTION

Maximum use of epoxy resins is being made in the aviation industry as adhesives and as matrix materials in fibre reinforced composites for structural applications.

The main advantage of long fibre reinforced epoxy composites is their high strength to weight ratio when compared to metals; which make them suitable for applications where weight saving is a very important factor. The main problem associated with epoxy based composite is the brittle nature and notch sensitivity of the matrix. The damage can be initiated from pre-existing defects in the epoxy matrix, which compromise the structural integrity of a composite material.

To improve the fracture toughness of the composite matrix, the epoxy matrix can be replaced by a high toughness thermoplastic such as poly(ether ether ketone). The corresponding composite exhibits high toughness characteristics but the difficulty in preparing quality prepregs had made the fabrication cost relatively high.

The other alternative is the toughening of existing epoxy resins. Rubber modification has been found to increase greatly the fracture resistance of epoxy systems [1]. The in-situ phase separation process which inevitably leaves some rubber dissolved in the matrix results in compromising the material stiffness, heat and chemical resistance. The efficiency of the rubber modification upon fracture toughness enhancement ultimately depends upon the inherent epoxy matrix ductility. Epoxy systems with an envisaged service temperature above 150°C are highly crosslinked with low ductility, which makes them limited in their toughenability by rubber modification.

The main aim of this work is to study the effect of homogeneously blending in an amorphous high toughness thermoplastic with a highly cross-linked difunctional epoxy resin, upon the toughenability of the resulting epoxy matrix when modified by rubber particles.

We expect an increase of ductility with the dissolution of the thermoplastic into the epoxy matrix and so an increase in toughness when this matrix is modified by rubber particles in comparison to the rubber modified epoxy system without dissolved thermoplastic.

The thermoplastic chosen is polycarbonate. Polycarbonates with or without reactive end group are available.

Unreactive polycarbonates are expected to increase the ductility of the epoxy resin in the same way as dissolved rubbers do.

Polycarbonates with reactive end groups, most of which were manufactured and provided by UMIST, are expected to react with epoxy resin and increase its ductility after cure, by chain extension of the reactive epoxy monomer.

A recent development has been the change from rubber particles to thermoplastic particles to toughen epoxy systems. Thermoplastic particles can significantly improve the fracture toughness of epoxy systems without an accompanying loss in material stiffness [2].

Yamanaka et al [3] showed higher adhesive strength for a polyethersulfone modified epoxy system than for the unmodified epoxy system. In this thesis, we will also follow up these preliminary studies and investigate the properties of polyethersulfone modified difunctional epoxy systems.

CHAPTER 1

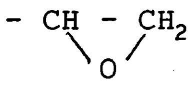
LITERATURE SURVEY

In this part chemistry of cure reaction of epoxy resin with amine hardener will be reviewed; polymer-polymer miscibility aspects will be dealt with, in relation to the phase separation of the rubber in epoxy resin. Then toughening of epoxy resin will be discussed. Most of the attention will be paid to the matrix toughenability for toughness enhancement in relation to the aim of this work : increasing the toughenability of a DGEBA epoxy matrix by dissolution of polycarbonate into it.

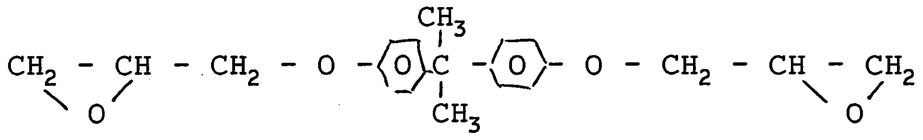
1.1 Chemistry of epoxy-resins

1.1.1. Chemistry of cure reactions

The basic unit, common to all epoxy resins, is the epoxide ring;



The most widely studied and commercially used group of epoxy resins are those based on the diglycidylether of bisphenol A (DGEBA):



A wide range of different epoxy resins is commercially available which differ in their functionality (from two to four) and molecular weight.

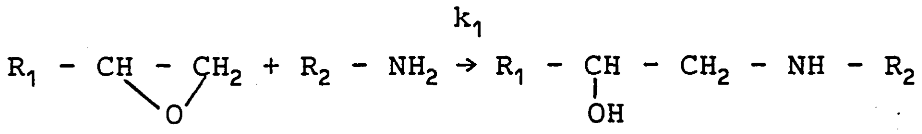
A wide range of hardeners (comonomers) can be used to cure epoxy resins (epoxy prepolymers). They can be classified in two different categories:

- the basic hardeners : e.g. Lewis bases, primary amines, secondary amines.
- the acid hardeners : e.g. Lewis acids, anhydride acids, phenols.

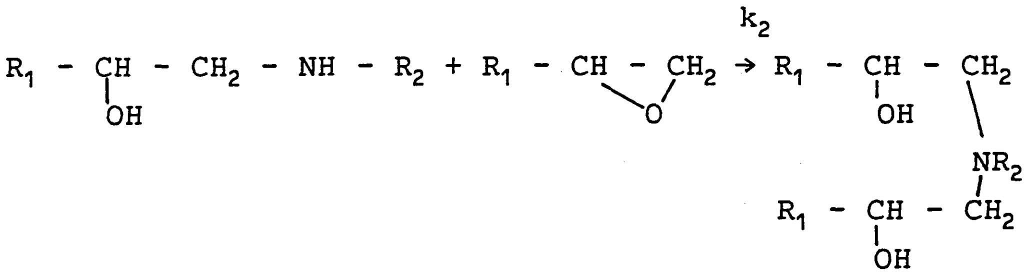
We are mainly interested in epoxy amine reactions as the amine hardeners are the most commonly used. The chemical reaction mechanisms between epoxy and amine groups can be summarised according to the following scheme [4-6].

Addition mechanism :

(1)

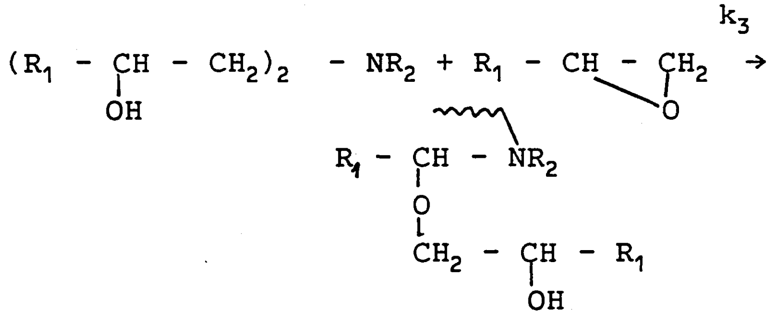


(2)



Etherification mechanism:

3.



Without any accelerator, in a stoichiometric mixture of epoxy resin and diamine hardener, reaction (3) is believed to be very rare because of the low reactivity of the tertiary amine caused by a sterical hindrance of this molecule [4]. The rarity of the etherification mechanism is now clearly admitted in DGEBA epoxy resin-aliphatic diamine systems [7, 8] but for epoxy aromatic-diamine blends, it may no longer be the case [8]. Riccardi and Williams [8] found that the etherification reaction in DGEBA-DDS (diaminodiphenylsulfone) system is significant at temperatures of cure above 150°C. It is however fair to point out that this reaction has not been found for other DGEBA epoxy resin-aromatic diamine systems [4,6].

Reactions (1) and (2) are autocatalysed by hydroxyl groups initially present in the DGEBA epoxy resin and also formed during the reaction [9].

When an accelerator is used, reactions such as oligomerisation involving the hydroxyl and epoxy groups through an ionic process may complicate the simple addition scheme [5].

There is a difference between primary and secondary amine reactivities with $k_2 < k_1$ [6, 7], and the ratio of reactivities depends upon the diamine used.

Riccardi et al [10] worked on a blend of DGEBA and EDA (ethylenediamine) and found that the reaction of polymerisation (step 1 and 2) takes place by two competitive paths. One is catalysed by the hydroxyls initially present in the DGEBA and those generated during the reaction (activation energy E_a = 14 kcal/mol). The other is a noncatalytic mechanism with a higher activation energy (E_a = 25.4 kcal/mol). The catalytic (k_1', k_2') mechanism does not operate at high temperatures whereas the non-catalytic mechanisms (k_1, k_2) takes place over all the temperature range.

1.1.2 Structural transformations during polymerisation

If the functionality of the epoxy hardener system is above 2 (for instance the functionality of the DGEBA is 2 and that of the diamine hardener is 4), a tridimensional system is formed as the polymerisation progresses. Two structural transformations occur during polymerisation : gelation and vitrification. Gelation marks the transition from a liquid to a rubbery state.

The gel point signals the formation of an infinite network, and for one epoxy system it always occurs at the same conversion ratio whatever the temperature of cure, provided that the reaction mechanism involved remains the same [7].

Dusek et al [7] have investigated the influence of the reactivity ratio between primary and secondary amines upon the conversion at gel point for difunctional epoxy resin cured with the stoichiometric ratio of diamine hardener. As k_2/k_1 varies from zero to infinity, the conversion level at gel point varies from 0.618 to 0.5.

Vitrification involves a transition from the liquid or rubbery state into the glassy state. The glass transition is due to the increase of the molecular weight of the epoxy resin if it occurs before gelation or the increase of the crosslink density if it occurs after.

The vitrification nearly stops the reaction because of the very low mobility of the reactive species in that state. The isothermal vitrification time is the time when the glass transition temperature is equal to the isothermal temperature of cure [11].

Galy et al [5] have determined that the T_g of several DGEBA-diamine cured blends is maximum when the hardener is used at the stoichiometric ratio, that corresponds to the maximum of cross-link density, or/and when aromatic rather than aliphatic diamine hardeners are used.

1.1.3 Kinetics of epoxy-amine reactions

Kinetics models are mainly used to determine specific rate constants of reaction and reactivities as well as activation energies.

Two kinds of kinetic models may be found in the literature. On one hand, pure phenomenological equations of the type

$$\frac{dx}{dt} = (K_A + K_B x^m)(1 - x)^p \qquad (1)$$

have been used to describe the autocatalytic cure of various epoxy resins [9, 12].

K_A and K_B are specific rate constants which are temperature dependent according to an Arrhenius relationship, m and p are adjustable parameters, and x and dx/dt are the conversion and rate of conversion of epoxy groups.

On the other hand, some authors like Riccardi and Williams [8] or Verchère [11] have developed more detailed kinetics models taking into account the etherification reaction and the reaction path. This knowledge is necessary for any study dealing with the analysis of the network structure [8].

The models were found to fit experimental results on DGEBA-3DCM (3.3'dimethyl4.4'diaminodicyclohexylmethane) for Verchère and DGEBA-DDS for Riccardi and Williams.

1.2 Polymer-polymer miscibility and phase separation

We are only interested in the case where the three components (epoxy resin, modifier and hardener) are initially miscible and the modifier phase separates as polymerisation progresses, as a result in the increase of molecular weight of the epoxy [13]. This can lead to a modifier-rich nodular structure dispersed in an epoxy-rich phase. This structure (dispersed particles in an epoxy matrix) can increase the fracture resistance of the epoxy matrix [1, 5, 14]. Addition of a liquid CTBN (carboxyl terminated butadiene - acrylonitrile random copolymer) rubber is a commonly used technique and has been found to greatly increase the fracture resistance of epoxy resins in many cases [15-22]. Thermoplastic modifications are part of a recent development in toughness improvements for epoxy resins.

Particle size or domain structure and the degree of phase mixing between the two phase boundaries are two primary factors for improving mechanical strength. In order to manipulate the morphology one must understand miscibility and phase separation in multi-component systems [23].

1.2.1 The Flory-Huggins theory

The liquid lattice, Flory-Huggins theory was initially developed in 1942 to describe polymer-solvent miscibility and has been extended to study polymer-polymer miscibility.

The isothermal free energy of mixing per unit of volume of polymer A and polymer B is given as follows:

$$\Delta G_m = \Delta H_m - T\Delta S_m = RT \frac{V}{V_R} \left(\frac{\phi_A}{X_A} \ln \phi_A + \frac{\phi_B}{X_B} \ln \phi_B + \chi_{AB}\, \phi_A\, \phi_B \right) \quad (2)$$

with $\Delta H_m = RT \frac{V}{V_R} \phi_A \phi_B \chi_{AB}$ (3)

is the enthalpy of mixing

and $\Delta S_m = \frac{RV}{V_R} \left(\frac{\phi_A}{X_A} \ln \phi_A + \frac{\phi_B}{X_B} \ln \phi_B \right)$ (4)

is the entropy of mixing per unit volume.

where

T : temperature of mixing

R : molar gas constant

V : total volume of the blend

V_R : reference volume of the constitutive unit

ϕ_i : volume fraction of component i

X_i : degree of polymerisation of component i

χ_{AB} : Flory's interaction parameter, $\chi_{AB} = V_R/RT\ (\delta_A - \delta_B)^2$

δ_i : solubility parameter of component i calculated for the constitutive unit of component i.

For two components to be miscible, ΔH_m should be either negative or as small as possible, i.e. the solubility parameters should be as close as possible.

Fedors [24] proposed a method to calculate δ_i at 25°C and at atmospheric pressure, which involves summation of constants representing chemical groups of the component i: In the case of a low molecular weight liquid, the solubility parameter is obtained by measuring the energy of vaporisation of the component (ΔE_V) and knowing its molar volume (V) at a given temperature and at a given pressure:

$$\delta = \left(\frac{\Delta E_V}{V}\right)^{\frac{1}{2}} \qquad (5)$$

For high molecular weight polymers, the volatility is much too low for ΔE_V to be obtained directly by experiment.

Fedors established a table of chemical group contributions to E_v and V which can be used to estimate δ for polymers at 25°C and at atmospheric pressure. For a given polymer, ΔE_V and V are obtained by summing the corresponding contributions of the chemical groups of the polymer structural formula. A correction to V is necessary for polymers the T_g of which is above 25°C, based on the number of main chain skeletal atoms.

This one dimensional solubility parameter approach is only valid when dispersive interactions (London, Van der Waals) are present. Specific polymer-polymer interactions such as polar and hydrogen bonding forces are important in the miscibility of binary polymer blends. In order to take them into account the solubility parameter has been considered in terms of separate components.

Hansen [25] suggested the use of a three-dimensional solubility parameter to allow for the unique characters of dispersive, polar and hydrogen bonding forces:

$$\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (6)$$

where δ_o is the total solubility parameter, δ_d, δ_p and δ_h the contributions due to dispersion, polar and hydrogen bonding forces. As a consequence of the separation of the solubility parameter into three solubility parameter components, for two polymers to be compatible, each of their three components must be as close to each other as possible.

If a polymer-polymer solution is miscible (equilibrium state), $\Delta G_m < 0$.
The theory is based on the following hypotheses:

i) the compressibility is negligible;
ii) the components are isomolecular;
iii) the constitutive unit concentrations are constant in all the blend;
iiii) the chains are ideal;
iiiii) there is no specific interaction, but only London - Van der Waals interactions, ΔH_m is constant.
iii) and iiii) are valid if the sizes of the chains are similar.

This model is quite difficult to apply in real cases as it is not easy to define the reference volume of the constitutive unit ($V_A \neq V_B$) and because RT χ_{AB} is supposed to be constant (hypothesis iiiii)).

The Flory-Huggins theory has therefore been modified through a simple phenomenological term. The free energy of mixing is expressed, per unit of volume as:

$$\Delta G_{m/cm^3} = RT \left(\frac{\phi_A}{V_A} \ln \phi_A + \frac{(1 - \phi_A)}{V_B} \ln (1 - \phi_A) \right) + \Lambda \phi_A (1 - \phi_A) \qquad (7)$$

where Λ is a parameter which depends on temperature, pressure, composition and can include some other entropic parts (due for example to intermolecular interactions). In the classical Flory-Huggins theory $\Lambda = \frac{RT}{V_R}$

V_A, V_B are the molar volumes of component A and B respectively.

This expression is generally used to describe polymer-polymer miscibility, with Λ only considered as temperature dependent [11, 21, 26, 27].

However, the theory has got some weaknesses. For instance, the polydispersity of polymers is not taken into account. A polymolecular system can be considered as a blend of components of same chain lengths, and can be thermodynamically treated in this way. In our knowledge only Pascault et al [27] attempted to take this effect into account in the description of the miscibility of CTBN rubber-difunctional epoxy blends. The case of specific interactions is not considered in the Flory-Huggins lattice theory. Nor is considered the possibility of demixing while the temperature is raised (LCST - Lower Critical Solution Temperature) but only the possibility of demixing upon cooling (UCST - Upper Critical Solution Temperature). The LCST behaviour is commonly observed in polymer-polymer solutions whereas it is relatively rare among binary blends of low molecular weight species [28].

Paul and Newman [28] and Olabisi et al [29] reviewed polymer-polymer miscibility aspects in two books which the reader is referred to for more detail.

1.2.2 Epoxy resin-modifier compatibility

In the case of CTBN rubber modified epoxy resins the compatibility of the rubber and epoxy can be controlled by the acrylonitrile content of the rubber modifier. The weight acrylonitrile content of commercial CTBN rubbers, supplied by BF Goodrich, varies between 10% and 25%. CTBN modifiers of higher acrylonitrile content are more compatible with epoxy resins because the interaction parameter is reduced as acrylonitrile content increases.

If we consider a copolymer A-B of two polymers A and B, the blend A-B/A or A-B/B is more compatible than the blend A/B, as a consequence of the reduction of the interaction parameter. This copolymer effect is used by some authors in CTBN-epoxy blends [11, 21, 26, 30-32]. These authors use a CTBN-epoxy adduct (ETBN epoxy terminated butadiene-acrylonitrile random copolymer), formed by pre-reacting a large amount of epoxy with the rubber, to increase the miscibility between the rubber and the epoxy.

At the same volume fraction the miscibility of a binary polymer blend is reduced as the molecular weight of one of its components is increased [21, 30, 33]. This is the result of the decrease of the entropy of mixing with increasing molecular weight of the components.

In all the cases, the more miscible the initial epoxy resin-modifier system, the later the phase separation in the epoxy resin-modifier-hardener blend occurs [13].

1.2.3 Phase separation in reactive epoxy systems

Phase separation studies in binary epoxy resin-modifier systems such as those referred to above, form the basis to understanding phase separation processes after the hardener is added, and the molecular weight of the resin increases as the polymerisation proceeds. The increase in the molecular weight of the epoxy-amine copolymer is at the origin of the phase separation process in rubber [33] or thermoplastic modified epoxies [3].

Each state of cure corresponds to a phase diagram involving the modifier and the epoxy-hardener copolymer (if the hardener alone is neglected or considered with the epoxy-hardener copolymer). This view indicates the difficulty of dealing with reacting systems as far as phase separation is concerned.

The main problem comes from the difficulty in applying thermodynamic theory which ignores time parameters to dynamic systems the nature of which changes very rapidly as a result of polymerisation.

Experimental studies of phase separation in reactive modified epoxy systems have shown that, the volume fraction, size distribution, nature, structure, chemical and physical properties of the dispersed phase all depend on a large number of parameters, such as [11]:

- nature and amount of modifier and epoxy resin [13, 34, 37]
- nature of hardener [32, 35, 36]
- temperature of reaction [3, 13, 21, 27, 32, 35, 36, 37].

1.3. Toughening of cured epoxy systems

1.3.1 Introduction

It has long been established that substantial toughness enhancement can be achieved by dispersing rubber particles, the useful diameter of which is below 20μm [35], within a polymer matrix [1].

The most well known procedure to accomplish this in a reactive system such as epoxy resin-hardener is to dissolve the rubber in the epoxy monomer in order to get a miscible mixture of epoxy resin-rubber-hardener from which the rubber will phase separate during the curing reaction. The addition of a low T_g modifier like a rubber ($T_g \approx -60°C$) leads to a loss in the modulus of the matrix and reduces its thermal properties. To get the best compromise between toughness enhancement and loss of other properties, the rubber concentration should be between 5% and 20% by weight; above 20 wt% phase inversion can occur resulting in a dramatic loss in stiffness due to the rubber being the continuous phase [1].

Bucknall and Yoshii [36] achieved an increase in G_{IC} from 0.72 kJ/m^2 to 5.3 kJ/m^2 by addition of 8.7 wt% CTBN rubber to an initial DGEBA epoxy system.

The use of a low molecular weight thermoplastic, as the dispersed phase in the epoxy matrix, for toughness enhancement of epoxy resins has been first introduced by Bucknall and Partridge in 1983 [34], where polyethersulfone was mainly used as a viscosity modifier.

The interest of using thermoplastics lies in their higher T_g, when compared to rubber. Also, thermoplastic modified epoxy systems show a higher stiffness than rubber 'equivalent' modified epoxy systems [38]. The thermoplastic is either dissolved in the epoxy matrix (the use of a solvent is sometimes required) and phase separates during the cure [34, 38-44] or it is directly introduced as particles in the liquid resin before cure [45]. This later procedure was not found to be successful because of the difficulties in obtaining optimum particle size (generally the particles obtained were too big) and sufficiently strong interface between particles and matrix [45].

Besides using rubber or thermoplastic as a toughening agent, several inorganic fillers such as ceramic whiskers can significantly increase the toughness of cured epoxy systems [45].

Fracture behaviour of epoxy systems is understood by the application of the linear elastic fracture mechanics, which is particularly suited to the study of crack propagation in brittle solids. Since the bulk of the material behaves in a linear elastic manner, LEFM may be applied.

The main plastic deformation ahead of the crack tip in neat epoxy systems is considered to be localised shear yielding. Toughening mechanisms in modified epoxy are more complicated due to the presence of a dispersed phase in the matrix.

Bucknall [1], Kinloch and Young [14], Yee and Pearson [46] presented toughening mechanisms of rubber modified epoxy systems, Garg and Mai [2] and Evans et al [47] recently reviewed the existing theories.

These mechanisms, based on studies of rubber modified difunctional (DGEBA) epoxy systems involve cavitation of the rubber particles and plastic deformation of the epoxy matrix by shear banding promoted by stress concentration around the particles or voids formed. Plastic deformation of the matrix by shear banding ahead of the crack tip absorbs most of the energy [15, 18, 20, 46, 48-50] and thus is the most important mechanism for toughening in rubber modified epoxy systems.

The reader is referred to these authors for details on rubber toughening mechanisms in modified epoxy systems.

There is at present a limited understanding of the mechanisms responsible for toughening in thermoplastic modified epoxy systems. It seems that drawing of the thermoplastic [51, 52] and crack front pinning [43] rather than plastic deformation of the epoxy matrix by shear banding might be the principal toughening mechanisms in these systems. It must however, be pointed out that most of the studies on thermoplastic modified epoxy systems have been carried out with highly crosslinked tri- or tetrafunctional epoxy resins [34, 40, 42, 43, 51-53], and that shear band formation is highly restricted in these systems because of their poor ductility.

The following section points out the importance of the epoxy matrix toughenability for toughness enhancement. This aspect will be also related to the purpose of this work : to study the effect of homogeneously blending in a thermoplastic with a DGEBA epoxy matrix, upon the toughenability of this matrix when modified by rubber particles. Influence on morphological and chemical parameters upon toughness improvement in rubber modified DGEBA epoxy systems will be also discussed.

1.3.2 Epoxy matrix toughenability.

Above all the considerations of the toughening mechanisms in modified epoxy systems, the toughenability of the epoxy matrix is a very important factor for toughness improvement:-

- Manzione et al in 1981 [19], have introduced the importance of the matrix ductility in the toughness improvement of rubber modified epoxies. The ductility of the DGEBA epoxy matrix was controlled by the amount of rubber dissolved in the matrix by varying the type of rubber chosen and the curing conditions. They showed best toughness properties for large amount of dissolved rubber and low volume fraction of phase separated rubber.

- Kirschenbaum et al [54] showed that impact strengths of rubber modified DGEBA epoxy systems modified by the same amount of different rubbers were greater at a lower cross-link density. The cross-link density was changed by varying the initial amount of hardener to the epoxy resin-rubber blends. No details about the morphologies observed in their different blends were given.

- Yee and Pearson [15, 16, 46, 49] have more precisely defined the role of the ductility of the epoxy matrix upon toughness enhancement: they found that large decrease in the cross-link density of a DGEBA epoxy system modified by the same amount of CTBN rubber largely increased the fracture toughness of the system, in contrast with the corresponding unmodified epoxy systems which showed only a modest increase [46]. Rubber toughening mechanisms become more effective when cross-link density decreases because at the same time, the capacity of the resin to deform in shear increases, the ductility of the matrix is increased [15, 16, 46, 49]. Yee and Pearson demonstrated this statement by examination of optical micrographs taken from sections perpendicular to the fracture surface of three point bend specimens [46]. These pictures showed that shear band density in the fractured epoxy systems modified by the same amount of CTBN increased when cross-link density of the epoxy matrix decreased. Changes in the morphology of the different systems tested by Yee and Pearson were not related to their results on toughness and matrix ductility.

Increasing the temperature of the fracture test or decreasing the rate of the fracture test are other ways of increasing the ductility of the epoxy matrix. In this case, the matrix ductility is changed without any change in the morphology of the rubber modified epoxy system, thus the effect of matrix ductility upon toughness enhancement can be examined on its own. Kinloch et al [20] and Kinloch and Hunston [55] showed that fracture toughness of rubber modified DGEBA epoxy systems increased with increasing temperature or decreasing rate of test and that this increase in fracture toughness was far more dependent upon the test rate and temperature than for the unmodified epoxy system.

The aim of this work is to increase the toughenability of a DGEBA epoxy matrix by two anticipated mechanisms :

- by homogeneously blending in an unreactive polycarbonate with the epoxy matrix which would act in the same way as dissolved rubber to increase the ductility of the epoxy matrix.

- by reacting a polycarbonate, with reactive OH end groups on both ends of its chain, with epoxy resin. The reactive polycarbonate would act as a chain extender and would increase the epoxy monomer molecular weight, and so the ductility of the epoxy matrix.

In our knowledge, chain extension of the DGEBA epoxy monomer has only been achieved by pre-reacting some bisphenol A with the epoxy or epoxy rubber blends before the hardener was added [19, 36, 44, 46, 49, 50].

The fracture toughness of the rubber bisphenol A modified DGEBA epoxy systems is greater than that of the corresponding rubber modified epoxy systems without bisphenol A, [36, 44, 46, 49, 50].

Yee and Pearson [46, 50] always obtained a higher fracture toughness for CTBN rubber modified DGEBA epoxy systems with 24 parts by weight of bisphenol A per hundred parts (phr) of DGEBA epoxy resin than for the corresponding epoxy systems modified by the same amount of CTBN rubber without bisphenol A. (see Figure 1.1). They believe that this is due to the higher ductility of the bisphenol A - DGEBA epoxy matrix when compared to the neat DGEBA epoxy matrix, rather than the possible difference in morphology of the rubber-bisphenol A modified DGEBA epoxy systems when compared to rubber modified DGEBA epoxy systems [46].

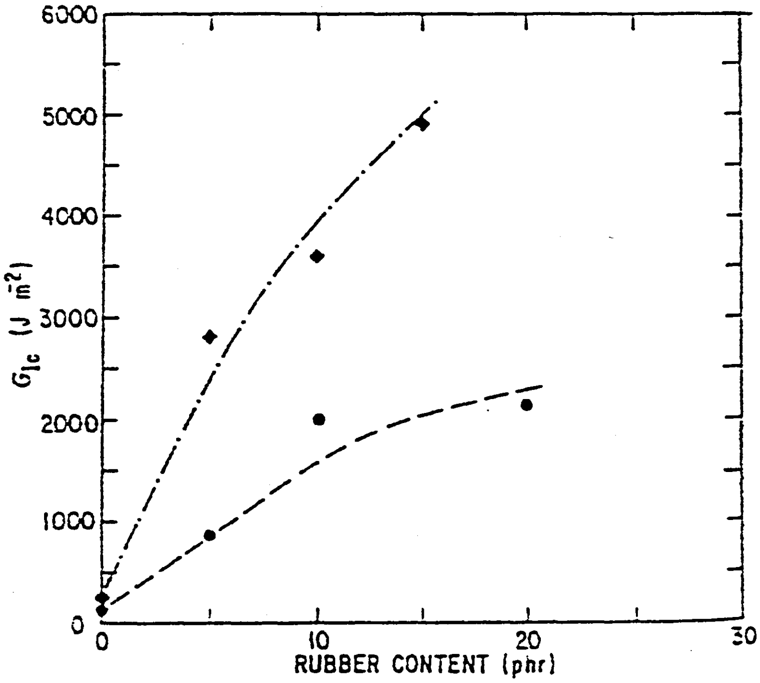


Figure 1.1: From [50]. Effect of the addition of 24 phr of bisphenol A to a CTBN rubber modified DGEBA epoxy system upon toughness enhancement.
●: rubber modified epoxy system.
◆: rubber modified epoxy system with 24 phr of bisphenol A.

Bucknall and Yoshii [36] believe that the higher toughness observed in their rubber-bisphenol A modified DGEBA epoxy systems was due to the higher volume fraction of the dispersed rubber phase in this case, in comparison to the volume fraction of the corresponding rubber modified system without bisphenol A. (see Section 1.3.3.1 for the relation between fracture toughness and volume fraction of the dispersed phase in rubber modified epoxy systems).

These differences point out one very important problem: it is very difficult to isolate and examine the effect of one parameter, such as the ductility of the epoxy matrix, upon the toughness of modified epoxy without changing other parameters in the corresponding modified epoxy systems, such as volume fraction of the dispersed phase.

Nevertheless, the above studies of the effect of the matrix ductility upon toughness enhancement in rubber modified epoxy systems tend to prove that it is the major important parameter for toughness improvement and that an epoxy matrix of low ductility limits the level of toughening that can be achieved even under the most favourable conditions [56]. For instance, the small level of toughness enhancement achieved in polyethersulfone modified tri- and tetrafunctional epoxy systems by Partridge and Gurnell [53] was independent of the different morphologies observed in these blends. This result was due to the poor ductility of their epoxy matrices.

1.3.3 Influence of morphological and chemical parameters on toughness of modified epoxy systems

1.3.3.1 Morphological parameters

a) Amount of modifier.

Typical influence of CTBN rubber content upon the Young's modulus and the critical strain energy release rate (G_{IC}) in rubber modified DGEBA epoxy system is shown in Figures 1.2 and 1.3. G_{IC} is maximum for about 15 wt% rubber.

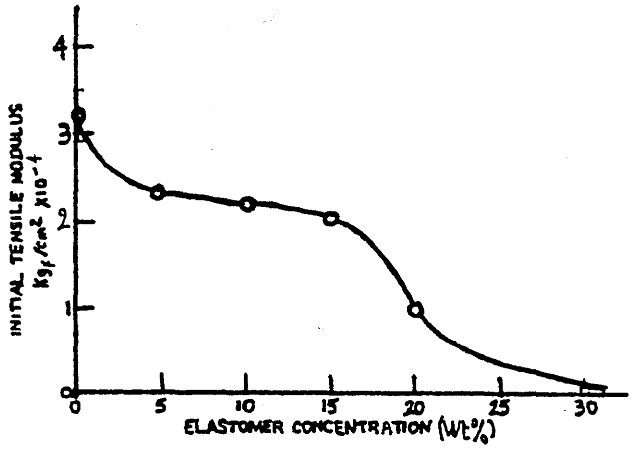


Figure 1.2: From [22]. Evolution of the Young's modulus with rubber content in CTBN rubber modified DGEBA epoxy system.

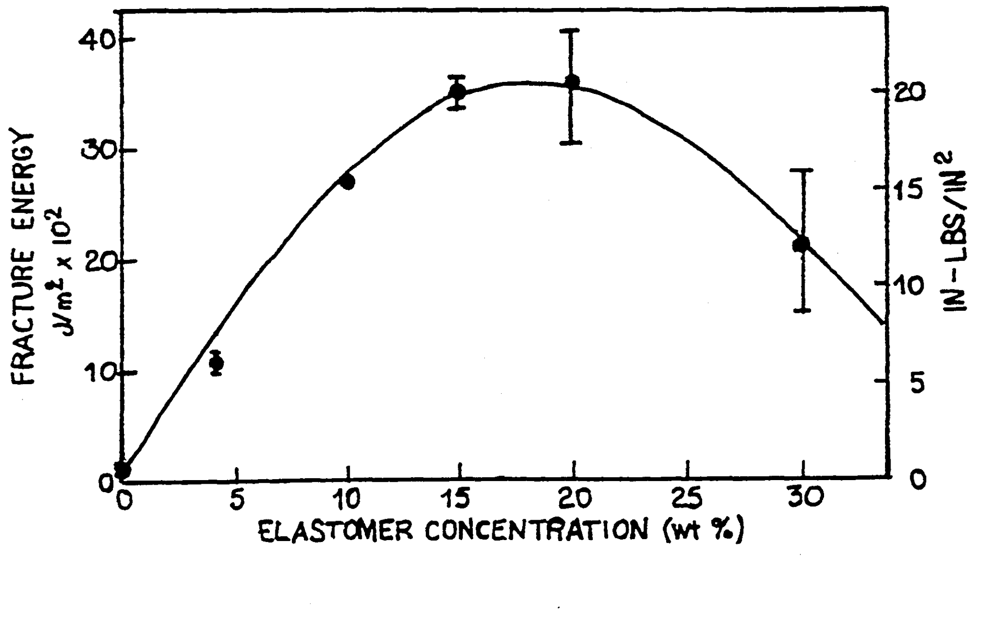


Figure 1.3: From [22]. Evolution of G_{IC} with rubber content in CTBN rubber modified DGEBA epoxy system.

Partridge and Gurnell [53] have shown an slight increase in G_{IC} with polyethersulfone content in polyethersulfone modified tri- and tetrafunctional epoxy systems. A similar evolution of G_{IC} with the amount of modifier was found by Gilbert [51] in polyetherimide modified tetrafunctional epoxy system.

b) Volume fraction of the dispersed phase

More than the modifier content, the volume fraction of the dispersed phase seems to be the crucial factor for toughness enhancement. Bucknall and Yoshii [36], Douglas et al [57], Kinloch et al [55], Verchère et al [58] have found that G_{IC} increases linearly with increasing volume fraction of the rubber dispersed phase. Kinloch [55] points out that this relation is not unique but that the rate of increase of G_{IC} with the volume fraction of the dispersed phase depends greatly upon the ductility of the matrix.

Volume fraction of the dispersed phase can be effectively increased by the presence of epoxy subinclusions within the rubber particles in rubber modified DGEBA epoxy systems [31, 36].

c) Particle size and distribution

The effect of particle size upon toughness enhancement in rubber modified DGEBA epoxy systems is subject to some controversy.

On one hand, Sultan and McGarry [35] found, by SEM investigations of fracture surface of rubber modified DGEBA epoxy systems, that small rubber particles (diameter below 0.1μm) promote shear band formation in the epoxy matrix whereas bigger particles (diameter between 1μm and 2μm) enhance microcavitation in the epoxy matrix around the particles. Two CTBN rubbers of different acrylonitrile contents were used which produced big or small particles in the epoxy matrix. No indication about volume fraction of the dispersed phase or the amount of dissolved in the epoxy matrix on which the ductility of the matrix depends were given.

On the other hand Bascom et al [18] believe that big rubber particles (2µm - 4µm) induce localised shear yielding in the epoxy matrix. But once again, there was no other indication about the morphologies or phase composition which makes the results inconclusive.

It is very difficult to examine the role of the particle size alone upon toughness enhancement as particle size and volume fraction vary simultaneously.

It seems, however, that particle size distribution [18, 55] is of more crucial importance upon toughness enhancement than particle size in itself [50, 58], even though inconclusive results could be found on this point, due to the simultaneous variation of parameters dealt with above.

1.3.3.2 Chemical parameters

Toughness of rubber modified DGEBA epoxy systems has been found to be affected by the acrylonitrile content of the CTBN rubber. This is shown to be the highest with acrylonitrile content between 12 wt% and 18 wt% [36]. This result is related to the initial miscibility of CTBN rubber with epoxy resin which increases with acrylonitrile content (see Section 1.2.3). The initial degree of miscibility between these two components affects the resulting morphology obtained in the cured system and so the toughness of these systems. Generally, as the initial degree of miscibility between epoxy resin and CTBN rubber increases, the volume fraction of the dispersed phase in the cured system decreases [13] and so the toughness of the system also decreases.

The importance of a strong interface between particle and matrix for toughness enhancement has also been discussed [31, 38, 54, 59]. The stress concentration around a particle on which depends the toughening mechanisms in rubber modified epoxy system (see Section 1.3.1) is improved with a good interfacial adhesion [59].

The interfacial bonding in CTBN modified epoxies can be improved by pre-reacting the CTBN with epoxy resin to form a new adduct usually called ETBN (epoxy terminated rubber). This procedure has been successfully used by Manzione et al [13, 19], Verchère et al [58], Yamanaka et al [32] and is of particular relevance to the work presented here.

The most commonly used rubbers are carboxyl terminated rubbers (CTBN); some authors have also used amine terminated rubbers (ATBN) which show greater interfacial bonding than CTBN. The use of ATBN rubbers results in a higher toughness [31] and sometimes not [60].

CHAPTER 2
MATERIALS AND METHODS

2.1 Materials

Structural formulae of the following materials are found in Appendix A.

2.1.1 Epoxy resins

Araldite MY750. Product of Ciba-Geigy Ltd

This diglycidylether of bisphenol A (DGEBA) epoxy resin is widely used in rubber toughened formulations. It contains two epoxy rings per monomer unit, and its average molecular weight, Mn, is about 380 g/mol (polymolecularity n = 0.15). Its relatively low viscosity at ambient temperature makes it easy to manipulate.
Specific gravity : 1.17 g/cm^3 at 25°C.

DER332. Product of DOW Chemical Ltd

Another DGEBA epoxy resin, but of lower molecular weight than MY750 (Mn = 348 g/mol, polymolecularity n = 0.03) which also contains two epoxy rings per monomer unit. It crystallises at ambient temperature and so needs to be melted, at around 60°C, before use.
Specific gravity : 1.16 g/cm^3 at 25°C.

ERL0510. Product of Ciba-Geigy Ltd

This triglycidylparaaminophenol (TGPAP) epoxy resin contains three epoxy rings per monomer unit. At ambient temperature, it is a low viscosity liquid epoxy resin of molecular weight about 300 g/mol.

In this project, we mainly used the MY750 epoxy resin.

2.1.2 Curing agents

HT972. Product of Ciba-Geigy Ltd

A solid aromatic diamine available as light yellow coloured crystals, this hardener is otherwise known as 4.4' diaminodiphenylmethane, DDM. Its molecular weight is around 198 g/mol and its melting point is about 90°C.

The stoichiometric ratio of DDM is 26 phr (parts by weight per hundred parts of resin) and 28 phr when used with MY750 and DER332 respectively.

HT976. Product of Ciba-Geigy Ltd

This is another solid aromatic diamine hardener, available as a tan coloured powder and otherwise known as 4.4' diaminodiphenylsulfone DDS. Its molecular weight and melting point are about 236 g/mol and 175°C respectively.

HY917 (and DY070). Products of Ciba-Geigy Ltd

HY917 is a low viscosity liquid anhydride hardener also known as methyltetrahydrophthalic anhydride. To cure epoxy resins this hardener is normally used with an accelerator such as the accelerator DY070 (2 ethyl 4 methylimidazole : EMI).

DDM was the most commonly used hardener in this work.

2.1.3 Modifiers

2.1.3.1 Thermoplastics

Polycarbonate grade L141. Product from General Electric

This commercial amorphous engineering polycarbonate of high molecular weight (Mn approximately 28.7 kg/mol) combines excellent toughness properties and high Young's modulus. It is used for great many industrial applications such as in the fabrication of compact discs. It is available as transparent granules of around 3 mm diameter.

Throughout this work this polycarbonate has been named PC.H. H stands for high molecular weight. PC.H is not thought to have any reactive end groups.
Specific gravity : 1.20 g/cm^3.

Polycarbonate Jupilon FR40. Product of Mitsubishi Gas Chemical Comp. Inc

It is a difunctional polybrominated carbonate terminated with phenolic OH groups, available as a white powder. Its molecular weight is around 2.8 kg/mol. In this project, this polycarbonate has been renamed fP(BrC).O. O stands for oligomer.

Polycarbonate prepared at the Manchester Materials Science Centre of the University of Manchester & UMIST

A selection of three difunctional polycarbonates terminated with phenolic OH groups, of different molecular weights was available as white powders. They were PC_8 (Mn = 7.1 kg/mol), PC_6 (Mn = 9.2 kg/mol) and PC_7 (Mn = 26 kg/mol), which have been renamed fPC.L, fPC.M and fPC.H respectively. L, M and H stands for low, medium and high molecular weight.

Polyethersulfones Victrex 4100P and 5003P. Products of ICI

They are two amorphous high temperature engineering thermoplastics available as white powder of mixed particle size.

Polyethersulfone 5003P is the thermoplastic additive used as a viscosity modifier in tetrafunctional TGDDM based resin. It confers excellent processing characteristics on these systems. OH groups terminate about 80% of one of the chain ends of the polyethersulfone 5003P, the other end being of unreactive groups [39]. Its molecular weight, Mn, is approximately 24.0 kg/mol.

4100P grade is an unfunctionalised polyethersulfone of molecular weight around 17.7 kg/mol. Polyethersulfones 4100P and 5003P have been renamed PES and fPES respectively.

It is important to note that considerations about low or high molecular weight were made in a relative sense in order to compare the molecular weight of our thermoplastics between each other. The highest molecular weight thermoplastic, PC.H is still a thermoplastic of low molecular weight (Mn = 28.7 kg/mol) in terms of conventional processing.

2.1.3.2 Rubber

HYCAR CTBN 1300 x 8. Product of BF Goodrich

This carboxyl terminated butadiene-acrylonitrile random copolymer is one of the rubbers most widely used to toughen epoxy systems.

It contains 18 wt% acrylonitrile, its functionality is 1.8 and its molecular weight, Mn, is 3.6 kg/mol. It has been used prereacted with epoxy resin (see Section 2.2.2.5). Specific gravity : 0.948 g/cm^3.

Table 2.1 summarises the names and characteristics of the modifiers presented above.

2.2 Preparation of the blends and casting procedures

2.2.1 Epoxy resin polycarbonate solutions

They were prepared according to two procedures:

Procedure A:

Polycarbonate was first dissolved in dichloromethane (CH_2Cl_2) at concentration of 15 wt%. This solution was added to hot epoxy resin at 80°C in about 10 mins, with continuous stirring with a glass rod. The blend was then degassed in a vacuum oven at 100°C - 110°C for about 1 hour.

Procedure B:

Polycarbonate was first dissolved in dichloromethane at concentration of 15 wt%. This solution was added very slowly to hot resin at 120°C, with continuous stirring with a glass rod, as at this stage the solvent was violently flashed off from the blend. It took around 10 mins, 30 mins and 1 hour to add 10 phr of fPC.M, 10 phr of PC.H and 20 phr of PC.H to hot epoxy resin at 120°C respectively. The blend was then degassed in a vacuum oven at 100°C - 110°C for about 1 hour.

Material original name	Type	Reactive end groups	Mn (kg/mol)	Specific gravity (g/cm^3)	Material name in this report
PCL141	polycarbonate	no	28.7[a]	1.20	PC.H
PCFR40	polycarbonate	yes	2.8	-	fP(BrC).O
PC_8	polycarbonate	yes	7.1	-	fPC.L.
PC_6	polycarbonate	yes	9.2	-	fPC.M.
PC_7	polycarbonate	yes	26.0	-	fPC.H
PES4100P	polyethersulfone	no	17.7	-	PES
PES5003P	polyethersulfone	yes	24.0	-	fPES
CTBN1300 x 8	rubber	yes	3.6	0.948	CTBN

Table 2.1 : Name and principal characteristics of the modifiers used in the present work. Data specified by manufacturers.

[a]: Mn - calculated by GPC at Kobe Steel Ltd Laboratory in Guildford.

Adding the polycarbonate-solvent mixture to hot resin at 120°C instead 80°C flashes a bigger amount of solvent off from the blend which makes the subsequent degassing of the blends easier to perform.

2.2.2 Casting of epoxy resin and polycarbonate plaques

2.2.2.1 The mould

The resin plaques were cast between two parallel glass plates with a steel frame used as a spacer. All the parts of the mould (glass plates and steel frame) were coated with Frekote 44 release agent.

The demoulded plaques had dimensions 24 cm x 12 cm x 0.6 cm. Except for the polycarbonate modified epoxy plaque cured with the anhydride hardener without accelerator, the dimensions of which were 24 cm x 3 cm x 0.6 cm.

2.2.2.2 Neat and polycarbonate modified epoxy resin cured with DDM hardener

The stoichiometric ratio of DDM (26 phr) was melted at 105°C and mixed with the hot MY750 epoxy resin or hot MY750 epoxy resin-polycarbonate solutions, prepared following procedure A or B as specified, at 80°C with a glass rod until the blends were homogeneous. The mixtures were then poured into the preheated mould at 60°C.

Degassing was carried out under vacuum at 60°C for 1 hour, followed by curing for 6 hours at 80°C with post-curing for 2 hours at 150°C. The oven was switched off and the plaques were allowed to cool down gradually to room temperature before demoulding.

2.2.2.3 Polycarbonate modified epoxy resin cured with DDS hardener

MY750 epoxy resin-PC.H polycarbonate solutions were prepared following procedure B. The stoichiometric ratio of DDS (30 phr) was dissolved in these solutions at 120°C for about 30 mins while continuously stirring with a glass rod. The mixtures were then poured into the preheated mould at 93°C.

Degassing was carried out under vacuum at 93°C for 2 hours followed by curing for 5 hours at 93°C, 16 hours at 121°C, 2 hours at 149°C, 2 hours at 177°C and postcuring for 4 hours at 200°C. The plaques were allowed to cool down gradually to room temperature before demoulding.

2.2.2.4 Polycarbonate modified epoxy resin cured with anhydride hardener

With accelerator DY070

MY750 epoxy resin-PC.H polycarbonate solution was prepared following procedure B.

85 phr of hardener HY917 and 1 phr of accelerator DY070 was added to the epoxy resin-polycarbonate solution at 60°C while continuously stirring with a glass rod. The mixture was then poured into the preheated mould.

Degassing was carried out under vacuum at 60°C for 2 hours followed by curing for 3 hours at 80°C and postcuring for 4 hours at 150°C. The plaque was allowed to cool down gradually to room temperature before demoulding.

Amount of hardener, accelerator and the curing procedure used were taken from Ciba-Geigy technical data sheets about the MY750-HY917-DY070 system.

Without accelerator

MY750 epoxy resin-PC.H polycarbonate solution was prepared following procedure B.

85 phr of hardener was added to the epoxy resin-polycarbonate solution at 60°C.

The solution was degassed under vacuum for 2 hours at 60°C. The mixture was then poured into the preheated mould at 100°C and cured for 6 hours at 100°C followed by 6 hours at 150°C and 6 hours at 200°C. The plaque was allowed to cool down gradually to room temperature before demoulding.

There were many bubbles within the plaque and it was fractured in many places too. This is believed to be due to the absence of accelerator and the final high temperature of cure used in this case.

2.2.2.5 Rubber and rubber-polycarbonate modified epoxy resin cured with DDM hardener

i) Preparation of the rubber adduct : CTBN rubber was prereacted with epoxy resin in order to get epoxy capped CTBN rubber, also called ETBN (epoxy terminated butadiene-acrylonitrile random copolymer).

Epoxy resin and CTBN rubber were degassed separately for 3 hours at 60°C.

They were mixed together at 50°C in appropriate proportions in order to get a carboxyl groups to epoxy rings ratio equal to 0.065.

The epoxy resin-CTBN mixture was degassed 1 hour at 50°C. The catalyst triphenylphosphine was then added at 0.18 wt%.

The epoxy-CTBN reaction was carried out under a nitrogen stream with continuous stirring and was believed to be completed after 4 hours at 85°C [27, 30]. Typically 300 ml of adduct were prepared at a time. The adduct was kept in the fridge at -18°C.

ii. Casting of the rubber and rubber-polycarbonate modified epoxy resin cured with DDM hardener.

<u>Procedure C</u> :

The rubber adduct was added to hot epoxy, or hot epoxy resin polycarbonate solutions prepared following procedure B, at 60°C. The mixtures were degassed for about 2 hours at 60°C. Melted DDM at 105°C was then added at the stoichiometric ratio (26 phr when used with MY750, 28 phr with DER332) to the epoxy resin-ETBN or epoxy resin-polycarbonate - ETBN blends at 80°C (the total number of unreacted epoxy rings was calculated in the epoxy resin - ETBN or epoxy resin polycarbonate - ETBN blends, taking into account the number of unreacted epoxy rings present in the rubber adduct). The blends were mixed thoroughly with an electric mixer until homogeneous. They were then poured into the preheated mould at 60°C.

Degassing was carried out under vacuum for 1 hour at 60°C followed by curing for 6 hours at 80°C and postcuring for 3 hours at 150°C. The plaques were then allowed to cool down gradually to room temperature before demoulding.

Procedure D:

This procedure has only been used with the polycarbonate fP(BrC).O to prepare a rubber-polycarbonate modified epoxy system at 15 wt% rubber and 5 wt% polycarbonate. The only difference to the previous procedure lay in the preparation of the epoxy resin-polycarbonate solution : instead of dissolving the polycarbonate in dichloromethane and adding this solution to hot epoxy resin at 120°C, the polycarbonate was directly dissolved in the hot epoxy resin at 80°C in about 1 hour.

2.2.2.6 Compression moulded polycarbonate

A plaque of pure polycarbonate PC.H was cast. The polycarbonate was dried under vacuum for 10 hours at 80°C. The plaque was moulded between two highly polished steel plates, using a compression moulding machine, at 245°C for 30 mins under a pressure of 31 kg/cm^2.

The plaque was then allowed to cool down gradually to room temperature before completely releasing the pressure and demoulding.

2.2.2.7 Polyethersulfone modified epoxy resin cured with DDM hardener

Procedure E:

The polyethersulfone was dried at 100°C for 5 hours. It was then dissolved in dichloromethane at concentration of 20 wt%. Melted DDM was added at the stoichiometric ratio (26 phr) to hot MY750 epoxy resin at 80°C. The polyethersulfone-solvent solution was added to the epoxy - DDM blend at 80°C and mixed thoroughly until homogeneous.

The mixture was then poured into the preheated mould at 60°C. Degassing was carried out at 60°C for 2 hours to remove the maximum of solvent. The blend was cured at 80°C for 6 hours and postcured at 150°C for 3 hours.

2.2.3 Nomenclature used

A simplified nomenclature has been used to name the different plaques cured with DDM hardener.

2.2.3.1 Neat, polyethersulfone or polycarbonate modified epoxy systems cured with DDM hardener

For example 750-fPC.M7.4 is the abbreviation which names the MY750 epoxy system modified by 7.4 wt% of fPC.M polycarbonate.

2.2.3.2 Rubber and rubber-polycarbonate modified epoxy systems cured with DDM hardener

All the rubber or rubber-polycarbonate modified epoxy systems were modified by 5 wt% polycarbonate and 15 wt% rubber, 15 wt% rubber meaning 15 wt% of CTBN (and not ETBN) in the plaque.

332-PC.H5-R15 is the abbreviation which names the DER332 epoxy system modified by 15 wt% of CTBN rubber and 5 wt% of PC.H polycarbonate.

All the other systems are named with their compositions in parts by weight.

After demoulding and when not used, all the plaques cast were kept at 23°C in a desiccator to avoid moisture absorption and in the dark to avoid photooxidation.

2.3 Characterisation methods

2.3.1 Transmitted light microscopy

This technique was used to study phase separation at 23°C in epoxy resin polycarbonate liquid blends. Samples were observed between two microscope slides with an Olympus microscope.

2.3.2 Scanning electron microscopy

To study the morphology of our different systems, scanning electron microscopy was performed on fracture surfaces of samples prepared in the same way as for the three point bend test (see Section 2.4.3) but broken in impact after cooling in liquid nitrogen for about 10 mins. The samples were cut down to the required length (5 mm) and mounted on aluminium SEM stubs using a conducting cement. They were coated with gold/palladium alloy and examined under an ISI/ABT 55 scanning electron microscope with an accelerating voltage of 15 kV.

Etched samples were prepared by simply immersing the fractured sample into dichloromethane for 1 hour or 3 hours when specified, before mounting onto the SEM stubs in the usual way.

2.3.3 Dynamic scanning calorimetry analysis

The dynamic scanning calorimetry analyses were performed on a Perkin-Elmer system which includes:

- DSC 4 working station
- system 4, thermal analysis microprocessor controller
- thermal analysis data station run with the TADS programme.

Heat flow variations of the sample of about 10 mg in an aluminium pan were recorded, under a slight nitrogen stream between 40°C and 300°C at a heating rate of 10°C per minute.

For reactive blends, the heat of reaction ΔH, and the minimum of the exothermal peak, T_{min} were measured. The heats of reaction, in joules per gramme were 'normalised' for the different blends MY750/polycarbonate/DDM = 100/polycarbonate phr/26, using the expression:

$$\Delta H_{100\%} = \Delta H \times \frac{126 + \text{polycarbonate phr}}{126} \qquad (8)$$

where ΔH is the heat of reaction in joules per gramme in the epoxy resin-polycarbonate-hardener blend and $\Delta H_{100\%}$ is the 'normalised' heat of reaction (in J/g) in this blend. One experiment is carried out on each two different blends prepared from the same composition. ΔH is measured with a scatter of around 10% whereas T_{min} is known within an error of ± 1°C.

Glass transition temperatures were taken as the temperature of the onset of the transition. No significant variation of this temperature was observed between two experiments on the same material.

2.3.4 Dynamic mechanical thermal analysis

Dynamic mechanical thermal measurements were performed in the single cantilever bending mode, on the Polymer Laboratories DMTA.

Sample size was kept as closely as possible to a cross section of 11.4 mm x 1.9 mm. The free length imposed by the single cantilever bending mode rig was 14 mm. The peak amplitude and the frequency of the sinusoidally varying strain were set at 64 μm and 10 Hz respectively. The stress response of the sample was measured between 0°C and 250°C or -100°C and 250°C with a constant heating rate of 3°C per minute.

Storage modulus (E') and loss factor $\tan\delta$ were plotted over the given temperature range.

For a given material two experiments on two different specimens were carried out.

The glass transition temperature was taken as the temperature of the maximum of loss factor tanδ curve.

No significant difference in glass transition temperature was found between two samples from the same plaque (maximum difference found 0.5°C). But a scatter of ± 4°C was found between experiments carried out for two different plaques cast of the same initial composition (neat MY750 epoxy system cured with the stoichiometric ratio of DDM hardener). These results indicate the experimental plaque to plaque variations induced by the casting procedure and justify the fact that all the experiments carried out in this work for a given composition were performed on the same plaque.

The glass transition temperatures measured from DMTA experiments are given without any error bars except when specified.

2.3.5 Image analysis

Results on morphology of the cured phase separated modified epoxy system were obtained with a Joyce Loebel image analyser system and the Genias 2.5 software. SEM pictures of non etched fracture surface samples were used for the analysis.

Prior to investigation by the image analyser system, the particles on the SEM pictures were manually darkened with a pen in order for the particles to be correctly recognised by the analyser system. By this method, small particles, the diameters of which were below 0.5 µm, could not be taken into account. The number of particles counted by the image analyser was between 177 and 864 particles for each of the pictures investigated.

The analysis results gave access to surface fraction of the dispersed phase and particle dimensions observed in the SEM pictures.

The volume fractions of the dispersed phase, V_D, in our systems were taken as the surface fractions of the dispersed phase observed on the SEM fracture surface pictures. Indeed, the surface fraction of the dispersed phase observed on a plane randomly sliced in the bulk of a material is equal to the volume fraction of the homogeneously dispersed phase in this material [61].

Particle diameters are the averages between the horizontal and vertical Feret diameters [61] for each particle. Statistical analyses were performed on the particle diameters to give average particle diameter, d, with the population standard deviation, $d\sigma n$, and the particle size distribution for each system.

The estimated errors, coming from the operation when the particles were manually darkened, are 10% and 5% on the volume fraction of the dispersed phase and particle average diameter respectively.

2.3.6 Infra red analysis

The tests were performed on a Perkin Elmer 1420 Ratio Recording Infra Red Spectrophotometer. Spectrum acquisition time was set at three minutes.

Liquid samples were sandwiched between two KBr pastilles. When heating up the sample was required, the samples were fitted into an IR hot cell, a small temperature controlled furnace, through which the IR beam could pass.

Liquid blends investigated were mainly based on epoxy resin-polycarbonate solutions all prepared following procedure B, but without degassing except when specified.

2.3.7 Gel permeation chromatography analysis

This was carried out at the Kobe Steel laboratory in Guildford, on a Perkin Elmer system fitted with three columns of 5 µm diameter particles of cross-linked polystyrene. The guard column was of mixed pore size, the porosities of the first and second column were 500 Å and 10^4 Å respectively.

Samples were dissolved in dichloromethane at 0.2 wt% a day before the tests. Injections (100 µl) of solutions were made into the dichloromethane flowstream at 1 cm^3/min and 70 bars and at 23°C. The concentration of the eluted species was monitored using a UV detector the wavelength of which was set at 255 nm.

The chromatograms were analysed using the PK Nelson Software (model 2900 GPC revision 5.0) based upon a polystyrene calibration.

Epoxy resin-polycarbonate solutions were prepared following procedure B with different degassing times.

2.4 Mechanical testing

All the dimensions of the specimens used for the mechanical tests presented in this part as well as for DMTA experiments were measured to ± 0.01mm.

2.4.1 Compression testing

Yield stress of our brittle epoxy systems could not be obtained by tensile experiments because in tension such systems break before yielding. In compression testing, the yield stress can be reached before the sample breaks.

The tests were carried out at 23°C between two hard steel plates, on a Nene tensile machine used in compression with a cross-head speed of 0.5 mm/min. The displacements were measured by a displacement transducer (LVDT).

For uniform stressing of compression specimens, a circular section is to be preferred over other shapes. The length to diameter ratio is an important parameter for the results, and a ratio of 2 or more is commonly employed [62]. Machining circular section specimens would have been very difficult since the thickness of the plaques cast was only 6 mm.

Previous experiments carried out on the neat MY750 epoxy system cured with the DDM hardener showed that the yield stress was not dependent upon the height to width ratio, in the case where samples of square loaded section of 10 mm x 10 mm with three different heights 2 mm, 4 mm and 6 mm were used (see Figure 2.1).

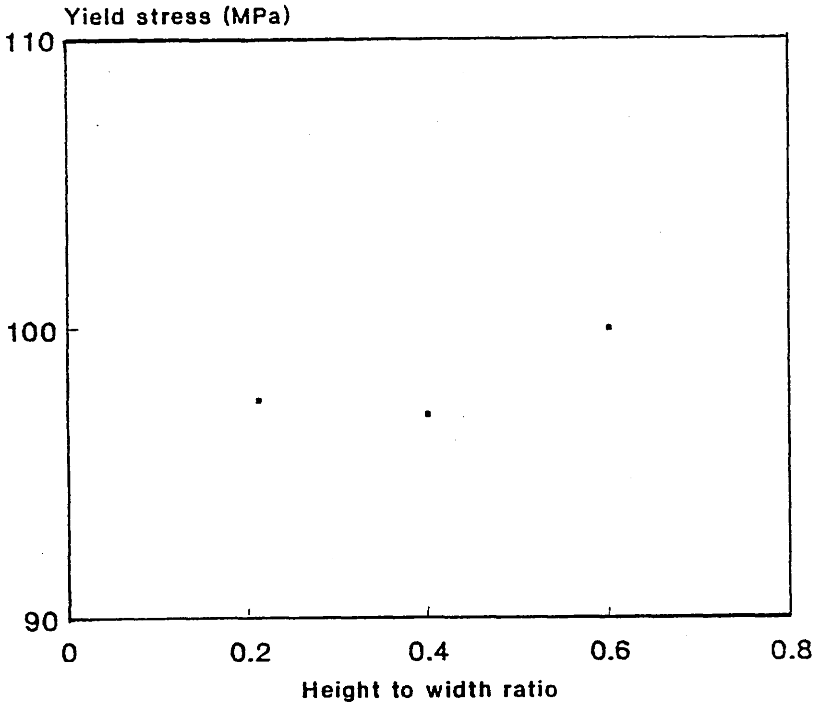


Figure 2.1 : Yield stress plotted against height to width ratio (square loaded section of 10 mm x 10 mm) for the system 750.

We chose to use samples of square section of 10 mm x 10 mm with a height of 4 mm.

Figure 2.2 shows the typical load displacement curve obtained and how the yield point was determined.

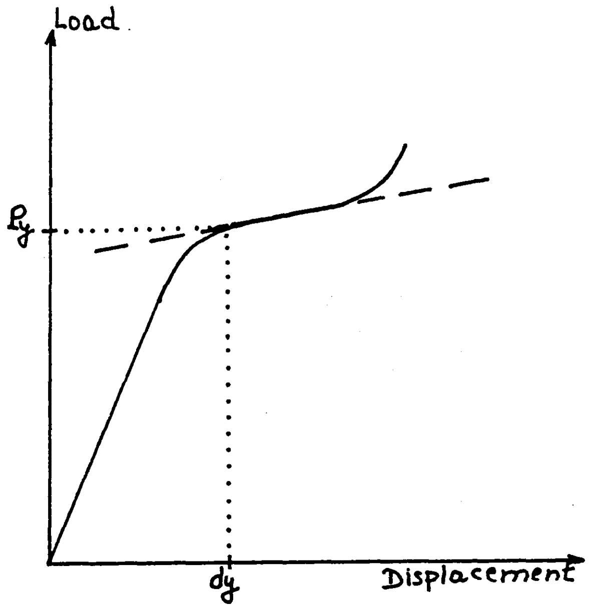


Figure 2.2 : Typical load-displacement curve obtained in compression test.

The yield stress σy is obtained as:

$$\sigma y = \frac{Py}{So} \left(1 - \frac{dy}{ho} \right) \qquad (9)$$

where

So : initial loaded surface of the sample
ho : initial height of the sample
Py : load at yield point
dy : displacement from initial height to height at yield point.

The final values for σy are the averages taken from tests on five specimens from the same plaque. They are given with their corresponding scatter. The estimated error in a single measurement is ± 7%.

2.4.2 Isochronous modulus measurements

They were performed to get the Young's modulus of the materials at very low strains (less than 0.5%).

The tests were carried out on a Darlington-Saunders creep machine at 23°C. The samples, the cross-section dimensions of which were typically 6 mm x 5 mm, were placed onto the machine with an extensometer fixed on it (initial gauge length approximately 27 mm). A preload of 1.02 kg stressed the samples for a night before the tests for stabilisation.

The test procedure was the following:

i) The sample was loaded with a weight and the corresponding displacement was taken after 100 seconds of loading. Displacements were determined to within ± 0.0001 mm.

Each load corresponds to a displacement and thus for each load a stress and a strain is found.

ii) The load is then removed and the sample is allowed to relax completely, in about 10 mins.

This procedure was repeated with ten different weights.

The curve, stress against strain, for each sample was a straight line, the slope of which was the isochronous Young's modulus E_{100}.

The final values for E_{100} are the averages taken from two different tested specimens for each material. They are given with their corresponding scatter. The estimated error in a single E_{100} measurement is ± 3%.

2.4.3 Fracture testing

Slow fracture testing was carried out with single edge notched three point bend specimens at 23°C, using an Instron testing machine, and following the linear elastic fracture mechanics (LEFM) standard for determining the critical stress intensity factor, Kc and the critical strain energy release rate, G_c (see Appendix B). This protocol has been created by the activities of the EGF Task Group on Polymers and drafted by Professor J. G. Williams.

The specimens were cut to the following dimensions: length: 55 mm, width: 12 mm, thickness: 6 mm.

The notch was a cut saw 'V' notch, extended by a sharp pre-crack made by tapping on a fresh razor blade placed in the notch.

The tests were performed at 23°C and at a cross-head speed of 1.13 mm/min; except for pure polycarbonate specimens, where the cross-head speed was 10 mm/min. The span to width ratio was 4:1 as stated in the protocol.

With these conditions all the specimens tested fractured in a brittle manner.

The size criteria for plane strain conditions were also respected. So K_{IC} was given as

$$K_{IC} = f\,(a/W)\ \frac{P_Q}{BW^{\frac{1}{2}}} \qquad (10)$$

where

a : initial crack length measured on the fracture surface after testing with a travelling microscope

W, B : width and thickness of the specimen respectively

P_Q : maximum load at crack initiation

f : calibration factor

G_{IC} was given as

$$G_{IC} = \frac{U_Q - U_i}{BW\,\phi\,(a/W)} \qquad (11)$$

where

a, B, W : as above

U_Q : energy calculated from the load point displacement diagram up to the load P_Q when the crack initiates

U_i : energy from indentation calculated following configuration 3b and 3c (see Appendix B), up to the same load point P_Q. This energy corresponds to the total energy absorbed during the fracture test by the indentation of the loading pins into the specimens and by the deformation of the testing machine between the cross-heads.

ϕ : energy calibration factor

The indentation tests were performed on broken fracture test specimens at half the speed of the fracture tests : 0.54 mm/min, except for polycarbonate samples : 5.12 mm/min.

The final values for K_{IC} and G_{IC} are the averages taken from eight valid tests ($0.45 < a/W < 0.55$). K_{IC} and G_{IC} are given with the population standard deviation calculated from the corresponding eight valid tests. The estimated error in a single K_{IC} and G_{IC} measurement is ± 10%.

CHAPTER 3

PHASE SEPARATION AND MORPHOLOGY IN THE MODIFIED EPOXY SYSTEMS

The following conditions should be met for successful toughening of a highly crosslinked thermoset:

- The thermoplastic should stay dissolved in the matrix while it is cured in an attempt to enhance the epoxy matrix ductility.

- The rubber must phase separate to get the rubber particles dispersed in the continuous matrix.

Thus, polycarbonate-epoxy resins compatibility has been investigated. Morphology and glass transition of the cured epoxy systems are presented as well as results on polyethersulfone modified epoxy systems.

The reader is referred to Chapter 2 for details of mixing and casting procedures of the blends as well as for SEM and DMTA sample preparation.

3.1 <u>Phase separation before cure</u>

This part presents the results of phase separation investigations on polycarbonate, rubber, rubber-polycarbonate and polyethersulfone modified epoxy blends before they were cured.

Details of the mixing procedures quoted in this part are presented in Section 2.2.2.

3.1.1 Solubility parameter calculations

To get an approximate idea of the compatibility between epoxy resins and modifiers, it is useful to determine the solubility parameter of each component involved in the different blends.

Their values, calculated by Fedors' method [24], are presented in Table 3.1 Details of the calculations are in Appendix C.

Epoxy resins and brominated polycarbonate oligomer solubility parameters were calculated from their structural formulae. Solubility parameters of polyethersulfone and higher molecular weight polycarbonate were calculated from their constitutive unit structural formula; the end group contributions to the solubility parameter were not taken into account. This contribution is very low compared to that of the long main chain.

Materials	Solubility parameter δ $(cal/cm^3)^{1/2}$
difunctional epoxy - MY750 trifunctional epoxy - ERL0510	9.2 10.0
polycarbonate functionalised brominated polycarbonate fP(BrC).0	10.3 11.0
polyethersulfone	11.3
CTBN rubber	8.8[a]

Table 3.1 : Solubility parameter values at 25°C for different materials.

[a] = from [13].

At 25°C polycarbonates and polyethersulfone should be more miscible in trifunctional than in difunctional epoxy resin because the difference in solubility parameter between the modifier and the epoxy resin is less in the case of the trifunctional epoxy.

3.1.2 Polycarbonate modified epoxy blends

3.1.2.1 Investigations on compatibility between epoxy resins and polycarbonates prepared by UMIST

Most of the work presented here has been carried out with the fPC.M polycarbonate.

a) 5 parts per hundred parts of resin by weight (phr) of fPC.L, fPC.M, fPC.H do not dissolve in MY750 in 8 hours either at 23°C or at 80°C.

Figure 3.1 shows the amount of fPC.M (in phr) added to difunctional and trifunctional epoxy resins (MY750 and ERL0510) at 130°C as a function of time to get clear solution at this temperature. As demonstrated, fPC.M is very difficult to dissolve in MY750. The dissolution of fPC.M in ERL0510 is much easier : it takes around 30 minutes to dissolve 5 phr of fPC.M in trifunctional epoxy at 130°C, whereas it takes 5 hours in difunctional epoxy. Attempt to dissolve the fPC.M at higher temperatures was not contemplated as high temperatures may promote resin homopolymerisation.

This confirms the conclusions of the solubility parameters approach : polycarbonate is more compatible with trifunctional than with difunctional epoxy resin.

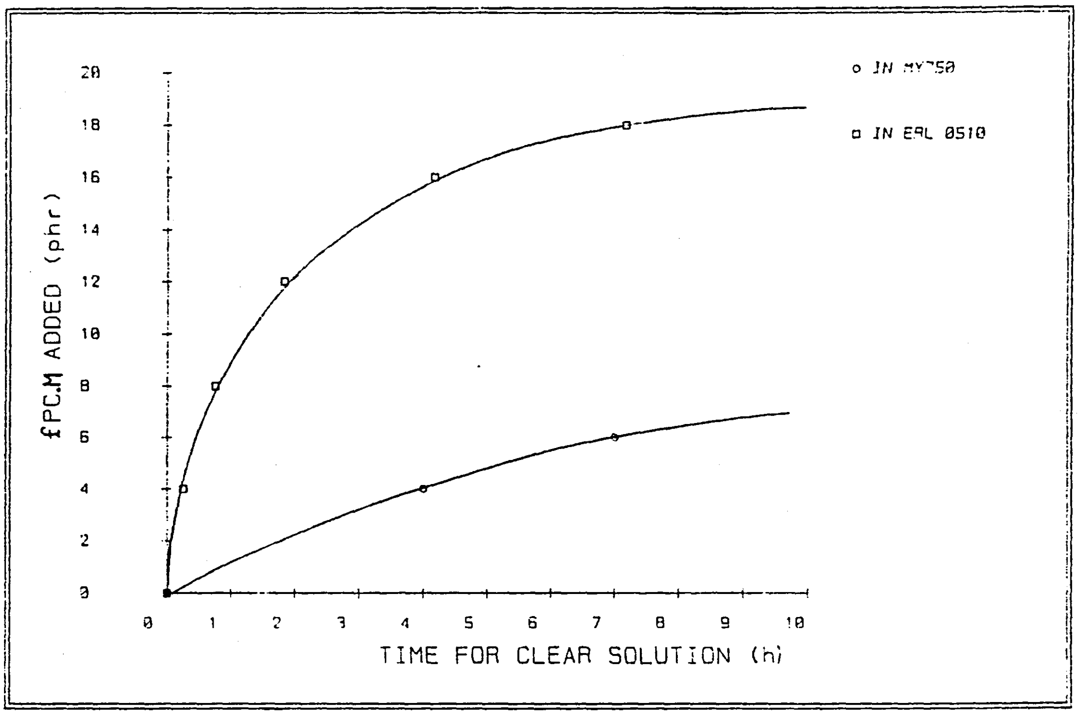


Figure 3.1 : Dissolution curve of fPC.M in difunctional and trifunctional epoxy resins at 80°C.

b) Thus, the use of a solvent common to polycarbonate and epoxy resin had to be considered to prepare epoxy polycarbonate blends.

Methylene chloride was found to dissolve polyethersulfone successfully at room temperature [3, 39-42, 53]. fPC.L, fPC.M, fPC.H dissolve in methylene chloride at room temperature and at concentrations of 15 wt% to form clear solutions.

To study the compatibility between fPC.M and MY750, MY750/fPC.M solutions in 100/5, 100/10, 100/20 and 100/30, 100/40 parts by weight ratios were prepared following procedure A. At the end of the degassing all the blends were turbid, except for the one containing 5 phr of PC.M. The 100/20, 100/30 and 100/40 blends exhibited putty-like consistency. Optical micrographs of these blends show that phase separation has occurred (see Figures 3.2 and 3.3).

The optical micrographs suggest that the PC 6 in the blends has re-crystallised into a spherulitic form, with diameters around 10μm. Similar re-crystallisation of initially amorphous polyethersulfone on repeated exposure to chlorinated solvents has been noted [63].

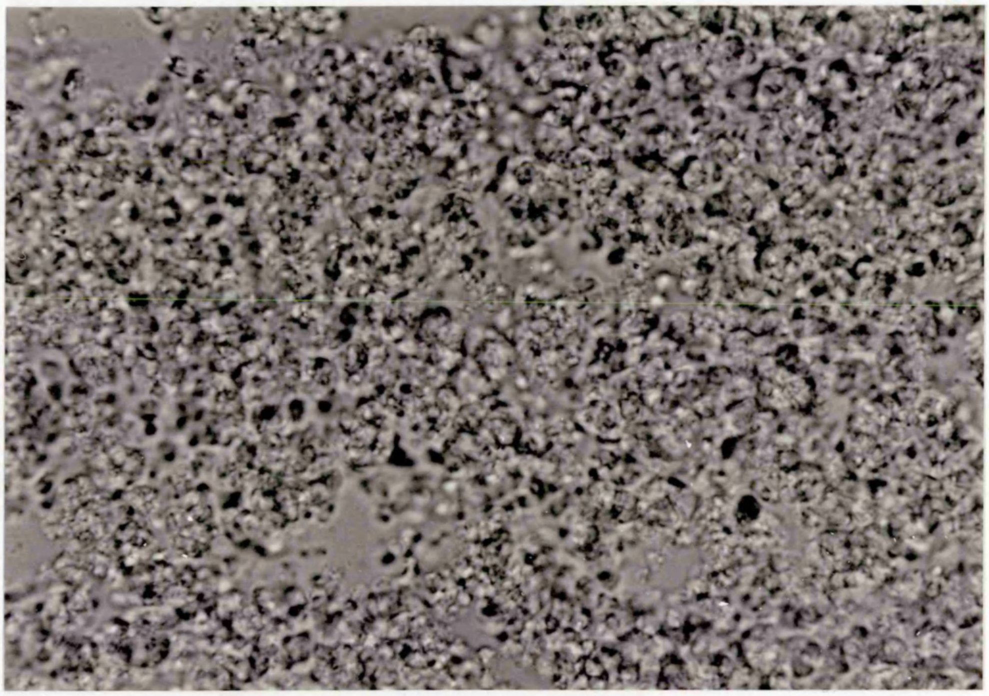


Figure 3.2 : Optical microscope picture of MY750/fPC.M = 100/30 blend at X680 on photograph.

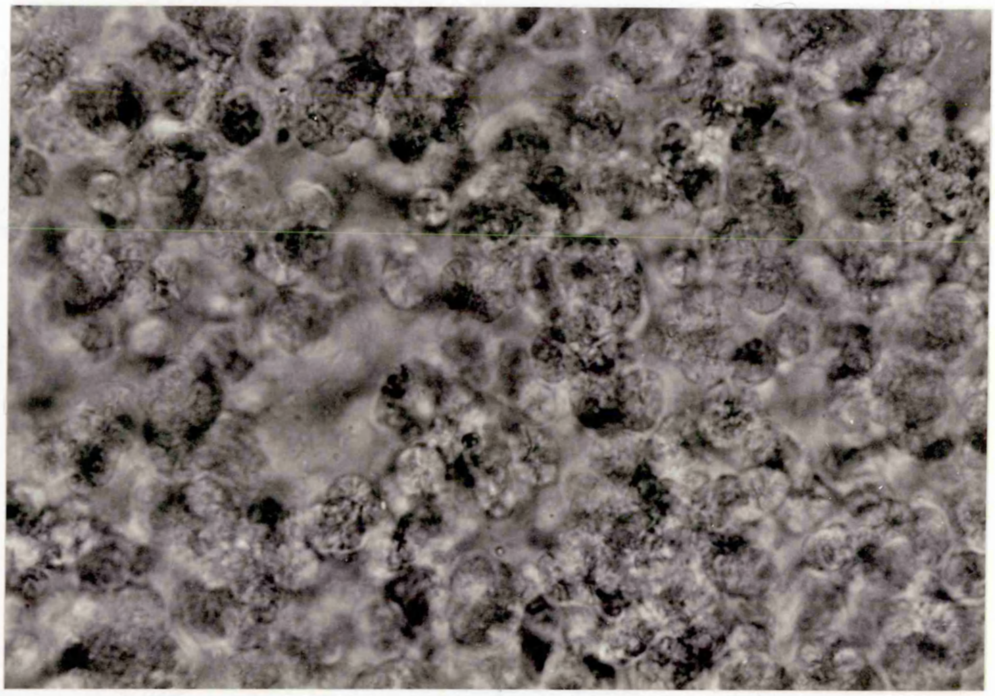


Figure 3.3 : Optical microscope picture of MY750/fPC.M = 100/40 blend at X680 on photograph

Yamamoto et al [64] performed light scattering experiments on blends of DGEBA epoxy resin -functionalised polycarbonate from UMIST-DDM hardener during cure at 170°C. The scattering pattern which appeared in these blends at around 100°C remained almost unchanged up to 170°C. This pattern, which could be confused with the spherulitic scattering pattern is nevertheless characteristic of the rodlike pattern.

Thus, the morphology observed in our blends MY750/fPC.M = 100/20, 100/30, 100/40 could be the result of a microfibril accumulation rather than a spherulite formation.

Four DSC runs have been performed on these blends. The DSC traces do not show any clear evidence of a fusion peak except at around 140°C (see Figure 3.4). Nevertheless, the features observed in these blends are believed to be due to a crystallised fPC.M-rich phase.

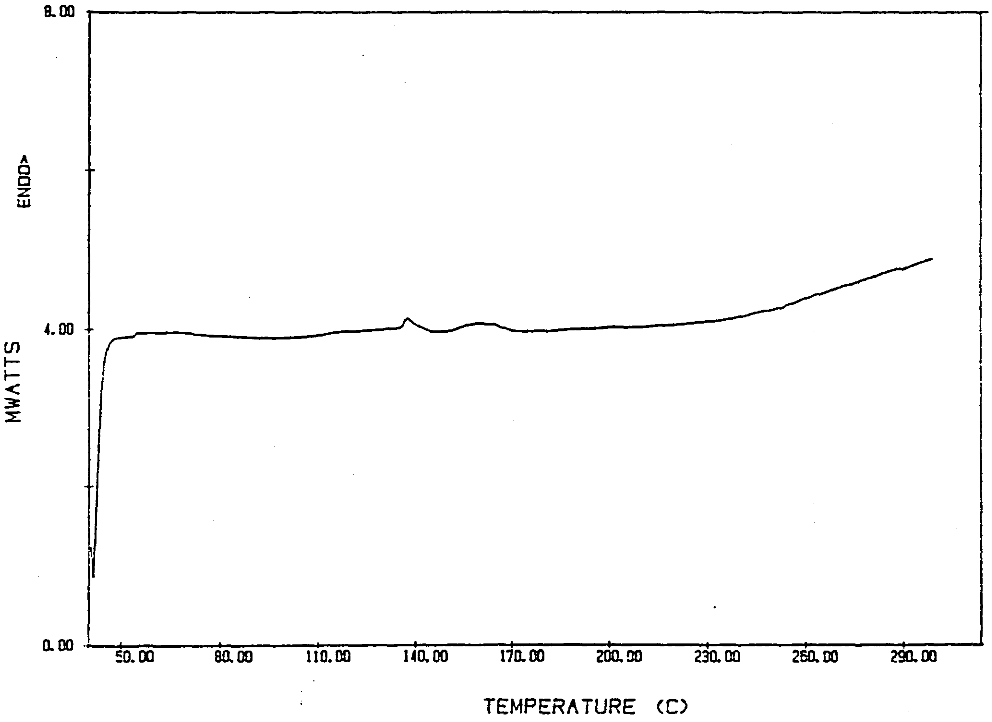


Figure 3.4 : Dynamic DSC run on the blend MY750/fPC.M = 100/30.

3.1.2.2 Investigations of compatibility between difunctional epoxy resin and commercial polycarbonates (PC.H and fP(BrC).O)

PC.H and fP(BrC).O dissolve in methylene chloride at 23°C, at a concentration of 15 wt%.

10 phr of fP(BrC).O dissolve in MY750 at 80°C in about 1 hour with continuous stirring.

Attempts to dissolve even a very small amount of the highest molecular weight polycarbonate PC.H in MY750 at 80°C have not been successful. MY750/PC.H solutions were prepared following procedure B. Degassing during procedure A was found to be peculiar : the large amount of solvent still present in the blends gave big bubbles during the degassing step. Blends prepared following procedure B did not show this problem because most of the solvent was removed from the blends before degassing.

Therefore procedure B was preferred to procedure A.

After the degassing, the MY750/PC.H = 100/10, 100/20 solutions were clear at 23°C.

20 phr of PC.H seems to be the upper limit which can be dissolved in MY750 at 120°C, the PC.H-solvent solution had to be added very slowly to the MY750 epoxy resin at 120°C, especially at the end, to avoid precipitation of polycarbonate particles.

No change concerning phase separation was noticed before and after the hardener, DDM at 26 phr, DDS at 30 phr or HY917 at 85 phr, was added to the MY750-polycarbonate blends listed in this section.

The results on phase separation in the polycarbonate modified epoxy systems are summarised in Tables 3.2 and 3.3.

3.1.3 Rubber and rubber-polycarbonate modified epoxy blends

Difunctional epoxy resin (MY750,DER332)/polycarbonate (fPC.L,fP(BrC).0, PC.H)/CTBN rubber solutions in 100/8/24 parts by weight ratios were prepared following procedure C or D (D : without solvent procedure). They did not show any evidence of turbidity at 60°C or 80°C which was not the case as soon as the stoichiometric ratio of DDM was added in these blends at 80°C. Thus, the mixtures : epoxy resin - polycarbonate (5 wt%) - CTBN rubber (15 wt%)-DDM are not fully compatible at 80°C.

3.1.4 Polyethersulfone modified epoxy blends

The mixtures MY750/Polyethersulfone/DDM = 100/30/26 prepared following procedure E were clear at the beginning of the cure for both the functionalised or not polyethersulfone: fPES or PES.

Parts per hundred parts of resin by weight of modifier added	5 fPC.L	10 fPC.L	5 fPC.M	10 fPC.M	20 fPC.M	30 fPC.M
Dissolution in epoxy resin MY750 at the specified temperature	80°C no	80°C no	-	-	-	-
After the specified mixing procedure observation at 23°C	A clear	A clear	A clear	A slightly turbid	A turbid	A turbid
At the beginning of cure with the specified hardener	DDM clear	DDM clear	DDM clear	DDM clear	-	DDM turbid
After cure with the specified hardener	DDM clear	DDM clear	DDM clear	DDM clear	-	DDM opaque

Table 3.2 : Summary of the observations of miscibility in polycarbonate modified MY750 epoxy systems

Parts per hundred parts of resin by weight of modifier added	40 fPC.M	5 fPC.H	10 fPC.H	10 fP(BrC).0	10 PC.H	15 PC.H	20 PC.H
Dissolution in epoxy resin MY750 at the specified temperature	-	80°C no	-	80°C Yes	80°C no	-	-
After the specified mixing procedure observation at 23°C	A turbid	-	A clear but yellow	B clear	B clear	B clear	B clear
At the beginning of cure with the specified hardness	-	-	DDM clear	DDM clear	DDM/DDS clear	HY917 clear	DDM/DDS clear
After cure with the specified hardener	-	-	DDM clear	DDM clear	DDM/DDS clear	HY917 clear	DDM/DDS clear

Table 3.3 : Summary of the observations of miscibility in polycarbonate modified MY750 epoxy systems.

3.2 Morphology and Dynamic mechanical behaviour of the cured blends

This part presents SEM and DMTA results on the cured modified epoxy blends, which include considerations of phase separation and glass transition temperature determinations.

Systems cured with DDM hardener are named with their codes specified in Section 2.2.3 SEM photographs of fracture surface of some of the modified epoxy systems are presented in Appendix D. DMTA tables of results and a selection of DMTA traces are presented in Appendix E.

3.2.1 Polycarbonate modified epoxy systems

Plaques were cast of the following mixtures (in parts by weight) :

MY750/fPC.L/DDM = 100/5/26, 100/10/26,
MY750/fPC.M/DDM = 100/5/26, 100/10/26, 100/30/26
MY750/fPC.H/DDM = 100/10/26
MY750/PC.H/DDM = 100/10/26, 100/20/26.
MY750/PC.H/DDS = 100/20/30
MY750/PC.H/HY917/DY070 = 100/15/85/1, 100/15/85/0.
(HY917 : anhydride hardener, DY070 : accelerator)

3.2.1.1 SEM, DMTA results and phase separation

With the exception of the blend MY750/fPC.M/DDM = 100/30/26 all the other blends cast are transparent. They exhibit brittle featureless fracture surfaces, even at high SEM magnification (x 20k). Etching with methylene chloride has no observable effect on the fracture surface appearance.

This suggests a high compatibility between polycarbonate and epoxy matrix in our blends.

Blend MY750/fPC.M/DDM = 100/30/26 is opaque and creates a rough fracture surface when broken in impact after cooling in liquid N_2. Etching with methylene chloride has the effect of smoothing the fracture surface slightly. A small amount of polymer appears to have been washed away but not enough to account for all the PC present. This, therefore, suggests that the PC has been insolubilised to a degree, probably by a reaction with the epoxy (re-crystallisation from a solvent is also a possible reason for reduced solubility). The phase separation observed in this cured blend arises from the initial phase separation existing in the MY750/fPC.M = 100/30 blend before the hardener was added.

This blend was unsuitable for DMTA specimen preparation because large bubbles were trapped in the final plaque.

The shapes of the DMTA traces are basically the same for all the polycarbonate modified epoxy systems investigated. There is no evidence of phase separation on these traces. This agrees with the SEM results.

3.2.1.2 Variation of the glass transition temperature with polycarbonate molecular weight and polycarbonate content

Glass transition temperature of pure polycarbonate has been able to determined only for the PC.H (T_g = 152.5°C). We could not cast any DMTA specimens for the other polycarbonates because too much material was required in comparison to what was available.

Figure 3.5 shows the difference between the experimental curve - T_g as a function of polycarbonate content in PC.H modified epoxy system - and the theoretical curve determined by the Fox's equation [65]; assuming complete miscibility.

If T_{g1}, T_{g2} and W_1, W_2 are the respective T_gs and weight fraction of component 1 and 2 in the blend, the Tg of the homogeneous blend predicted by the Fox's equation is given as

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{12}$$

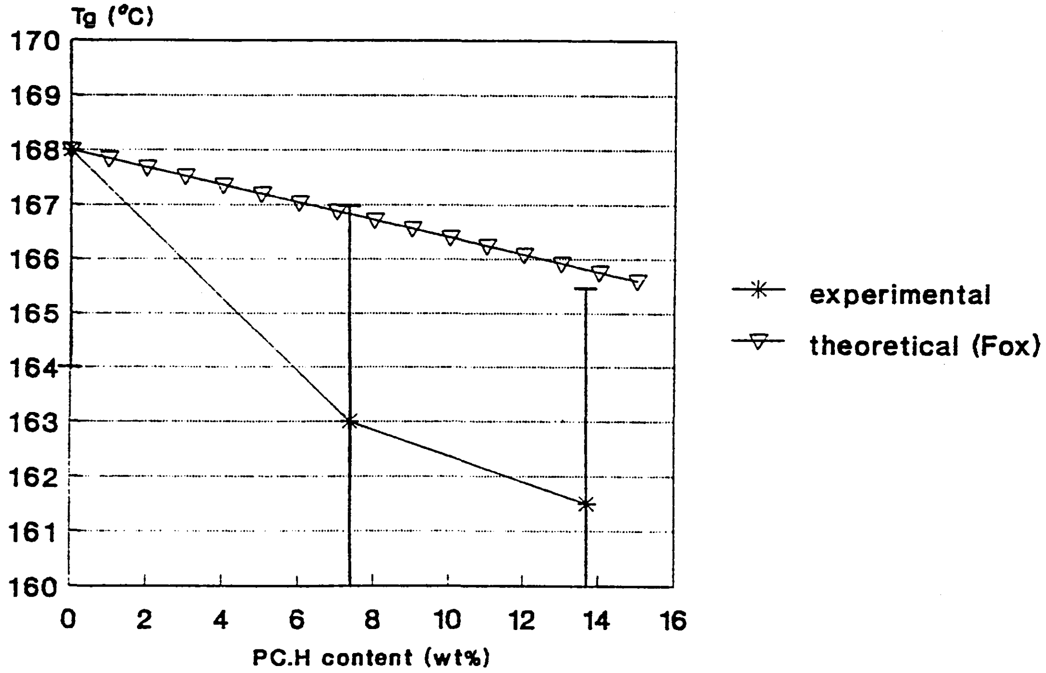


Figure 3.5: T_g as a function of PC.H content in cured blends 750-PC.Hn. Comparison between experimental and theoretical (Fox) curves.

The general theoretical trend of a decrease of T_g with increasing polycarbonate content is respected in our homogeneous PC.H modified epoxy systems.

However, the experimental curve is below the theoretical one. This could be due to experimental errors (see Section 2.3.4) or to some interactions between the polycarbonate and the epoxy resin which could reduce the T_g by affecting the network formation more than a simple and total dissolution of the PC.H in the epoxy matrix.

Within the limits of experimental errors on T_g measurements discussed in Section 2.3.4, the following results can be drawn:-

i) The T_g of the polycarbonate modified epoxy systems increases with increasing polycarbonate molecular weight at the same amount of polycarbonate added. This is the result of the increase of the glass transition temperature of the pure polycarbonate with their molecular weight [66]; (see Figure 3.6).

ii) The T_g of the polycarbonate modified epoxy systems decreases with polycarbonate content as the result of the increase of the amount of polycarbonate dissolved in the epoxy matrix (see Figure 3.7).

As required, phase separation does not occur in those epoxy resin-polycarbonate-hardener blends which are initially miscible, whichever of the three hardeners is used : DDS (low reactivity diamine hardener), DDM (high reactivity diamine hardener) or HY917 (anhydride hardener) with or without accelerator.

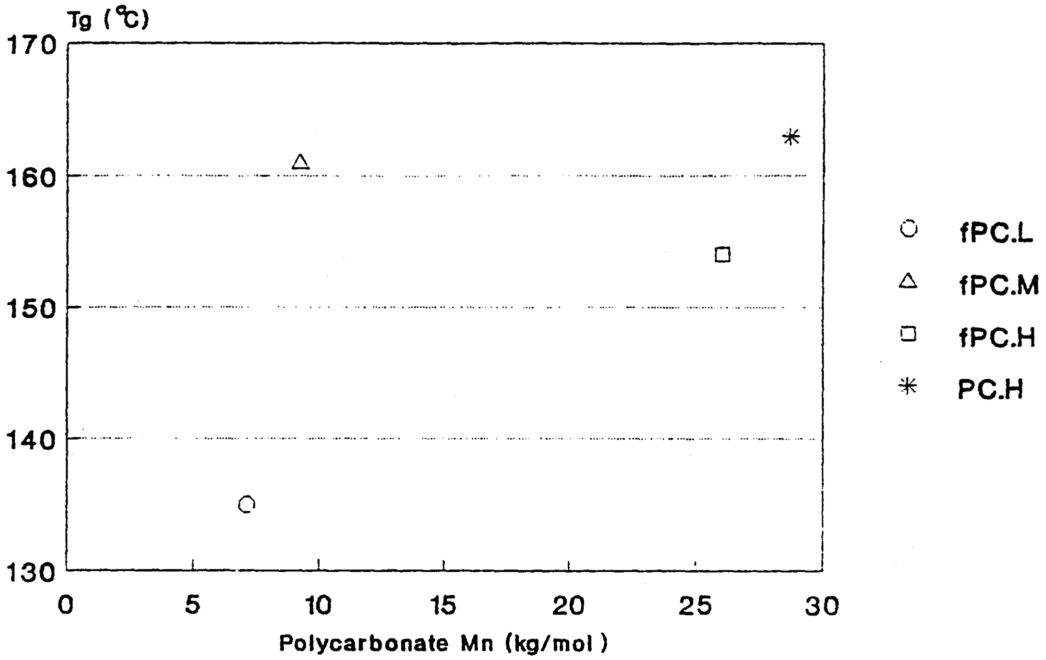


Figure 3.6 : T_g plotted against polycarbonate molecular weight in polycarbonate modified epoxy systems at 7.4 wt% polycarbonate.

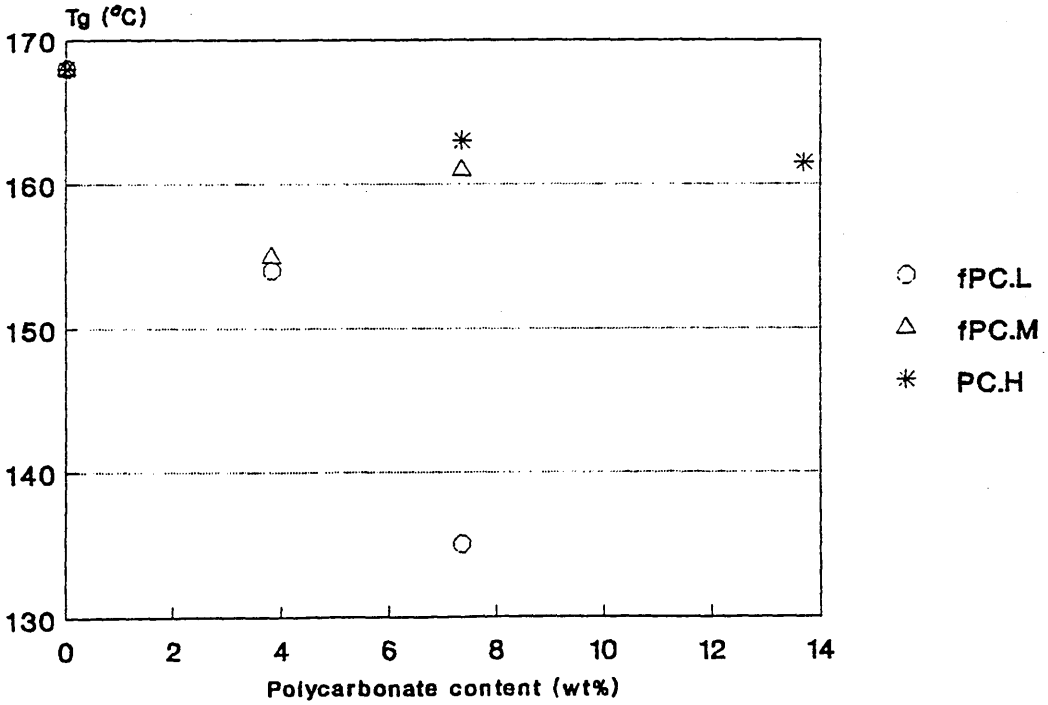


Figure 3.7 : T_g plotted against polycarbonate content in polycarbonate modified epoxy systems.

3.2.2 Rubber and rubber-polycarbonate modified epoxy systems

All the cured blends are opaque. SEM pictures of the fracture surfaces show spherical particles dispersed uniformly in a continuous matrix.

These particles can be washed away by etching with methylene chloride. Thus, these particles are not of epoxy-rich phase. The number and size of these particles can only account for rubber-rich phase particles. A great number of these particles are washed away after etching with methylene chloride and some others are not rinsed away even after etching for three hours. This suggests that the rubber has been insolubilised to a degree as the result of the reaction between the epoxy capped rubber and the hardener.

Examination of the fracture surface of the etched samples in methylene chloride did not show any clear evidence for subinclusions in the rubber particles, except for the blend 750-fPC.L5.R-15. This blend shows some rare very big particles (diameter around 40µm) with subinclusions which are believed to be of epoxy resin. These particles could result from a coalescence of small particles at the end of the phase separation process. Some smaller particles in this blend (diameter about 10µm) also show epoxy-rich phase subinclusions. Epoxy-rich phase subinclusions result from phase separation occurring within the particles.

As the polycarbonate stayed dissolved in the cured polycarbonate epoxy systems, it is supposed that it also does not phase separate in the rubber-polycarbonate modified epoxy systems, but forms an homogeneous blend with the epoxy resin. This supposition seems reasonable although it could not be clearly demonstrated by the experiments carried out here.

Some polycarbonate might be dissolved or have phase separated within the rubber particles.

Thus, the dispersed particles are believed to be of rubber-rich phase which are dispersed in a polycarbonate modified epoxy-rich phase matrix.

Further considerations of particle size and distribution and composition of the dispersed and continuous domains will be given in Section 3.3.

The DMTA traces of all epoxy blends modified by rubber or rubber and polycarbonate confirmed that phase separation occurred in these blends : for all these blends there is a shoulder in the LogE' trace at around -35°C with a small but broad tanδ peak appearing in the same temperature region. These characteristics are less pronounced in neat or polycarbonate modified epoxy systems. Thus, these are evidence of the glass transition of the rubber-rich phase [13, 20, 31]. The low temperature tanδ peak arises from the combination of three transitions : the ß transition of the epoxy resin (- 30°C), the ß transition of the polycarbonate (-74°C for PC.H) and the glass transition of the rubber-rich phase (T_g of pure liquid CTBN rubber, measured by DSC at 10°C per minute, has been reported to be -60°C [27]). Verchère [11] has carried out dynamic mechanical analysis on rubber modified epoxy systems and showed by deconvolution of the low temperature tanδ peak, that its maximum was the same as the one of the rubber-rich phase. The maximum of the low temperature tanδ peak was therefore considered in our work to correspond to the glass transition temperature of the rubber-rich phase in the rubber or rubber-polycarbonate modified epoxy systems.

The glass transition temperatures of the epoxy-rich phase (ET_g) are between 2°C and 10°C lower than the value for the neat MY750-DDM epoxy system. This indicates that some rubber and polycarbonate are dissolved in the epoxy matrix.

The glass transition temperatures of the rubber-rich phase (RT_g) are above the glass transition of the neat rubber (difference about 25°C) as a result of some epoxy (or polycarbonate) included in the rubber particles.

There is no dramatic change in ET_g or RT_g for all the rubber-polycarbonate modified epoxy systems, regardless of the polycarbonate used : from low to high molecular weight (fP(BrC).O to PC.H) and with or without reactive end groups and Bromine substitution (fP(BrC).0, fPC.L and PC.H).

3.2.3 Polyethersulfone modified epoxy systems

At the end of the cure the systems are opaque. SEM investigations of the fracture surfaces demonstrated that: The system containing the PES shows nodular features, resulting from phase separation of the thermoplastic from the epoxy. Etching a similar fracture surface in methylene chloride results in washing away the interconnecting ductile polymer from in between the nodules. This observation is consistent with the 'continuous phase' being the thermoplastic and is also in agreement with the results of Yamanaka and Inoue, obtained from thin films [3].

The equivalent system containing the fPES shows no such nodular features, but the appearance of the fracture surface is more 'ductile' than that of the unmodified epoxy. Etching with methylene chloride has no observable effect on the fracture surface, suggesting that the fPES has in this case become insolubilised, probably by reaction with the epoxy. This observation is in agreement with previous findings on related systems [34,39].

T_gs of pure polyethersulfone determined by DSC are:

-PES $T_g \approx 221°C$ (onset)
-fPES $T_g \approx 230°C$ (onset)

T_g of polyethersulfone obtained by dynamic mechanical analysis were reported to be about 225°C [34,42,53].

A shoulder on the low temperature side of the glass transition peak is noted in the case of the blend modified by the non reactive end group polyethersulfone. This could be interpreted as the result of the phase separation which occurred in this blend. The T_g of this system (159°C) does not fall between the T_g of both its components : the epoxy resin ($T_g = 168°C$) and the PES ($T_g \approx 225°C$). A similar effect has been noted by Raghava [42] and Ibrahim et al [41] in polyethersulfone modified tetrafunctional epoxy resin cured with an anhydride [42] or diamine [41] hardener. The only favourable explanation found by these authors is the reduction of the cross-link density of the epoxy matrix by the PES. The PES would prevent some reactions between epoxy groups and the hardener, and thus reduce the observed T_g.

The lack of phase separation between epoxy resin and the fPES shown by the SEM picture of fracture surfaces of the modified system specimen is confirmed by the DMTA traces observed on this blend : its T_g (170°C) is close to that of the neat epoxy system (168°C), and there is no shoulder peak on the glass transition peak.

A strange colour effect has been noted in these systems : their colour gradually turned from creamy white after the cure, to green when exposed to light. Photooxidation of the DDM cured epoxy resin is believed to be responsible for this effect: Bellenger and Verdu [67] studied the photooxidation in the solar UV range of the DGEBA.DDM system. They showed that the development of the green colour of oxidised samples was due to the absorption in the red region by a chromophore derived from the oxidation of the DDM methylene bridge. Iron chloride has a catalytic influence on this process.

Our neat, rubber or rubber-polycarbonate modified epoxy systems did not show the green colour observed in the polyethersulfone modified systems. Some iron chloride ions were perhaps introduced in the epoxy-polyethersulfone blends at the time of the mixing procedure by the steel spatula only used in this case.

3.3 Image analysis results of rubber and rubber-polycarbonate modified epoxy systems

The table of results is presented in Appendix F.

3.3.1 Particle size and volume fraction of the dispersed domains

SEM photographs of fracture surfaces have shown a bimodal distribution in the systems 750-fPC.L5-R15 and 750.PC.H5.R15. Very small particles of around 0.2 µm diameter were associated with particles of diameter about 4 µm. Particles of diameter below 0.5 µm could not be taken into account in our image analysis investigations (see Section 2.3.5). fP(BrC).O seems to promote a larger amount of small particles (diameter below 2μm) in the rubber-polycarbonate modified epoxy systems than fPC.L or PC.H. The widest particle size distribution is observed for the systems where PC.H. is used.

If the chemical aspects of polycarbonates, such as reactive end group or bromine substitution influence, are not taken into account, it is demonstrated that the particle average diameter in rubber-polycarbonate modified epoxy systems increases smoothly (from 3.1 μm to 4.1 μm) with polycarbonate molecular weight. Simultaneously the volume fraction of the dispersed phase decreases slightly (see Figure 3.8).

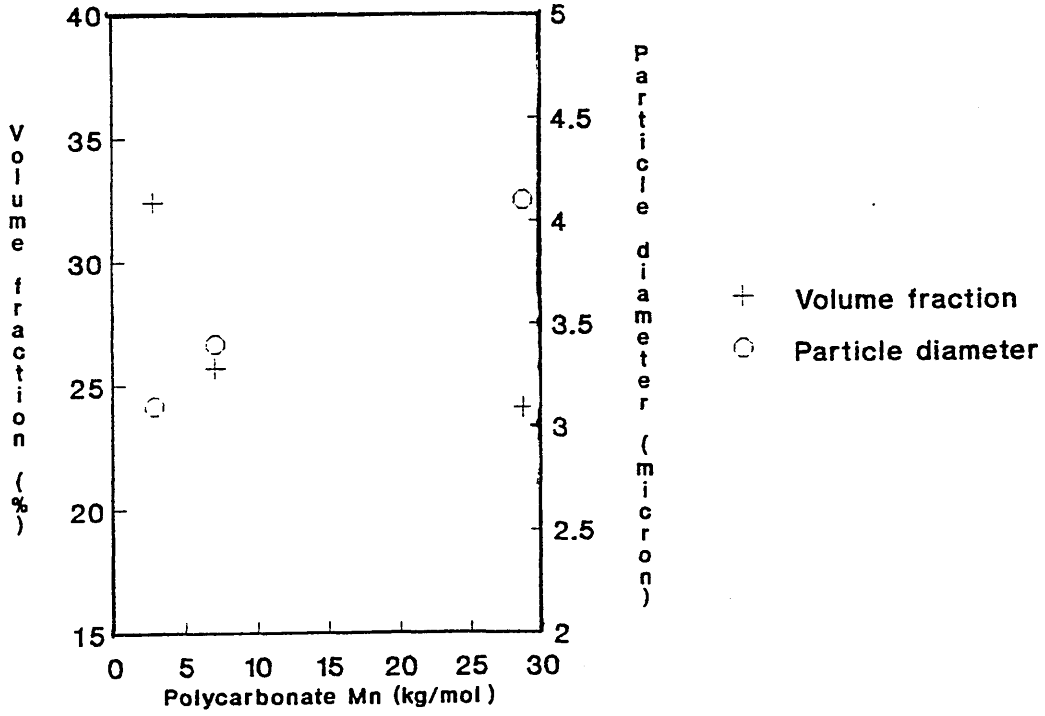


Figure 3.8 : Evolution of the particle average diameter and volume fraction of the dispersed phase with polycarbonate molecular weight in the rubber (15 wt%)-polycarbonate (5 wt%) modified MY750 epoxy systems.

If we consider that the rubber alone or the rubber and polycarbonate together would be completely phase separated in the rubber or rubber-polycarbonate modified epoxy systems, then the respective volume fractions of the dispersed phase should be 18% and 23%. The volume fractions of the dispersed phase obtained in our corresponding systems are between 24% and 35%. This is evidence that some epoxy is included in the dispersed rubber-rich particles.

3.3.2 Composition of the dispersed and continuous domains

3.3.2.1 Calculations

To be able to carry out the phase composition calculations in our rubber and rubber-polycarbonate modified systems, it has been necessary to suppose that there was no polycarbonate in the dispersed rubber particles but that the polycarbonate was homogeneously blended with the epoxy matrix.

The weight fraction of rubber dissolved in the polycarbonate modified epoxy matrix, W_R can be evaluated using the Fox equation (13):

$$W_R = \left(\frac{T_{g1} \times T_{g2}}{T_g} - T_{g2} \right) \times \frac{1}{T_{g1} - T_{g2}} \qquad (13)$$

where:

T_{g1} : T_g of the polycarbonate modified epoxy matrix taken as the T_g of the neat epoxy matrix (T_{g1} = 441 K). Figure 3.7 shows that at 5 wt% polycarbonate, the T_g of the polycarbonate modified epoxy systems are close to the T_g of the neat epoxy systems

T_{g2} : T_g of the pure rubber (T_{g2} = 213 K [27])

T_g : T_g of the system investigated.

The corresponding volume fraction $\phi_R{}^c$ is obtained as

$$\phi_R{}^c = \frac{\dfrac{W_R{}^c}{p_R}}{\dfrac{W_R{}^c}{p_R} + \dfrac{1 - W_R{}^c}{p_E}} \qquad (14)$$

where:

p_R : specific gravity of the rubber (p_R = 0.948 g/cm^3)

p_E : specific gravity of the polycarbonate modified epoxy matrix (p_E = 1.17 g/cm^3), calculated from the specific gravity of the pure epoxy resin (1.17 g/cm^3) and pure polycarbonate (P_{PC} = 1.20 g/cm^3) respectively.

The volume fraction of rubber in the dispersed phase, ϕ_R^D, is obtained by the equation expressing the conservation of the initial amount of rubber added into the blend:

$$\phi_R^o = \phi_R^D \times V_D + \phi_R^c\ (1 - V_D) \qquad (15)$$

or

$$\phi_R^D = \frac{\phi_R^o - \phi_R^c\ (1 - V_D)}{V_D} \qquad (16)$$

where:

ϕ_R^o = initial rubber volume fraction.

V_D = volume fraction of the dispersed phase determined by image analysis.

ϕ_R^o is given by:

$$\phi_R^o = \frac{\dfrac{W_R{}^o}{p_R}}{\dfrac{W_R^o}{p_R} + \dfrac{W_E^o}{p_E} + \dfrac{W_{PC}^o}{p_{PC}}} \qquad (17)$$

W_R^o : initial rubber weight fraction.

W_E^o : initial epoxy resin weight fraction (including the hardener)

W_{PC}^o : initial polycarbonate weight fraction

p_R, p_E, p_{PC} : the respective specific gravities of rubber (0.948 g/cm^3), epoxy resin (1.17 g/cm^3) and polycarbonate (taken as that of the PC.H : 1.20 g/cm^3).

3.3.2.2 Results (see Appendix F)

There is at least 30% by volume of neat or polycarbonate modified epoxy resin dissolved in the rubber particles for all the systems cast.

fP(BrC).O seems to promote the highest volume fraction of the dispersed phase (about 33%) and the highest polycarbonate modified epoxy resin volume fraction in the dispersed particles (about 48%).

Nevertheless for all the systems investigated, there is very little rubber dissolved in the neat or polycarbonate modified epoxy matrix (maximum 2.8% by volume).

CHAPTER 4

MECHANICAL PROPERTIES OF THE CURED EPOXY SYSTEMS

This part presents the mechanical properties : isochronous modulus (E_{100}), yield stress (σ_y) critical stress intensity factor (K_{IC}) and critical energy release rate (G_{IC}) of polycarbonate and of rubber and/or polycarbonate modified epoxy systems. Results on polyethersulfone modified epoxy systems are also considered.

The reader is referred to Section 2.4 for details of specimen preparation and testing procedures.

With our experimental conditions all the systems tested here fractured in a brittle manner. The tables of results are presented in Appendix G.

4.1 Polycarbonate modified epoxy systems

We only used the commercial polycarbonate PC.H at three concentrations (0%, 7.4% and 14.7% by weight). Using the functionalised polycarbonates from UMIST would have needed too much material in comparison to what was available.

E_{100} does not change significantly over the range of compositions investigated.

K_{IC} and G_{IC} decrease slightly when polycarbonate content is increased (see Figure 4.1). This result is inconsistent with the slight decrease of σy observed at the same time (see Figure 4.2). A decrease in σy usually leads to a better ability for plastic deformation which then yields a higher fracture toughness [15, 46, 48, 49, 50, 55], assuming that there is no change in the final network structure that could result in a counteracting effect.

However, this lack of toughness enhancement would not necessarily mean that the ability of the polycarbonate modified epoxy matrices to be toughened by rubber particles is not improved [46]. The slight decrease in σy and Tg observed in the PC.H modified epoxy systems could suggest that the effect of rubber particles to promote shear band formation in the matrix upon toughness enhancement could be more effective in the polycarbonate modified epoxy than in the neat epoxy systems.

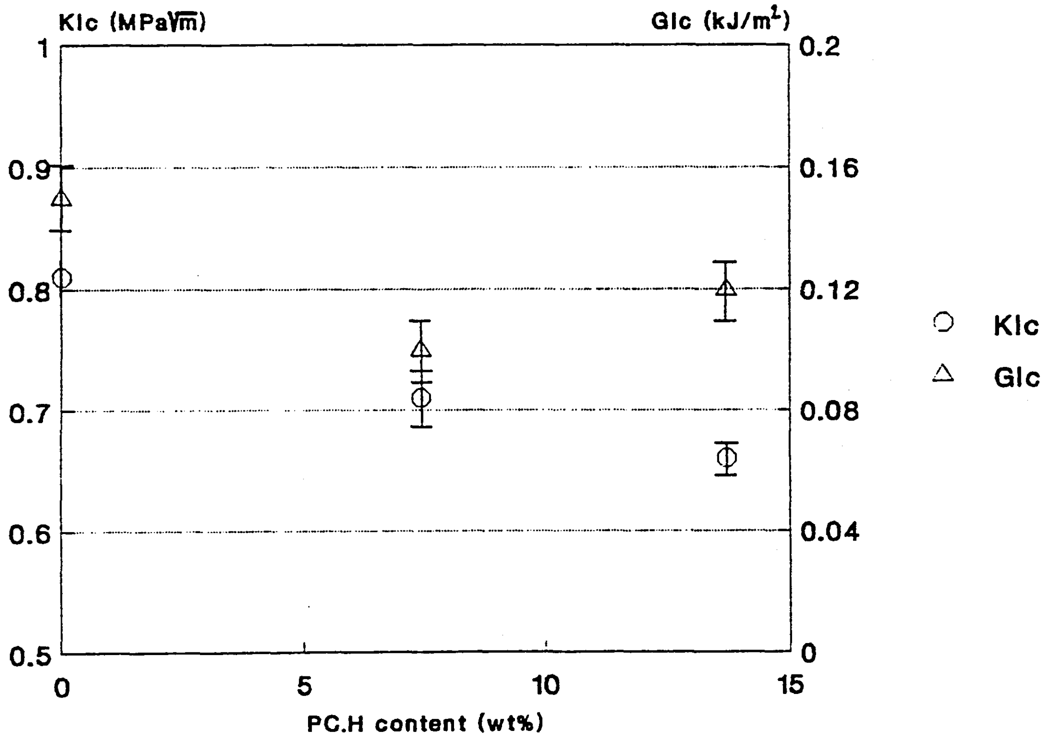


Figure 4.1 : K_{IC} and G_{IC} plotted against PC.H content in systems 750-PC.Hn.

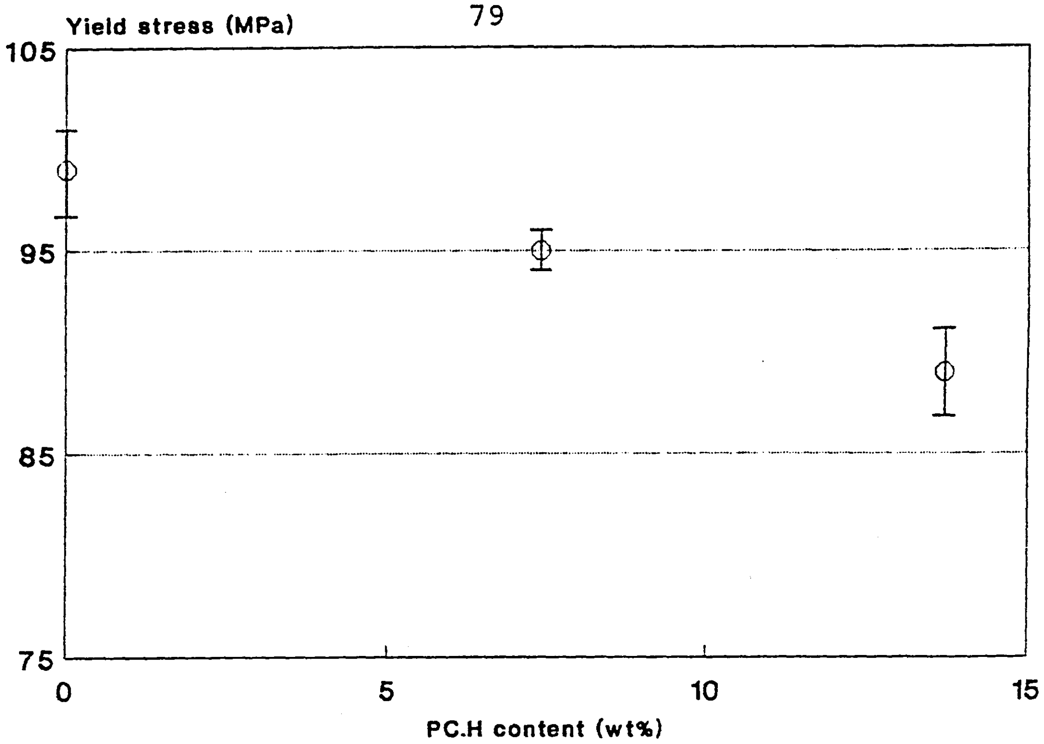


Figure 4.2 : σy as plotted against PC.H content in systems 750-PC.Hn.

4.2 Rubber and rubber-polycarbonate modified epoxy systems

In all the rubber and rubber-polycarbonate modified epoxy systems tested, the rubber and polycarbonate concentrations were 15% and 5% by weight respectively. Type of polycarbonate and of epoxy resin were the only parameters to vary.

4.2.1 Isochronous modulus and yield stress

As expected the epoxy modification by rubber or rubber and polycarbonate results in a large decrease in E_{100} and σy, when compared to the values obtained in the neat or polycarbonate modified epoxy systems (see Figures 4.3 and 4.4). This is mainly due to the presence of the dispersed rubber particles rather than the low amount of rubber dissolved in the polycarbonate modified epoxy rich-phase matrix.

However, E_{100} and σy, are almost unaffected by the choice of type of polycarbonate (fP(BrC).O, fPC.H, PC.H) or of resin (MY750 or DER332) used in the polycarbonate modified epoxy systems. E_{100} and σy vary between 1.7 GPa and 1.9 GPa, 61 MPa and 65 MPa respectively for all these systems.

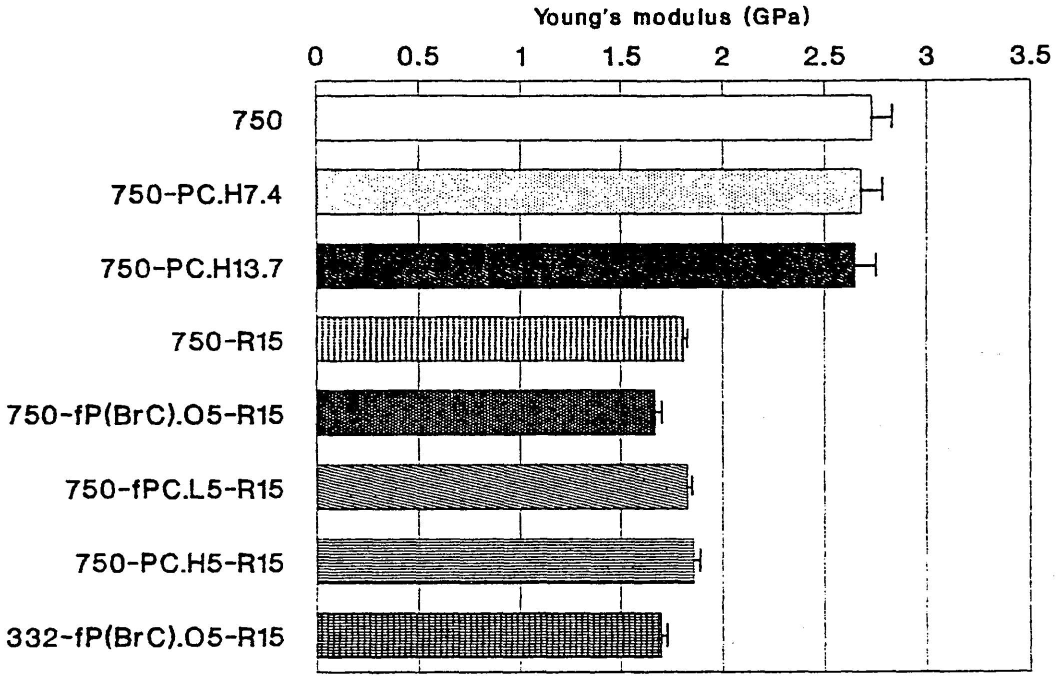


Figure 4.3 : E_{100} histogram for the corresponding systems.

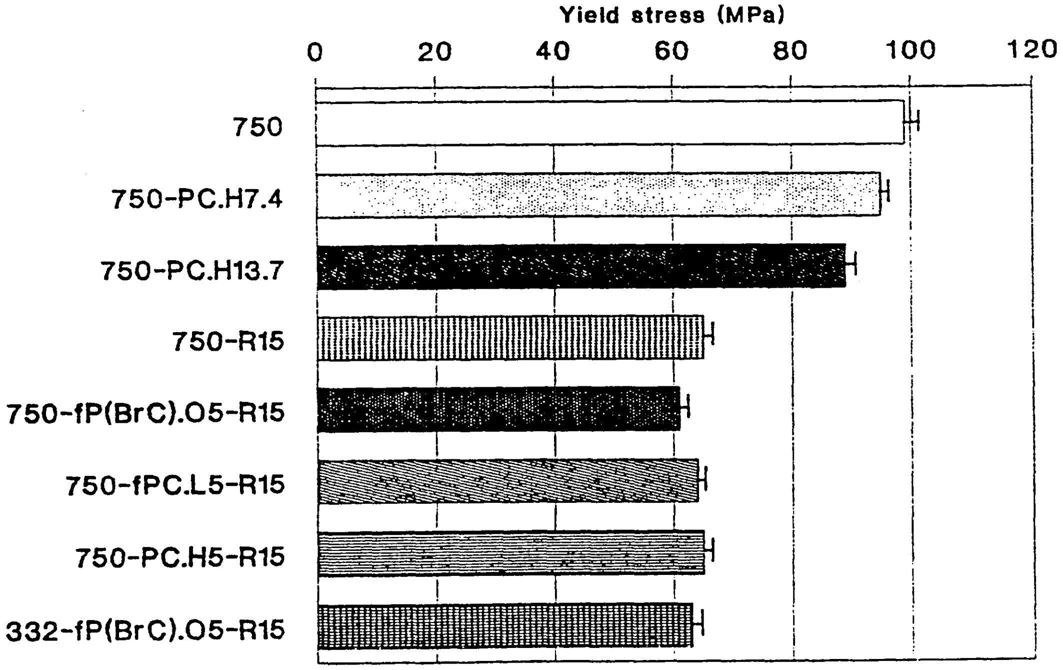


Figure 4.4 : σy histogram for the corresponding systems.

4.2.2 Fracture toughness

The increase in K_{IC} observed in the epoxy systems modified by rubber or rubber and polycarbonate is negligible, about 5%, in comparison to the neat epoxy system value. There is also no difference in K_{IC} between all these systems. Adding our polycarbonate modifiers to our rubber modified epoxy system does not enhance the fracture toughness of this system (see Figure 4.5).

Thus, adding polycarbonate to our neat epoxy system does not improve its ability to be toughened by rubber particles, despite the slight decrease of σy and T_g observed in the polycarbonate modified epoxy systems. This could be related to the lowering of toughness properties observed in the PC.H modified epoxy systems.

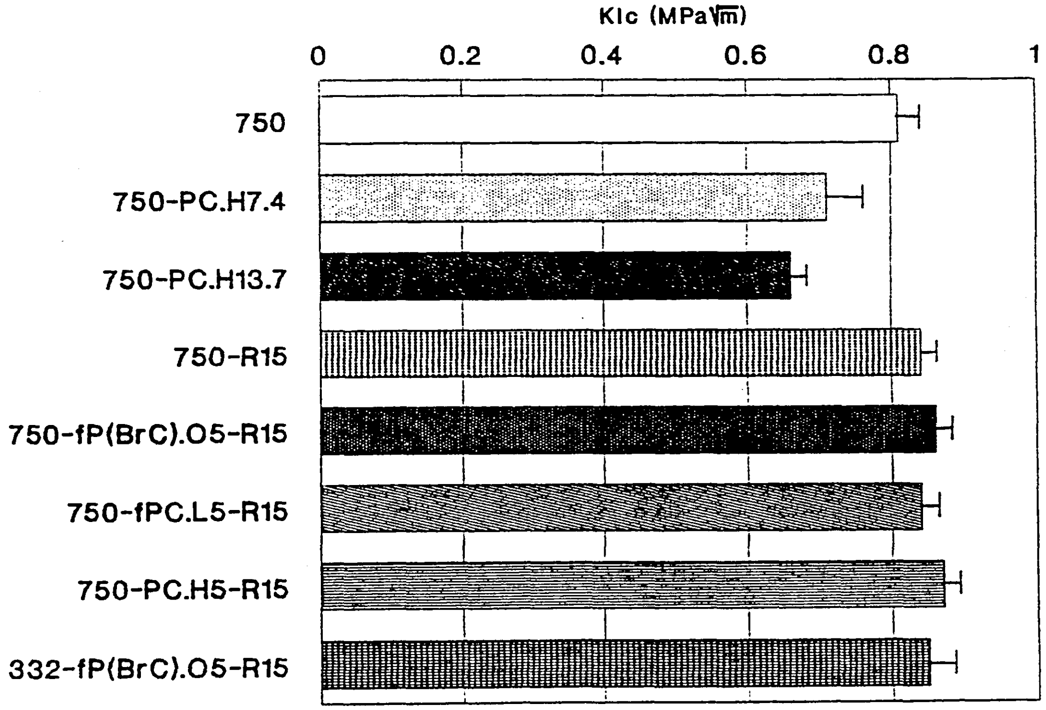


Figure 4.5 : K_{IC} histogram for the corresponding systems.

The large increase in G_{IC} observed in the rubber and rubber-polycarbonate modified epoxy systems about 100%, in relation to the neat epoxy system value (see Figure 4.6) is mainly due to the decrease of the Young's modulus E_{100}, for approximately the same K_{IC}, in these blends:

Indeed, G_{IC} is related to K_{IC} through

$$G_{IC} = \frac{K_{IC}^2 (1 - \nu^2)}{E_{100}} \tag{18}$$

where ν is the Poisson's ratio of the material. Assuming that the Poisson's ratio is constant for all the blends tested (ν = 0.35), Table G.1 shows that the experimental values for G_{IC} are in good agreement with the values calculated using equation (18).

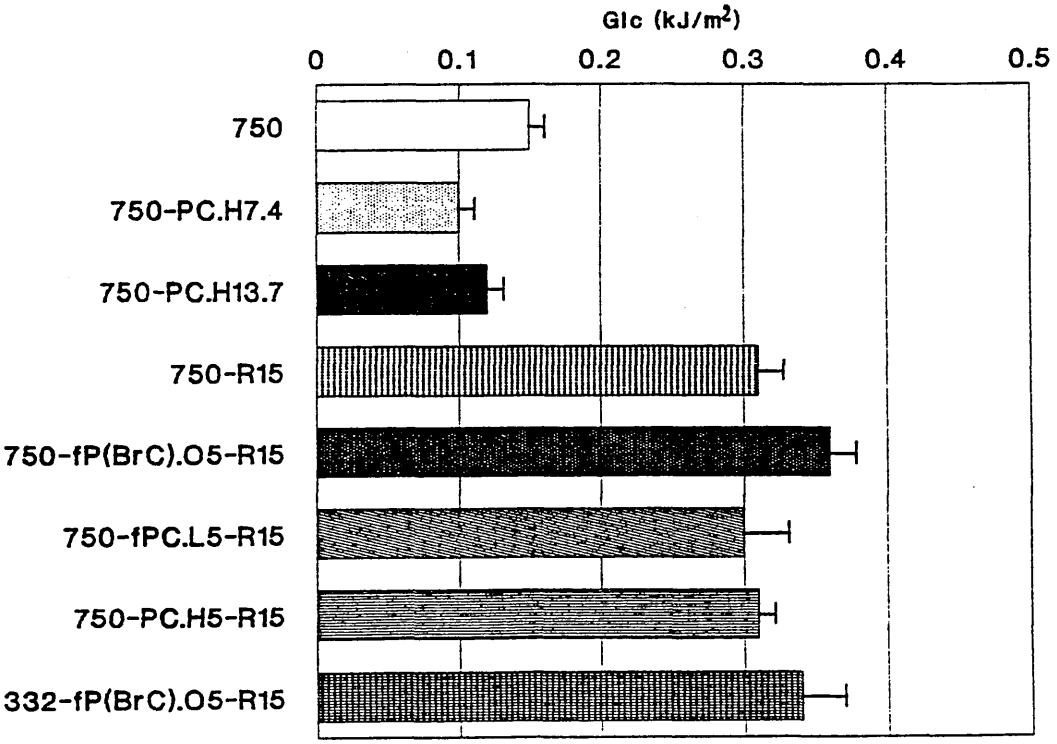


Figure 4.6 : G_{IC} histogram for the corresponding systems.

4.2.3 Conclusions

Whichever of the three polycarbonates is used, covering a wide range of molecular weights (from 2.8 kg/mol to 28.7 kg/mol), with or without reactive end group, bromine substituted or not; the mechanical properties of the rubber-polycarbonate modified epoxy systems are not significantly different from each other or even from the rubber modified epoxy system. Adding rubber or rubber and polycarbonate to the neat epoxy system does not significantly improve its fracture toughness.

Changing the epoxy resin from MY750 to DER332 does not lead to any differences in the mechanical properties of the rubber - fP(BrC).0 polycarbonate modified epoxy system.

4.3 Polyethersulfone modified epoxy systems

E_{100}, σy, K_{IC} and G_{IC} are almost unchanged when 19.2 wt% of fPES is added to the neat epoxy system. Reactive fPES forms a uniform matrix with the epoxy, the mechanical properties of which are not different from that of the neat epoxy matrix.

In contrast, the system 750.PES19.2 shows an appreciable increase in toughness, (50% in K_{IC} and 150% in G_{IC}), but with a larger scatter, in comparison to the neat epoxy system, without any significant loss in Young's modulus or yield stress.

The structure of this system which consists of a network of thermoplastic interpenetrated by a continuous network of thermoset globules is assumed to be responsible for this result. Since both of the phases are continuous, the toughness properties of this blend could be considered as a combination (probably following a rule of mixtures) of the toughness properties of its components: a high toughness thermoplastic-rich phase and a low toughness epoxy-rich phase. The difference of the nature of the area just ahead of the crack tip might explain the scatter observed in the toughness properties: if the epoxy rich phase is majority in this area the fracture toughness should be lower than if it is minority.

CHAPTER 5

INTERACTIONS BETWEEN POLYCARBONATE AND EPOXY RESIN AND INTERACTIONS BETWEEN POLYCARBONATE AND DIAMINE OR ANHYDRIDE HARDENER

The lowering of toughness observed in the polycarbonate modified epoxy systems despite the slight decrease in the yield stress when compared to that of the neat epoxy system, suggested that the epoxy network structure in the polycarbonate modified epoxy systems was different from that of the neat epoxy matrix (see Section 4.1).

The existence of some chemical interactions between polycarbonate and epoxy resin could also explain the observed decrease in the T_g of the PC.H polycarbonate modified epoxy systems below that predicted by the Fox's equation, assuming a complete dissolution of the pure polycarbonate in the epoxy matrix (see Section 3.2.1).

Therefore, IR, GPC and DSC experiments were performed on polycarbonate modified epoxy solutions, with or without hardener in order to find out whether or not chemical interactions between polycarbonate and epoxy or polycarbonate and hardener (diamine or anhydride) could be promoted in these blends during mixing, degassing or curing procedures.

Details of sample preparation for the various experiments dealt with here are given in Section 2.3.

5.1 Interactions between polycarbonate and epoxy resin

5.1.1 Anticipated reaction between carbonate and epoxy groups

Yunzhao Yu and J. P. Bell [68] have shown by DSC experiments on epoxy resin-polycarbonate (with OH end groups) blends, that BTMAC (benzyltrimethyl ammonium chloride) used at 0.2 phr, catalysed a reaction between epoxy resin and polycarbonate. Measurement of the epoxy equivalent value by a standard hydrochlorination method before and after the reaction suggested that the reaction between the epoxy rings and the phenol end groups of polycarbonate (BTMAC is a catalyst for the phenol-epoxy ring reaction) could not account for all the epoxy ring disappearance, and thus that another reaction should be involved.

Using diphenyl carbonate as a model compound they showed that epoxy ring reacted with carbonate group in the presence of the catalyst BTMAC, and that one carbonate group reacted with two epoxy rings.

The reaction is believed to be of an addition coupling type (see Figure 5.1, reaction between epichlorohydrin and diphenyl carbonate).

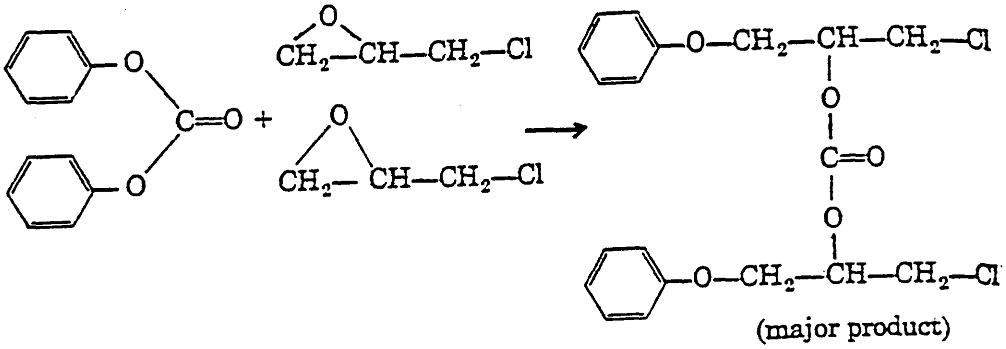


Figure 5.1 : From [68]. The anticipated reaction between epoxy rings and carbonate group.

The polycarbonate oligomers used in their studies were of very low molecular weights, below 0.6 kg/mol and the epoxy resin was similar to the MY750 used in the present study.

They finally showed that the reaction of aromatic carbonate with epoxides could also be catalysed by materials other than quaternary ammonium salt, such as tertiary amines or metal alkoxides.

5.1.2 DSC comparisons between catalysed and uncatalysed epoxy resin-polycarbonate blends

Comparative studies between uncatalysed and BTMAC catalysed polycarbonate-epoxy resin blends have been carried out in order to determine if the epoxy ring-carbonate group reaction occurs in our polycarbonate modified epoxy systems.

All the DSC experiments have been performed using two of the polycarbonates: the functionalised polycarbonate fPC.M and the non functionalised polycarbonate PC.H. Epoxy resin-polycarbonate solutions were prepared following procedure B. BTMAC was added to the blends at 23°C before they were tested.

Comparative dynamic DSC experiments carried out on catalysed and uncatalysed systems (composition in parts by weight ratios) MY750/PC.H/BTMAC = 100/10/0.2 and MY750/PC.H = 100/10 or MY750/fPC.M/BTMAC = 100/10/0.2 and MY750/fPC.M = 100/10 showed the presence of an exothermal peak for the catalysed systems.

This peak could not be seen in the uncatalysed epoxy resin-polycarbonate blends (see Figure 5.2). No exotherm peak could be observed on the DSC trace obtained on the blend

MY750/BTMAC = 100/0.2; this confirms the results of Yu and Bell [68], that BTMAC does not catalyse the homopolymerisation reaction of the epoxy resin. These authors demonstrated that the epoxy value measured by a standard hydrochlorination method did not change significantly in a blend of epoxy resin and BTMAC (at 0.2 phr) before and after 1h at 120°C.

Thus, the peak observed in our catalysed epoxy resin-polycarbonate blends is evidence for some reaction between polycarbonate and epoxy resin.

The absence of exotherm peak in the uncatalysed systems does not necessarily mean that the polycarbonate-epoxy reaction does not occur in these blends. It could also mean that the reaction is very slow or/and does not involve enough epoxy and carbonate groups to be detected by DSC.

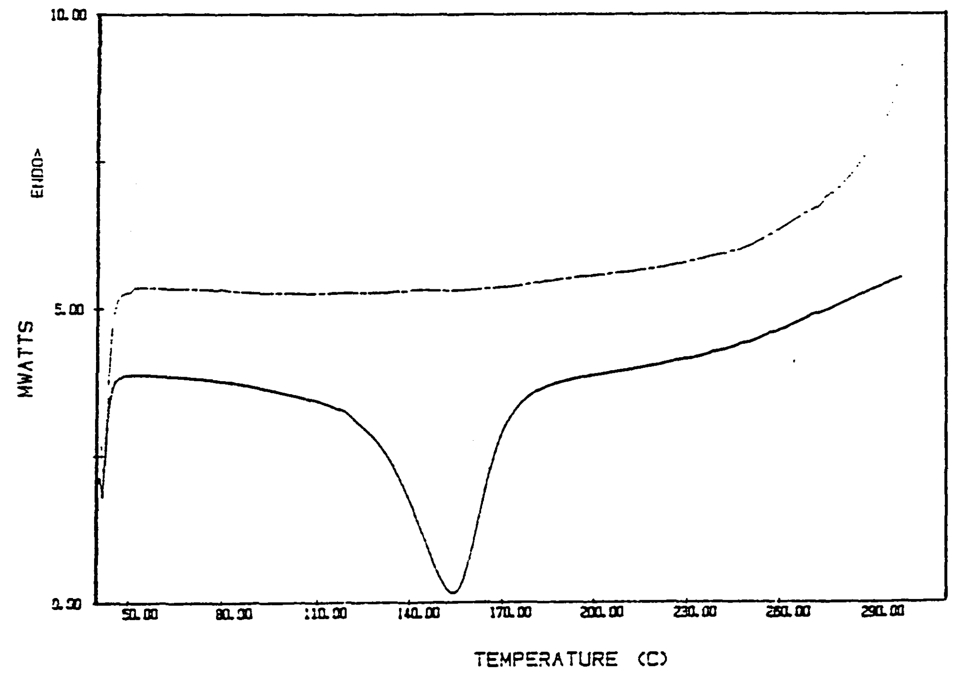


Figure 5.2 : Dynamic DSC comparison between catalysed and uncatalysed polycarbonate-epoxy resin blends.
—— - ——: blend MY750/PC.H = 100/10
————: blend MY750/PC.H/BTMAC = 100/10/0.2.

5.1.3 IR characteristics of the epoxy ring - carbonate group reaction

To obtain more specific information about the epoxy polycarbonate reaction, IR experiments have been carried out on the relevant blends. All the experiments were performed, using the two polycarbonates fPC.M and PC.H at 23°C and 80°C, 150°C, the curing temperatures of the epoxy resin plaques cured with DDM.

In order to check if the KBr itself might promote a reaction between polycarbonate and epoxy resin, dynamic DSC run experiments have been carried out on the blend MY750/PC.H/KBr = 100/10/4 (KBr was added to the epoxy resin-polycarbonate solution at 23°C, before the DSC run). They showed an exothermal peak the maximum of which occurs at around 220°C, suggesting that the KBr (i.e. K^+ or Br^-) is a catalyst for the polycarbonate-epoxy reaction (see Figure 5.3). Its catalytic power is lower than that of the BTMAC (the maximum of the peak for the BTMAC catalysed epoxy resin-polycarbonate blends occurs at 154°C).

Thus precise conclusions from IR experiments about polycarbonate-epoxy reaction are difficult to draw. The catalytic effect of the KBr could be considered as a 'baseline' for all the experiments on polycarbonate modified epoxy blends carried out at temperatures above 23°C between two KBr discs in the IR hot cell.

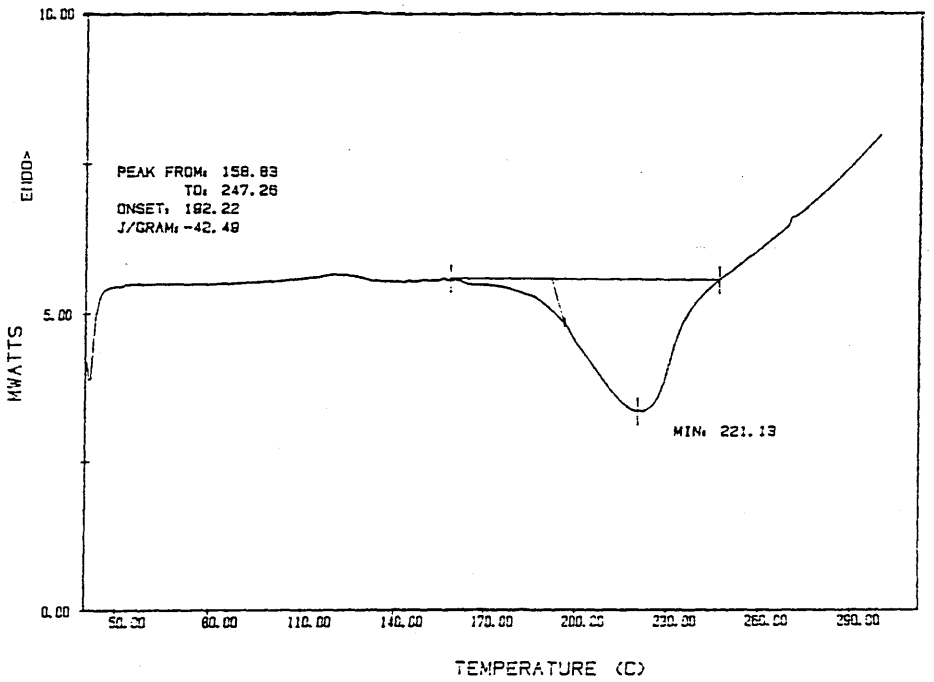


Figure 5.3 : Dynamic DSC run on the blend MY750/PC.H/KBr = 100/10/4.

Figures 5.4 and 5.5 show the variation of the transmittance in IR between 1600 cm^{-1} and 1950 cm^{-1} with time and temperature (23°C, 80°C, 150°C) for the blends MY750/fPC.M/BTMAC = 100/10/0.2 (BTMAC was added to the epoxy resin-polycarbonate solutions at 23°C) and MY750/fPC.M = 100/10. The evolution of the transmittance, in this area, is the same for the blends with PC.H.

In the catalysed systems, the shoulder that appears around 1810 cm^{-1} on the carbonate group peak and turns into a peak with increasing time and temperature is due to a reaction involving the carbonate group. It is believed that this reaction is the epoxy ring-carbonate group reaction proposed by Yu and Bell [68], although no significant decrease in the epoxy ring concentration (established by looking at the height of the epoxy peak at 915 cm^{-1} could be observed).

The same phenomenon happens in the uncatalysed blends but the amount of reaction is lower than in the catalysed blends. The shoulder on the carbonate group peak is less pronounced, at a given time and temperature, in the uncatalysed blends than in the catalysed blends.

Looking at the OH group peak (around 3200 cm^{-1}) could not bring any clear evidence for a reaction between epoxy resin and functionalised polycarbonate through their OH end groups in either the catalysed or uncatalysed epoxy resin-polycarbonate blends. Indeed, OH groups initially present in the epoxy resin and those generated during the epoxy-DDM reaction did not let us conclude about the evolution of the OH group peak related to this polycarbonate OH end group-epoxy ring reaction.

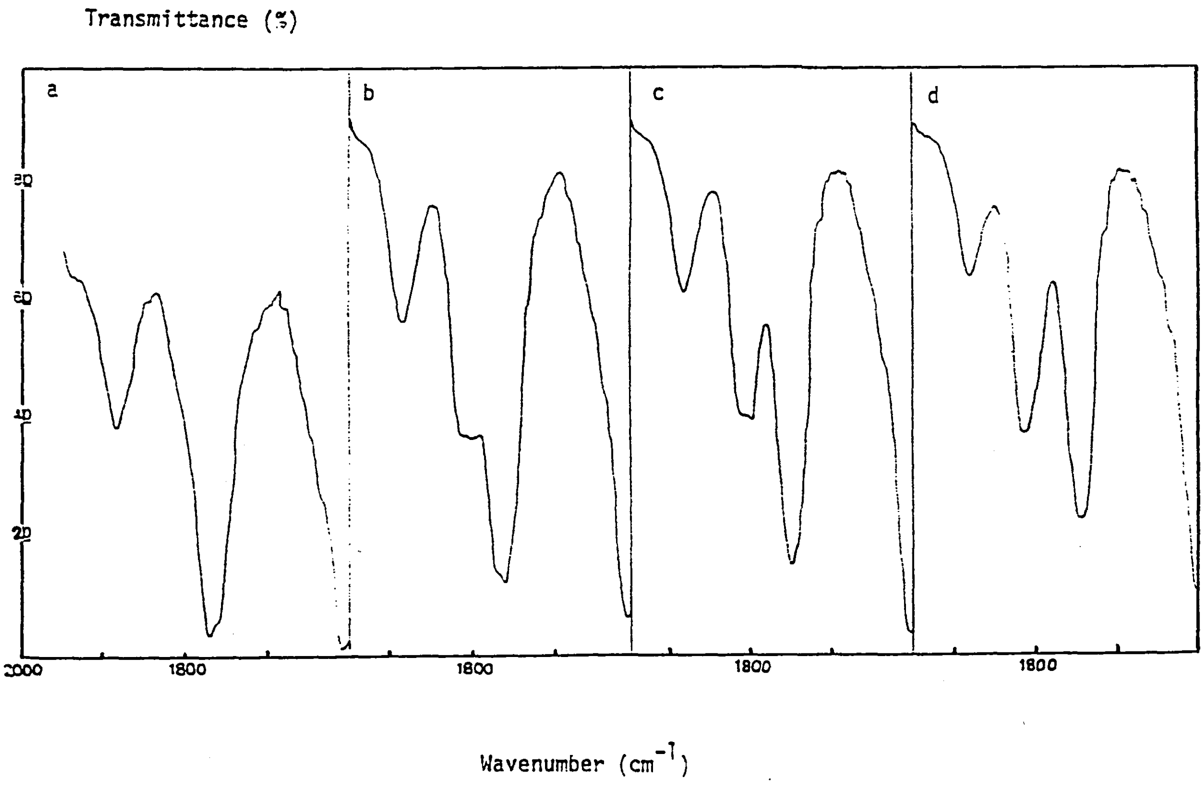


Figure 5.4 : IR spectra of MY750/fPC.M/BTMAC = 100/10/0.2 blend.
a: 23°C - b: 35 mins at 80°C - c: 3h 32 mins at 80°C - d: 4h 10 mins at 80°C and 20 mins at 150°C.

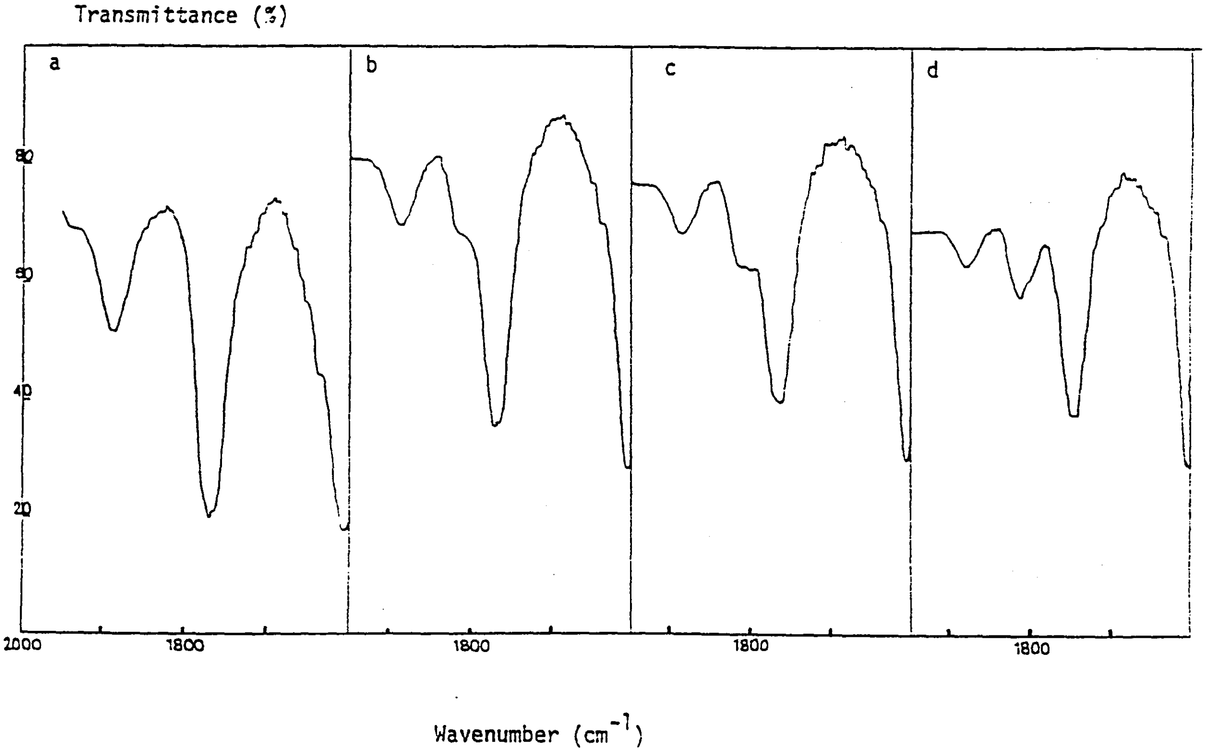


Figure 5.5: IR spectra of MY750/fPC.M = 100/10 blend. a: 23°C - b: 31 mins at 80°C - c: 3h 07 mins at 80°C - d: 3h 07 mins at 80°C and 1h 04 mins at 150°C.

5.1.4 The epoxy ring-carbonate group reaction during cure of the polycarbonate -epoxy resin blends with DDM.

The rate of the epoxy ring-carbonate group reaction is lower in the epoxy resin-polycarbonate-hardener blends than in the epoxy resin-polycarbonate blends as the epoxy groups preferentially react with the reactive group of the hardener. A comparison is to be made between the height of the shoulder on the carbonate group peak of the same polycarbonate-epoxy resin blend with an without the DDM hardener at the end of the epoxy-DDM reaction (Figure 5.5 and 5.6).

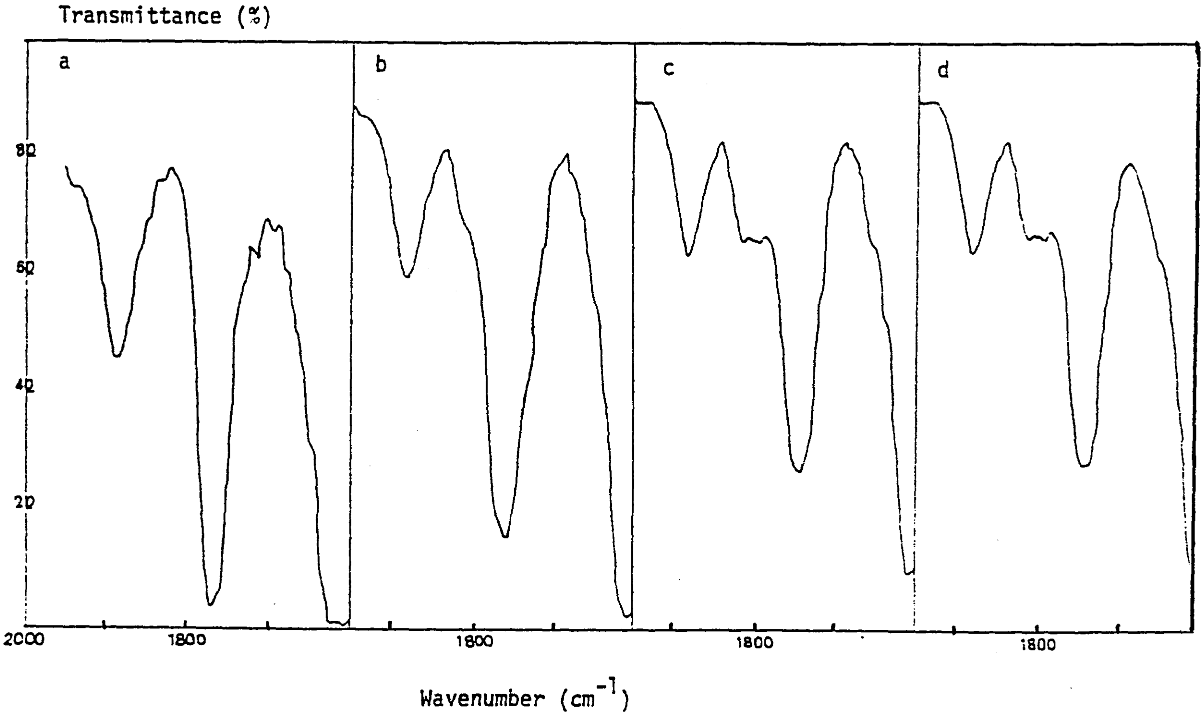


Figure 5.6 : IR spectra of MY750/fPC.M/DDM = 100/10/26 blend. a: 23°C - b: 3h 32 mins at 80°C - c: 7h 16 mins at 80°C and 1h 14 mins at 150°C - d: 7h 16 mins at 80°C and 3h 31 mins at 150°C.

Thus, most of the epoxy ring-carbonate group reaction should occur during the mixing and degassing steps of the preparation of our polycarbonate modified systems than after the hardener is added and the cure starts.

Therefore, the effect of the mixing and degassing procedures upon the epoxy-polycarbonate reaction has been investigated.

5.1.5 The epoxy ring-carbonate group reaction during the mixing and degassing of the epoxy resin-polycarbonate blends

Figure 5.7 shows the evolution of the IR spectra of the carbonate group peak obtained at 23°C from small samples taken at regular time intervals from the blend MY750/PC.H = 100/10 kept in a beaker at 120°C, the temperature of the mixing of the procedure B used to prepare most of the polycarbonate-epoxy resin blends (see Section 2.2.1).

Figure 5.8 shows the evolution of the IR spectra of the carbonate group peak of the same blend but obtained directly at regular intervals in the IR hot cell with the sample between two KBr discs at 120°C.

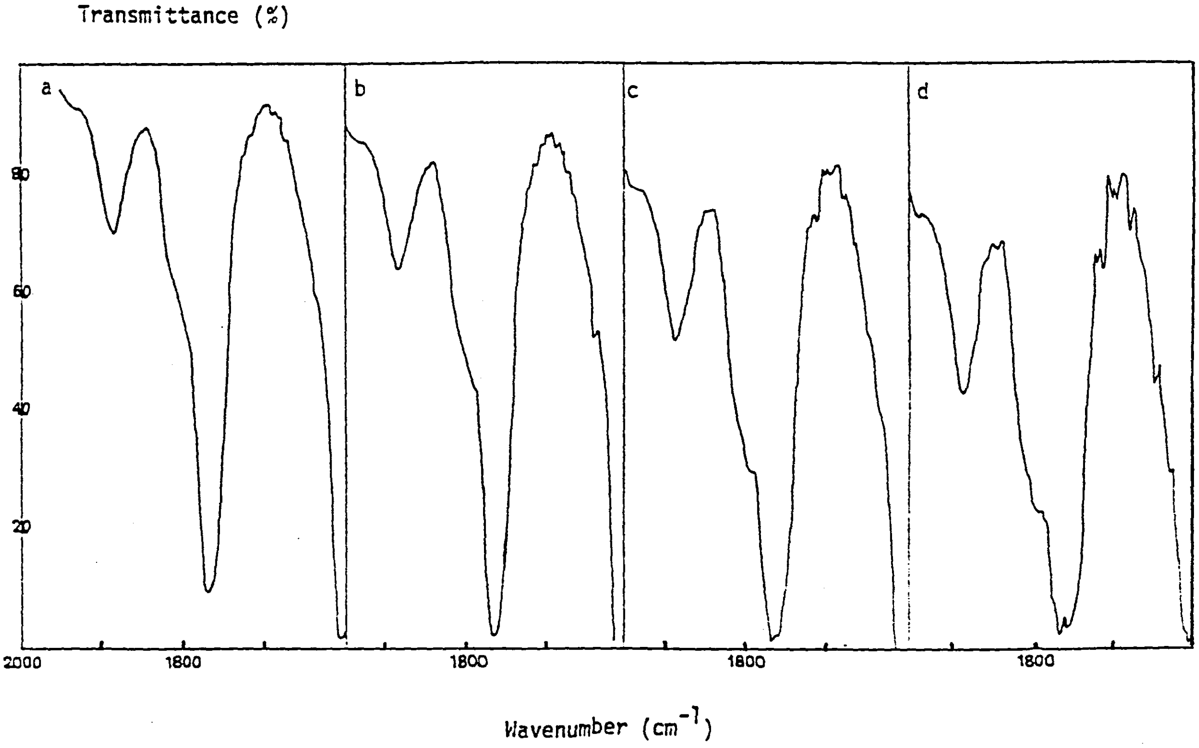


Figure 5.7 : IR spectra of MY750/PC.H = 100/10 blend; reaction in a beaker at 120°C.
a: 30 mins - b: 1h - c: 2h - d: 3h 25 mins.

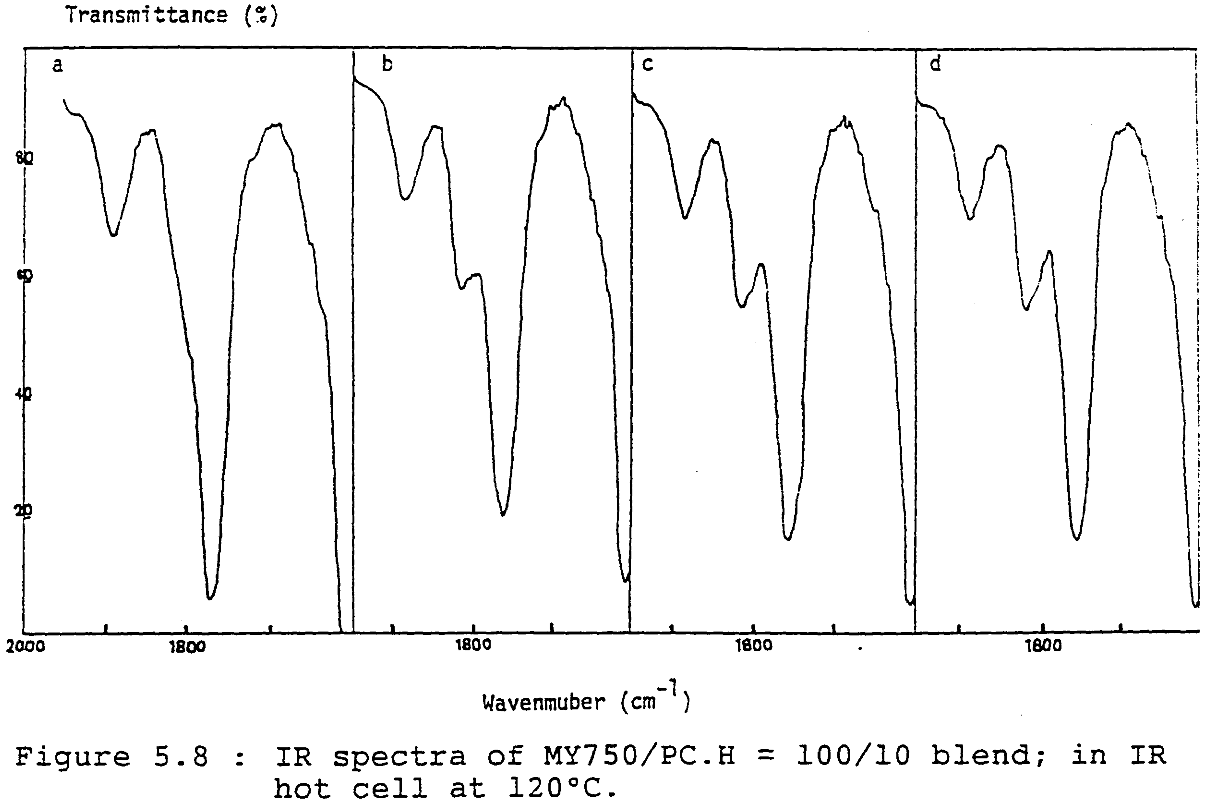


Figure 5.8 : IR spectra of MY750/PC.H = 100/10 blend; in IR hot cell at 120°C.
a: 30 mins - b: 1h - c: 2h -d: 3h 10 mins.

There is only a shoulder on the carbonate group peak even after 3h in the beaker at 120°C compared to the fairly big peak, characteristic of the epoxy ring-carbonate group reaction, after the same time in the IR hot cell at 120°C. This suggests that, in epoxy resin-polycarbonate blends, without any catalyst (BTMAC or KBr), the epoxy-carbonate reaction might be considerably lowered, to such a degree it cannot be detected by dynamic DSC experiments for instance.

Comparing Figure 5.7 and 5.8 also brings to the fore the catalytic effect of KBr upon this reaction.

The effect of the degassing procedure upon the epoxy-polycarbonate reaction is shown on the IR spectra obtained from the blends MY750/fPC.M = 100/10 and MY750/PC.H = 100/10 before and after the degassing procedure (1h at 100°C - 110°C) (see Figure 5.9).

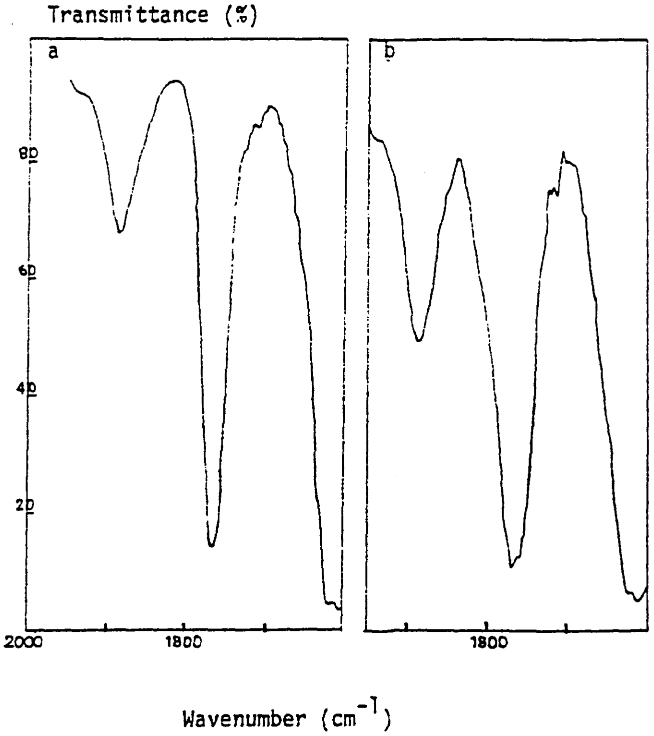


Figure 5.9 : IR spectra of MY750/fPC.M = 100/10 blend.
a: 23°C without degassing procedure
b: 23°C after degassing procedure.

The carbonate peaks for the non-degassed epoxy resin-polycarbonate blends are spread from 1700 cm^{-1} to 1820 cm^{-1} and are quite sharp whereas those for the degassed epoxy resin-polycarbonate blends are spread from 1700 cm^{-1} to 1840 cm^{-1} with a slight bulge around 1820 cm^{-1} (see Figure 5.9).

The mixing (at 120°C for a maximum of 1h) and degassing (1h at 100°C - 110°C) procedures employed with the epoxy resin-polycarbonate blends seem to promote some interactions between epoxy resin and carbonate groups rather than a reaction between epoxy rings and carbonate groups, because the features appearing on the carbonate group peak in IR after these procedures are less pronounced and different from those characteristic of the epoxy-carbonate reaction.

In order to check the validity of this assumption, GPC experiments have been performed on the corresponding blends.

5.1.6 Reaction or degradation ?

The GPC chromatogram obtained on the blend MY750/PC.H = 100/10 after the degassing procedure of 1h at 100°C - 110°C show the absence of the pure polycarbonate peak and the presence of a new broad round peak that falls between the pure PC.H and pure MY750 peaks. Increasing the time of the usual degassing procedure from 1h to 2h at 100°C - 110°C slightly shifts the position of this new peak to the higher elution times (see Figures 5.10 and 5.11). This round peak is absent from the chromatogram of the epoxy resin MY750 after 1h at 100°C - 110°C, thus it cannot be accounted for by any unexpected homopolymerisation of the resin.

This round peak is believed to correspond to a degraded polycarbonate of lower molecular weight than the pure PC.H.

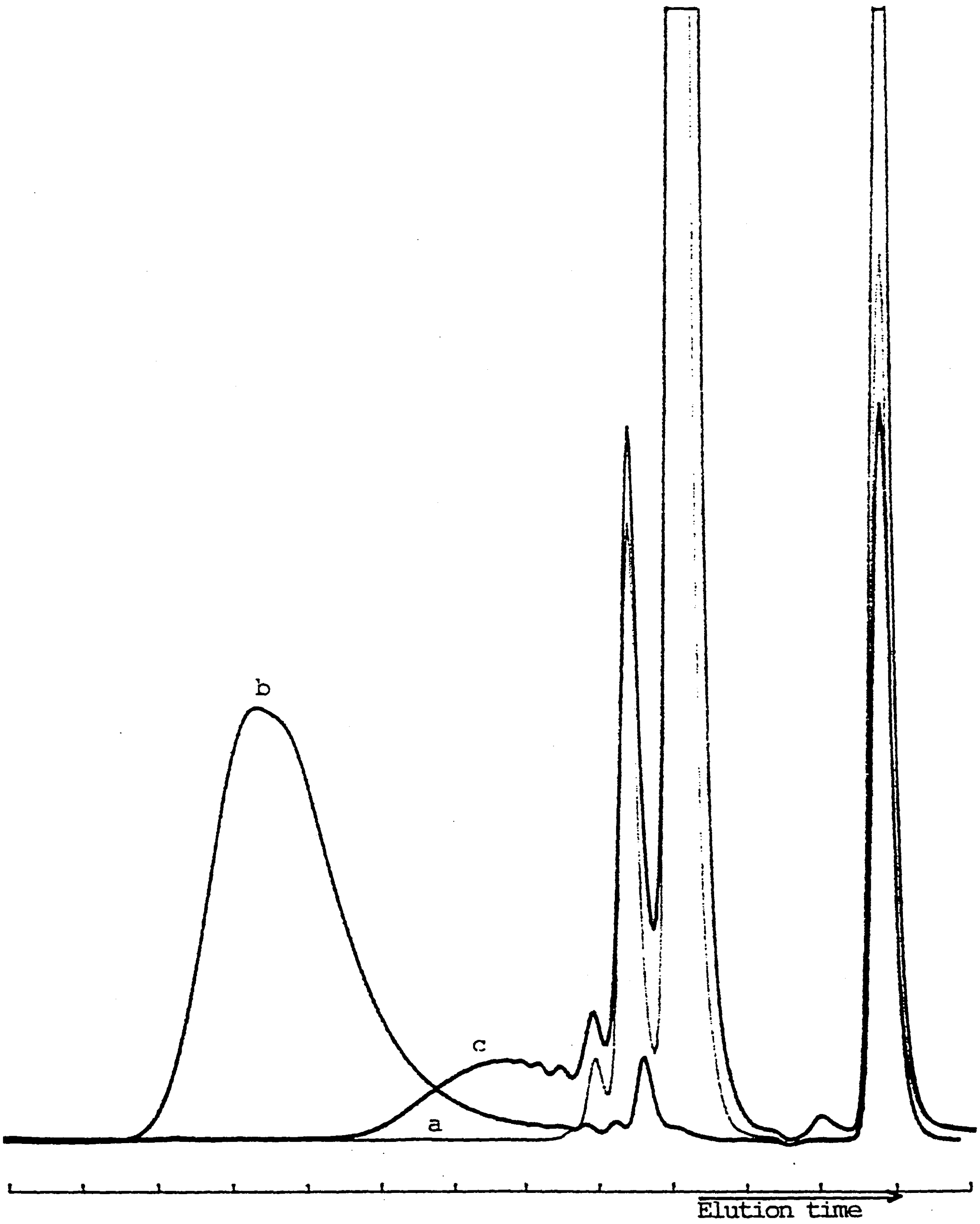


Figure 5.10 : Chromatogram comparison.
a: epoxy resin MY750
b: polycarbonate PC.H
c: blend MY750/PC.H = 100/10 after 1h at 100°C-110°C under vacuum.

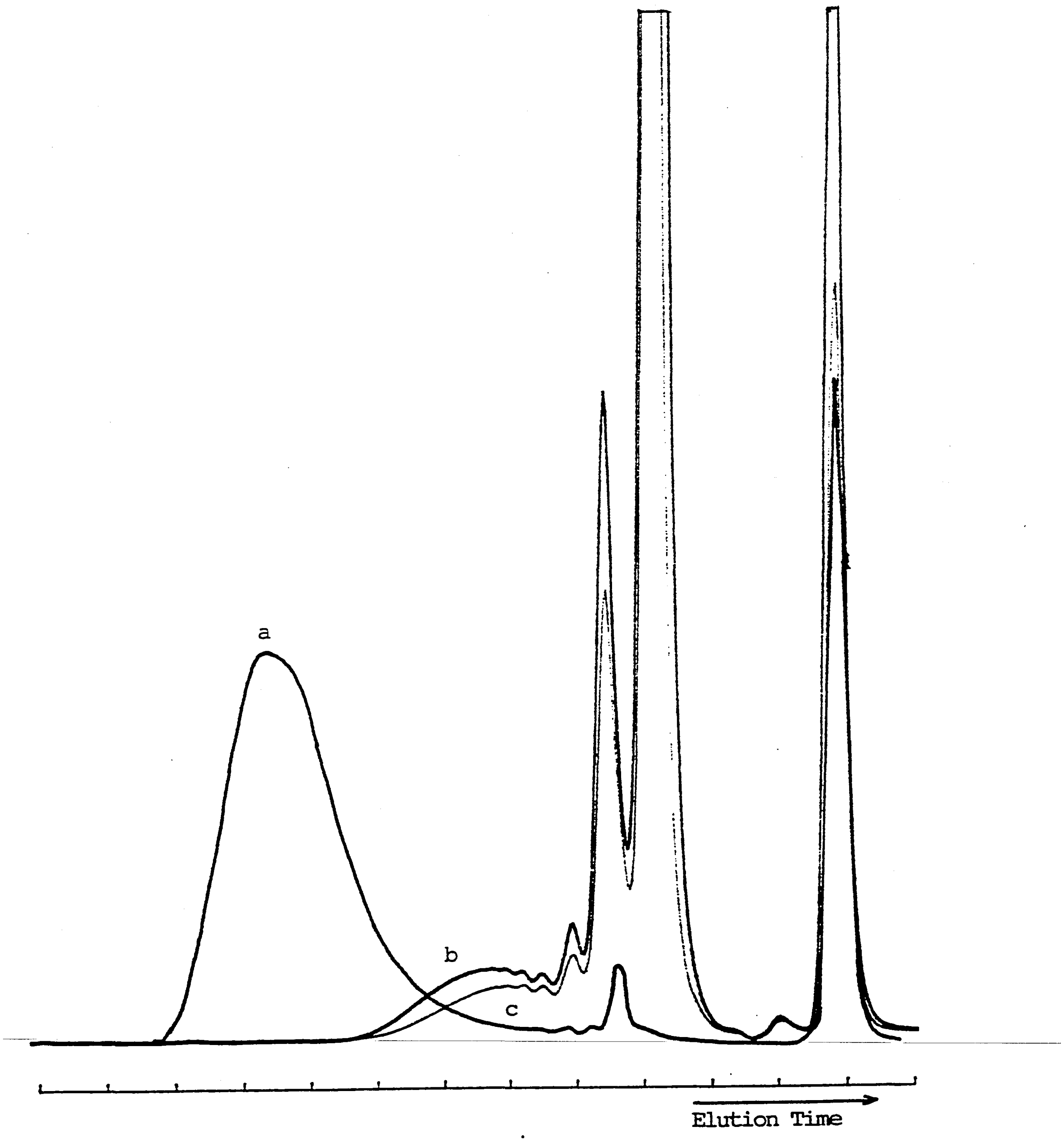


Figure 5.11 : Chromatogram comparison.
a: polycarbonate PC.H
b: blend MY750/PC.H = 100/10 after 1h at 100°C - 110°C under vacuum
c: blend MY750/PC.H = 100/10 after 2h at 100°C - 110°C under vacuum.

Thus, the polycarbonate chains are cleaved in the presence of epoxy resin at 100°C - 110°C. This split of the polycarbonate chains increases with time at 100°C - 110°C as demonstrated by the simultaneous slight shift of this new round peak to the higher elution times. If there was a reaction between epoxy resin and the degraded polycarbonate, it should be less important than the degradation of the polycarbonate. Indeed, the opposite would have shifted the position of the round peak to the lower elution time when increasing the time of reaction from 1h to 2h at 100°C - 110°C.

The small peak corresponding to a species of lower molecular weight than epoxy resin that appears in the blend MY750/PC.H = 10/10 after 1h or 2h at 100°C - 110°C could also indicate some degradation of the epoxy resin.

The widely spread peak shown on the GPC chromatogram of the catalysed blend MY750/PC.H/BTMAC = 100/10/2 after 2h at 100°C - 110°C, the position of which is between the polycarbonate and epoxy resin peaks, is evidence for some reaction between the degraded polycarbonate and the epoxy resin (see Figure 5.12). This peak is believed to result from two competitive phenomena : the degradation of the polycarbonate and the reaction between epoxy resin and this degraded polycarbonate which shift the position of this peak to the lower and higher molecular weights respectively.
The presence of degraded polycarbonate in the epoxy polycarbonate blends, resulting from the mixing procedure at 120°C, before the BTMAC was added, might also influence the molecular weight of the epoxy-carbonate compound formed and so the position of the corresponding peak.

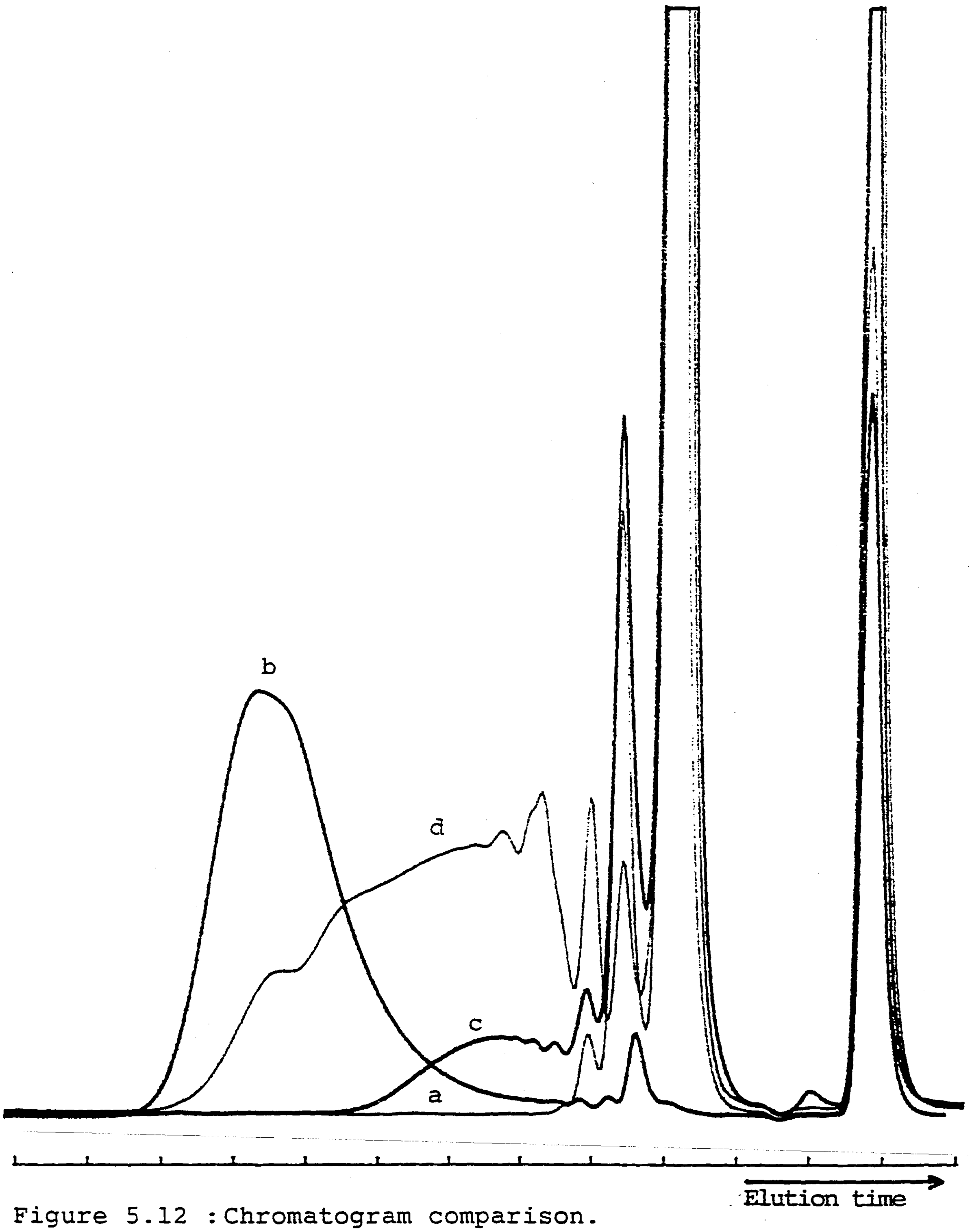


Figure 5.12 : Chromatogram comparison.
a: epoxy resin MY750
b: polycarbonate PC.H
c: blend MY750/PC.H = 100/10 after 1 h at 100°C - 110°C under vacuum
d: blend MY750/PC.H/BrMAc = 100/10/2 after 2h at 100°C - 110°C under vacuum.

In this catalysed blend (as in the uncatalysed) no formation of a material of higher molecular weight than PC.H (i.e. no peak of shorter elution time than that of PC.H) could be demonstrated.

5.2 Degradation of the polycarbonate by the hardener or accelerator

5.2.1 Degradation of polycarbonate with DDM

During the cure of the blends MY750/fPC.M/DDM = 100/10/26 or MY750/PC.H/DDM = 100/10/26 in the IR hot cell, as soon as the temperature reached 150°C, after the first cure step at 80°C for 6 hours, a very sharp peak, which could be identified as the CO_2 peak appeared and disappeared, in about 50 mins at 2330 cm^{-1}. This peak was not observed in the blend MY750/DDM = 100/26 and MY750/fPC.M or PC.H = 100/10. Hence, the reaction between polycarbonate and DDM was investigated.

This CO_2 peak could not be seen in the blends DDM/fPC.M = 100/10 or DDM/PC.H = 100/10. The CO_2 produced by a reaction of the polycarbonate could be removed very quickly because of the very low viscosity of these blends at temperatures above 90°C and the very small thickness of the samples. That probably is the reason why it could not be detected by IR measurements. But because of the very high viscosity at 150°C of the polycarbonate modified epoxy systems cured with DDM, the CO_2 produced could be trapped in the IR sample for a while and detected before getting out of the blend. Figure 5.13 shows the evolution of the carbonate group peak in the DDM/PC.H = 100/10 sample with time and temperature (23°C to 150°C). The height of the carbonate group peak decreases with time and temperature as a new peak appears at 1735 cm^{-1} (Fig. 5.13c), then the carbonate group peak disappears, as well as the peak at 1735 cm^{-1}. This is evidence for degradation of the polycarbonate and perhaps of the hardener. This degradation seems to be very fast at temperatures above 120°C.

The CO_2 peak observed in the polycarbonate modified epoxy blends is believed to be due to a degradation of the polycarbonate by the DDM.

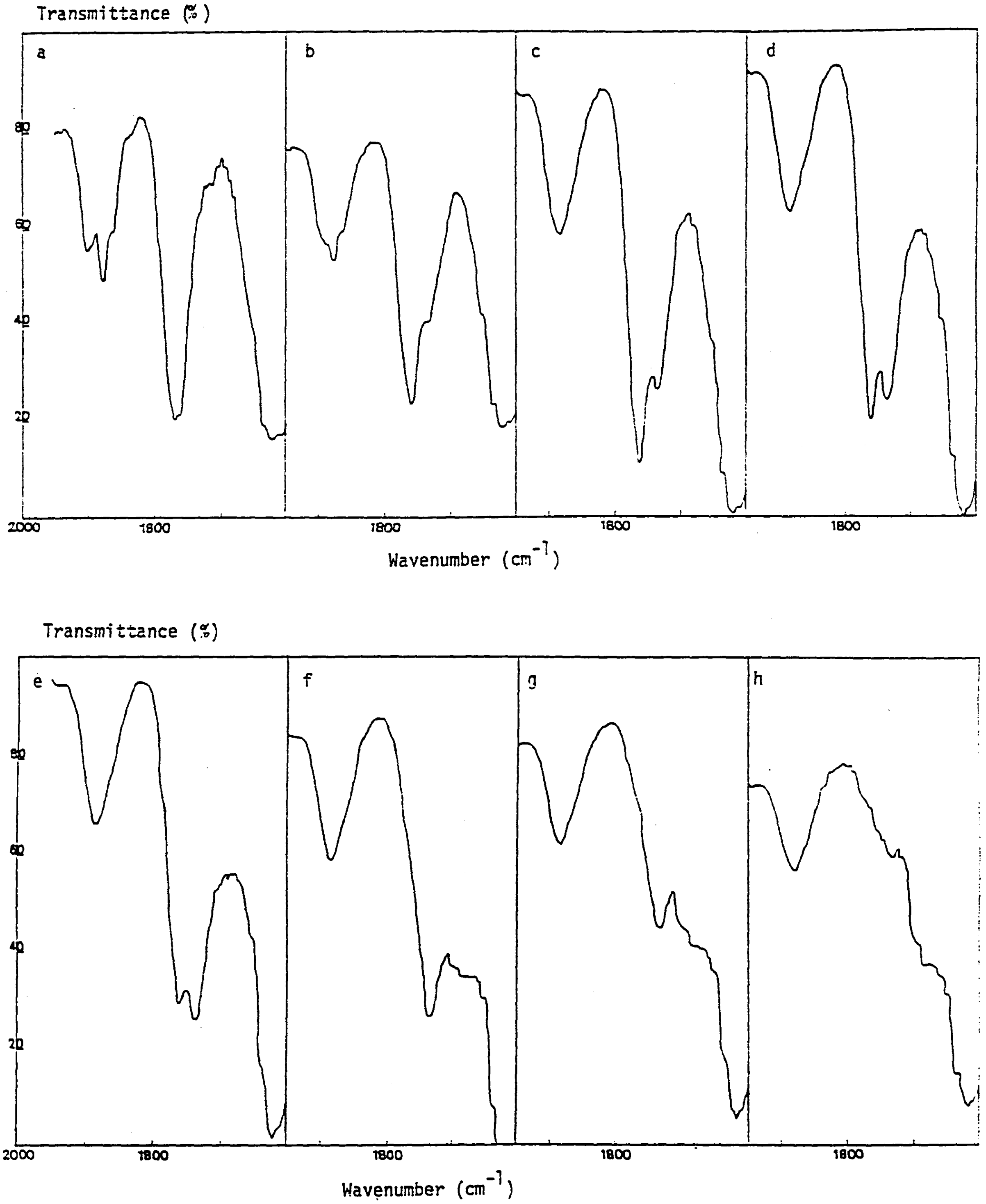


Figure 5.13 : IR spectra of DDM/PC.H = 110/10 blend. a: 23°C - b: 3h at 80°C - c: plus 97 mins at 90°C - d: plus 74 mins at 100°C - e: plus 6 mins at 120°C - f: plus 83 mins at 120°C - g: plus 19 mins at 130°C - h: plus 13 mins at 150°C.

The degradation of polycarbonate with DDM is believed to follow the scheme shown in Figure 5.14.

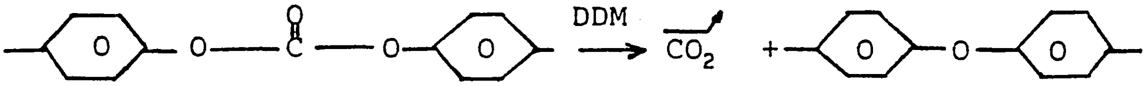


Figure 5.14 : Degradation of polycarbonate with DDM through its carbonate group.

Nevertheless, no decrease of the carbonate group peak was observed in the polycarbonate modified epoxy blends cured with DDM. Because most of the DDM preferentially reacts with the epoxy rings during the cure of these blends; this prevents a large amount of polycarbonate from being degraded by the DDM.

5.2.2 Degradation of the polycarbonate, in the polycarbonate-epoxy resin blends cured with anhydride hardener and accelerator

Figure 5.15 shows the evolution of the carbonate group peak in IR with time at 80°C, in a blend of epoxy resin, polycarbonate and the accelerator used with the anhydride hardener.

A new peak appears very quickly at around 1810 cm^{-1}. This peak is believed to be evidence for some reaction between polycarbonate and epoxy, (see Section 5.1). Meanwhile, the carbonate group peak at 1770 cm^{-1} decreases as the CO_2 peak at 2300 cm^{-1} appears and disappears in less than 30 mins. This is evidence for some degradation of the carbonate group.

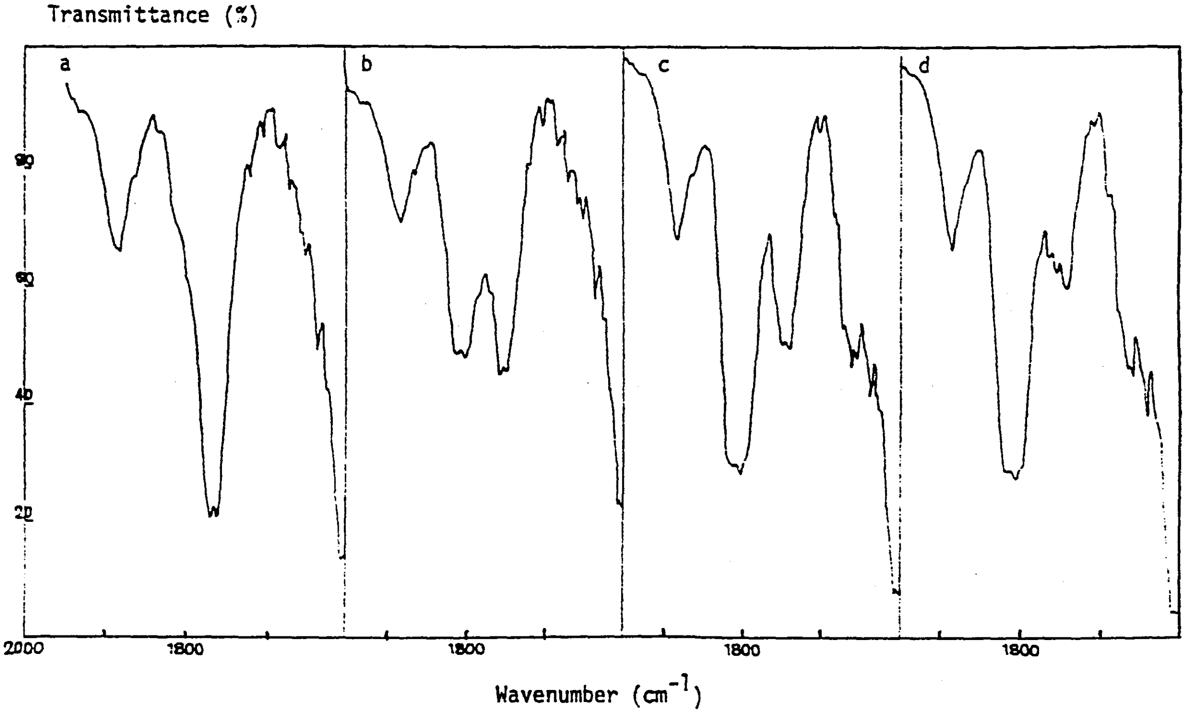


Figure 5.15 : IR spectra of MY750/PC.H/DY070 = 100/10/1 blend. a: 23°C - b: 5 mins at 80°C - c: 30 mins at 80°C - d: 2h 20 mins at 80°C.

The accelerator promotes the epoxy ring-carbonate group reaction and the degradation of the carbonate group.

This phenomenon is believed to be still present when the polycarbonate modified epoxy blends are cured with the anhydride hardener and the accelerator, although the IR examination of the carbonate group peak area during the cure of the corresponding blends in the IR hot cell did not show any clear evidence for this assumption. The superposition of the two strong anhydride group peaks at 1750 cm^{-1} and 1800 cm^{-1} (cyclic anhydride) with the carbonate group peak at 1770 cm^{-1} made the examination of this area very difficult to follow. The shape evolution of that area was dominated by the reaction mechanisms involving the anhydride group.

The absence of CO_2 peak in these blends does not mean that the polycarbonate was not degraded. Because of the very low viscosity of these blends at 80°C, before gelation, the CO_2 could be removed very easily and not detected by IR measurement.

5.3 Accelerating effect promoted by the polycarbonate on the epoxy resin-diamine hardener (DDM) reaction

This effect was studied by dynamic DSC in neat and polycarbonate modified epoxy blends, by the examination of the temperature of the minimum of the exothermal peak corresponding to the epoxy-DDM reaction.

Tables of results and an example of the DSC thermograms are in Appendix H.

5.3.1 Influence of polycarbonate molecular weight and polycarbonate content upon the catalytic effect

Figures 5.16 and 5.17 show the variations of the temperature of the minimum of the exothermal peak in the functionalised polycarbonate modified epoxy blends, prepared following procedure A, against polycarbonate content and polycarbonate molecular weight. The position of this minimum is shifted to lower temperatures, which means that the rate of the epoxy-DDM reaction is increased, with the increase of the polycarbonate content or the polycarbonate molecular weight.

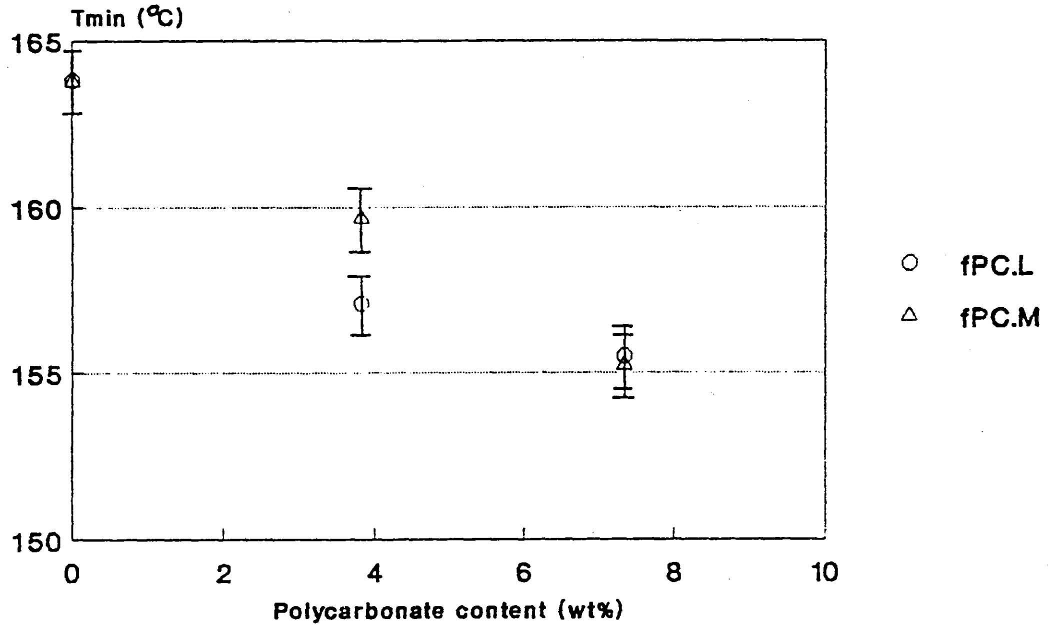


Figure 5.16 : Variation of the minimum of the exothermal peak in DSC for the functionalised polycarbonate modified epoxy blends cured with DDM, against polycarbonate content.

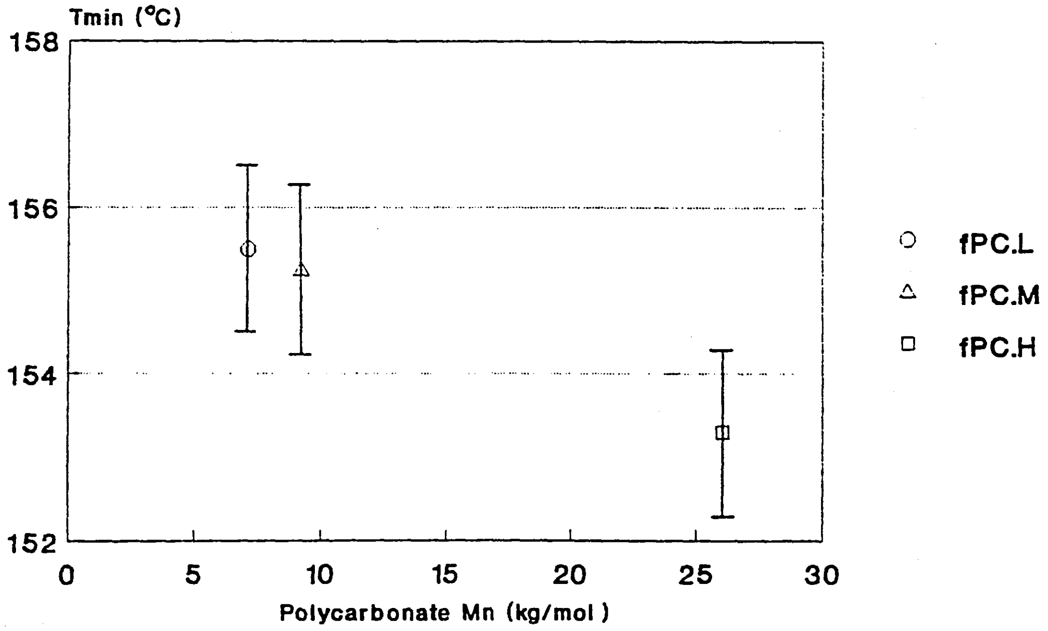


Figure 5.17 : Variation of the minimum of the exothermal peak in DSC for the functionalised polycarbonate modified epoxy blends (polycarbonate content 7.4 wt%), against polycarbonate molecular weight.

5.3.2 Influence of the degassing time upon the catalytic effect

The rate of the MY750-DDM reaction also increases with the degassing time of the epoxy polycarbonate blends at 100°C - 110°C, before the DDM hardener is added (see Figure 5.18).

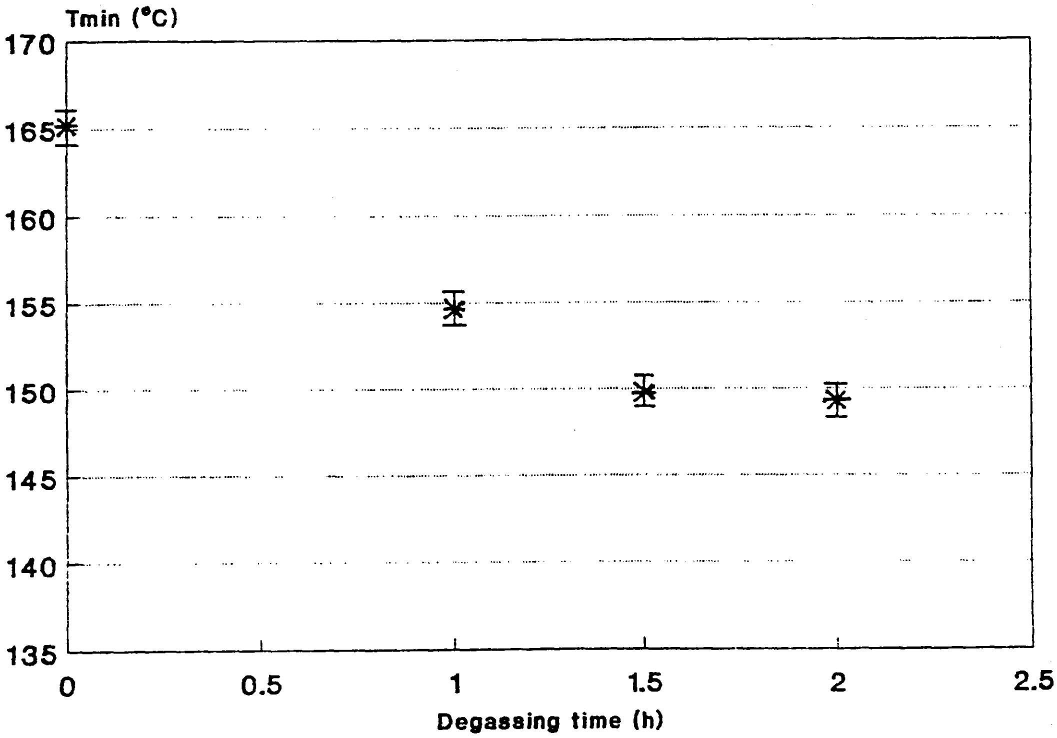


Figure 5.18 : Variation of the minimum of the exothermal peak in DSC for the blend MY750/PC.H/DDM = 100/10/26, against the degassing time of the epoxy polycarbonate blend at 100°C - 110°C.

5.3.3 Influence of the solvent upon the catalytic effect

This influence has been shown by the following experiment:

i) The blend MY750/PC.H = 100/10 has been degassed for 2h at 100°C - 100°C.

ii) The stoichiometric ratio of DDM was added to give the blend MY750/PC.H/DDM = 100/10/26.

iii) The position of the minimum of the exothermal peak for this blend was 149.0°C.

iiii) Then, this blend has been dissolved in a larger amount of dichloromethane than was present at the end of the degassing procedure in i).

iiiii) The position of the minimum of the exothermal peak for the blend MY750/PC.H/DDM = 100/10/30 dissolved in solvent was then 153.1°C.

This decrease of the rate of the MY750-DDM reaction when some solvent is added to the epoxy resin-polycarbonate-hardener blend has not been noted when the same amount of solvent was added to the neat blend MY750/DDM = 100/26.

5.3.4 Discussion

It seems reasonable to assume that for a given time at a given temperature, the number of 'degraded polycarbonate entities', in an epoxy resin-polycarbonate blend, increases with polycarbonate molecular weight or polycarbonate content and that for the same epoxy resin-polycarbonate blend, it increases with time, at the same temperature.

The catalytic effect promoted by polycarbonate upon the epoxy-DDM reaction follows the same tendencies: it increases with polycarbonate molecular weight or polycarbonate content and with degassing time at 110°C - 120°C.

This catalytic effect is therefore believed to be due to the 'degraded polycarbonate entities'.

It can be proposed that the catalytic effect is not due to these 'degraded polycarbonate entities' but to the polycarbonate on its own and its increase with time of degassing is due to the removal of the solvent from the epoxy polycarbonate blend since the solvent can hide the catalytic effect (see Section 5.3.3). Though, a total reversibility of the catalytic effect would have been noticed when some solvent had been added to a polycarbonate modified epoxy hardener blend, this was not found to be the case (see Section 5.3.3).

Thus, the catalytic effect is believed to be dependent upon the number of 'degraded polycarbonate entities' present in the epoxy resin-polycarbonate blend when the DDM hardener is added. This catalytic effect increases with the number of these 'entities'.

5.4 Conclusions

It is important to summarise the results of this section by detailing what happens during the different steps of the preparation of our polycarbonate modified epoxy systems cured with DDM.

The cleaving-degradation of the polycarbonate by the epoxy resin begins during the mixing of the polycarbonate solvent solutions with the hot epoxy resin at 80°C or 120°C, depending on the procedure used (A or B). It carries on during the degassing of the epoxy resin-polycarbonate blends at 100°C - 110°C for 1h. Simultaneously, it is likely that some epoxy resin is also degraded.

These 'degraded polycarbonate entities' accelerate the epoxy-DDM reaction. Some degradation of polycarbonate by the

DDM can also occur, but it is nevertheless restricted since the hardener preferentially reacts with the epoxy resin.

The degradation of the polycarbonate which increases with time and temperature is likely to happen the most before the hardener is added, that is during the mixing and degassing steps.

Finally, no clear evidence of a reaction between epoxy resin and polycarbonate or 'degraded polycarbonate' has been found in our uncatalysed blends. It seems reasonable to assume that a reaction between polycarbonate OH end groups and epoxy rings in epoxy resin-functionalised polycarbonate blends should be of lower importance in comparison to the degradation of the polycarbonate.

CHAPTER 6
DISCUSSION

6.1 Overall view of the programme

As discussed in Section 1.3.2, toughenability of the matrix is a very important parameter in the toughening of epoxy systems by rubber or thermoplastic particles.

The initial objective of this programme was to improve the toughenability of a highly cross-linked DGEBA epoxy matrix by homogeneously blending in an amorphous thermoplastic.

Polycarbonate was the thermoplastic chosen. Different grades and types of polycarbonates were available : from low molecular weight functionalised to high molecular weight with no reactive end group polycarbonates.

The work carried out is divided in three main parts:

i) We investigated the compatibility between epoxy resin and the different polycarbonates. The polycarbonate did not phase separate in most of the epoxy resin-polycarbonate systems cured with DDM, DDS or anhydride hardener (see Chapter 3).

ii) To study the effect of the polycarbonates upon enhancement of the toughenability of the matrix when modified by rubber particles, we decided that the type of polycarbonate should be the parameter to vary.

Three polycarbonates were selected : a bromine substituted polycarbonate oligomer with phenolic OH end groups (fP(BrC).O), a low molecular weight polycarbonate with phenolic OH end groups (fPC.L) and a high molecular weight polycarbonate with no reactive end group (PC.H).

They were used at 5 wt% in combination with 15 wt% rubber. The characteristics (see Chapter 3) and mechanical properties of polycarbonate, rubber and rubber-polycarbonate modified epoxy systems as well as those of the corresponding unmodified epoxy system were investigated.

iii) The catalytic effect of polycarbonate upon the DGEBA-DDM reaction noted during the curing of the plaques, as well as the observed decrease in toughness of the polycarbonate modified epoxy systems with increasing polycarbonate content suggested a need for a study of possible chemical interactions between epoxy resin and polycarbonate and between hardener and polycarbonate (see Chapter 5).

The major results that come out of this work are the unexpected degradation of the polycarbonate by the epoxy resin and the lack of toughness improvement achieved either in the rubber or in the rubber-polycarbonate modified epoxy systems. The discussion will be structured in three parts:

i) The relationship between degradation of the polycarbonate and phase separation in epoxy resin-polycarbonate blends will be drawn.

ii) The reasons why no significant toughness enhancement was achieved in the rubber modified epoxy system will be examined.

iii) The failure of the polycarbonate to increase the toughenability of the epoxy matrix will be related to its degradation.

6.2 <u>Phase separation and degradation of polycarbonate in epoxy resin-polycarbonate blends</u>

The absence of phase separation noted in most of the polycarbonate modified epoxy blends, is closely linked to the degradation of polycarbonate by epoxy resin, which mainly occurs during the mixing and degassing procedure : This degradation reduces the molecular weight of the polycarbonate and so increases its compatibility with the epoxy resin (see Section 1.2.3) up to a level when the degraded polycarbonate can stay dissolved in the uncured or cured epoxy blends (during curing of epoxy-polycarbonate blends the polycarbonate is also degraded by the DDM hardener or the accelerator used with the anhydride hardener).

Moreover, a possible reaction between the epoxy resin and the degraded polycarbonate would also increase the compatibility between the epoxy resin and the degraded polycarbonate due to the formation of a epoxy-polycarbonate copolymer (see Section 1.2.3). But no clear evidence of such a reaction could be found in our blends.

This absence of phase separation has been noted even at high concentration (13.7 wt%) of the highest molecular weight polycarbonate (PC.H) and in the cured blends whichever of the three hardeners, low and high reactivity diamine hardeners DDS and DDM or methyltetrahydrophthalic anhydride hardener, was used.

The phase separation observed in the epoxy resin-polycarbonate liquid blends when fPC.M functionalised polycarbonate was used at concentration above 7.4 wt% is related to the lower mixing temperature used in this case : 80°C instead of 120°C when PC.H was concerned.

This lower temperature reduced the degradation of the polycarbonate, and hence also the degree of compatibility between degraded polycarbonate and the epoxy resin. It also allowed a larger amount of solvent to be present in the MY750-fPC.M solutions for a longer time during the degassing procedure. This led to the observed phase separation and crystallisation of the fPC.M polycarbonate in the epoxy resin. Similar re-crystallisation of initially amorphous polyethersulfone on repeated exposure to chlorinated solvents has been noted by other authors [63].

6.3 Toughenability of the epoxy matrix : the rubber modified epoxy system

6.3.1 Controlling factors of the epoxy matrix toughenability

It is now commonly accepted that the key to successful toughening of epoxy resins with rubber particles is to have a toughenable matrix : a matrix in which shear band formation, the main plastic deformation and so energy absorption mechanism in glassy epoxies, is easily promoted ahead of the crack tip by the rubber particles before catastrophic failure occurs (see Section 1.3.2).

The toughenability of the matrix is controlled by its ductility which is controlled by its cross-link density [15, 16, 46, 49, 54] and the amount of rubber dissolved in the matrix [19].

Manzione et al [19] showed best toughness properties in their two phase rubber modified epoxy systems for a large amount of rubber dissolved in the matrix (around 10% by wt).

The effect of cross-link density upon matrix toughenability has been clearly demonstrated by the work of Yee and Pearson [46] which is illustrated in Figure 6.1 : in the absence of rubber modification, variation in the molecular weight between cross-links, Mc, has little effect on G_{IC} of the neat DGEBA-type epoxy systems cured with a stoichiometric ratio of DDS. But when 10 wt% of a suitable rubber is added to the formulation, G_{IC} increases linearly with Mc. These results demonstrate that, while reducing cross-link density in itself does not significantly increase toughness, the toughenability of the epoxy matrix is greatly increased.

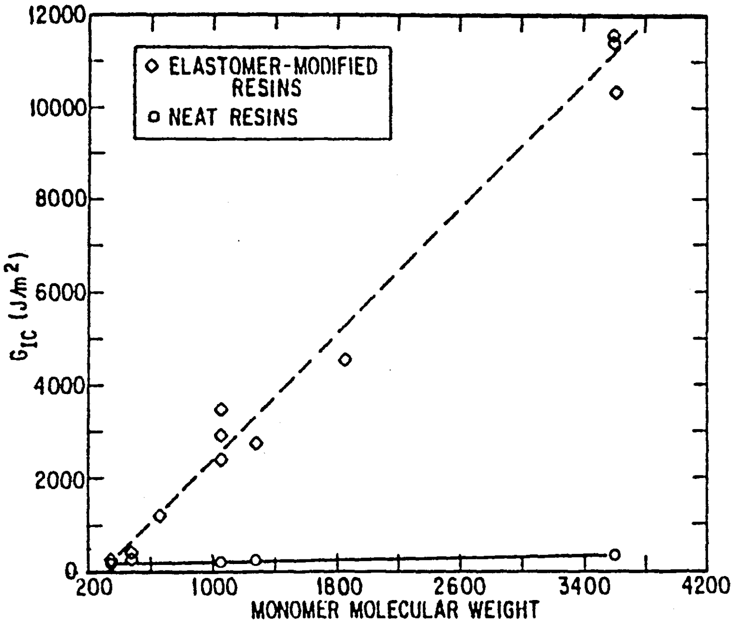


Figure 6.1 : From [46]. Effect of 10 wt% CTBN rubber on toughness properties of epoxy resins of different epoxy monomer molecular weight cured with the stoichiometric ratio of DDS.

6.3.2 Toughenability of the DGEBA-DDM epoxy matrix : toughness of the rubber modified epoxy system

Previous studies of rubber modified epoxy systems have demonstrated that the type of epoxy resin (DGEBA) rubber (CTBN 1300x8 prereacted with epoxy resin) and the initial amount of rubber used (15 wt%), the volume fraction of the dispersed phase (V_D between 20% and 30%), the rubber particle size (d between 2µm and 4µm) observed in our own rubber modified epoxy system and the selected testing conditions (temperature 23°C and low cross head speed 1.12 mm/min) should have been optimum to get substantial toughness improvements [11, 18, 15, 20, 22, 31, 46, 49, 50, 55, 60].

For example, Bascom et al [22] have shown that the critical strain energy release rate, G_{IC} of a DGEBA epoxy resin can be increased from 121 J/m^2 to 2150 J/m^2 by addition of 15 wt% of a liquid CTBN rubber.

Thus, the choice of the DDM hardener is believed to be responsible for the lack of toughness enhancement observed in our rubber modified epoxy system (G_{IC} is only increased from 150 J/m^2 to 350 J/m^2 by addition of 15 wt% CTBN rubber). DDM when used at the stoichiometric ratio gives a structure which cannot be successfully toughened by rubber particles.

The toughenability of the DDM cured epoxy matrix is poor, because it is highly crosslinked (due to the combination : low molecular weight epoxy monomer (Mn = 380 g/mol) cured with the stoichiometric ratio of DDM hardener) and because there is too little dissolved rubber (about 1% by volume) in the matrix to increase its ductility. This is partially indicated by the high T_g of our rubber modified epoxy matrix (165°C) in comparison to those of systems showing high toughness enhancement (see Table 6.1).

Authors	System	wt% (n%) rubber	d (μm)	V_D (%)	$\frac{K_{IC}\ (n\%)}{K_{IC}\ (0\%)}$	$\frac{G_{IC}\ (n\%)}{G_{IC}\ (0\%)}$	ET_g (°C)
Bucknall and Yoshii [36]	DGEBA + piperidine + CTBN8 (n = 0.15)	8.7	1.7	12.7	-	7.4	-
Yee and Pearson [50]	DGEBA + piperidine + CTBN8 (n = 0.15)	4.5 8.7 16	1 1-2 2	5 10 18	1.6 3.6 3.6	3 8 8	- 86 87
Kinloch et al [55]	DGEBA + piperidine + CTBN8 (n = 0.15)	4.5 15	1.2 2-8	10 22	- -	6.6 14.3	99 100
Kunz et al [60]	DGEBA + jeffamine T403+CTBN8 (ETBN) (n = 0.15)	11.5	1.7	21.5	2.5	5.7	86
Verchère et al [58]	DGEBA + 3DCM + CTBN8 (ETBN) (n = 0.15)	15	0.27	29.7	1.4	2.71	155
Present work	DGEBA + DDM + CTBN8 (ETBN) (n = 0.15)	15	3.3	28.9	1.04	2.07	165

Table 6.1 : Properties and characteristics of different rubber modified epoxy systems.
CTBN8 = CTBN1300 x 8.
ETBN = epoxy terminated butadine acrylonitrile random copolymer.

Our results on the system 750-R15, which are in good agreement with those reported by Kunz-Douglas et al [57] on the same system (see Table 6.2) clearly showed that over and above the considerations about optimal morphology and structure of the separated rubber phase, toughenability of the epoxy matrix is a primary factor in determining toughness enhancement by rubber modification.

Parameter	Present work	Kunz-Douglas et al [57]
d(μm)	3.3	3.3
don (μm)	2.0	3.1
V_D (%)	28.9	28.9
G_{IC} (kJ/m^2)	0.16[a]	0.5[b]
$\frac{K_{IC}\ (15\%)}{K_{IC}\ (0\%)}$	1.04	-
$\frac{G_{IC}\ (15\%)}{G_{IC}\ (0\%)}$	2.07	-
ET_g (°C)	165	-

Table 6.2 : Comparison between the results obtained by Kunz Douglas et al [57] and our results on the same system 750-R15 (DDM hardener.
[a]: measured by 3PB test
[b]: measured by double torsion test.

6.4 Toughness of rubber-polycarbonate modified epoxy systems and degradation of the polycarbonate

6.4.1 The anticipated effects of polycarbonate upon matrix toughenability enhancement

The purpose of blending polycarbonate with the epoxy matrix was to increase its ductility. Thus, the rubber particles would have been more effective to promote shear band formation in the surrounding matrix and hence increase the toughness to a higher level than that reached by the rubber modified epoxy system 750-R15.

Three different polycarbonates were used. They were supposed to increase the epoxy matrix ductility following two different ways:

i) The polycarbonate fPC.H and fP(BrC).0 terminated with reactive phenolic OH groups could have acted as chain extenders by reacting with the epoxy rings:

An evaluation of the theoretical average monomer molecular weight obtained by the presence of 5wt% (about 8 phr) of polycarbonate in the rubber polycarbonate modified epoxy system can be made assuming that all the molecules of polycarbonate are capped with one molecule of epoxy at each end. The value of the average monomer molecular weight is then estimated as being equal to 414 g/mol. If we assume the validity of the results of Yee and Pearson [46] about the effect of monomer molecular weight upon toughness improvement, for our systems (see Figure 6.1), the increase in G_{IC} would have been of 30% when the monomer molecular weight increased from 380 g/mol, in rubber modified epoxy system, to 414 g/mol, in rubber-polycarbonate (fPC.L or fPC(BrC).O) modified epoxy systems.

Unfortunately, in practice, we did not see any significant variations in G_{IC} (and K_{IC}) between these three systems.

ii) The high molecular weight unfunctionalised polycarbonate PC.H staying dissolved in the epoxy matrix could have increased the toughenability of the matrix as suggested by the slight increase in ductility observed in the PC.H polycarbonate modified epoxy systems by the slight lowering of σy and T_g, when compared to the unmodified system (see Table 6.3). But once again no significant difference in toughness was seen between the rubber and rubber-polycarbonate modified epoxy systems.

6.4.2 Final results

The fracture toughness of our epoxy system modified by rubber and different polycarbonates was not significantly changed compared to the rubber modified epoxy system, whichever of the three polycarbonates was used. Table 6.3 shows that this absence of variation in toughness properties was not due to dramatic changes in other properties or characteristics between these systems.

Thus, the polycarbonates did not successfully increase the toughenability of our MY750-DDM matrix. The degradation of the polycarbonate by the epoxy matrix and somehow by the hardener is believed to be responsible for this result : it alters the network structure, resulting in a more brittle matrix; as the decrease in fracture toughness of PC.H polycarbonate modified epoxy systems would suggest (see Table 6.3).

This network alteration outweighs the benefit of the slight ductility improvement observed in the unfunctionalised polycarbonate modified epoxy systems.

System	K_{IC} (MPa$\sqrt{m}$)	G_{IC} (kJ/m^2)	σy (MPa)	E_{100} (GPa)	T_g (°C)	V_D (%)	d (μm)
750	0.81	0.15	99	2.7	168	0	0
750-PC.H7.4	0.71	0.10	95	2.8	163	0	0
750-PC.H13.7	0.66	0.12	89	2.7	161.5	0	0
750-R15	0.84	0.31	63	1.7	165	28.9	3.3
750-fP(BrC)0.5-R15	0.86	0.36	61	1.7	166	32.4	3.1
750-fPC.L5-R15	0.84	0.30	64	1.8	157.5	25.7	3.4
750-fPC.H5-R15	0.87	0.31	65	1.9	159	24.1	4.1

Table 6.3: Principal properties and characteristics of our systems.

CONCLUSION

From this work, one major point can be retained :

the MY750-DDM epoxy matrix is very difficult to toughen by rubber modification even under the best conditions because it is highly cross-linked. No significant difference in K_{IC} was observed between the rubber modified epoxy system and the neat epoxy system. The toughenability of this epoxy matrix is not improved by the addition of polycarbonates, either terminated by OH groups or not, which stayed dissolved within it. Polycarbonate is in fact degraded by the epoxy resin when the two are mixed together at a high temperature (100°C - 120°C) leading to a more brittle matrix, when cured with DDM, than the neat epoxy matrix. Moreover, polycarbonate can also be degraded by the DDM hardener.

It has also been shown that:

The choice of using or not using dichloromethane to prepare epoxy-polycarbonate blends of same composition (i.e. polycarbonate dissolved in dichloromethane and then added to hot epoxy resin or polycarbonate directly dissolved in hot epoxy resin when this polycarbonate can be effectively dissolved in hot epoxy resin) does not lead to any significant differences in the dynamic mechanical thermal properties, morphology or mechanical properties of the resulting rubber-polycarbonate modified epoxy systems.

The co-continuous structure, epoxy matrix-thermoplastic, observed in the MY750 epoxy system modified by 19.2 wt% of PES and cured with DDM is responsible for the toughness enhancement observed in this system when compared to the neat epoxy system.

Further work should be concentrated on the selection of other appropriate thermoplastics which would not phase separate from the cured epoxy matrix and would not be degraded. This is in order to investigate if the toughenability of a highly cross-linked epoxy matrix such as MY750-DDM can be improved and controlled by the presence of these thermoplastics when the epoxy is modified by CTBN rubber particles.

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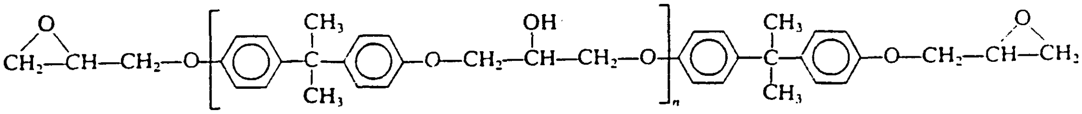
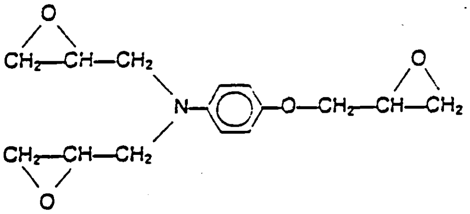
APPENDIX A
STRUCTURAL FORMULAE OF DIFFERENT MATERIALS USED IN THE PRESENT WORK

i) Epoxy resins

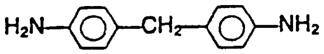


Diglycidylether of bisphenol A : DGEBA
DER332, n = 0.03
MY750, n = 0.15

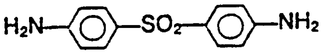


Triglycidylparaaminophenol : TGPAP

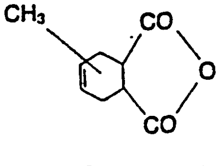
ii) Diamine hardeners



4.4' diaminodiphenylmethane : DDM.

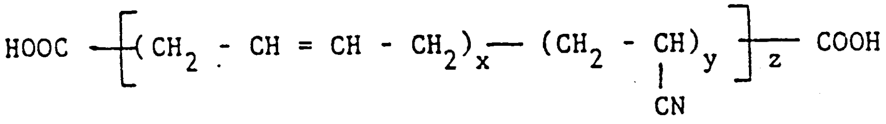


4.4' diaminodiphenylsulfone : DDS.



methyltetrahydrophthalic anhydride

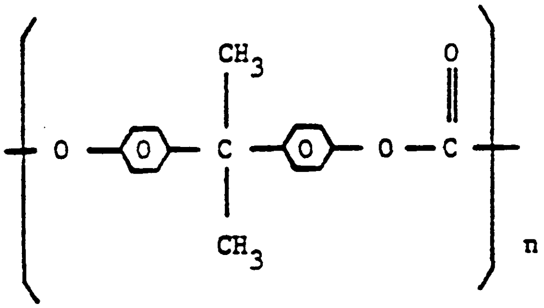
iii) Rubber modifier



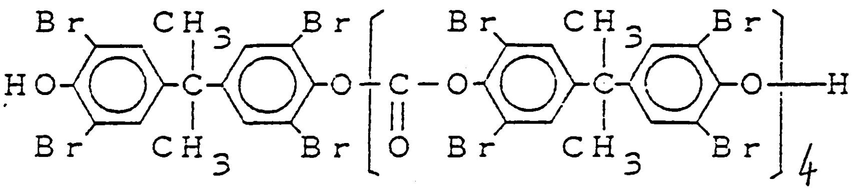
$$HOOC-\left[(CH_2-CH=CH-CH_2)_x-(CH_2-\underset{\displaystyle CN}{\underset{|}{CH}})_y\right]_z-COOH$$

Carboxyl terminated butadiene-acrylonitrile random copolymer : CTBN

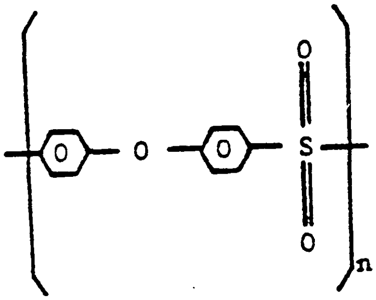
iiii) Thermoplastic modifiers.



Polycarbonate



Polybrominated carbonate : fP(BrC).0



polyethersulfone

APPENDIX B

PROTOCOL FOR DETERMINING K_{IC} AND G_{IC}

A LINEAR ELASTIC FRACTURE MECHANICS (LEFM) STANDARD FOR DETERMINING K_C AND G_C FOR PLASTICS

TESTING PROTOCOL - OCTOBER 1989

This protocol has been created by the activities of the EGF Task Group on Polymers and Composites and is the result of a series of Round - Robin tests. It is intended to form the basis of national and international standards. It has been drafted by Prof. J G Williams, Mech.Eng.Dept., Imperial College, London, U.K. to whom enquiries and comments should be addressed.

1. Introduction

These tests are designed to characterise the toughness of plastics in terms of the critical stress intensity factor, K_C, and the energy per unit area of crack, G_C, at fracture initiation. The scheme used assumes linear elastic behaviour of the cracked sample, so certain restrictions on linearity of the load - displacement diagram and specimen width must be imposed to ensure validity. In addition a state of plane strain at the crack tip is required so that thickness normal to the crack front must be sufficient to ensure this state. Finally the crack must be sufficiently sharp to ensure that a minimum value of toughness is obtained. These requirements are common to the ASTM metals standard E399 and much of what follows is drawn from this source. There are, however, special problems associated with plastics and these are accommodated in what follows. Items not covered here will be found in E399. It should also be noted that G_C is of particular importance for plastics and this protocol covers its determination while E399 does not.

2. Specimen Preparation

Three point bend (also called single edge notched bend, SENB) and compact tension (CT) geometries are recommended because these have predominantly bending stress states which require smaller sizes to achieve plane strain than other configurations. It is usually helpful to maximize the thickness used from a sheet sample and this is best achieved by making the sheet thickness that of the specimen i.e. B in fig. 1.where the two configurations are shown. In both tests the crack length range should be; $0.45 < a/W < 0.55$ and it is usually convenient to make $W = 2B$ initially.

3. Notching

The ideal case is when a natural crack is re-initiated and this is embodied in the metals test by requiring that an initial machined notched sample is fatigued to give some growth. This method may be used for plastics but it often is difficult to do because of unstable fatigue crack growth and the necessity of using low frequencies (<4Hz in some plastics) to avoid hysteretic heating. In plastics it is possible to produce sufficiently sharp initial cracks by other methods and particularly by first machining a sharp notch and then further sharpening it by using a razor blade.This is generally a much simpler technique than growing cracks in fatigue.The procedure to be followed is:

i) Machine or saw a sharp notch in the specimen. Then generate a natural crack by tapping on a new razor blade placed in the notch. It is essential to persevere with this since in brittle specimens a natural crack can be generated by this process but *some skill is required* in avoiding too long a crack or local damage. (Some precompression of the specimen may be helpful). The cracks grown should be several times longer than the pre- notch tip radius. Failure to generate a natural crack will result in too high values.

ii) If a natural crack cannot be generated, as in some tough specimens, then the notch can be sharpened by sliding or sawing a new razor blade across the notch. Again the depth of this extension should be greater than the original notch tip radius.

iii) Pressing the blade into the notch is not recommended because of induced residual stresses.

4. Test Conditions

Since plastics are viscoelastic materials it is necessary to specify both the temperature and time scale under which the result was obtained. As a basic test condition it is recommended that 23°C and a crosshead rate of 10 mm/min be used. In all cases the loading time should be quoted.

If it is not possible to obtain valid results at 23°C it is often possible to do so by decreasing the temperature which usually does not change K_c greatly but increases the yield stress rendering the fractures more brittle. If this procedure is used then again both temperature and loading time must be stated.

It is recommended that speeds of greater than 1 m/s or loading times of less than 1ms should be avoided because of the danger of dynamic effects causing errors.

5. Loading Rigs

For SENB a rig with moving rollers of sufficiently large diameter to avoid plastic indentation is recommended. That shown in **fig.2** is based on **E.399**. For the CT test the loading is via pins in the holes.

For either sample configurations, the displacement measurement can be performed using the loading machine's internally provided stroke (position) transducer. The fracture test displacement data must then be corrected for total system compliance, loading pin penetration and sample compression. This can be performed by a simple calibration of the testing system. The procedure is as follows.

A test configuration as shown in figs. 3a or 3d using identically prepared, but unnotched, samples is used to generate a load-displacement correction curve. This correction curve is then "subtracted" from the load-displacement curve obtained during the actual fracture test with notched samples. This subtraction is performed by subtracting the correction curve displacement from the fracture test displacement at corresponding loads.

In practice, a linear correction curve can usually be obtained (up to the maximum loads recorded in the fracture test). Use of a linear correction simplifies the displacement correction. Any initial non-linearity due to penetration of the loading pins into the sample is observed during both the calibration test and the actual fracture test, so a linearisation of the near-zero correction data and the fracture test data can effectively correct for this initial non-linearity.

This displacement correction must be performed for each material and at each different temperature or rate. Polymers are generally temperature and rate sensitive and the degree of loading pin penetration and sample compression can vary with changes in these variables.

If the internally provided displacement transducer is not available, then externally applied displacement measuring devices may be used. For this case, displacement should be taken at the load point.

For CT samples, this is preferred to crack mouth opening since the load point displacement is required for the energy calculation used in finding G_c. For CT a clip gauge near the pins will be satisfactory. (If a stiff metals gauge is used it may be necessary to correct the loads in a plastics test.)

For SENB a displacement transducer can be placed between the load point and the base as indicated in fig.2. In the G_c tests it is necessary to correct the measured displacement for indentation effects and this can be done by the arrangements shown in fig.3. A load displacement curve from that in fig.3a may be subtracted from that in the fracture test to obtain the true displacement. The value here would be slightly high because of flexing so a more precise result can be obtained using that in fig 3b + 3c from which

$$u\ (\mathit{corrected}) = u\ (\mathit{measured}) - \left[u_p + u_{p/2} + u_{\mathit{machine}}\right]$$

where u_p is the indentation displacement at the load point at which u is measured, $u_{p/2}$ is the displacement at load P/2 and $u_{machine}$ is the displacement due to the compliance of the testing machine. $u_{machine}$ may be determined from the test shown in fig 3c. This term is then subtracted from the displacement measured in test fig 3b. The remaining displacement is the displacement u_p.

The indentation tests should be performed such that the loading times are the same as the fracture tests. Since the indentations are stiffer this will involve lower rates to reach the same load ; in many cases about half the speed. (More details on energy calculations are given in section 8).

6. Test Procedure

It is recommended that three replicates be used. The test is performed and the load versus load-point displacement curve obtained. In the ideal case this is a linear diagram with an abrupt drop of load to zero at the instant of crack growth initiation. In some cases this occurs and K_Q can be found from the maximum load. (In such a case a natural crack will be required, see section 3). In most cases there is some non-linearity in the diagram and this can be due to plastic deformation at the crack tip, non-linear elasticity, general visco-elasticity and stable crack growth after initiation but prior to instability. The first three effects violate the LEFM assumption and the fourth one means that the true initiation load is not defined by the maximum. Indeed it is doubtful if an exact definition of initiation could be made and with this, and a need for simplicity in mind, the arbitrary rule of E.399 is used here. The diagram is shown (exaggerated) in fig.4 and a best straight line is drawn to determine the initial compliance C as shown. This is then increased by 5% and a further line drawn. If P_{max} falls within these two lines then P_{max} is used to find K_Q. If the C + 5% intersects the load curve then $P_{5\%}$ is found and this is taken as the load at crack initiation. In fact if all the non-linearity is due to crack growth then it corresponds to a particular amount of crack growth given by

$$\frac{\Delta a}{a} = \frac{\phi}{(a/W)} \cdot \frac{\Delta C}{C}$$

where $\phi(a/W)$ is the calibration factor discussed in section 8. For the configuration in SENB used here $\phi/(a/W) \sim 0.5$ so we have $\Delta a/a \sim 2.5\%$, i.e. a 2.5% increase in crack length.

To stay within the LEFM condition it is further specified that :

$$\frac{P_{max}}{P_{5\%}} < 1.1$$

i.e. a 10% non-linearity is allowed. If $P_{max}/P_{5\%} > 1.1$ then the test is invalid. If $P_{max}/P_{5\%} < 1.1$ then $P_{5\%}$ is used in the calculation of K_Q, or P_{max} if it falls within the two lines. (It should also be noted that crack 'pop-in' can occur in which the crack jumps forward a small distance and then arrests. This results in a short drop in the curve and then a continued rise. This value of load can be used and quoted as a 'pop-in' value.)

Values of K_Q are computed from the original crack length a which is best determined from the fracture surface after testing. An average value may be used but the difference between the shortest and longest length should not exceed 10%. Care should be taken that it is the original crack which is being observed since slow growth can occur. K_Q is then calculated from the following relationship:

$$K_Q = f \frac{P_Q}{BW^{\frac{1}{2}}}$$

The calibration factor f is defined for both geometries in Appendix 1. Tabulated values of f are presented in Table 1.

7. Size Criteria

The validity of K_Q should now be checked via the size criteria;

$$B,\ a,\ (W - a) > 2.5 \left(\frac{K_Q}{\sigma_y}\right)^2$$

Since the specimen dimensions require that $W = 2B$ initially (see section 2) and $a/W \sim 0.5$ then usually all are satisfied if one is. In fact the criteria covers two limitations in that B must be sufficient to ensure plane strain but $(W - a)$ has to be sufficient to avoid excessive plasticity in the ligament. If $(W - a)$ is too small the test will usually violate the linearity criteria but not necessarily so. If the linearity criteria is violated a possible option is to increase W for the same B. Values of W/B of up to 4 are permitted. It should also be noted that if the specimen is too small B will result in K_Q being high whilst $(W - a)$ will result in it being low. The nett effect may be close to correct but unfortunately in an unpredictable way since the dependence on B cannot be quantified.

σ_y is the uniaxial tensile yield stress and for polymers this is conventionally taken at the maximum load. Because of visco-elastic effects the 0.2% offset value as used in metals is not a yield stress and gives too low a value. Shear yielding in tensile tests in most polymers can be achieved by carefully polishing the specimen edges but if brittle fracture does occur then, since yielding is at a larger load, the stress at fracture may be used in the criteria to give a conservative size value. An alternative is to use 0.7 times the compressive yield stress. In all cases the time to yielding should be within ±20% of the fracture loading time and the method of finding σ_y given.

If these criteria are met then, $K_Q = K_{c1}$.

8. G_c Calculations

G_{c1} can, in principle, be obtained from,

$$G_{c1} = \frac{(1 - \nu^2)\, K_{c1}^2}{E} \quad , \qquad \text{(for plane strain)}$$

but for plastics E must be obtained at the same time and temperature conditions because of viscoelastic effects. Many uncertainties are introduced by this procedure and it is considered preferable to determine G_c directly from the energy derived from integrating the load versus load-point displacement diagram. The procedure to be followed is via K_Q for validity testing and then to determine the energy U_Q up to the same load point as used for K_Q, (as shown in fig. 5a). The indentation curve, as sketched in fig 5b, is usually quite linear and the energy from indentation, U_i can be estimated from C_i from,

$$U_i = 1/2\, P^2 C_i \quad \text{for method in fig 3a and 3d)}$$

$U_i = 3/4\ P^2\ C_i$ for method in fig 3b)

where $P = P_{5\%}$ or $P_{\max}$

The corrected fracture energy is,

$$U = U_Q - U_i$$

It is considered easier to correct for initial curvature by extrapolation as shown, but subtracting the total curves is permitted. Total energy corrections are usually < 20%.

G_c may be calculated from this energy U via,[+]

$$G = \frac{U}{BW\phi} \quad or \quad \frac{\eta_e U}{B(W - a)}; \qquad \eta_e = \frac{1 - a/W}{\phi}$$

(The η_e form is of the same form to that used for J tests). Values of η_e are given in Table 1.

The energy calibration factor ϕ is defined as

$$\phi = C / dC / d(a/W)$$

and may be computed as shown in Appendix 1. Values for the test geometries used are also given in table 1.

A useful cross check on accuracy may be made since $E/1-\nu^2$ can be found from the corrected compliance C_c, i.e, $C_c = C - C_i$ or $C_c - 3/2\ Ci$ for the two methods, from:

$$\left(\frac{E}{1-\nu^2}\right) BC_c = 2f^2\phi = \psi$$

and the factor ψ is given in table 1. This value of $E/(1-\nu^2)$ should be compared with that obtained from K^2_{c1}/G_{c1} and the former value should be the larger but the difference should be <15%. If the discrepancy is greater then the results should be examined for possible errors.

[+] J.G.Williams, "Fracture Mechanics of Polymers", Ellis Horwood/Wiley, 1985

9. Reporting

The following format for reporting results is suggested;

i) Specimen Configuration and Dimensions

ii) Notching method

iii) Temperature and Loading Rate

iv) One example of Load - Displacement diagram

v) P_{max} and/or $P_{5\%}$ values for all (3) specimens plus loading times

vi) $P_{max}/P_{5\%}$, $<$ or $>$ 1.1 ?

vii) K_Q value

viii) σ_y value at maximum load and loading time

ix) $2.5\,(K_Q/\sigma_y)^2$; $<$ or $>$ B, W - a ?

x) Energy value (indentation corrected?)

xi) G_c value via ϕ or η

xii) $E/(1-\nu^2)$ via C_c

xiii) $E/(1-\nu^2)$ via K_c^2/G_c

Table 1. Calibration Factors

SENB$^+$, S/W = 4

a/W	f	ϕ	ψ	η
0.05	2.50	1.502	18.7	0.63
0.10	3.39	0.857	19.7	1.05
0.15	4.07	0.641	21.2	1.33
0.20	4.70	0.526	23.2	1.52
0.25	5.36	0.449	25.7	1.67
0.30	6.09	0.391	28.9	1.79
0.35	6.93	0.345	33.1	1.89
0.40	7.93	0.307	38.5	1.96
0.45	9.14	0.275	45.9	2.00
0.50	10.65	0.246	55.9	2.03
0.55	12.57	0.220	69.6	2.04
0.60	15.09	0.195	88.7	2.05
0.65	18.51	0.170	116.4	2.06
0.70	23.40	0.145	158.5	2.07
0.75	30.84	0.120	228.2	2.08
0.80	43.21	0.096	357.7	2.09
0.85	66.76	0.072	643.7	2.08
0.90	123.30	0.049	1484.6	2.05
0.95	351.62	0.025	6148.3	2.01

+ Values calculated using
A. Bakker
Compatible Compliance and Stress Intensity Expressions for the Standard three-point Bend Specimen
Paper submitted for publication in: International Journal of Fatigue and Fracture of Engineering Materials and Structures (March 1989)

CT*

a/W	f	ϕ	ψ	η
0.25	4.92	0.199	9.6	3.77
0.30	5.62	0.208	13.2	3.36
0.35	6.39	0.213	17.4	3.05
0.40	7.28	0.213	22.5	2.82
0.45	8.34	0.208	28.9	2.64
0.50	9.66	0.199	37.1	2.51
0.55	11.36	0.186	48.1	2.42
0.60	13.65	0.170	63.6	2.35
0.65	16.86	0.152	86.6	2.30
0.70	21.55	0.133	123.2	2.26
0.75	28.86	0.112	186.3	2.23

*Values calculated using,
J.A.Kapp, G.S.Leger & B.Gross;
Fracture Mechanics Sixteenth Symposium, ASTM, STP 868.
pp 27 - 44.

Appendix 1

Compact Tension Specimen (0.2 < a/w < 0.8)

$$f = \frac{(2+\alpha)}{(1-\alpha)^{\frac{3}{2}}}\left[0.886 + 4.64\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.6\alpha^4\right]$$

$$\phi = \frac{(1.9118 + 19.118\alpha - 2.5122\alpha^2 - 23.226\alpha^3 + 20.54\alpha^4)(1-\alpha)}{(19.118 - 5.0244\alpha - 69.678\alpha^2 + 82.16\alpha^3)(1-\alpha) + 2(1.9118 + 19.118\alpha - 2.5122\alpha^2 - 23.226\alpha^3 + 20.54\alpha^4)}$$

where $\alpha = a/w$

Single Edge Notched Bend Specimen (0 < a/w <1)

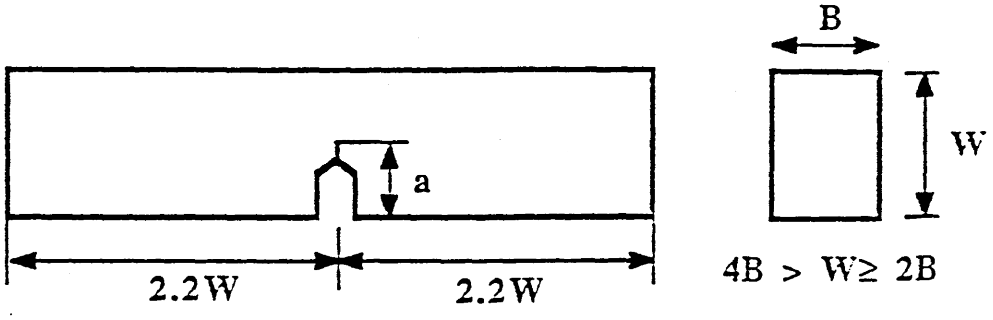
$$f = 6\alpha^{\frac{1}{2}}\frac{[1.99 - \alpha(1-\alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)]}{(1+2\alpha)(1-\alpha)^{\frac{3}{2}}}$$

$$\phi = \frac{A + 18.64}{dA/d\alpha}$$

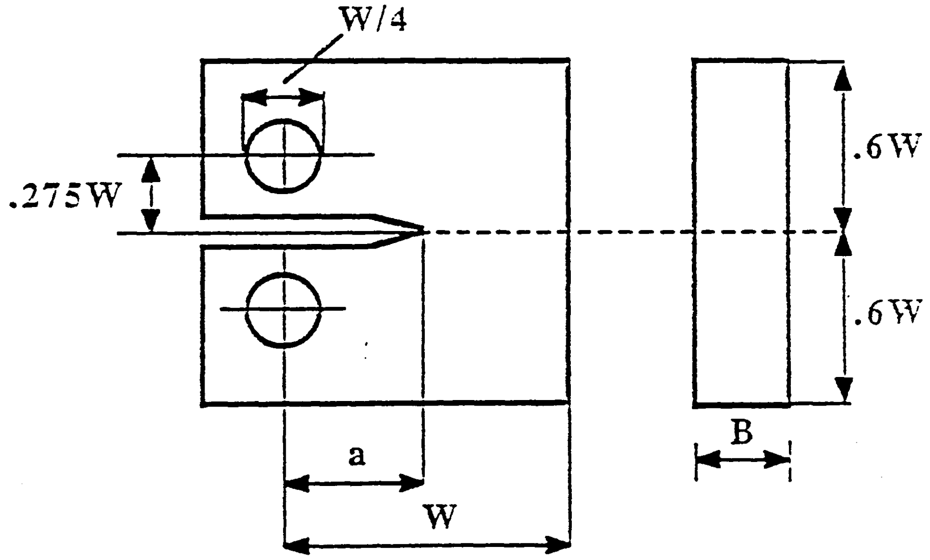
$$A = \frac{16\alpha^2}{(1-\alpha)^2}\left[8.9 - 33.717\alpha + 79.616\alpha^2 - 112.952\alpha^3 + 84.815\alpha^4 - 25.672\alpha^5\right]$$

$$dA/d\alpha = \frac{16\alpha^2}{(1-\alpha)^2}\left[-33.717 + 159.232\alpha - 338.856\alpha^2 + 339.26\alpha^3 - 128.36\alpha^4\right] +$$

$$16\left[8.9 - 33.717\alpha + 79.616\alpha^2 - 112.952\alpha^3 + 84.815\alpha^4 - 25.672\alpha^5\right]\left[\frac{2\alpha(1-\alpha) + 2\alpha^2}{(1-\alpha)^3}\right]$$



a) THREE POINT BEND SPECIMEN (SENB



b) COMPACT TENSION CONFIGURATION. (CT)

FIG.1. SPECIMEN CONFIGURATIONS - AS IN E399

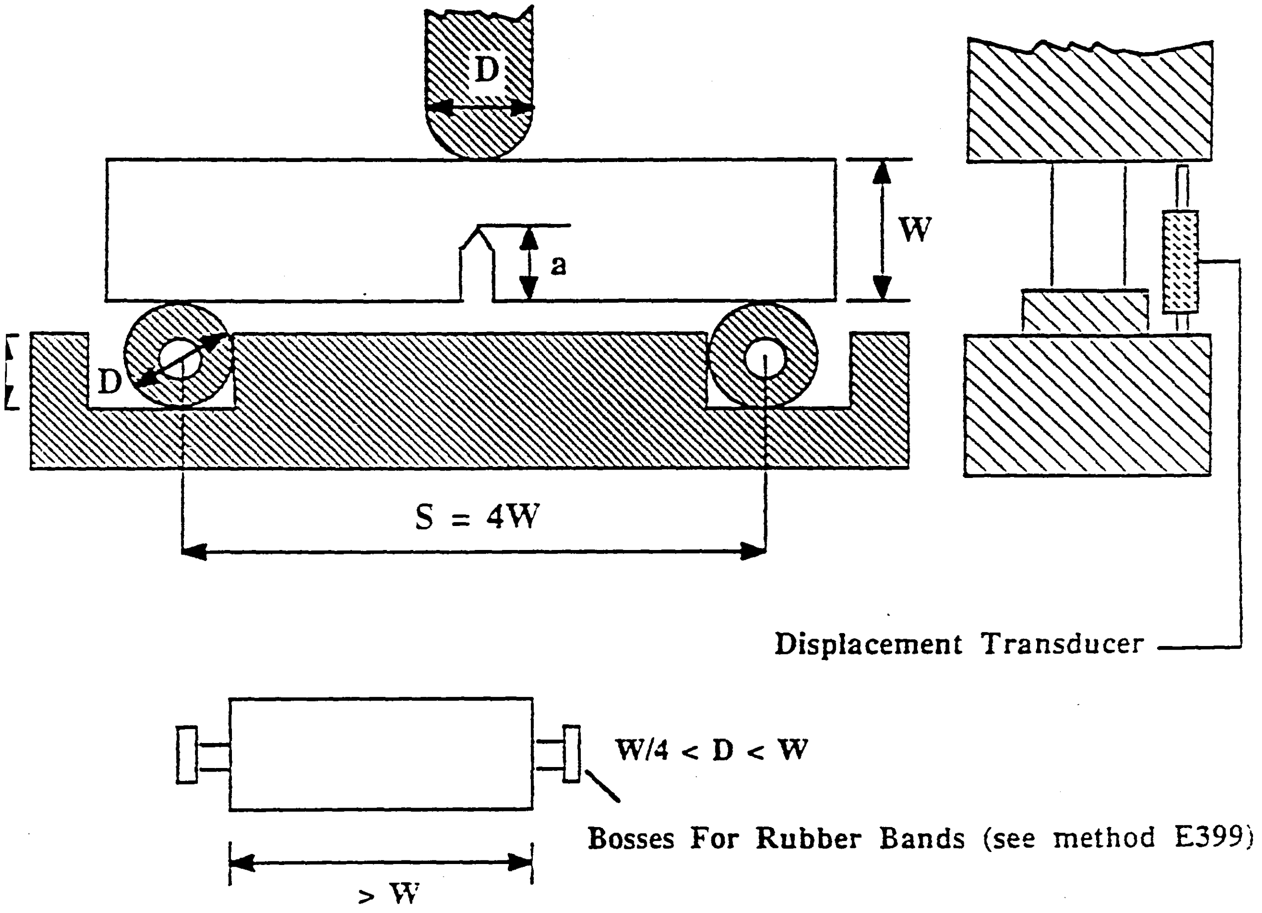


FIG. 2. BENDING RIG

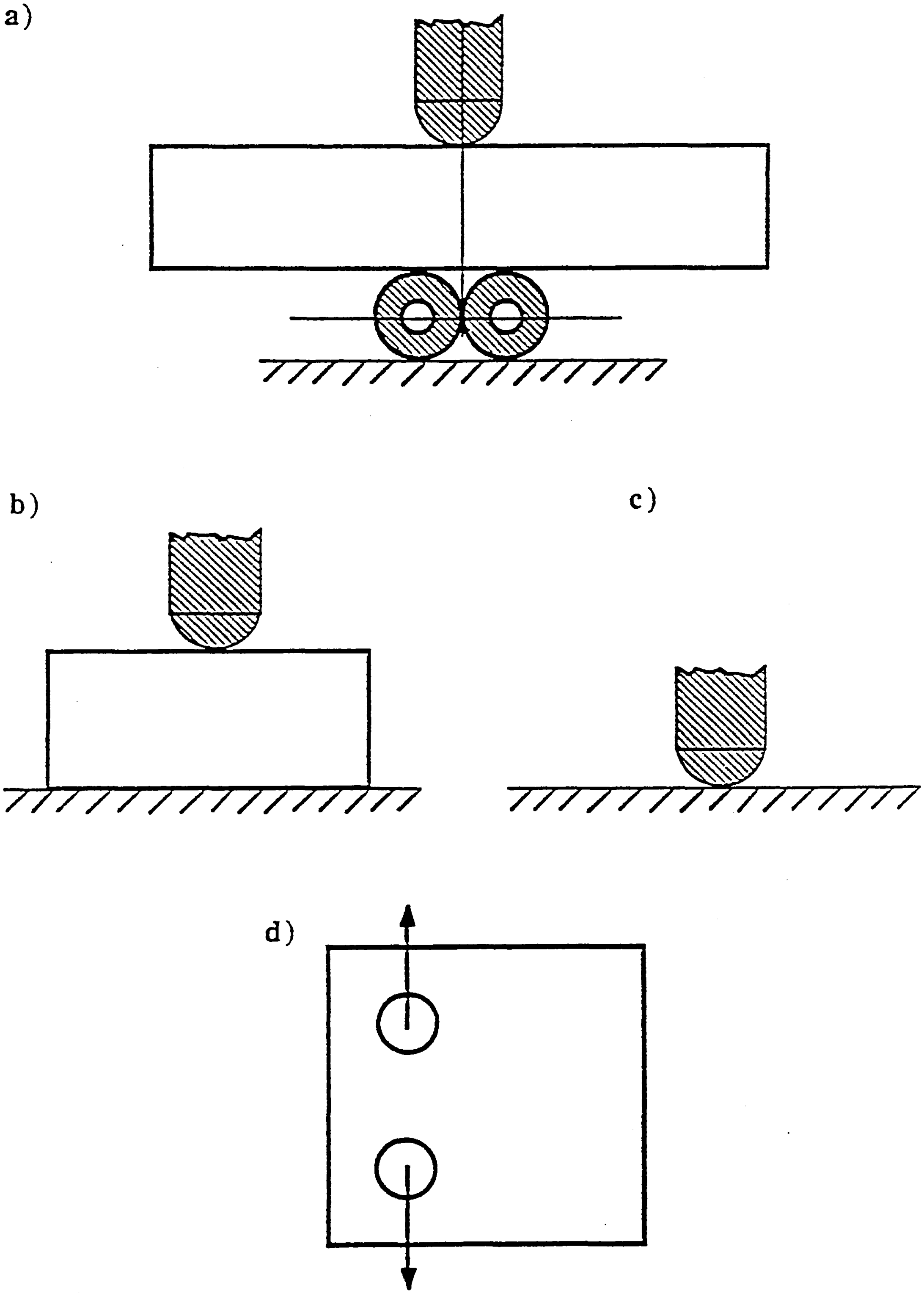


FIG.3. ARRANGEMENTS FOR FINDING INDENTATION DISPLACEMENT.

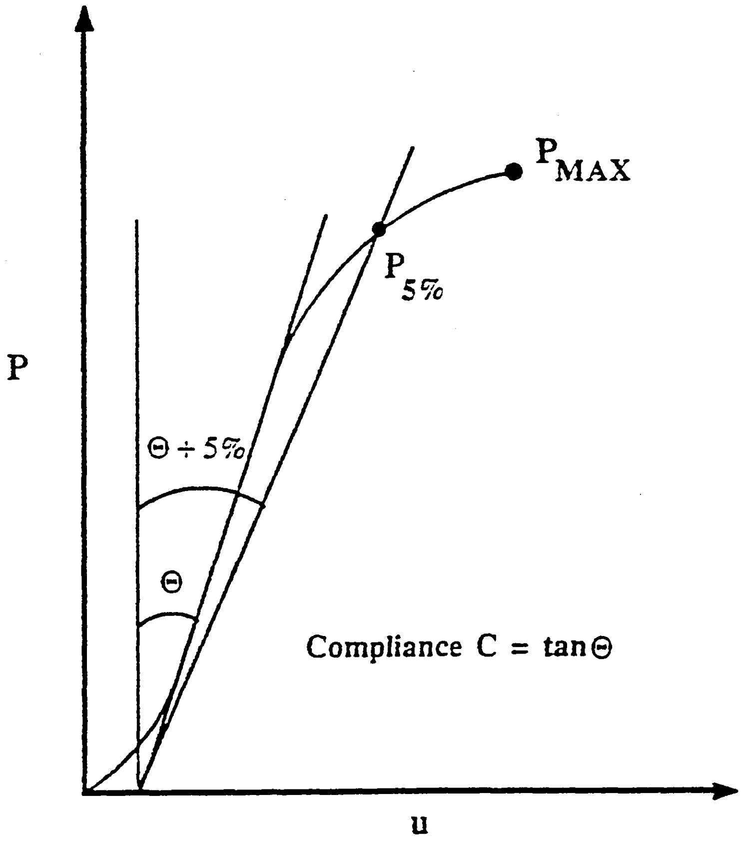
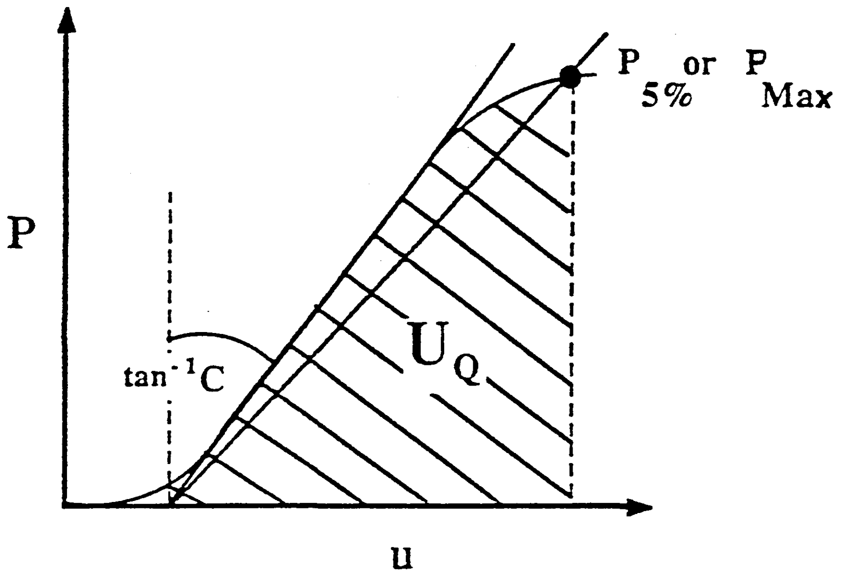
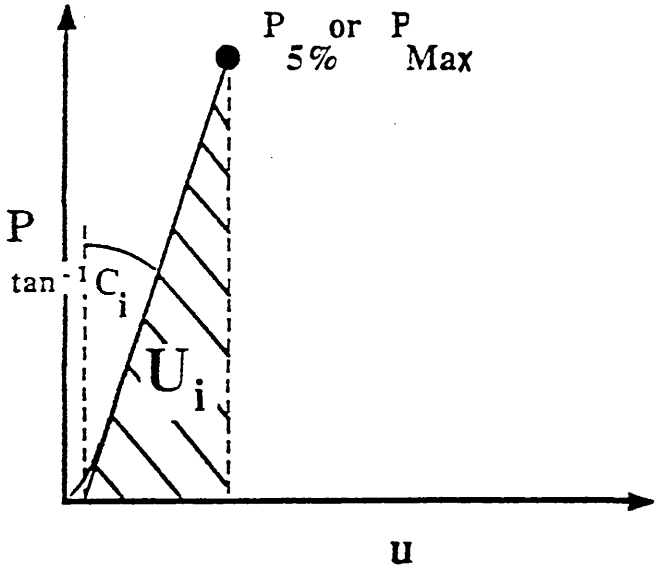


FIG.4. DETERMINATION OF $P_{5\%}$ and C



a) LOAD - DEFLECTION; FRACTURE TEST

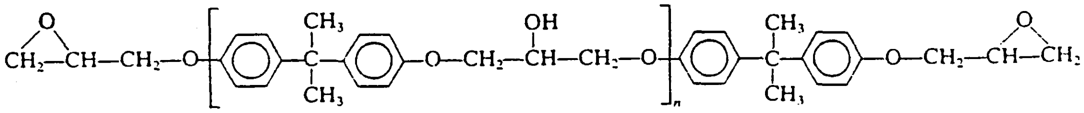


b) LOAD - DEFLECTION; INDENTATION

FIG 5. METHOD OF CORRECTING FOR INDENTATION

APPENDIX C
SOLUBILITY PARAMETER CALCULATIONS

MY750

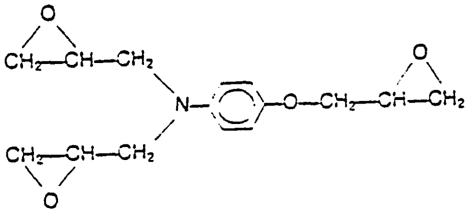


25.7 main chain skeletal atoms

Group	Δei (cal/mol.)		Δvi (cm^3/mol)
2.3 x disubstituted ring	17549		120.52
1.5 x C	402.5		-22.08
2.15 x CH	1763		-2.15
4.3 x CH_2	5074		69.23
2.3 x CH_3	4837.5		144.05
4.3 x O	3440		16.34
0.15 x OH	783		1.95
2 x ring closure of 3 atoms	1500		36
	35349		**363.86**
		'2n'	**51.4**
			415.26

$\underline{\delta = 9.2\ (cal/cm^3)^{1/2}}$

ERL0510

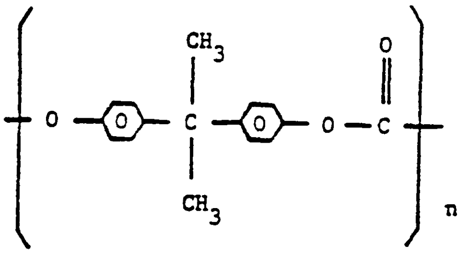


16 main chain skeletal atoms

Group	Δei (cal/mol)	Δvi (cm^3/mol)
1 x disubstituted ring	7630	52.4
1 x N	1000	-9
3 x CH	2460	-3
6 x CH_2	7080	96.6
4 x O	3200	15.2
3 x ring closure (3 atoms)	2250	54
	-----	-----
	23620	**206.2**
	'2n'	**32**
		238.2

$\underline{\delta = 10.0\ (\mathrm{cal/cm^3})^{1/2}}$

PC

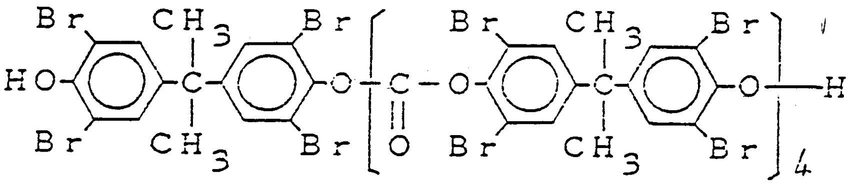


16 main chain skeletal atoms

Group	Δei (cal/mol)		Δvi (cm^3/mol)
2 x disubstituted ring	15260		104.8
1 x C	350		-19.2
2 x CH_3	2250		67
1 x CO_2	4200		22
	-----		-----
	22060		**174.6**
		'2n'	**32**
			206.6

$\underline{\delta = 10.3\ (cal/cm^3)}^{\frac{1}{2}}$

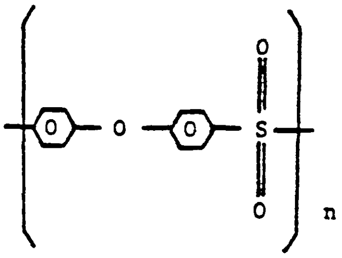
fP(BrC).0



Group	Δei (cal/mol)	Δvi (cm^3/mol)
10 x disubstituted ring	76300	524
5 x C	1750	-96
6 x CH_3	6750	201
4 x CO_3	12600	88
2 x OH	10440	26
29 x Br	74000	600
	-----	-----
	181840	**13436**
	'2n'	**158**
		1501

$\delta = 11.0\ (cal/cm^3)^{1/2}$

PES



14 main chain skeletal atoms

Group	Δei (cal/mol)		Δvi (cm^3/mol)
2 x disubstituted ring	15260		104.8
1 x 0	800		3.8
1 x sulphone group [39]	3940		20
	-----		-----
	20000		**128.6**
		'2n'	**28**
			156.6

$\underline{\delta = 11.3\ (cal/cm^3)}^{1/2}$

APPENDIX D
SEM PICTURES OF DIFFERENT SYSTEMS INVESTIGATED

i) Polycarbonate modified epoxy systems

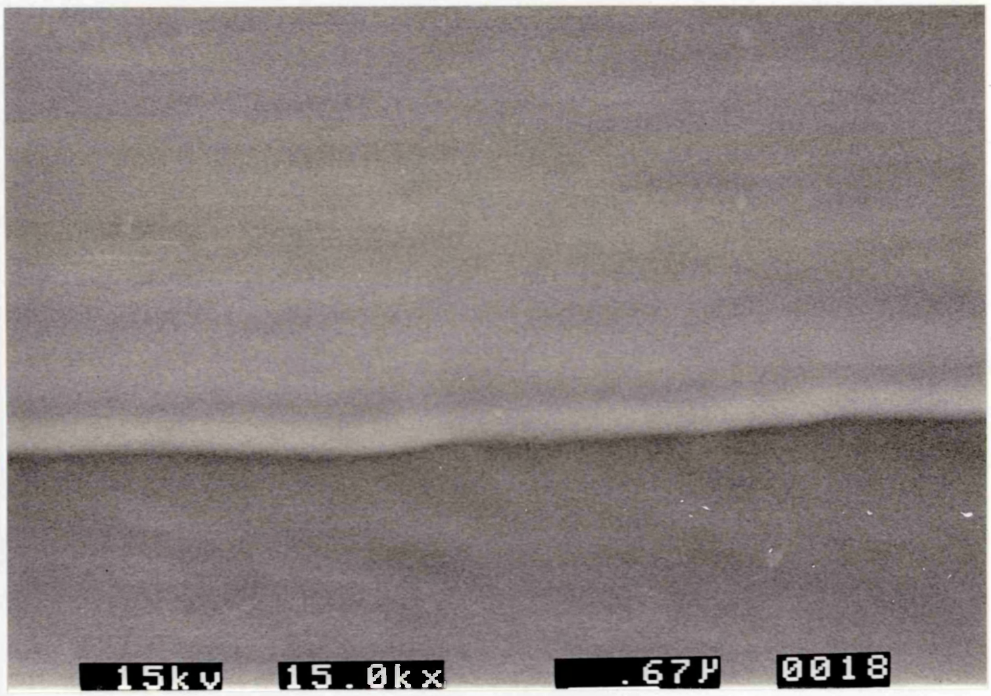


Figure D1 : Fracture surface of sample 750-PC.H13.7.

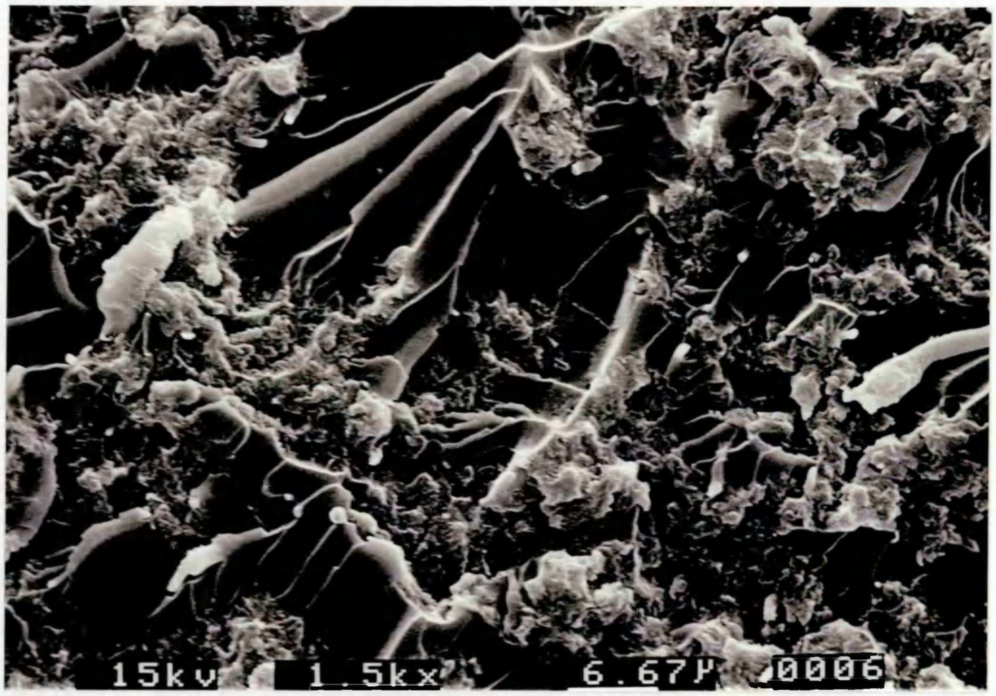


Figure D2: Fracture surface of sample 750-fPC.M19.2.

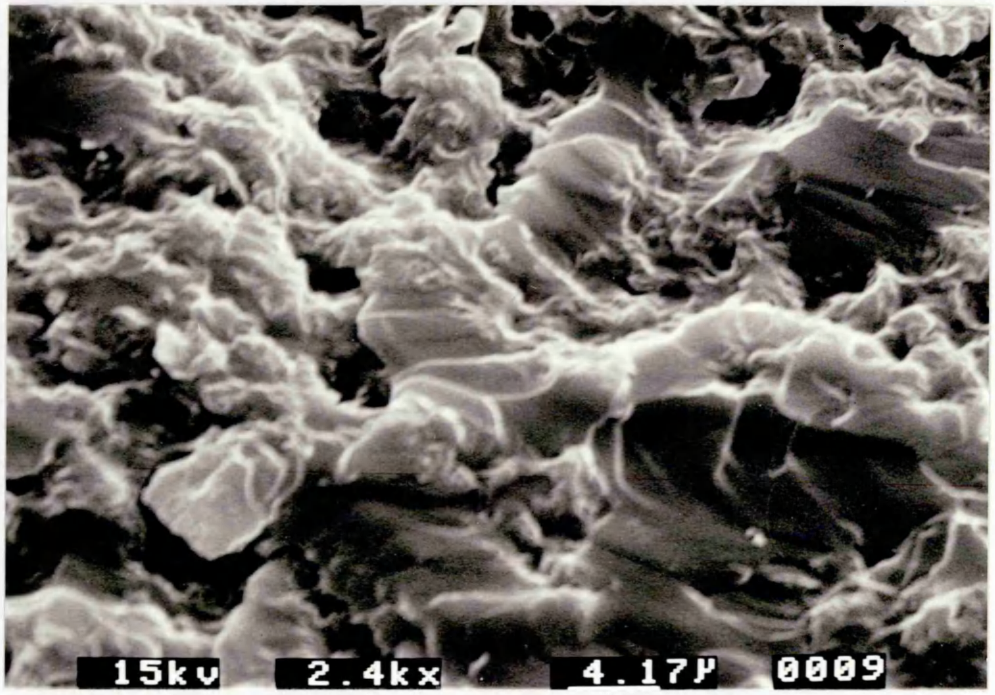


Figure D3: Fracture surface of sample 750-fPC.M19.2 etched in methylene chloride.

ii) rubber and rubber-polycarbonate modified epoxy systems

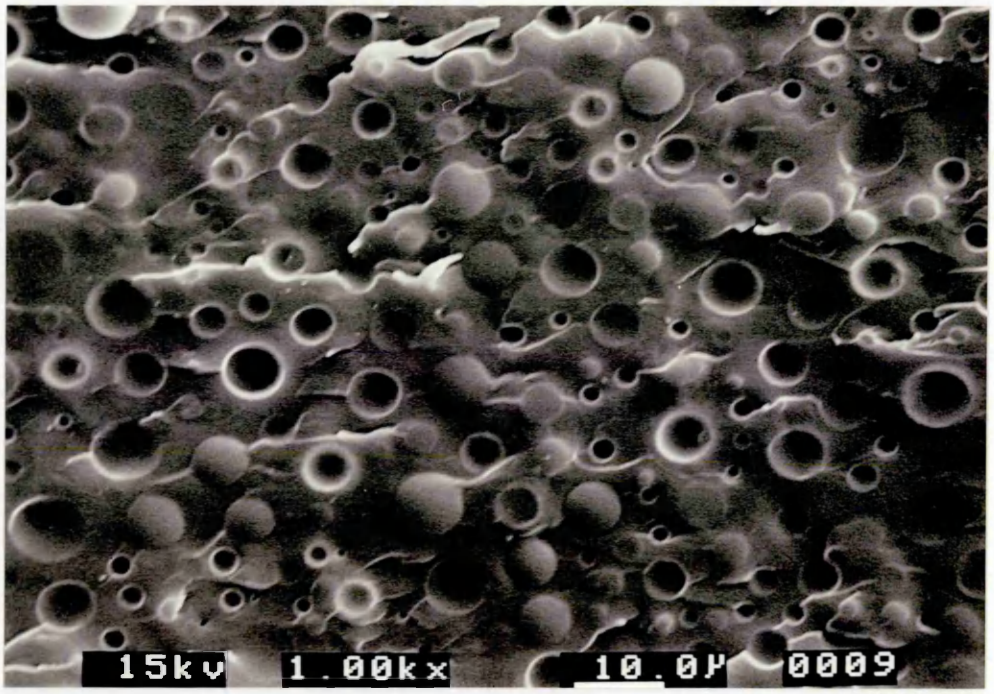


Figure D4: Fracture surface of sample 750-R15.

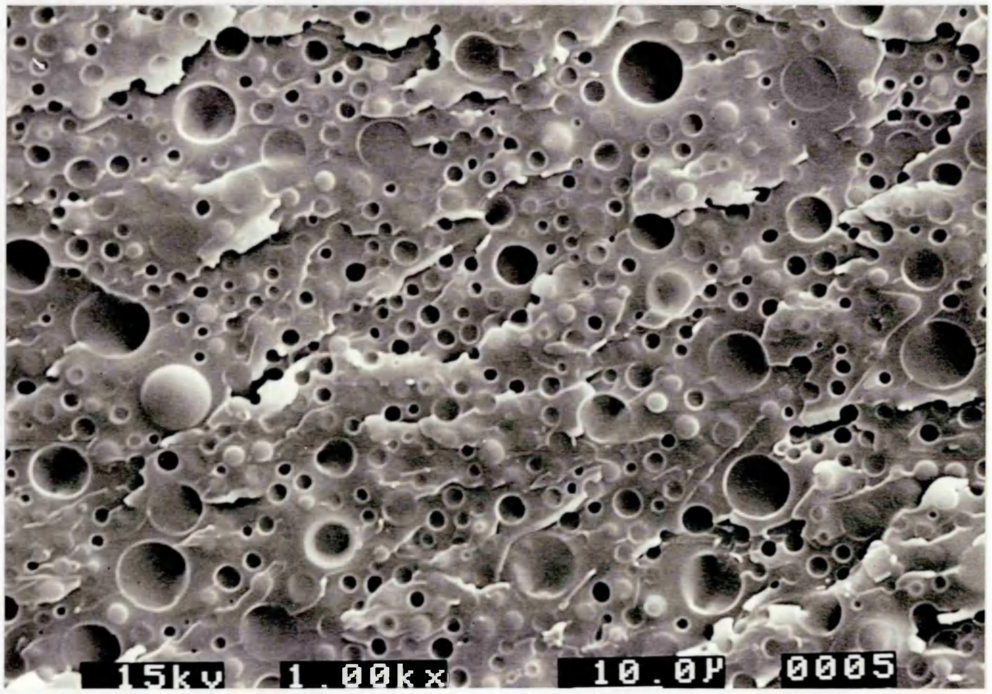


Figure D5: Fracture surface of sample 332-fP(BrC).05-R15.

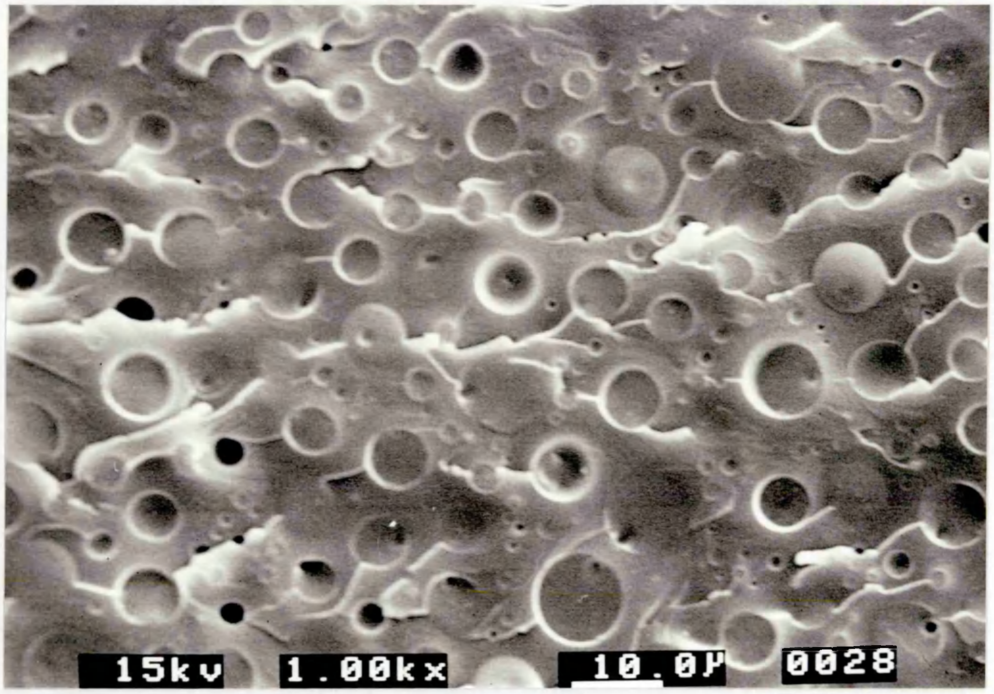


Figure D6: Fracture surface of sample 750-fP(BrC).05-R15.

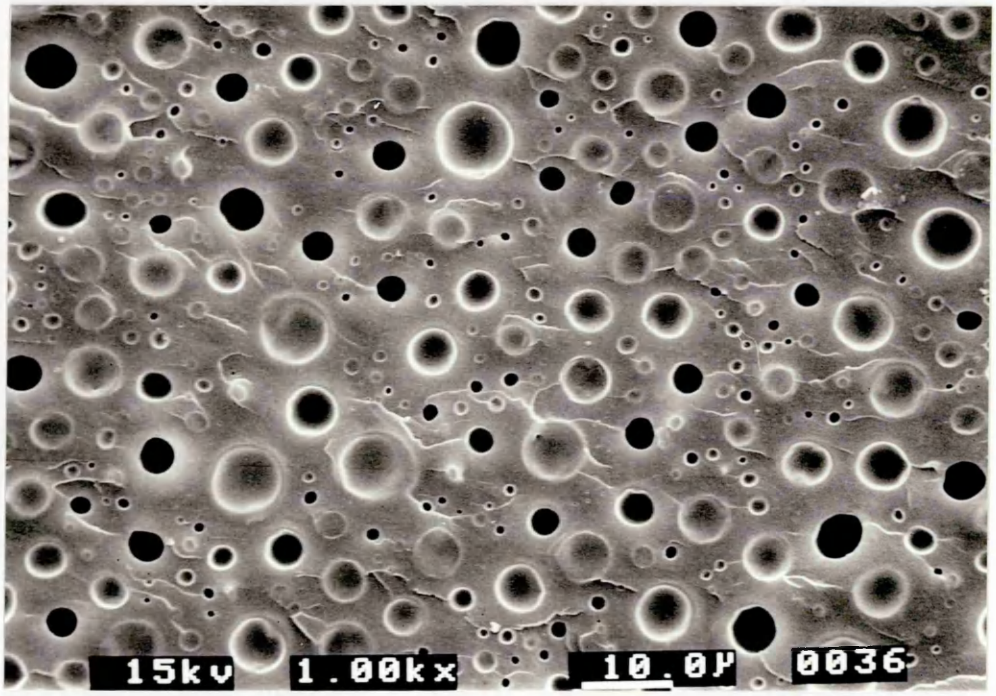


Figure D7: Fracture surface of sample 750-fP(BrC).05-R15 etched in methylene chloride.

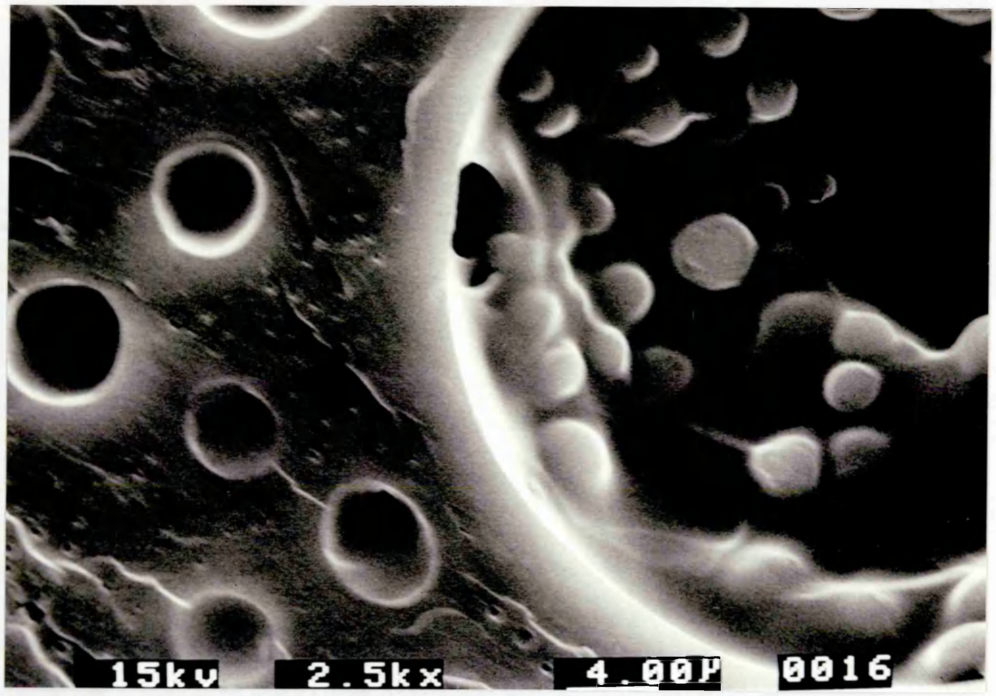


Figure D8: Fracture surface of etched sample 750-fPC. L5-R15. Note the very small holes (0.2µm diameter).

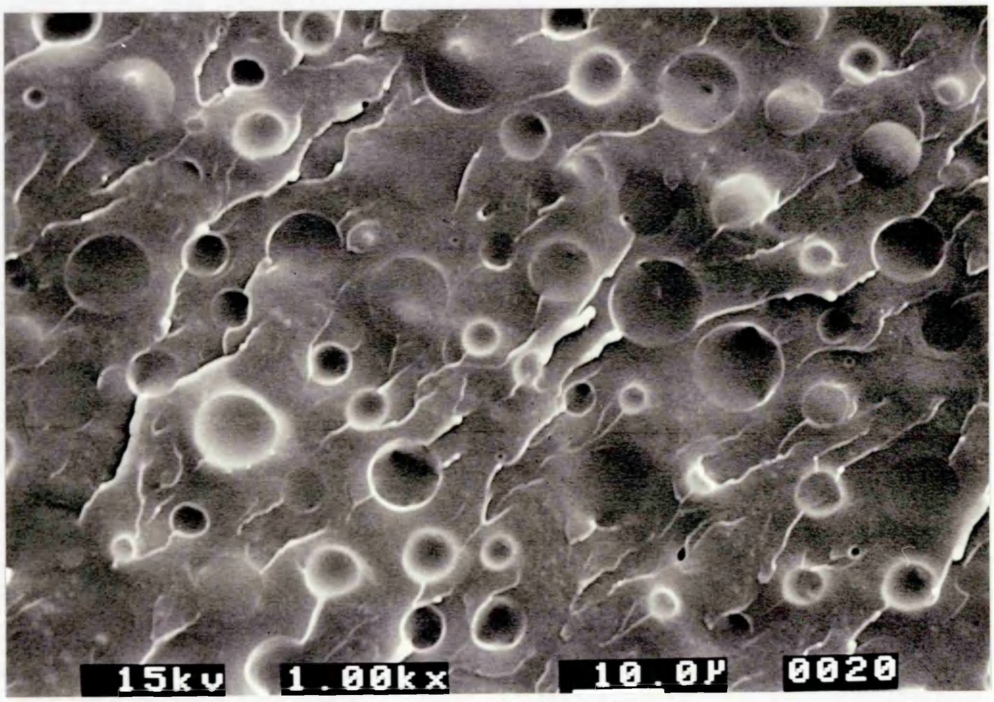


Figure D9: Fracture surface of sample 750-PC.H5-R.15.

iii) Polyethersulfone modified epoxy systems

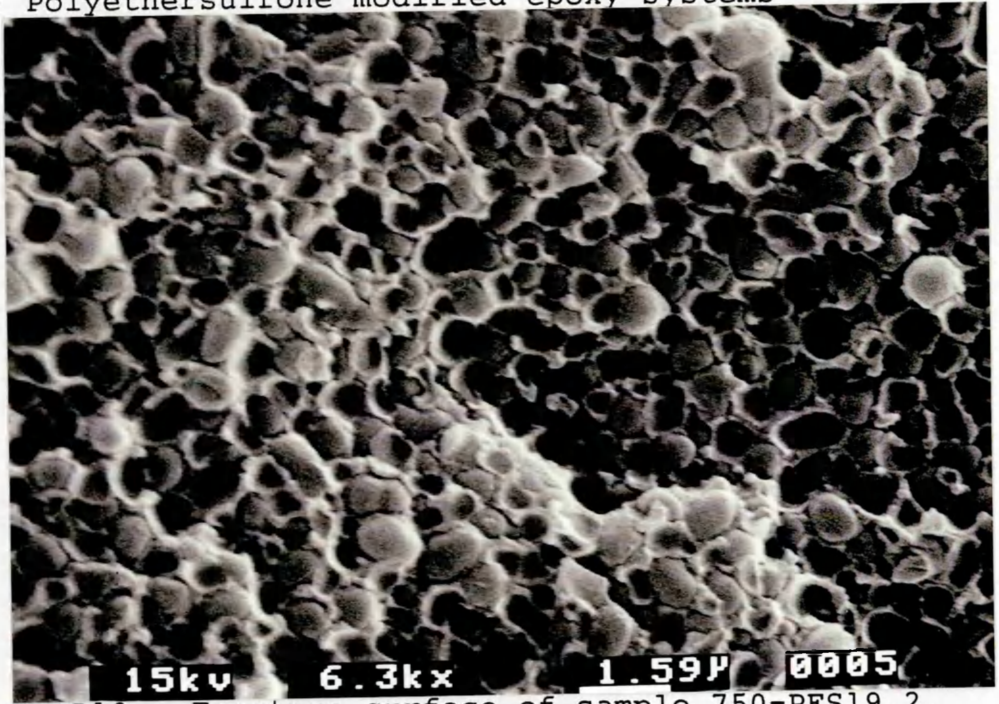


Figure D10: Fracture surface of sample 750-PES19.2.

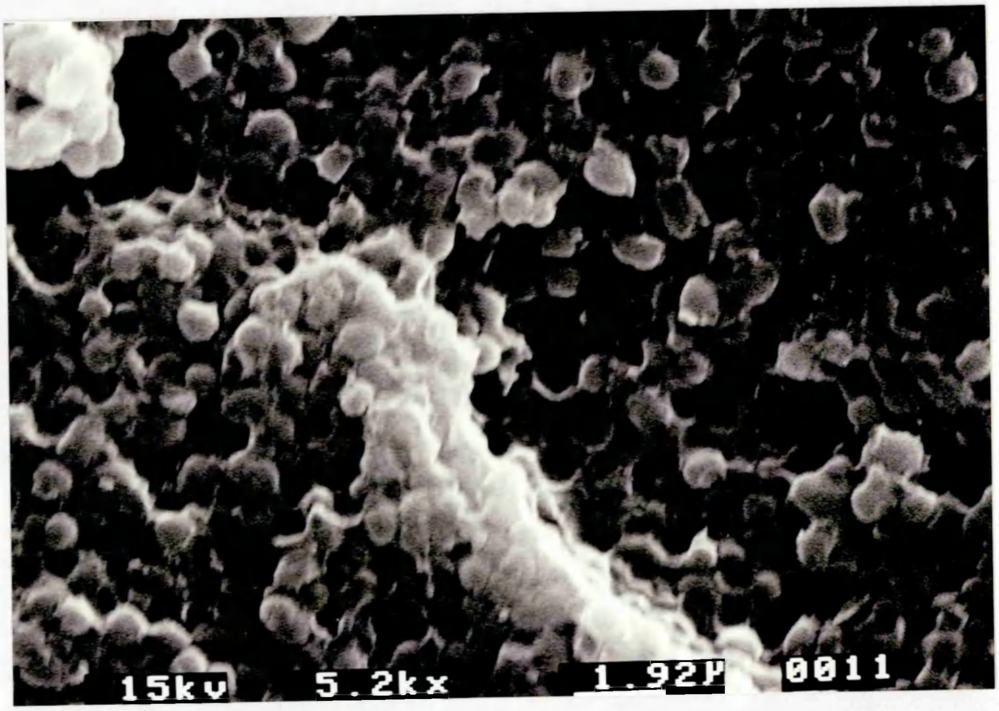


Figure D11: Fracture surface of etched sample 750-PES19.2.

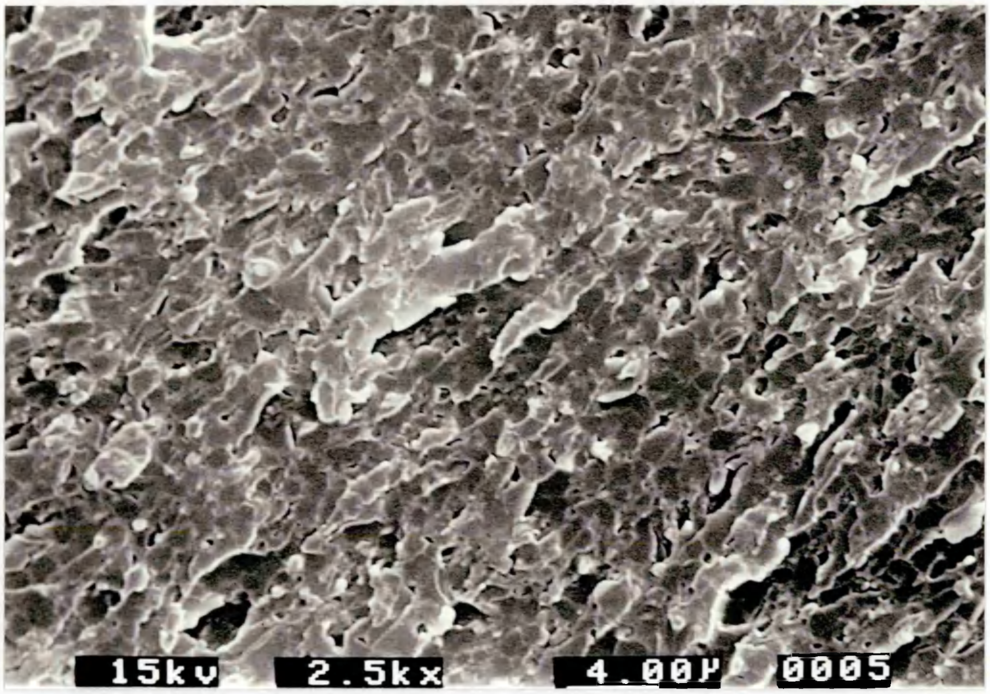


Figure D12: Fracture surface of sample 750-fPES19.2.

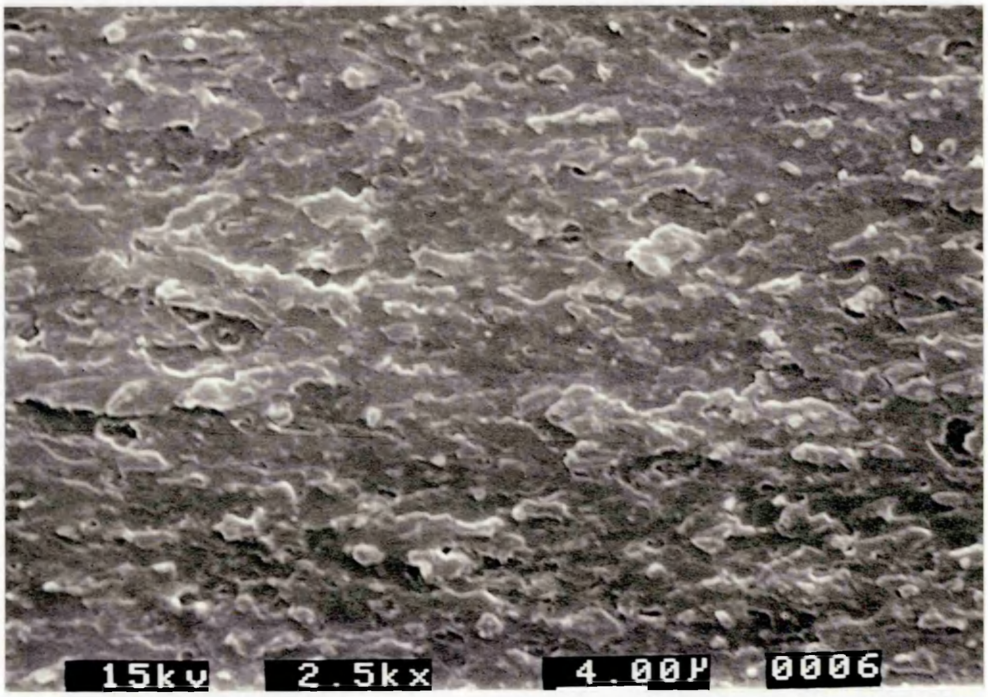


Figure D13: Fracture surface etched sample 750.fPES19.2

APPENDIX E
DMTA RESULTS

i) PC.H Polycarbonate and polycarbonate modified epoxy systems cured with DDM

System	T_g (°C)
750 (neat)	168
PC.H	152.5
750-PC.H7.4	163
750-PC.H13.7	161.5
750-fPC.M3.8	155
750-fPC.M7.4	161
750-fPC.H7.4	154
750-fPC.L3.8	154
750-fPC.L7.4	135

Table E1: T_g values for the corresponding systems.

System	Mn of PC (kg/mol)	T_g (°C)
750-fPC.L7.4	7.1	135
750-fPC.M7.4	9.2	161
750-fPC.H7.4	26	154
750-PC.H7.4	28.7	163

Table E2: T_g dependence on Mn of polycarbonates in polycarbonate modified epoxy systems at 7.4 wt% polycarbonate.

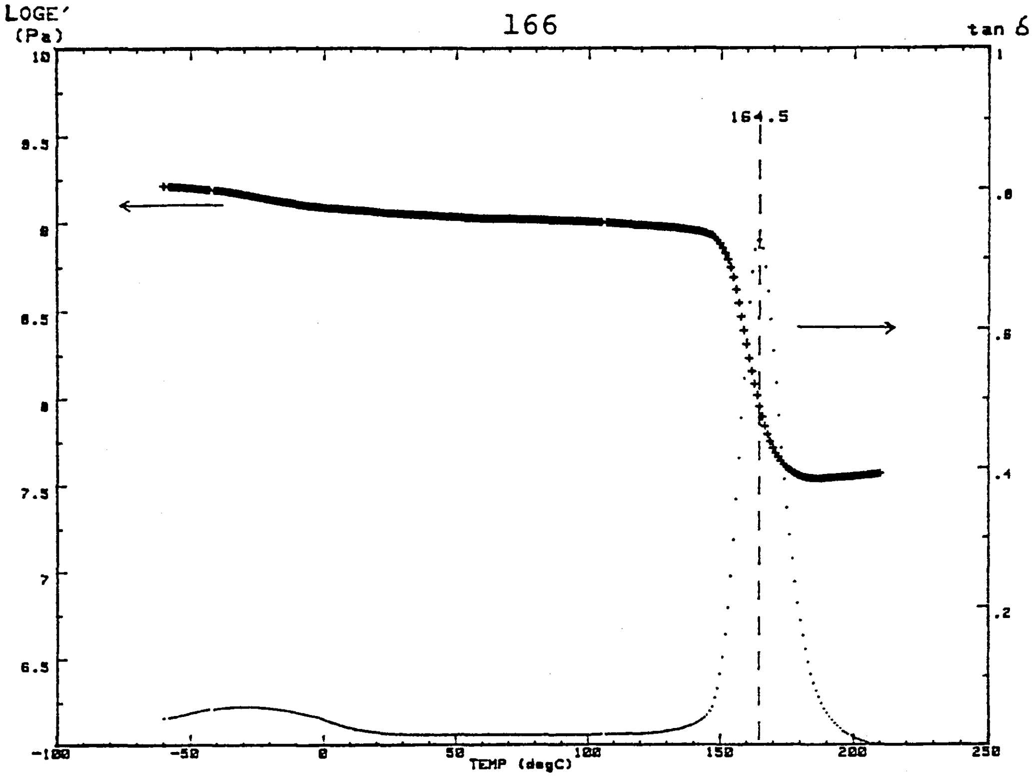


Figure E1: DMTA trace (logE' and tanδ) for the neat epoxy system.

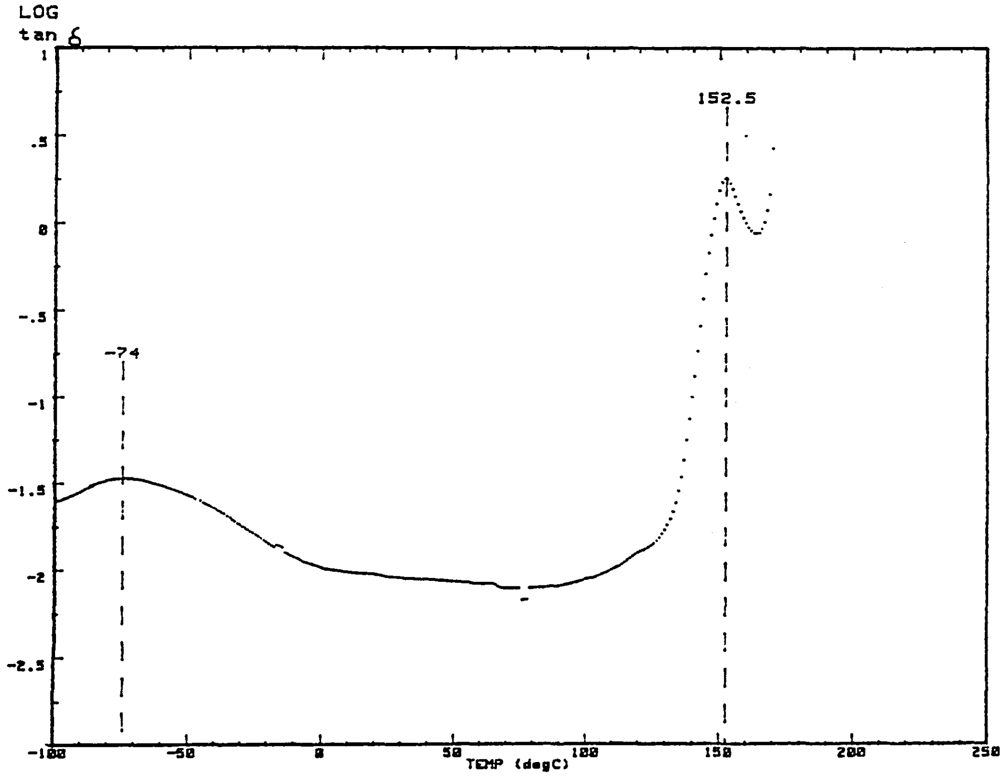


Figure E2: DMTA trace (log tanδ) for the neat PC.H polycarbonate.

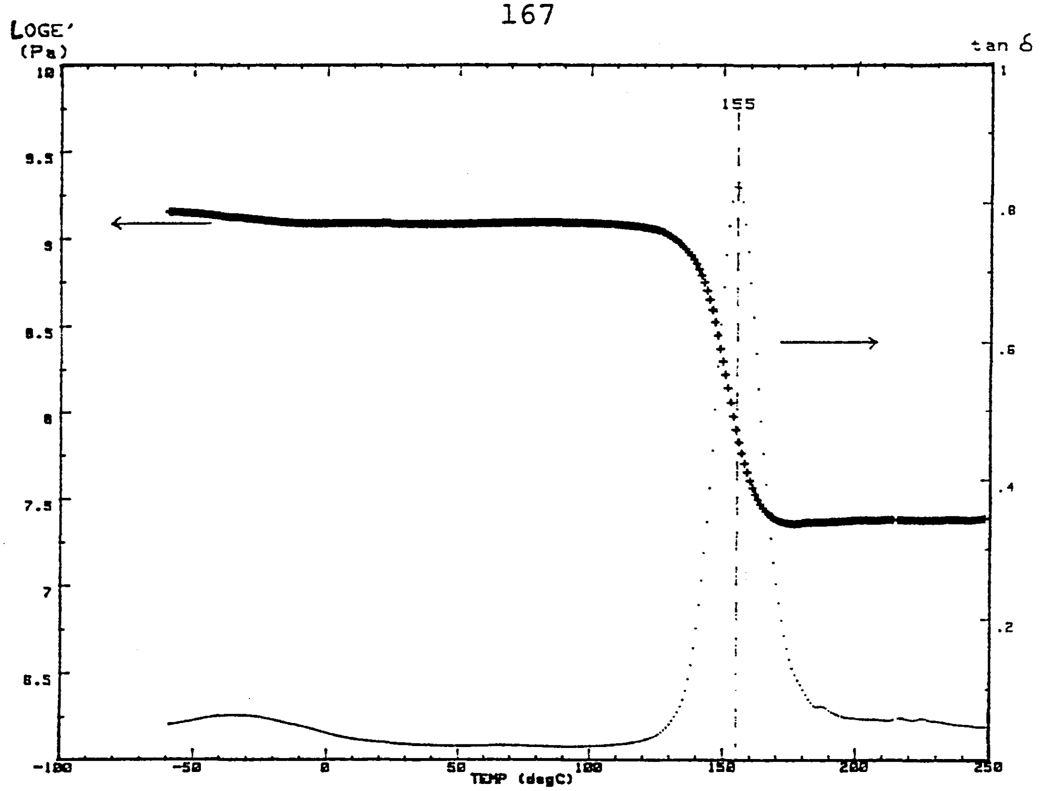


Figure E3: DMTA trace (logE' and tanδ) for the system 750-fPC.L3.8.

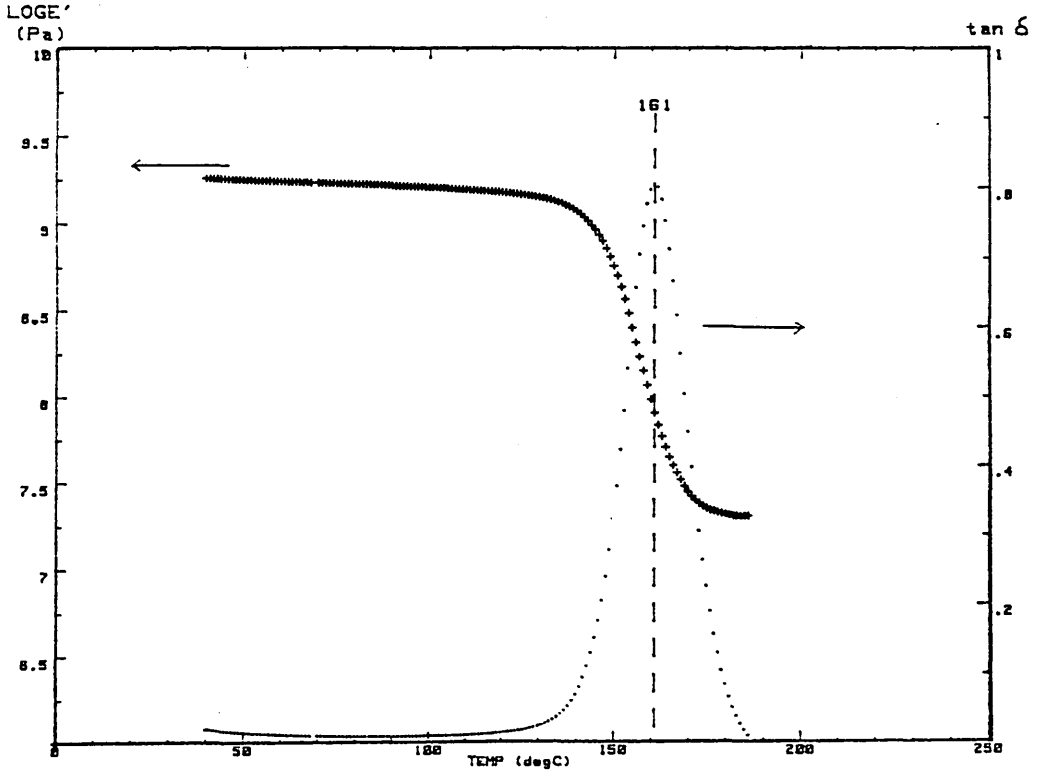


Figure E4: DMTA trace (logE' and tanδ) for the system 750-PC.H13.7.

ii) Polycarbonate modified epoxy systems cured with DDS or HY917

MY750	PC.H	DDS	HY917	DY070	PC.H content (wt%)	T_g (°C)
100	10	30	0	0	7.1	198
100	20	30	0	0	13.3	185
100	15	0	85	1	7.5	154.5
100	15	0	85	0	7.5	73

Table E3: T_g of PC.H modified epoxy systems cured with DDS and HY917 (with and without accelerator DY070). Composition in parts by weight.

iii) Rubber and rubber-polycarbonate modified epoxy systems (cured with DDM)

System	RT_g (°C)	ET_g (°C)
750 (neat)	- [T_β = -30]	168
750-R15	-38	165
750-fP(BrC).05-R15	-31	166
750-fP(BrC).05-R15*	-31	165.5
750-fPC.L5-R15	-36	157.5
750-PC.H5-R15	-35.5	159
332-fP(BrC).05-R15	-33.5	170

Table E4: DMTA results on cured epoxy systems modified by rubber and polycarbonate.

RT_g = glass transition temperature of the rubber-rich phase

ET_g = glass transition temperature of the epoxy-rich phase

* = blend prepared by dissolution of the polycarbonate directly into the hot resin at 80°C (without solvent) : Procedure D.

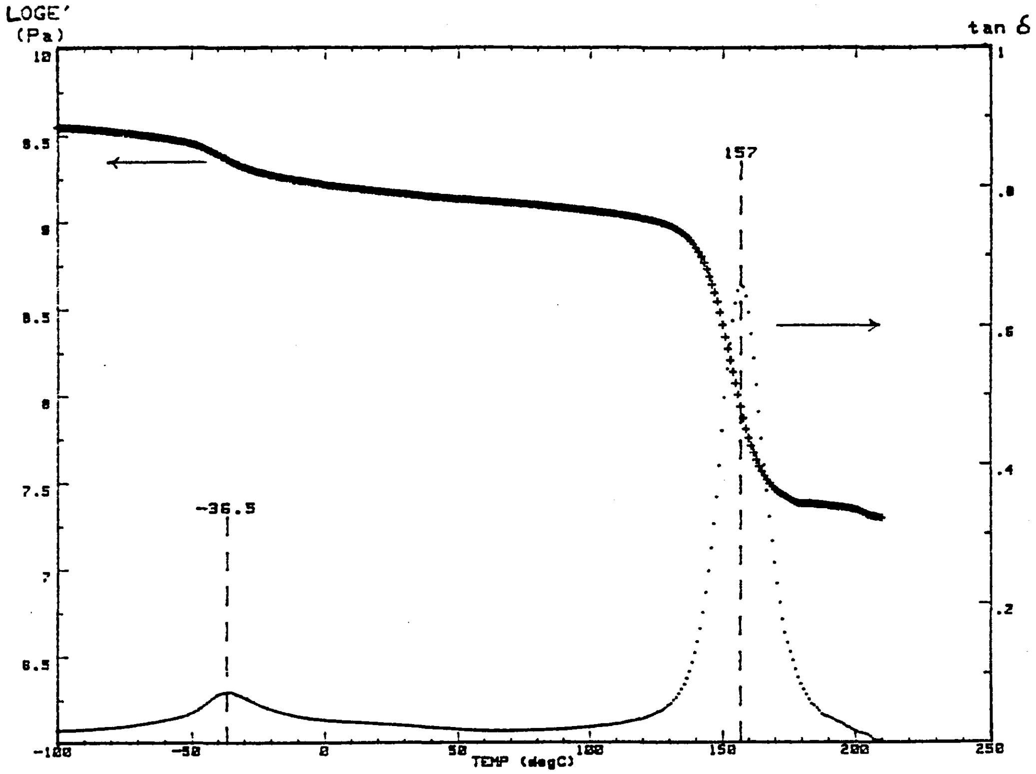


Figure E5: DMTA trace (logE' and tan δ) for the system 750-fPC.L5-R15

iiii) Polyethersulfone modified epoxy systems (cured with DDM)

System	T_g (°C)
750-PES19.2	159
750-fPES19.2	170

Table E5: T_g of polyethersulfone modified epoxy systems.

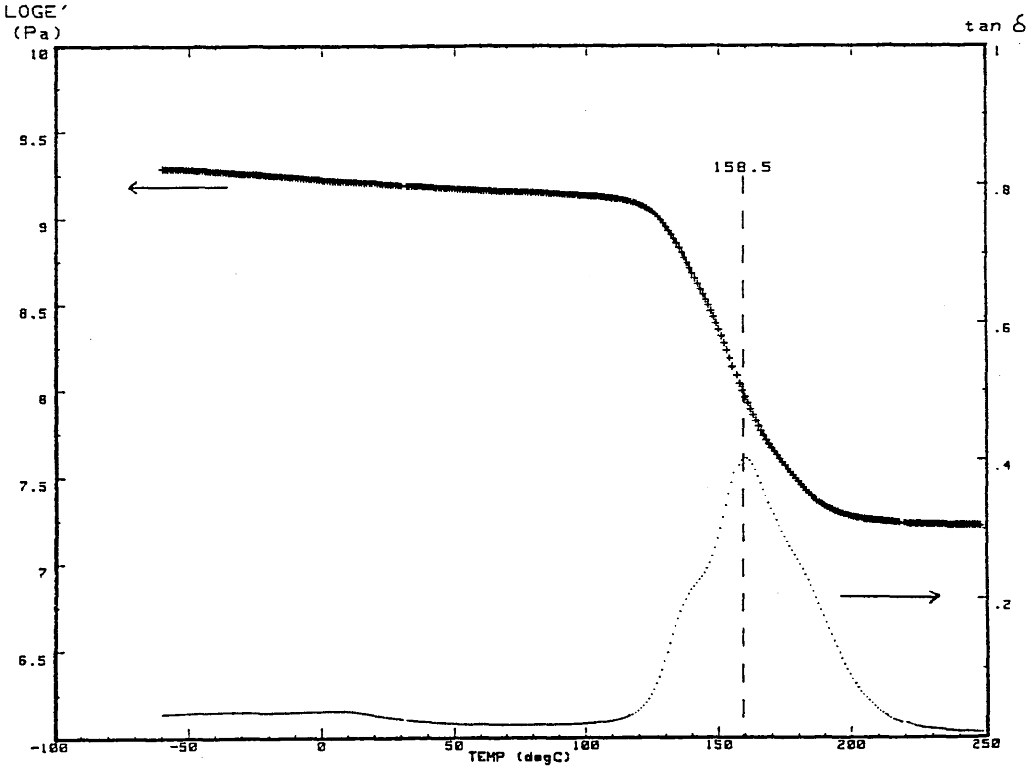


Figure E6: DMTA trace (logE' and tanδ) for the system 750-PES19.2.

APPENDIX F

IMAGE ANALYSIS RESULTS AND PHASE COMPOSITIONS OF RUBBER AND RUBBER-POLYCARBONATE MODIFIED EPOXY SYSTEMS

System	ϕ_R (%)	V_D (%)	d (µm)	dσn (µm)	T_g (°C)	ϕ_E (%)	ϕ_E (%)	ϕ_R (%)	ϕ_R (%)
750-R15	17.9	28.9	3.3	2.0	165	99.2	38.5	0.8	61.5
750.fP(BrC).05-R15	17.9	32.4	3.1	2.4	166	99.5	46.2	0.5	53.8
750-fP(BrC).0.5-R15*	17.9	35.4	2.8	2.2	165.5	99.3	50.9	0.7	49.1
750-fPC.L5-R15	17.9	25.7	3.4	2.8	157.5	97.2	38.8	2.8	61.8
750-PC.H5-R15	17.9	24.1	4.1	2.6	159	97.6	33.3	2.4	66.7
332-fP(BrC)0.5-R15	17.9	28.9	2.0	1.3	170	T_g of the neat cured 332 not determined			

Table F1. Image analysis results and phase composition of epoxy systems modified by rubber and polycarbonate.
* : blend cast following procedure D (without solvent procedure).

System	PC molecular weight Mn (kg/mol)	V_D (%)	d (µm)
750-fP(BrC).0.5-R15	2.8	32.4	3.1
750-fPC.L5-R15	7.1	25.7	3.4
750-PC.H5-R15	28.7	24.1	4.1

Table F2: V_D and d dependence of Mn of polycarbonates in rubber-polycarbonate modified epoxy systems.

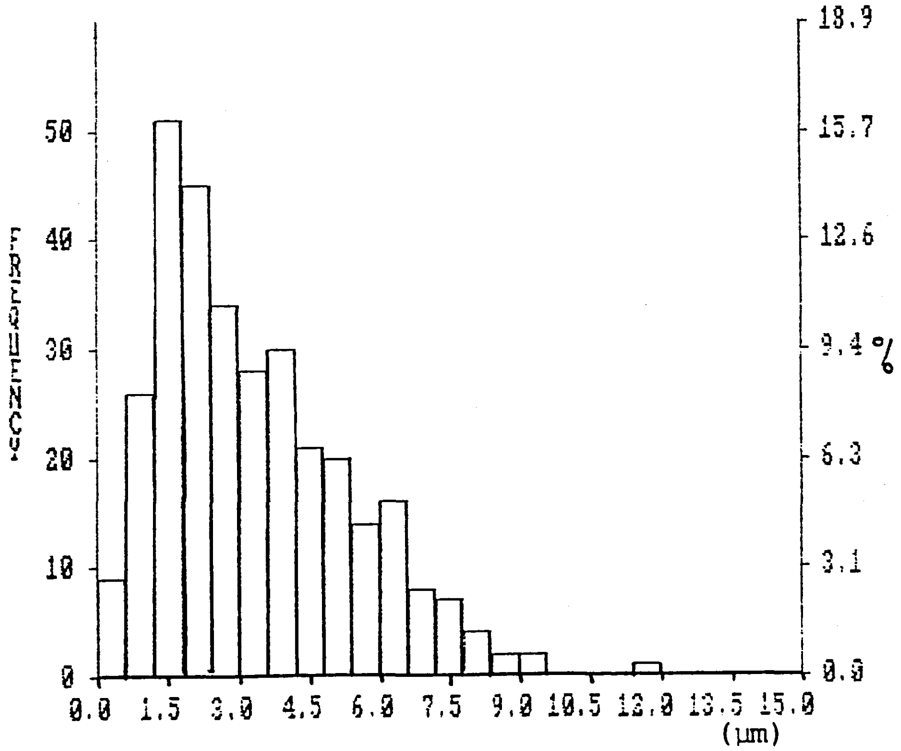


Figure F1: Particle diameter distribution in system 750-R15.

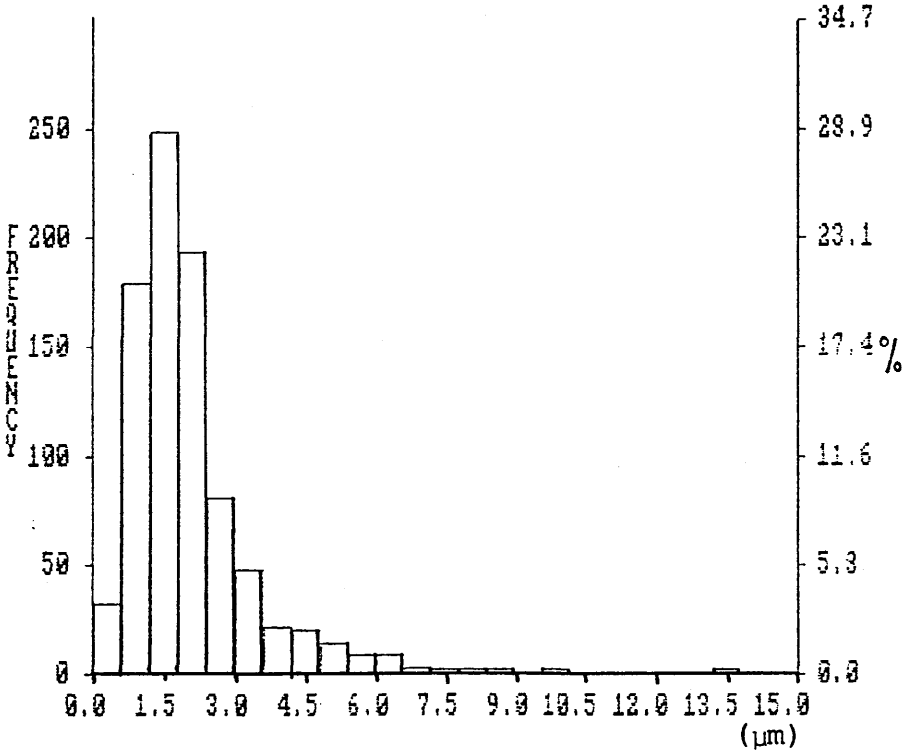


Figure F2: Particle diameter distribution in system 332-fP(BrC)0.5-R15.

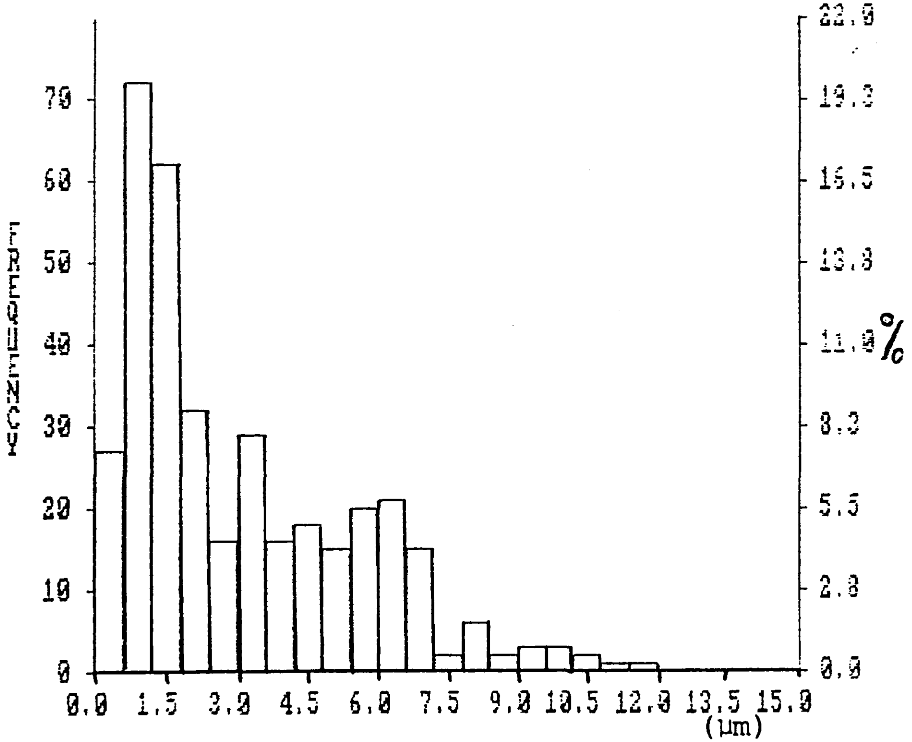


Figure F3: Particle diameter distribution in system 750-fP(BrC).05-R15.

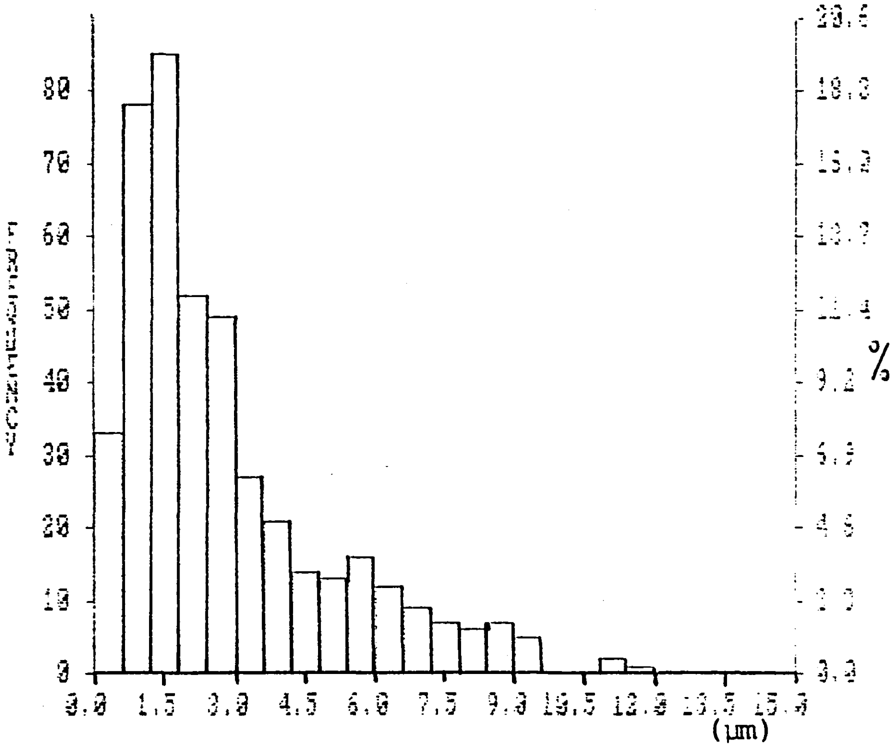


Figure F4: Particle diameter distribution in system 750-fP(BrC)0.5-R15* (without solvent procedure : D).

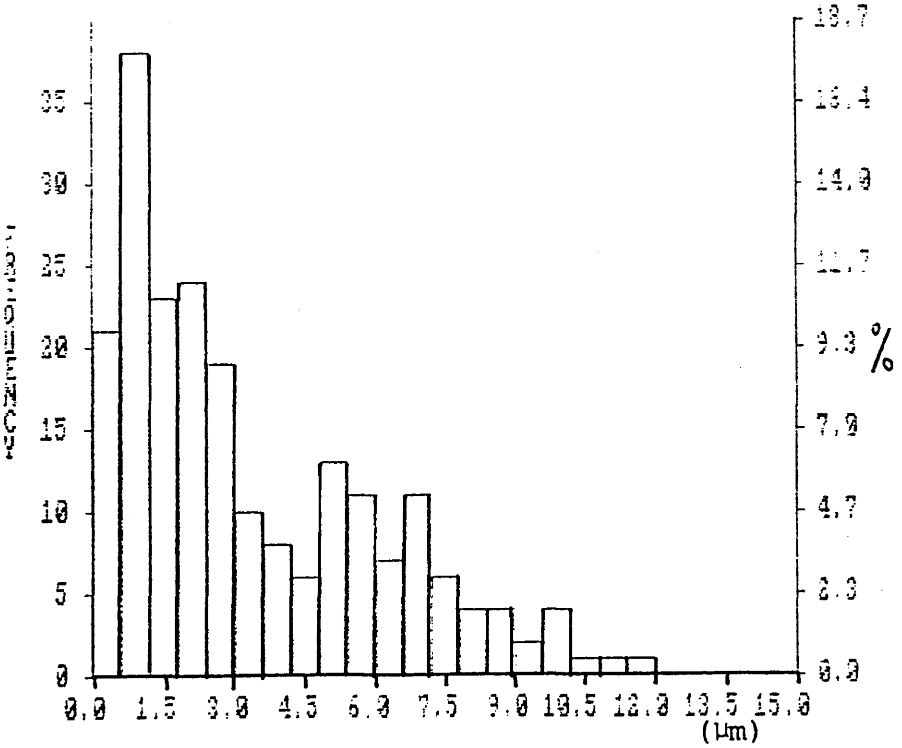


Figure F5: Particle diameter distribution in system 750-fPC.L5-R15.

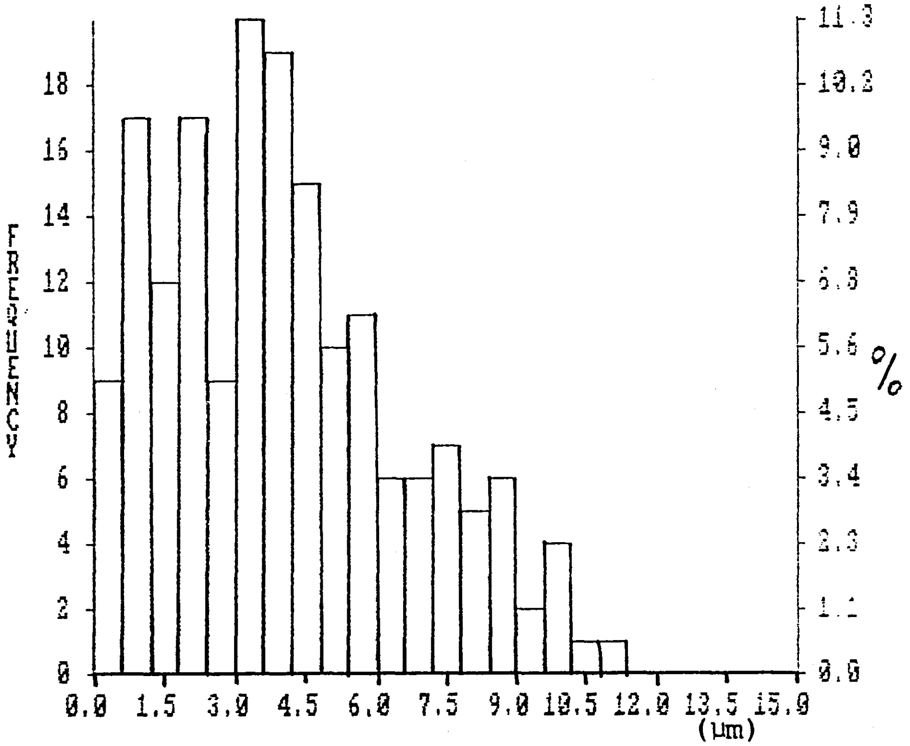


Figure F6: Particle diameter distribution in system 750-PC.H5-R15.

APPENDIX G

MECHANICAL PROPERTIES RESULTS

System	E_{100} (GPa)	σy (MPa)	K_{Ic} ($MPa\sqrt{m}$)	G_{Ic} (kJ/m^2)	G_{Ic} calculated using eqn. (18) (kJ/m^2)
750 (neat)	2.70 ± 0.1	99 ± 2	0.81 ± 0.02	0.19 ± 0.01	0.26
PC.H (neat)	2.21 ± 0.05	66 ± 3	2.80 ± 0.15	3.50 ± 0.43	3.11
750.PC.H7.4	2.80 ± 0.1	95 ± 1	0.71 ± 0.05	0.10 ± 0.01	0.17
750.PC.H13.7	2.70 ± 0.1	89 ± 2	0.66 ± 0.02	0.12 ± 0.01	0.14
750.R15	1.18 ± 0.01	65 ± 2	0.84 ± 0.02	0.31 ± 0.02	0.34
750.FP(BrC).05.R15	1.67 ± 0.03	61 ± 1	0.86 ± 0.02	0.36 ± 0.02	0.39
750.FP(BrC).05.R15*	1.71 ± 0.05	62 ± 1	0.84 ± 0.02	0.31 ± 0.03	0.36
750.FPC.L5.R15	1.83 ± 0.01	64 ± 1	0.84 ± 0.02	0.30 ± 0.03	0.34
750.PC.H5-R15	1.86 ± 0.02	65 ± 1	0.87 ± 0.02	0.31 ± 0.01	0.36
332.FP(BrC).05.R15	1.70 ± 0.03	63 ± 1	0.85 ± 0.04	0.34 ± 0.01	0.37

Table G1: Mechanical properties of neat epoxy, polycarbonate rubber modified epoxy system, and rubber and polycarbonate modified epoxy systems.
* : system cast following procedure D.

System	E_{100} (GPa)	σy (MPa)	K_{IC} (MPa$\sqrt{m}$)	G_{IC} (kJ/m^2)	G_{IC} calculated using eqn. (18) (kJ/m^2)
750.PES19.2	2.71 ± 0.03	96 ± 3	1.20 ± 0.20	0.40 ± 0.12	0.48
750.FPES19.2	2.79 ± 0.01	103 ± 4	0.84 ± 0.08	0.21 ± 0.03	0.21

Table G2: Mechanical properties of polyethersulfone modified epoxy systems.

APPENDIX H

DSC RESULTS ON THE CATALYTIC EFFECT PROMOTED BY POLYCARBONATE IN POLYCARBONATE MODIFIED EPOXY BLENDS CURED WITH DDM

MY750	fPC.L	fPC.M	fPC.H	PC.H	DDM	Procedure	ΔH (J/G)	$\Delta H_{100\%}$ (J/g)	T_{min} (°C)
100	0	0	0	0	26	MY750 degassed[a]	425±18	424±18	163.8±1
100	5	0	0	0	26	A	359±4	388±4	155.5±1
100	10	0	0	0	26	A	425±7	443±7	157.1±1
100	0	5	0	0	26	A	392±4	408±4	159.7±1
100	0	10	0	0	26	A	386±11	417±11	155.3±1
100	0	10	0	0	26	A without degassing	383±13	413±13	162.8±1
100	0	0	10	0	26	A	375±7	404±5	153.3±1
100	0	0	0	10	26	B	415±6	448±6	154.7±1
100	0	0	0	10	26	B without degassing	424±10	458±10	165.2±1

Table H1: DSC results on the polycarbonate modified epoxy blends composition in parts by weight.

[a]: MY750 degassed 1h at 100°C - 110°C before adding DDM.

Polycarbonate	Polycarbonate Mn (kg/mol)	T_{min} (°C)
fPC.L	7.1	157.1
fPC.M	9.2	155.3
fPC.H	26	153.3

Table H2: T_{min} variations against polycarbonate molecular weight in polycarbonate modified epoxy blends cured with DDM at 7.4% wt polycarbonate.

Degassing time (h)	T_{min} (°C)
0	165.2
1	152.7
1.5	129.8
2	129.3

Table H3: T_{min} variations in blends MY750/PC.H/DDM = 100/10/26 against degassing time of the epoxy resin-polycarbonate blend before the hardener was added.

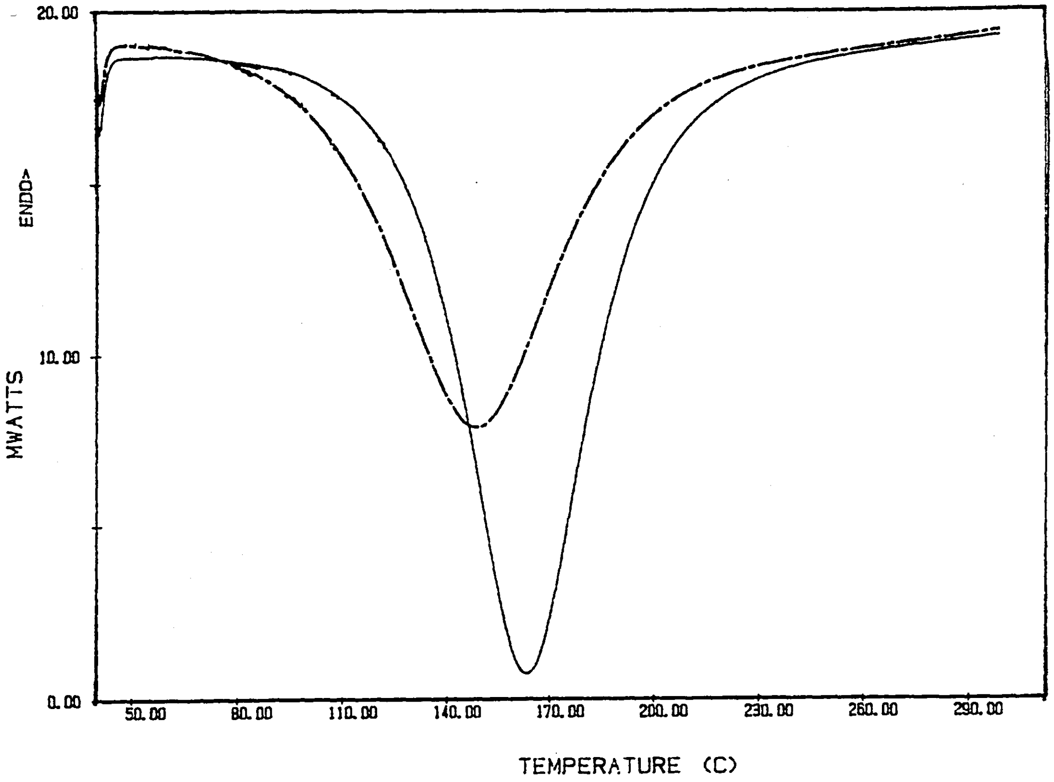


Figure H1 : Comparative dynamic DSC runs.
———— : blend MY750/DDM = 100/26
——-—— : blend MY750/PC.H/DDM = 100/10/26
the blend MY750/PC/H = 100/10 of
which was degassed for 2 hours at
100°C - 110°C