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## CONTROL OF THE PROPERTIES OF THE INTERFACE IN ORGANIC MATRIX COMPOSITES

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## 1. Introduction

### 1.1 The Interphase in Organic Matrix Composites

Many recent studies on the properties of organic matrix composites have been reported. An area of considerable interest is the properties of the matrix in the vicinity of the reinforcing fiber (1). Some studies assume that the matrix is homogeneous up to the fiber, and the material inhomogeneity exists as a plane surrounding the fiber (2-5). This plane of material is a true interface. The interface is associated with a single mechanical property, the interfacial bond strength. Other work has suggested that a volume of material surrounding the fiber is significantly different from the bulk matrix (6-9). This volume of material is an interphase. Drzal (6) has suggested that the interphase is more rigid than the bulk matrix while Piggott (7) has postulated that the interphase is softer.

### 1.2 Evidence for a Soft Interphase

Recent studies have examined the properties of matrix material near the fiber (8-11). This work has produced evidence that the interphase material has a lower modulus than unmodified matrix material (approximately 1/2th of the normal matrix modulus) and that it extends for about 1/10th of a fiber diameter into the matrix. These findings were based on three experiments.

The first experiment used a model composite based on a disk of resin with a single fiber embedded in the center (Figure 1). The sample was loaded through the fiber and the deformation in the matrix was measured near the fiber on the free surface. Figure 2 shows typical deformation maps for three composites in which the fiber had different surface treatments. Analysis of the deformation in this type of sample was carried out using finite element and shear lag methods (12,13). If no interphase was present the deformation expected was as is shown for the phenolic coated fiber in Figure 2. The deformation maps for the oxidized and the sized fibers show large elastic deformations near the fiber. This was interpreted as indicating the presence of a soft interphase and this was confirmed through finite element and shear lag modelling of the system (12).

One of the issues that became apparent during this study was that the properties of the material near the fiber were very dependent on time (8,10). In order to obtain elastic data it was found necessary to condition the sample by loading the sample to a higher load than used for the elastic deformation for a long period (creep relaxation) or to cycle the sample to a high load several times before testing (fatigue relaxation). The inelastic deformation was about five times greater than the elastic deformation at the same load. It was also observed that the inelastic deformation was greater for a thicker sample and was

not recoverable on unloading. If the sample was exposed to elevated temperature near cure temperature the time dependent deformation reappeared. It was assumed to be related to thermal stresses from differential cooling from cure temperatures.

The second set of experiments addressed the variation of the load necessary to debond a fiber when loaded in compression in a bulk composite (12). The configuration tested is shown in Figure 3. Experimental data quoted from the literature (14) suggested that the dependence of fiber bond strength on interfiber spacing was much lower than expected. Again, the use of finite element and shear lag analysis indicated that this effect could be interpreted as indicating the presence of a soft interphase.

Raman spectroscopy was used to examine the chemistry of the interphase material (11). The smallest area that can be examined using spectroscopy is ultimately limited by diffraction problems of point sources and this limitation is governed by the wavelength of the radiation used. Infrared spectroscopy is sensitive to the chemistry of the sample but the minimum spot size is about 10 microns. Raman spectroscopy is also sensitive to sample chemistry but uses visible light and the minimum spot size is near 2 microns. Preliminary study of raman spectra of the matrix near a fiber (using the same sample as for the first method) shows that the chemistry changes in the region of the first few microns away from the fiber and is constant thereafter. This is of the same order of magnitude as the variation of mechanical properties observed using the first two methods. The data could be interpreted as suggesting that the region near the fiber was chemically more complex than normal.

### 1.3 Possible Mechanisms for Formation of an Interphase

A major problem is associated with the possible mechanism of formation of the interphase. Initially it was postulated that chemical activity of the fiber surface could be invoked to explain the observations (6,15,16). However, the concentration of acid functionalities ( $-\text{COOH}$  and  $\text{Ar-OH}$ ) is inadequate to give any significant change of reactant ratios in the volume of resin affected. In addition, the observed effect of change of reactant ratios in this system (6,17) shows that off-stoichiometric mixtures have significantly higher moduli than the stoichiometric mixture. Recent work (18) has suggested that entropy effects could change the properties of polymers near interfaces. The restrictions imposed on large molecules near impenetrable interfaces has a greater entropic penalty than for smaller molecules. This allows a thermodynamic mechanism leading to fractionation of disperse thermoplastics near an interface. It is possible that similar effects could affect the course of the polymerization in the region, leading to an accumulation of

chain ends near the fiber. This could affect the Tg of the interphase. Such a mechanism remains only speculation at this time.

## **2.0 Work at MTU on Interface Effects on Matrix Solidification**

An alternative mechanism is presently being studied at Michigan Technological University (19). In this mechanism, the interface modifies the mechanism of solidification of the matrix during cure.

The work done under this contract addresses possible mechanisms for the formation of interphases in organic matrix composites.

## **2.1 The Mechanism of Solidification of Epoxy Resin Matrices**

At least three mechanisms are possible for the liquid-solid phase change during matrix cure. Two involve an abrupt change occurring over a limited time frame i.e. mechanisms covered by catastrophe theory. These are gelation through formation of an infinite network, and vitrification through increase of viscosity of a homogeneous reacting mixture. The third mechanism is through gradual precipitation of large molecular species from the mixture. This may be subdivided depending on whether the precipitated material is over or under its glass transition temperature.

The gelation mechanism is most commonly proposed for solidification of epoxy resins and has been described in detail by Gillham (20-22). He constructs a time-temperature transformation diagram (TTT plot) to summarize the changes that occur during resin cure. A typical TTT plot is shown in Figure 4. The point of initial solidification is shown in these plots as the gelation line for the majority of systems over most of the temperature ranges studied. The evidence for gelation is based on the onset of insolubility in strong organic solvents and the formation of dual damping peaks during determination of dynamic properties of curing systems measured on a braided fibrous support (torsional braid technique).

The viscoelastic properties of gels at the point of gelation have been studied by Winter (23). He used the scaling approach developed by de Gennes (24) and considers the relationship between degree of cure and viscosity and the relationship between real and loss modulus and test frequency at the point of gelation. According to this work, the onset of gelation is characterized by a time when the viscosity can be described by a power law relationship with a degree of cure function and the real and loss moduli are equal and their frequency dependence

can be described by a power law.

This work was extended by Martin et al (25-27) to an epoxy resin cure system cured with diethanolamine. Several epoxy resin systems have now been shown to be described by the scaling laws at gelation provided that the cure temperature is greater than the maximum achievable glass transition temperature. Curing agents used include diethanolamine (19,25), Jeffamine D400 (19,26) cured at temperatures 60°C and over, and butane diol diglycidyl ether systems (27). Jeffamine D400 is a commercial polymeric curing agent based on a polypropylene oxide polymer with a molar mass of 400 dalton, terminated at each end with an amine group. It has the formula:



where n has a value of about 5. Each system can be cured at temperatures well over the glass transition temperature of the fully cured system. Figures 5 and 6 show typical results for a Jeffamine D400 cured system at 80°C. We conclude that these systems solidify by gelation.

The majority of epoxy resin systems, however, do not show this type of behavior as is illustrated in Figures 7 and 8 for a system cured with ethylene diamine (EDA). We have studied EDA and its N-methyl derivatives, PACM 20, as used by Gillham (20), m-phenylene diamine, as used in the interphase studies described above, and Jeffamine D400 cured below 40°C. These systems do not obey scaling laws. We conclude that these systems do not solidify by gelation.

Some workers have suggested that the reason that some systems do not scale at the solidification point is related to the onset of vitrification (17). Examination of the curve for the glass transition temperature ( $T_g$ ) for the EDA cured resin shows that the  $T_g$  for the reaction mixture at the point of phase change is still well below 0°C and well below the cure temperature of 40°C. Vitrification cannot be the cause of solidification for the system. De Gennes has suggested that two pathways for gelation are possible (ref 24 pp129-130). In one mechanism, small molecules grow in size and degree of branching at similar rates. In the second, long chains form initially, or are formed separately, and cross link as a distinct process. Some workers have suggested that the reactivity of primary and secondary nitrogen functions have different reaction rates. This could cause a variation in solidification mechanism. However, N-methylation of EDA does not change the solidification mechanism, even for N,N'-dimethyl ethylene diamine which only forms a very lightly crosslinked network (28). It would seem unlikely that the degree to which linear polymer forms prior to gelation was a significant variable in determination of the mechanism for solidification in this case.

We propose that the phase change mechanism for most epoxy resin systems is through precipitation of high molecular weight material as a glassy solid. The reactivity of the precipitated material is substantially lower than that of material in the liquid phase and consequently the precipitated particles do not grow. The proportion of insoluble material builds up rapidly as polymerization proceeds. As the volume fraction of precipitate increases, the viscosity increases rapidly. When it becomes space filling in the reaction vessel the material solidifies as a loose conglomerate of glassy particles with lower molecular weight, fluid material trapped in the interstitial spaces. Reaction proceeds in the liquid material. The material polymerizing in the interstitial regions will be constrained geometrically by the glassy particles and will grow as extended, highly branched networks of complex shape and may not suffer the limitation on molecular dimension caused by insolubility. This material could solidify by gelation or by vitrification.

The final product of this solidification mechanism would be a conglomerate of vitrified molecular dimension particles suspended in a distinct glassy matrix. In contrast, the final product of the gelation mechanism would be a complex network of infinite extent. It would be anticipated that materials formed by such different mechanisms would have different properties. It is recommended that further work be done to compare the properties of networks solidified by alternate mechanisms.

## 2.2 Degree of Reaction at the Point of Solidification

Prediction of the degree of reaction at the gelpoint has been attempted by Flory and Stockmayer (29,30) using a statistical approach referred to as a mean field theory. The degree of reaction,  $p_g$ , at gelation for a system with a resin of functionality 2 and amine of functionality  $f$ , mixed such that the ratio of the epoxide concentration to the amino proton concentration is  $\rho$ , is given by the equation:

$$p_g = \frac{1}{[1 + \rho(f-2)]^{1/2}}$$

For a tetrafunctional amine mixed in stoichiometric ratio, the predicted degree of reaction is 0.577. The derivation of this equation assumes that the primary and secondary amino protons react at the same rate. Various attempts to allow for different reactivities (31,32) only change this value by a small amount and the expected range for  $p_g$  is 0.58-0.62. Data from the



present work for the degree of reaction at the point of solidification is shown in Table 1:

Table 1: Critical Degrees of Cure for Solidification of Epoxy Resin Systems

Curing Agent	Cure Temp	$P_g$
Jeffamine D400	80°C	0.55
Jeffamine D400	40°C	0.75
Ethylene Diamine	40°C	0.38
DMHDA	60°C	0.64

Of the systems studied, only those systems which obey scaling laws are observed to solidify at the degree of reaction predicted by Flory. Systems which are postulated to solidify by phase separation may solidify before (eg cured with ethylene diamine) or after (eg cured with Jeffamine D400 at 60°C) the predicted gel point. For systems showing an early solidification point, it is natural to postulate that the molecular weight of the largest molecule at the time in the reaction when insolubility first is observed, is well below that required for gelation. For systems in which bulk solidification occurs at a stage well beyond the predicted point of gelation, a natural explanation is not obvious. The assumptions of the statistical theory are not fulfilled. For these systems, we postulate that the vitreous molecules, which are precipitated early in the reaction, are statistically more likely to include amine functionalities with three or more amino protons reacted (ie the molecular branch points). The fluid phase then contains a reduced concentration of branches which inhibits formation of an infinite network and, therefore, gelation. We suggest that the observed delay in the solidification, past the point of gelation, is strong evidence that phase separation has occurred which allows partitioning of the molecular species between the branched, insoluble species and the linear, fluid species.

#### 2.4 Differentiation Between Systems Solidifying by Alternate Mechanisms

It has been suggested (23-27) that the major difference between systems that exhibit scaling properties at solidification, and those which do not is the difference between the temperature at which the system is cured ( $T_{cure}$ ) and the glass transition temperature of the fully cured system ( $T_g$ )

When the curing temperature is well above  $T_g$ , the glass transition temperature of the largest molecule at any time during cure is always lower than the curing temperature. Vitrification

of the largest molecule, as suggested in the phase separation mechanism, is impossible. The largest molecules remains in equilibrium with the small molecules in or near to the theta condition and the reaction mixture remains homogeneous. The free volume of the largest molecules is still large enough to allow the smaller molecules to approach and to react with them. Every molecule grows larger individually in a statistically determinable manner, and the distribution of molecular weight becomes broad. The concentration of the largest molecules increases as the reaction continues. At some point, a network with infinite molecular weight will be attained and gelation will occur. The reaction vessel will be filled with interpenetrating gel particles containing embedded small molecules. The reaction mixture is homogeneous throughout the reaction.

When  $T_{cure}$  is above  $T_g$ , it is postulated that solidification is by phase separation.

### 3.0 Influence of an Interface on the Solidification Mechanism

De Gennes has discussed the influence of reducing the dimensionality of a system on the process of gelation (ref 24, pp88-97). Although he does not consider the influence of vitrification on a gelling system, he does discuss the stability of the polymerization in solution toward phase separation. He has predicted that solution polymerizations carried out in a tube of molecular dimensions or on a surface would be much less stable toward phase separation than if carried out in the bulk. Bulk polymerization of epoxy resins could be considered as equivalent to polymerization in solution, where the solvent is the material of lower degree of polymerization. In view of the chemical similarity of the solvent to the highest molecular weight polymer, the conditions would be effectively theta conditions when molecular dimensions are unperturbed by the solvent. Under theta conditions, entropic considerations play an important role. The destabilizing influence of restricting the dimensionality of the reaction is through such entropic effects.

We propose that the influence of the interface on the resin solidification mechanism is through the destabilization of the surface toward phase separation. Near the surface the largest molecules precipitate earlier in the polymerization reaction, and at a lower degree of polymerization and create a layer with a lower glass transition temperature than in the bulk. We recommend that further study be done to investigate the influence of the surface on the mechanism of solidification.

### 4.0 Generalization of the Solidification Mechanisms of Thermoset Resins

On the basis of the experimental evidence presented here, it

is postulated that the mechanism of solidification of epoxy/amine networks during cure may be through gelation or through progressive phase separation depending on the cure temperature compared to the highest attainable glass transition temperature of the system. It is also suggested that the primary experimental criterion for gelation should be the occurrence of scaling properties of the viscosity with the reaction variable,  $\epsilon$ , and the real and loss modulus with frequency, as proposed by Martin (25). Some generalization of these mechanisms is possible, and a broad classification of solidification mechanisms for multifunctional, step polymerizations is presented.

In the cases when gelation is observed, it is not clear at this time whether gel particles are precipitated from the reaction mixture prior to gelation or, if they do, what effect would be predicted. It is clear from the fit of a general kinetic equation to the data throughout the gelation region, that gelation does not affect the kinetics of the reaction to a large extent. It is possible therefore that precipitation of gel particles also may not affect the kinetics or the course of the reaction: the presence of the insoluble particles would not be detectable. It could be postulated that, if gel particles precipitated, they would affect the viscosity. Analysis of the numerical viscosity data would not be practicable, however, firstly because the viscosity is diverging catastrophically and few data points are available, and secondly, because the viscosity divergence would imply large increases in the characteristic time, for translation (25). This has the effect of preventing the shear viscosity from reaching steady state as gelation is approached. These effects degrade the precision of the viscosity measurement.

One reported observation may be relevant. Winter (33) has reported that off-stoichiometric step- polymerizations do not show scaling at the  $G'/G''$  crossover point. There is no apparent reason for this. Non-stoichiometric systems, however, would show a gradual enrichment of the reaction mixture in the component in excess as reaction proceeds. This would tend to cause the parameter describing interaction between the largest molecules and the reaction medium to rise, increasing the free energy of mixing and increasing the probability for phase separation to occur. It is postulated here that systems showing  $G'$  and  $G''$  scaling with frequency at the point when  $G'=G''$  are homogeneous at gelatin. Systems that scale at a time other than when  $G'=G''$  have phase separated prior to gelation.

The general classes of alternate mechanisms of solidification of epoxy- amine systems postulated are shown in Figure (9).

Of epoxy resin/amine systems reported in the literature, and those studied here, almost all appear to solidify via mechanisms

Ib and Ic. The product of the reaction at gelation would appear to be a conglomerate of thermodynamically similar glassy spheres.

Amines giving rise to less rigid backbone systems (e.g., polyoxypropylene diamines and possibly polyamido-polyamines) may be cured at temperatures over  $T_g$ . Jeffamine D400, at stoichiometric ratios, and cured at over  $T_g$  (40°C) cures via mechanism II. Epoxy resin cured with 5% diethanolamine at temperatures over  $T_g$  (80°C) appears to cure via mechanism II, but the mechanism is via cationic chain polymerization probably initiated by the diethanolamine-epoxy resin adduct as has been reported for 4-ethyl-(2-methyl)imidazole cured systems (34).

Non-stoichiometric epoxy resin/Jeffamine D400 systems over  $T_g$  may also solidify by mechanism II but due to the lack of scaling of  $G'$  and  $G''$  with frequency at the  $G'/G''$  crossover it is suggested that these systems solidify by mechanism Ia.

A special case of epoxy resin cure using 1,4 dimethylhexane 1,4 diamine (DMHDA) has been reported (35). It is claimed that at temperatures below 50° C the system forms a glass which is chemically stable below 50° C. It is reported to "melt" and continue to cure if heated over 50°C. It is postulated that this system solidifies by mechanism III.

## 5.0 Conclusions for Solidification Studies

This work indicates that the network structure of the epoxy-amine resins is significantly different for the reactions cured above the highest attainable glass transition temperature,  $T_g$ , and the reactions cured below  $T_g$ . The following conclusions can be obtained from the present work:

- (1) For the reaction in which  $T_{cure}$  is greater than  $T_g$ , gelation is responsible for the liquid to solid transition. The reaction proceeds from the liquid state through gelation to the rubbery state. The reaction is homogeneous. A homogeneous network structure of the final product can be obtained.
- (2) For the reaction in which  $T_{cure}$  is less than  $T_g$ , the largest molecules precipitate from the reaction bath and form glassy particles. This results in a progressive phase separation occurring during the liquid to solid transition. A network structure containing a conglomerate of many glassy particles is formed as a result of solidification. The reaction is heterogenous during and after phase separation. Gelation may or may not occur in this condition.
- (3) In the regime near the gel point, a power law dependence of  $G'$  and  $G''$  on frequency,  $G'(\omega) \sim G''(\omega) \sim \omega^\Delta$ , with  $\Delta=0.70\pm0.03$  was obtained near the time when  $G'$  and  $G''$  cross over. A scaling law,

$\eta \sim \epsilon^{-k}$ , with  $k=1.3 \pm 0.2$  was also observed. These results agreed with Martin's dynamic scaling theory.

(4) Gelation is a catastrophic transition, whereas phase separation is a progressive transition. During the liquid to solid transition, the buildup of viscosity due to gelation is much faster than the buildup of viscosity due to phase separation.

(5) The structures of networks formed for the epoxy-amine systems proceeding through gelation and those proceeding through phase separation are predicted to be different because the structures of the final products are cure-path dependent.

A general classification of solidification mechanisms for network polymers is suggested which describes those mechanisms described here, and other systems reported in the literature. The classification includes phase separation to give rubbery particles (Type Ia), mixed particles (Type Ib), or glassy particles (Type Ic), gelation (Type II) and vitrification (Type III).

## 6.0 Studies of Material Properties Near Fibers

As a part of the work done at MTU under the Interface Contract, attempts were made to characterize material near the interface in carbon/epoxy composite specimens. The majority of the work done in this area was associated with development of a Perkin Elmer DMA-7 to measure  $T_g$  of a small area of a polymer surface.

### 6.1 Introduction to Interface Characterization Studies

Instruments have been developed recently designed to explore mechanical properties of very small regions of materials. Much of the research has been directed toward the measurement of modulus of thin films (36). Material scientists have used hardness testing on a micron to millimeter scale for many years (37-39). The information obtained is usually interpreted in terms of the plastic deformation mechanism of materials, particularly for metals, although approximate estimates of elastic moduli have been made. Recently, ceramicists have reduced the scale for indentation tests to the nano-level. With ceramics, the information has been interpreted in terms of elastic modulus and strength. Work on bond strength in ceramic composites has been reported using a nano-indentor (40). Indentors have also been applied to the determination of bond strength in composites (41,42) and a commercial instrument is now available. Studies on the structure of polymers at these scales are complicated by the time and temperature dependence of

mechanical properties of plastic materials.

Recent work has addressed the measurement of mechanical properties on an atomic scale using the scanning tunnelling microscope and the atomic force microscope (43,44). This work is providing deep insights into molecular interactions and current applications are addressing material properties on a nano scale.

The present work is directed toward measurement of time and temperature dependent properties of polymers on a sub-micron scale. The approach has been to use a dynamic indentation test and to interpret the resulting information in terms of variation of real and loss modulus with temperature across the specimen.

## 6.2 Application of Dynamic Mechanical Analysis to Interface Studies

Perkin Elmer have recently released an instrument (identified as the DMA-7) with interesting capabilities in mechanical analysis. It is capable of indentation type tests with high sensitivity in probe displacement and load, similar to the nanoindenter, but with the added capability of temperature control over a wide range. As supplied, it does not have the capability to move the probe over a sample.

Some initial development of the DMA-7 has been completed. A precision X,Y stage with mechanical and with piezoelectric positioning capabilities has been installed. The X,Y stage mount included an air bearing to ensure that the probe was held in a fixed position. Preliminary calibration of the unit indicated that the friction in the system was too high so the lower sapphire bearing of the DMA-7 was removed. A photograph of the unit is shown as Figure 10. Preliminary experiments were carried out to determine the sensitivity of the instrument to modulus variations. Figure 11 shows a series of runs on an epoxy resin, polycarbonate, poly acrylic, aluminum, and glass. Figure 12 shows a log/log plot of the recoverable indentation at maximum load against literature modulus data. It is apparent that the instrument can successfully interpret indentation at low loads (3mn) in terms of modulus. The instrument was also programmed to apply a cyclic load between 0 and 5mn and to monitor indentation at a fixed point as temperature is ramped. Figure 13 shows the results using an epoxy matrix as target. It is apparent that T<sub>g</sub> can readily be estimated from this data.

Attempts to prepare a series of indents on a soft surface in a form which could be imaged on a SEM were only partially successful. This is an important step toward tracing the precision with which the indentation can be placed on a sample. The problem was traced to the technique used to detect the surface. Currently, the DMA-7 lowers the tip until the probe force exceeds one gram. This impact load was sufficient to

destroy the probe tip and to damage the resin surface. Figure 15 shows a resolution pattern drawn on the surface of an aluminum sample using the surface detection load. The instrument was programmed to move in 100 micron steps to trace out a series of 100 micron steps in a line (Figure 15 i) and a square triangle with indentations at the corners (Figure 15 ii). It can be seen that the precision of the trace is poor and that the indentation size is comparatively large. This problem has been discussed with Perkin Elmer and future work will address techniques to find the surface without damaging the specimen. Improved temperature control of the stage will also improve the resolution.

## 7.0 Samples Supplied to NADC

As a part of the contract, specimens were prepared and supplied to Naval Air Development Center for distribution to other contractors and for study at NADC. The majority of these specimens were C-samples as illustrated in Figure 1. Table 2 lists the properties of all C-specimens produced under the current and an earlier contract (N62269-89-9208-5385, 8 Aug 1989).

Table 2: C-Samples Prepared for NADC

Number	Description	Recipient
M36	100% stoichiometry, unsized fiber, not cured in an atmosphere of amine	NADC
M37	100%, unsized	Rockwell
M38	100% sized fiber	NADC
M39	100% sized	Rockwell
M40	100%, hydrogenated fiber	
M41	100%, hydrogenated	Rockwell
M42	75% stoichiometric; unsized	MTU
M43	75% sized, cast in two stages	NADC
M44	75% unsized	Rockwell
M45	125% stoichiometric; fiber off center	NADC
M46	125 % unsized	NADC
M47	125% unsized	Rockwell

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A second type of specimen prepared and supplied to NADC was also a single fiber, model composite. It took the form of a tensile dogbone sample with a single fiber placed in the center of the sample with the axis of the fiber normal to the plane of the dogbone. The fiber was unsized and the resin system was Epon 828/MPD at 100% stoichiometry. Two samples were despatched.

The third type of sample was a multi-fiber specimen, more typical of conventional composites. In this group of samples fiber tows were dipped in the liquid matrix and pulled into an aluminum tube prior to cure. The final sample was sectioned from the tube. A number of specimens containing a wide range of fiber contents were supplied.

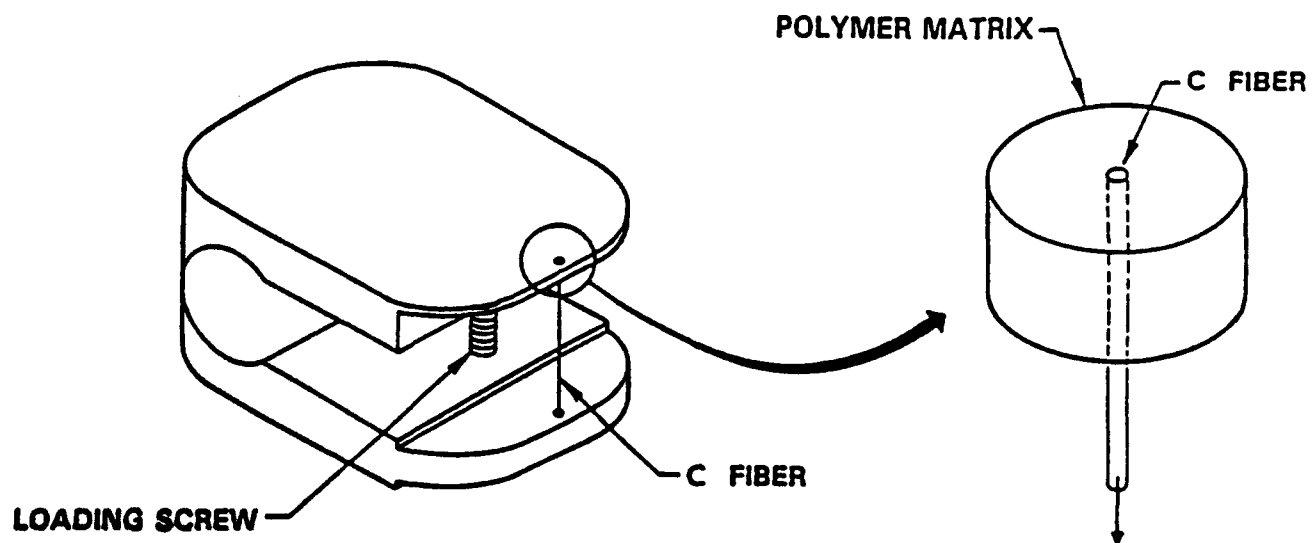


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**Figure 1** Sample configuration for determination of deformation around a fiber: "C-sample"

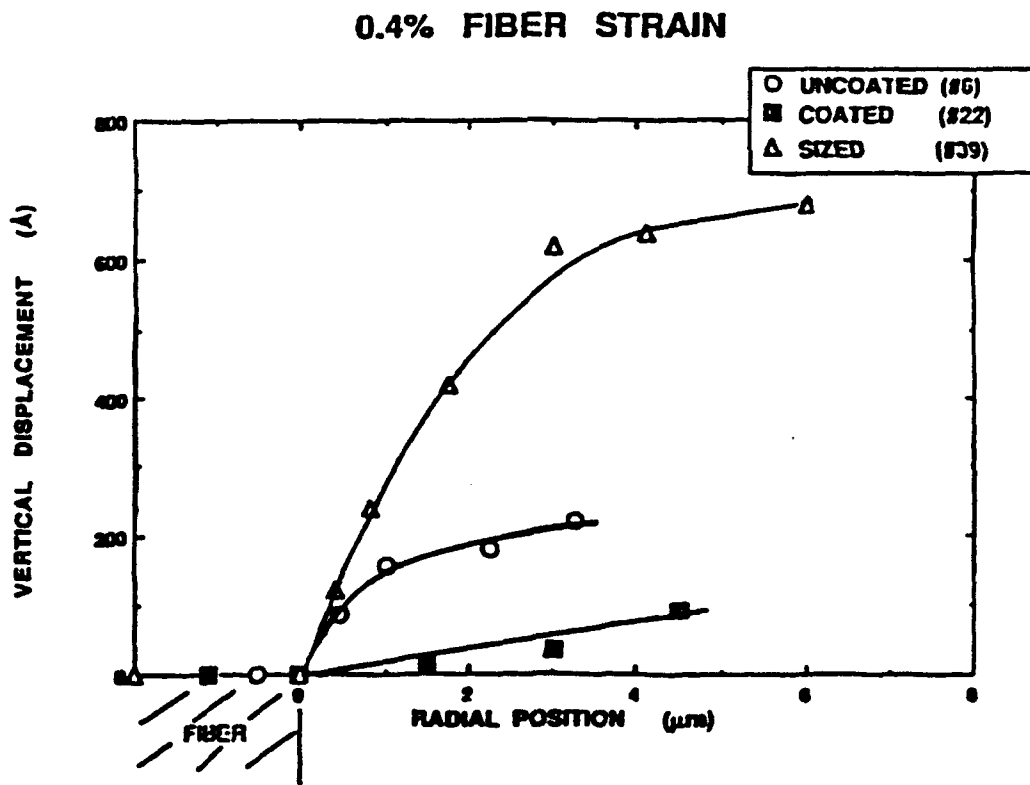
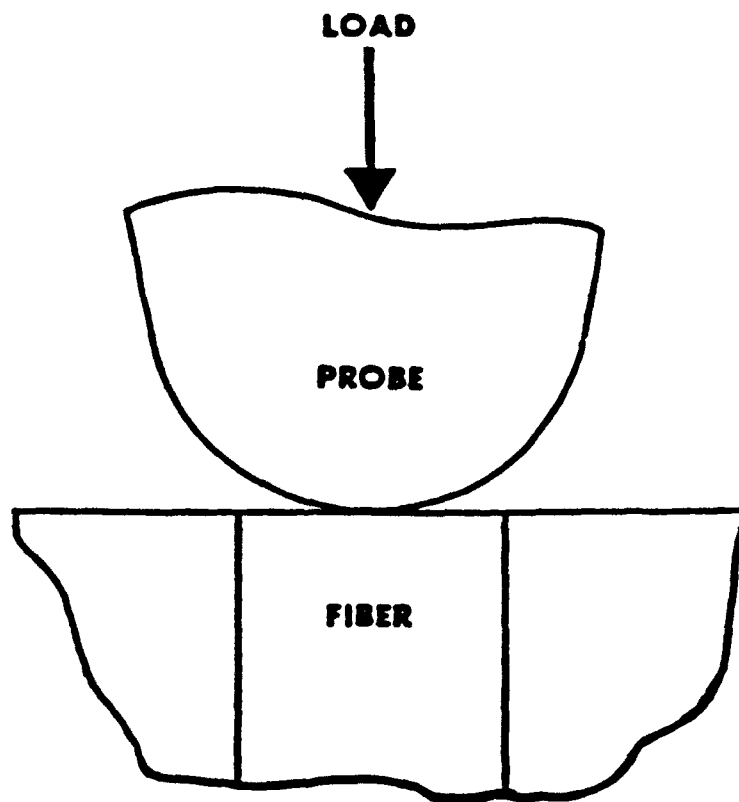


Figure 2 Elastic deformations near a fiber



**Figure 3 Schematic of loading for the microdebonding test**

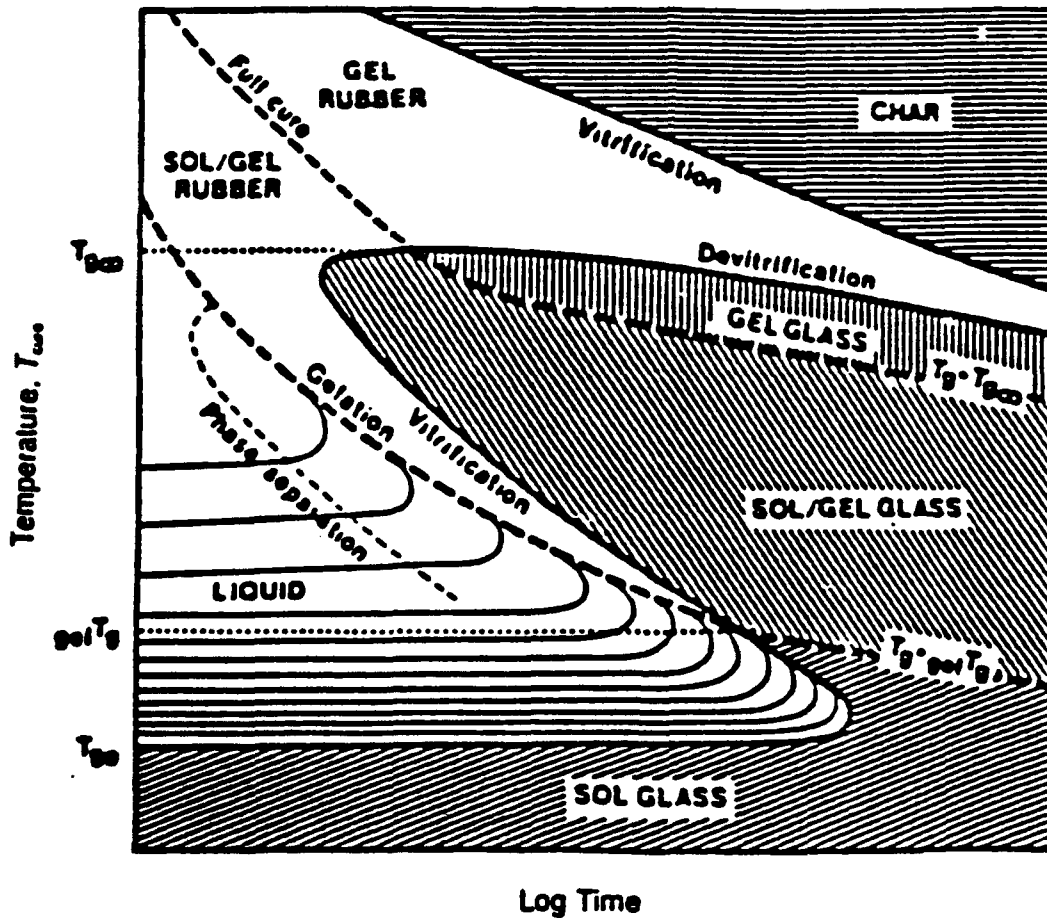


Figure 4 Time-temperature-transformation (TTT) cure diagram (reproduced from reference 21)

Dynamic Modulii for EDA/Epoxy with Frequency  
Near Phase Separation

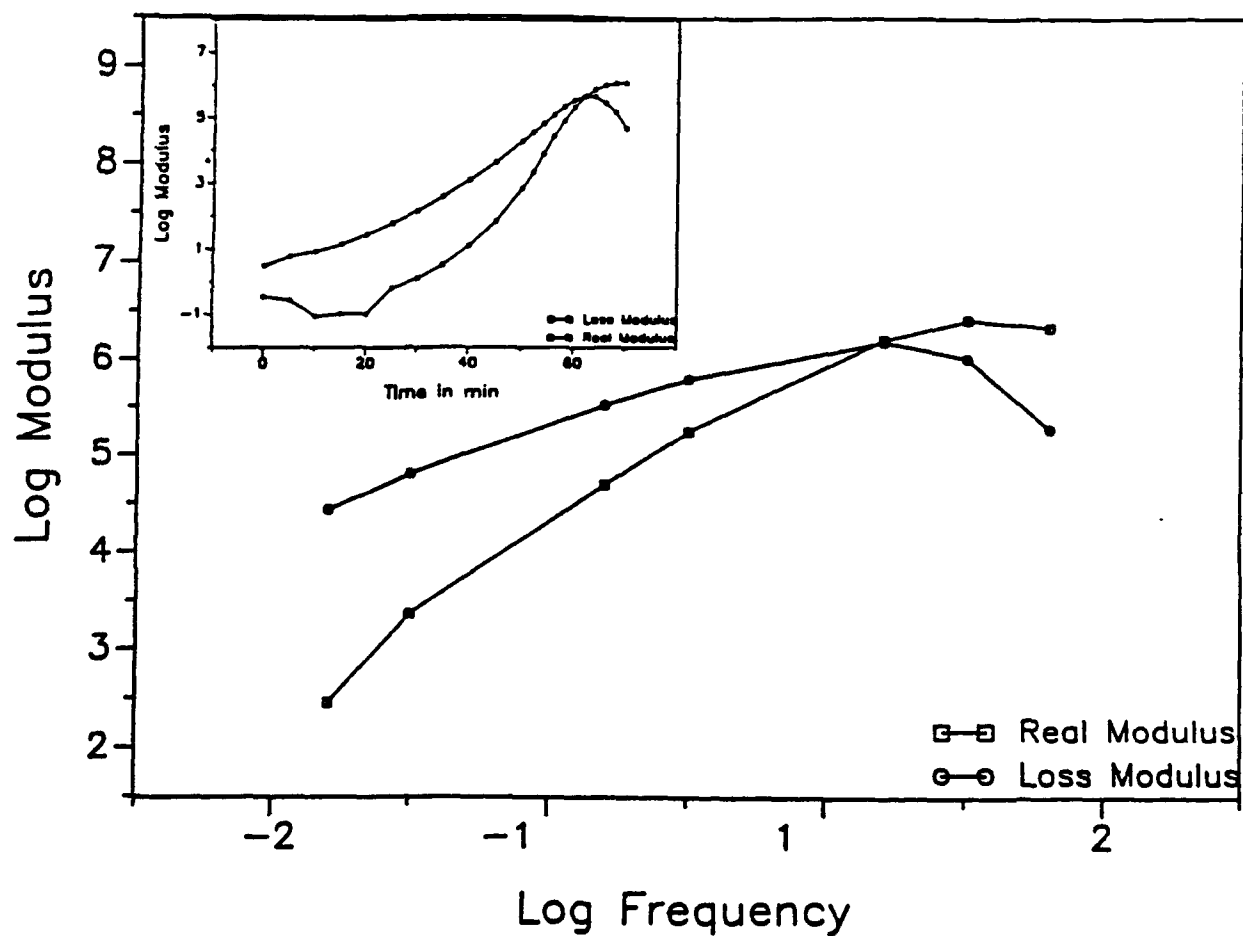


Figure 5 Variation of dynamic modulii for EDA/Epoxy with frequency near phase separation at 40°C

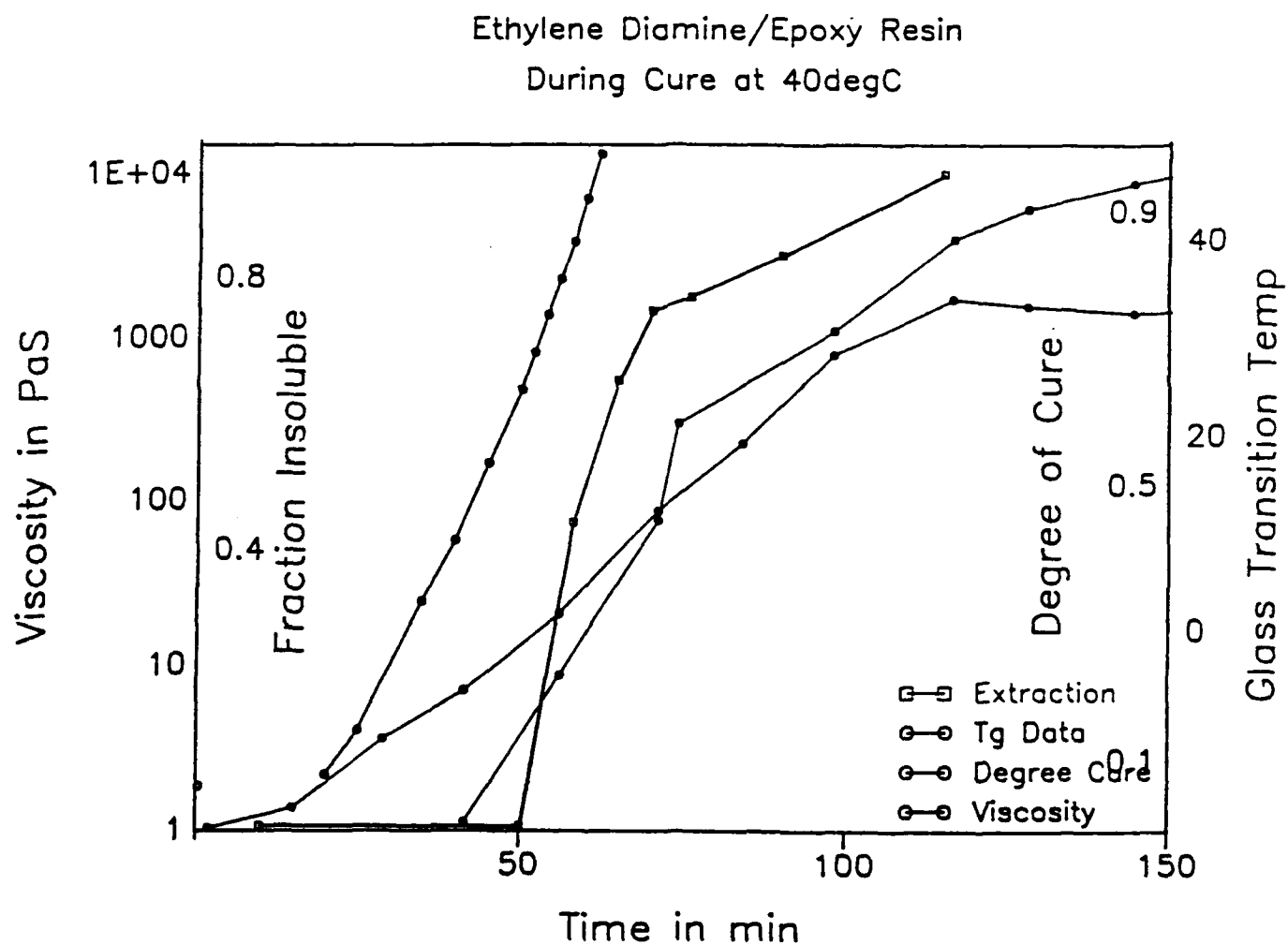


Figure 6 The properties of Ethylene diamine/Epoxy resin during cure at 40°C



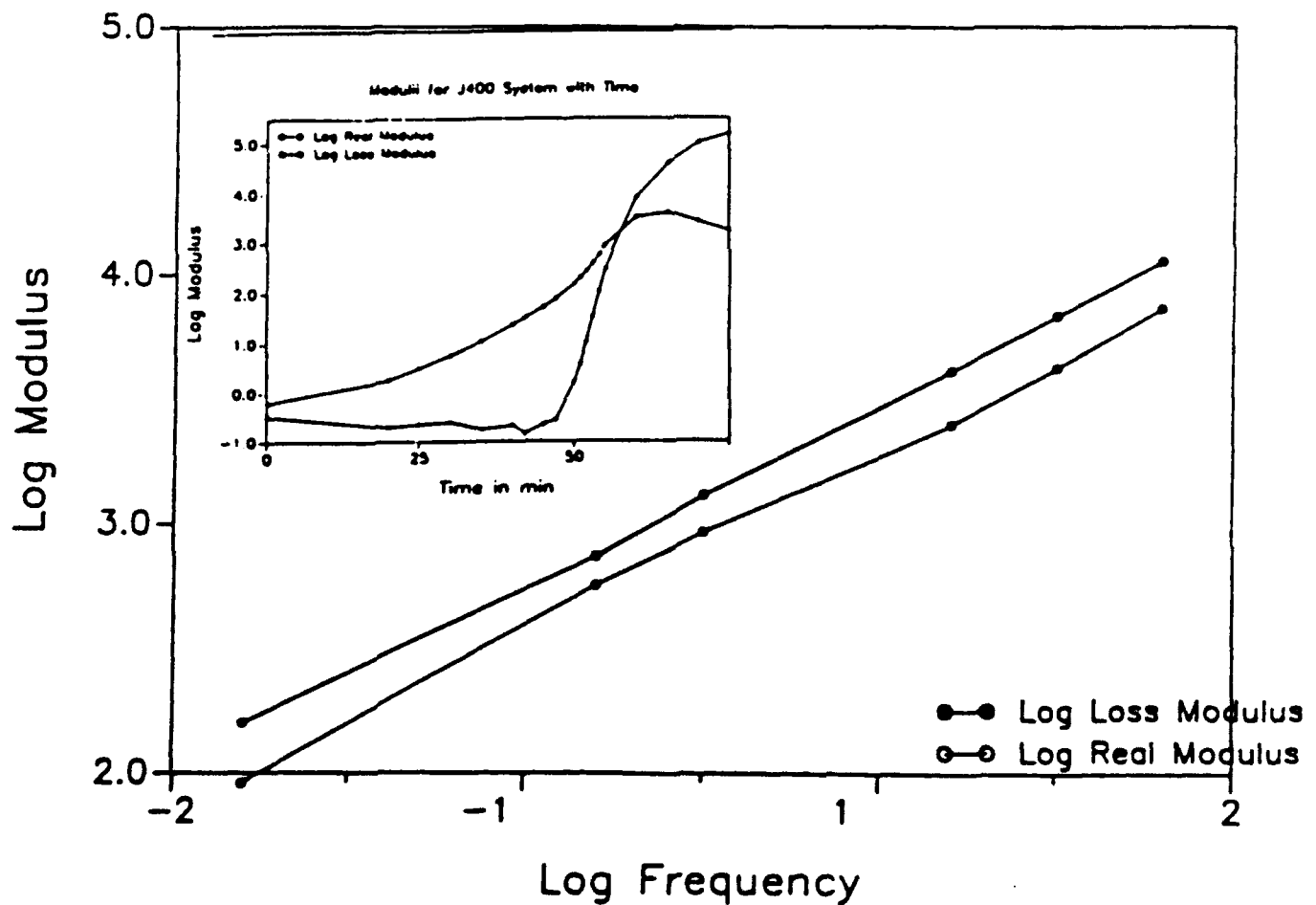
Modulii for J400 System with Frequency  
near Gelation

Figure 7 Variation of dynamic modulii for Jeffamine D400/Epoxy with frequency near phase separation at 80°C

Jeffamine 400/Epoxy Resin  
During Cure at 80degC

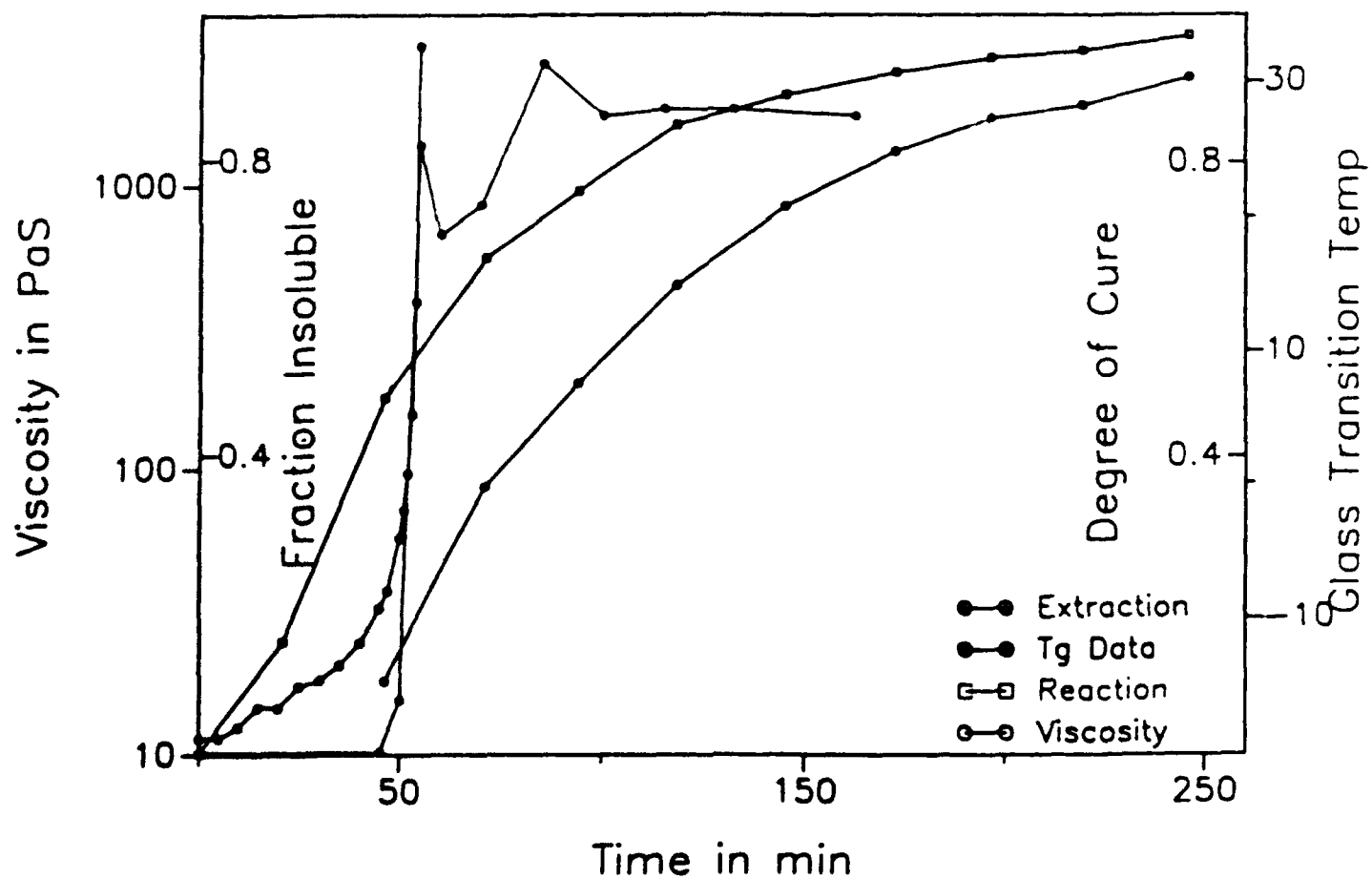


Figure 8 The properties of Jeffamine D400/Epoxy resin during cure at 80°C

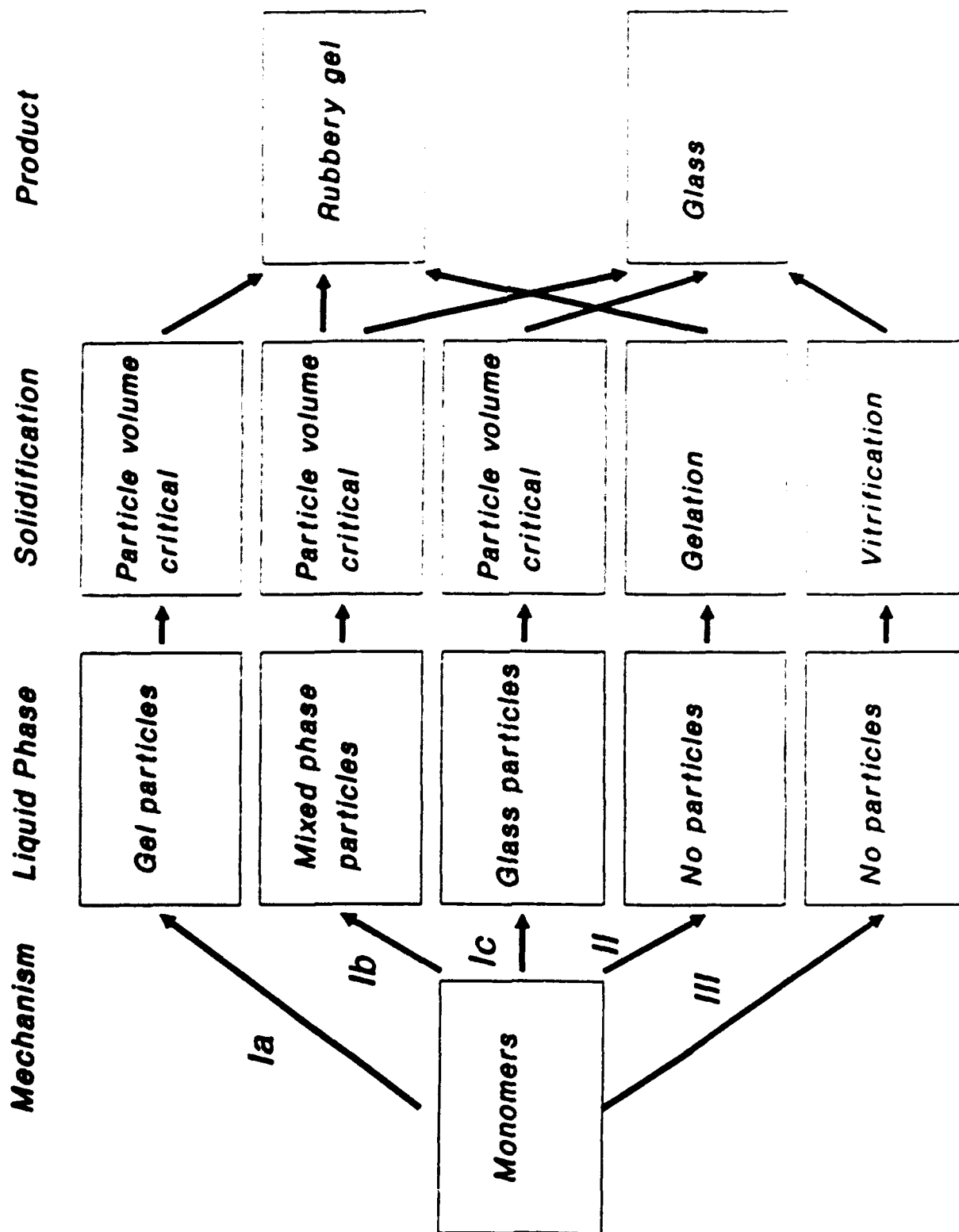


Figure 9 A proposed classification system for solidification mechanisms for network forming polymers

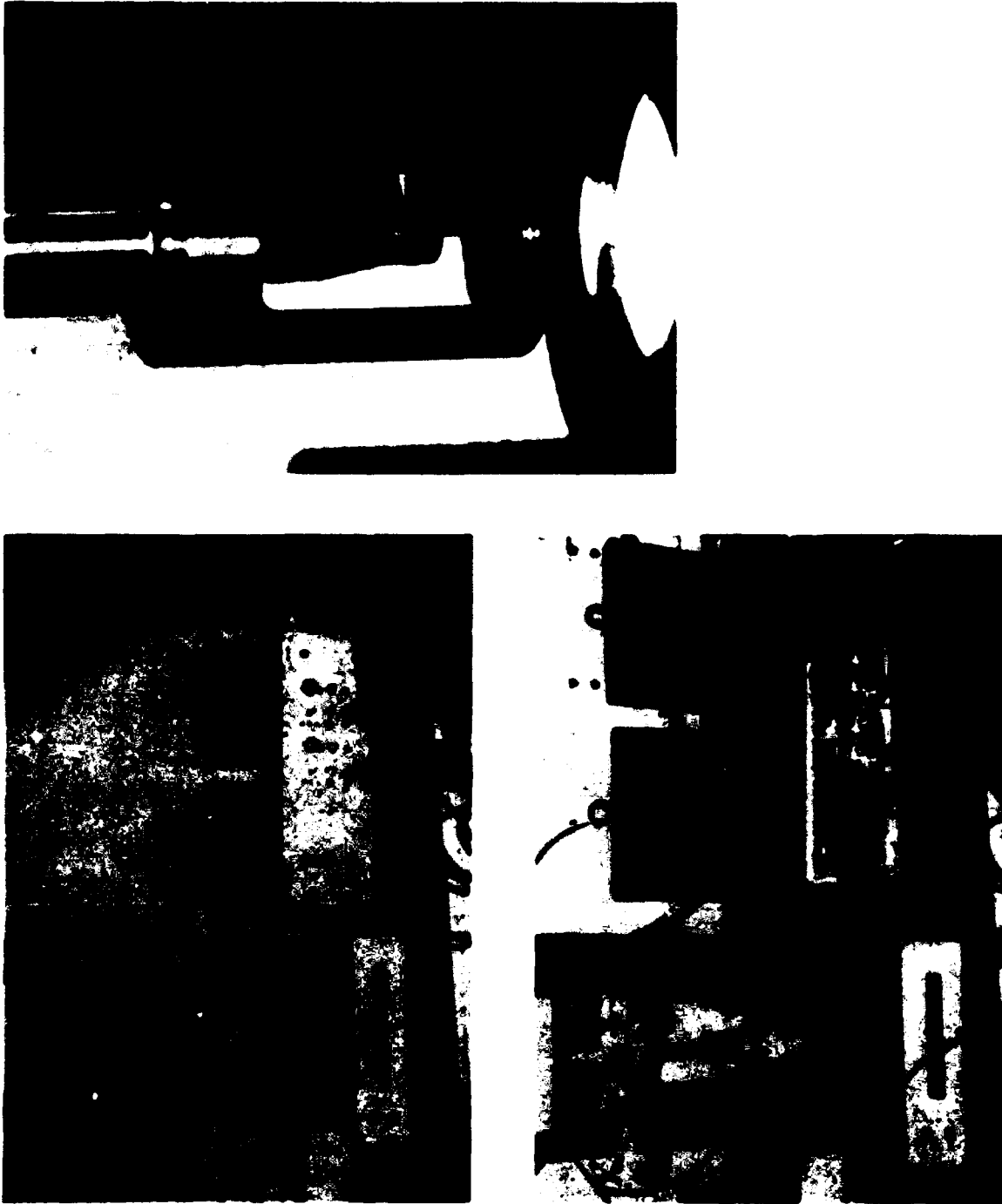


Figure 10 Views of the modified DMA-7 showing aspects of the X,Y-  
stage and its controls

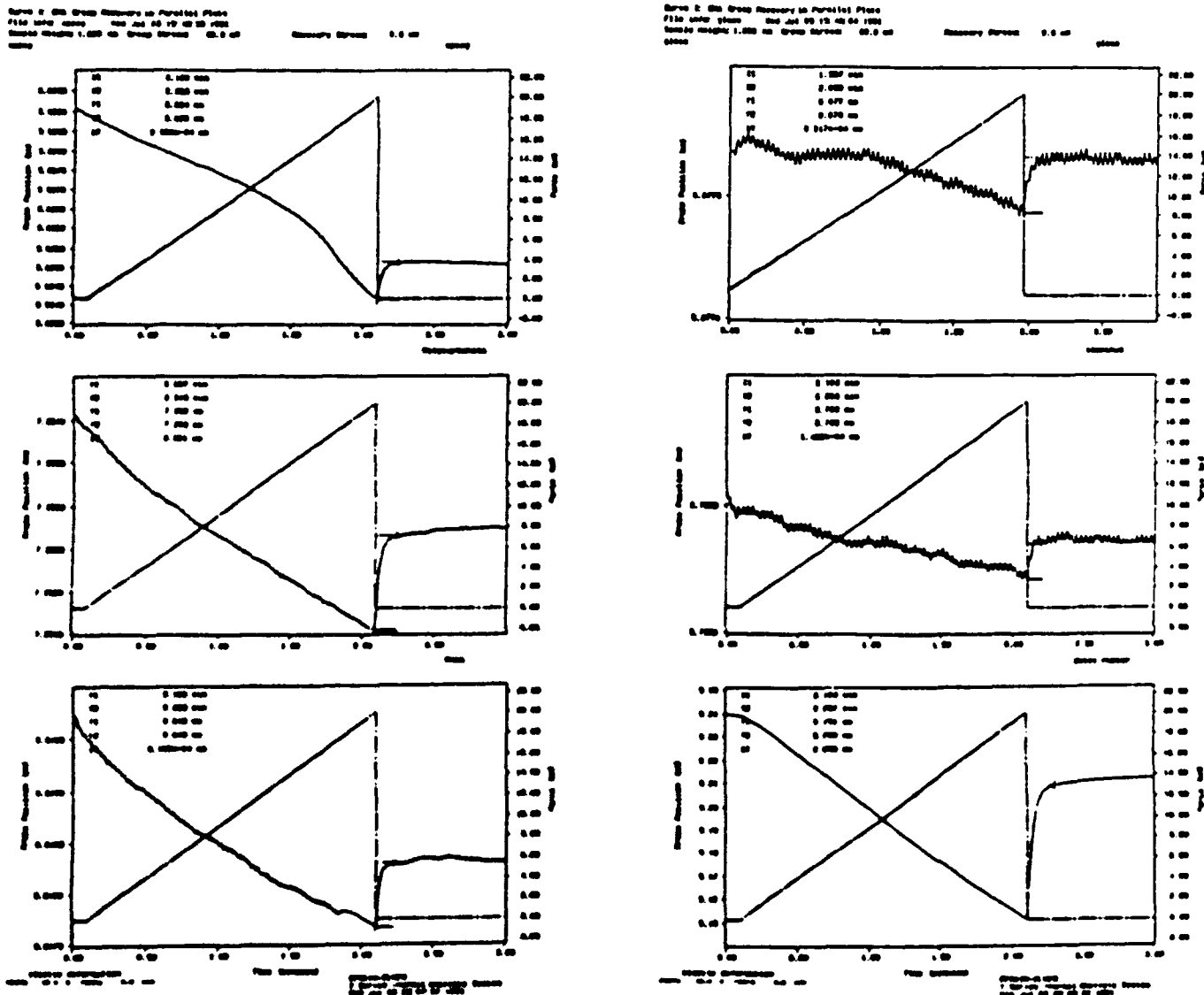


Figure 11 Load/indentation curves for a series of materials. The dashed curves show the load/time applied to the indenter, and the solid curves show the displacement response. The elastic indentation was taken as the recovered indentation on removing the load. The curves are labelled in the top right corner: epoxy, glass, polycarbonate, aluminum, PMMA, and butyl rubber.

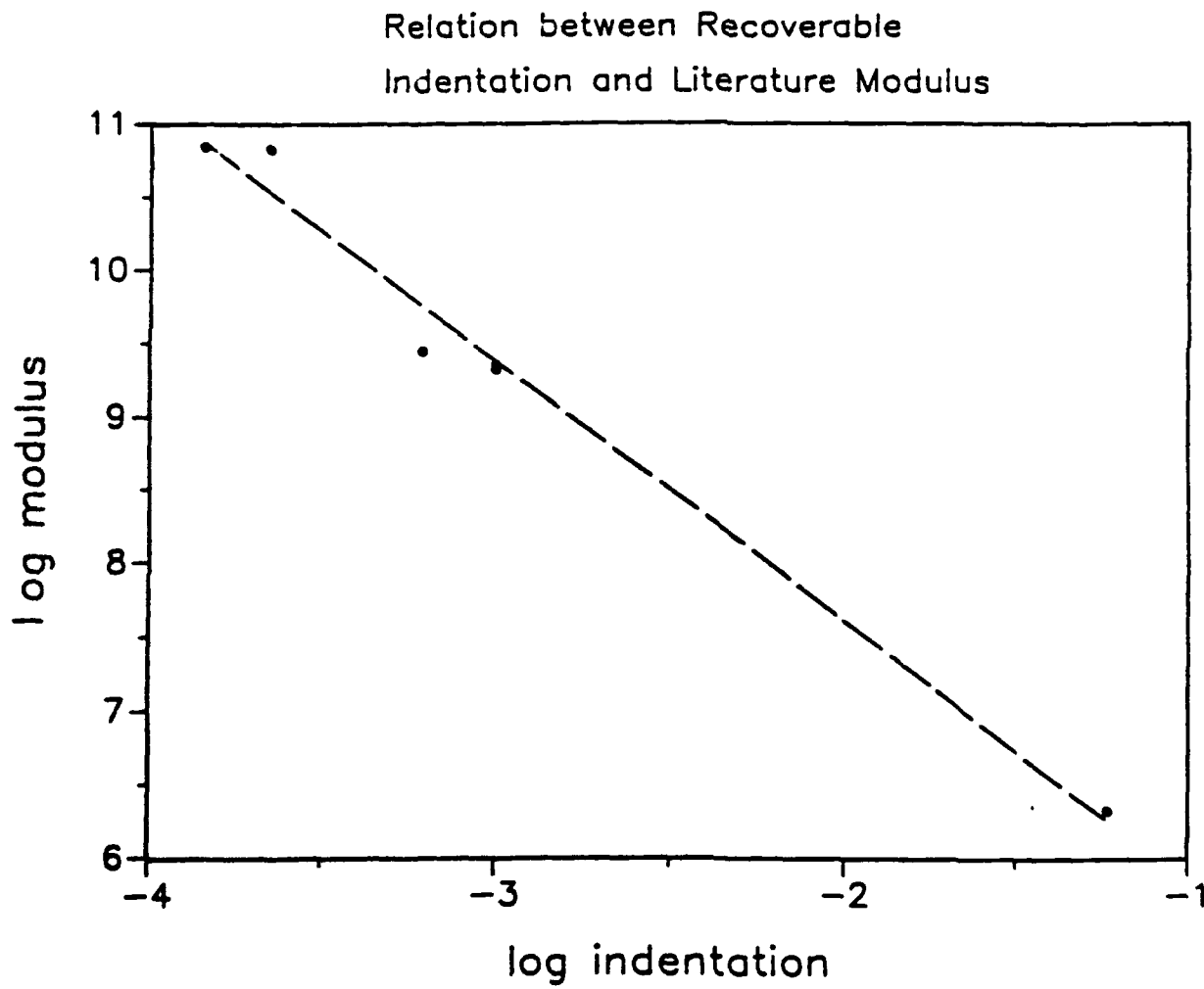


Figure 12 Relation between recoverable indentation and literature modulus

Curve 1: DMA Temp/Time Scan in Parallel Plate  
 File info: ep2 Fri Jul 05 01:14:24 1991  
 Frequency: 1.00 Hz Dynamic Stress: 4.0 mN  
 epoxy

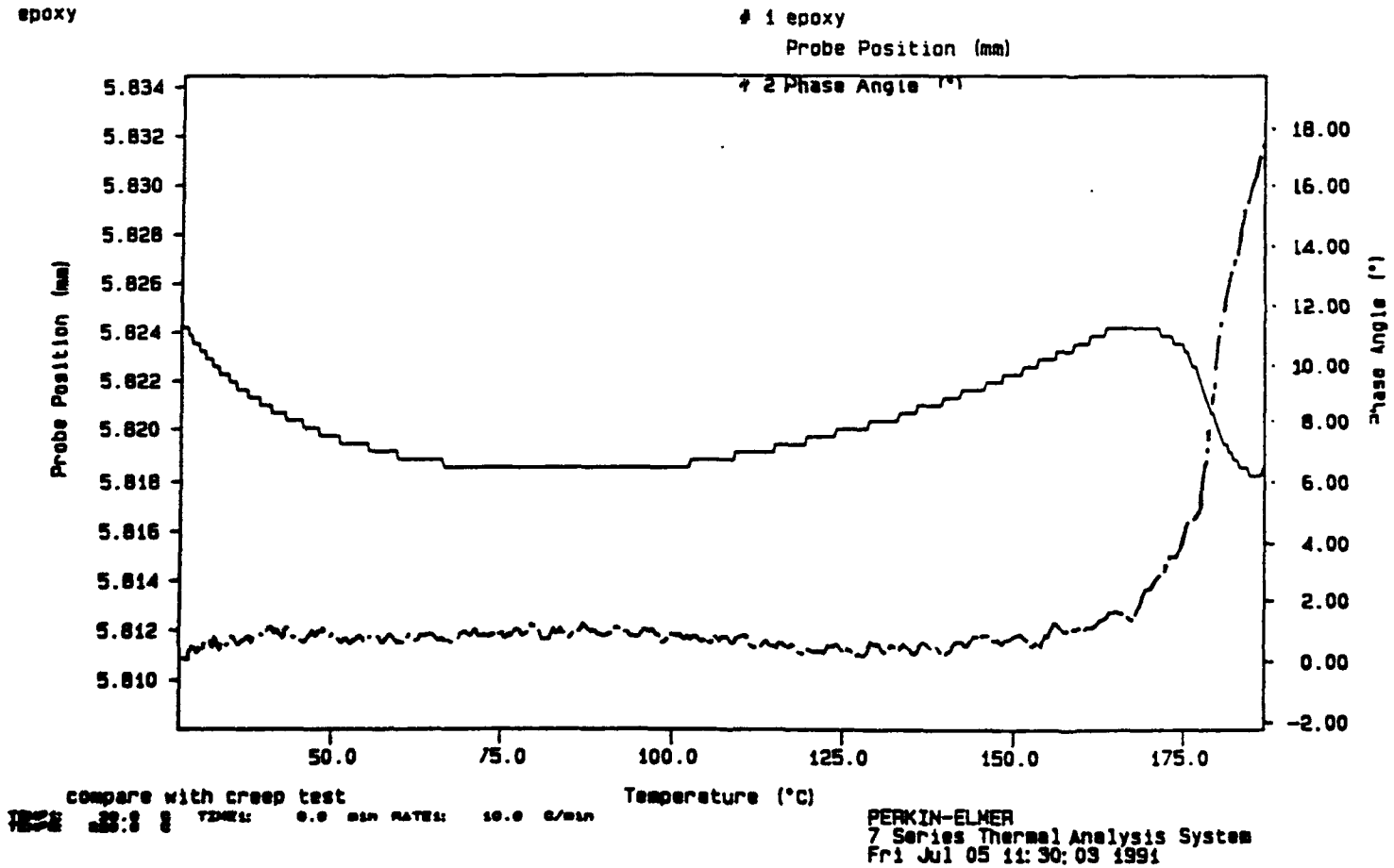


Figure 13 Variation of the dynamic indentation and energy loss on indentation with temperature for an MPD/Epoxy sample



**Figure 14** Scanning electron micrographs showing the indentation pattern on an aluminum sample following minimum load indentations (i) in line with 100 micron steps and (ii) in a square-triangular pattern returning to the point of origin



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