1985

NASA/ASEE SUMMER FACULTY

RESEARCH FELLOWSHIP

PROGRAM

MARSHALL SPACE FLIGHT CENTER

THE UNIVERSITY OF ALABAMA IN HUNTSVILLE

INVESTIGATIONS OF TOUGHENING MECHANISMS

OF EPOXY RESINS

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NASA/MSFC:

Division: Non-Metallic Materials

Branch: Polymers and Coatings

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Date: August 1, 1985

Contract No.:   NASA-NGT-002-099

                The University of Alabama in Huntsville

INVESTIGATION OF TOUGHENING MECHANISMS

## OF EPOXY RESINS

by

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ABSTRACT

Composite material technology has been applied to the solid rocket booster by the development of a carbon filament-epoxy resin case which yields a net increase of 4000 lbs. in payload in the shuttle. The question of reusability of the new composite tanks has not yet been answered and will depend on the toughness of the matrix resin. The present study was aimed at providing conditions whereby test specimens of the epoxy resin (EPON/825) and curing agents of systematically varied structures could be produced in a controlled manner. Three sets of conditions were found that might allow the isolation of the structural effects on toughness from the cure effects. The kinetic methods leading to the determination of these conditions are described.

I. Introduction and Objective

A composite material tank for the solid rocket booster of the space shuttle is being developed. This development will result in a net increase of 4000 lbs. in payload in the shuttle. The composite material consists of a carbon filament in an epoxy-diamine matrix resin. One of the unanswered questions about the new filament wound tanks concerns their reusability. The answer to this question will depend on the impact strength and fracture toughness of the matrix resin. The present project involved a study of the kinetics of polymerization of epoxy[1] EPON/825 (E)[2] with curing agents of systematic variation in structure (M, D, T)[2].
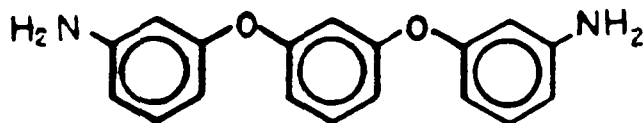
CH₃ CH₃ structure E
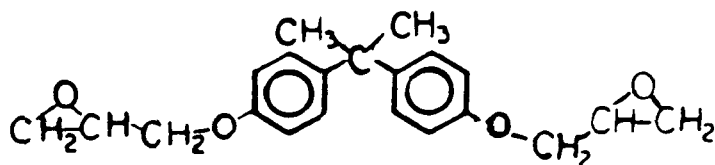
E
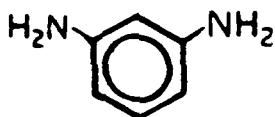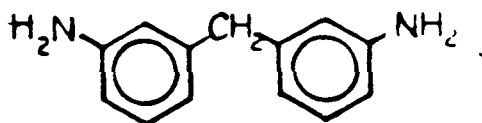
M   D

T

The important features of the structural variation of the diamines are the number of aryl groups (M, monaryl; D, diaryl and T, triaryl) and the meta arrangement of all arene linkages. Scheme I shows the overall reactions[1] responsible for formation of the matrix resin. As indicated in the top reaction between T and E, each of the four H atoms bound to the nitrogen atoms of the starting diamine is transformed to an OH group in the resinous product through reaction with one epoxy unit on E. The chemical stoichiometry thus requires 2 moles E for each mole diamine (M, D or T). The lower three equations are simplified representations of the reaction of 2E with the three respective diamines. There

is a good theoretical basis to expect that the present variation of
meta-aryl diamines should produce materials of variable impact strength
as suggested by the simplified representation of the three products in
Scheme I. An increase in the number of meta-aryl groups between the
cross-linked chains should provide a mechanism for dissipation of the
energy of impact through the increased number of random coil conforma-
tional possibilities associated with the increase in number of meta-aryl
subgroups.

SCHEME 1
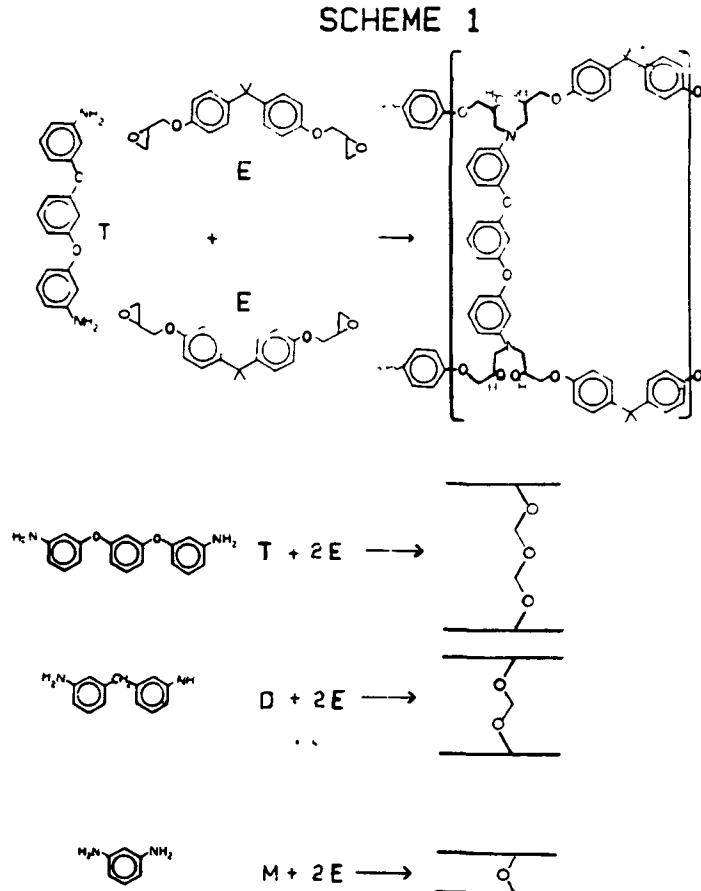
The objective of the present work was to find reaction conditions
that will allow the production of test specimens of matrix resins with
variable diamine structure and common (E) epoxy structure. The challenge
in this objective is to be able to produce specimens that will isolate
the effects of the diamine structural variation from effects simply due
to the extent of polymerization. Meeting this challenge requires a
fairly detailed study of the kinetics of the polymerization reaction with
each of the three diamines. The results of these studies suggest several
conditions where specimens can be produced that will allow the desired
isolation of the structural variation effects.

II. Materials and Methods

Some attention was paid to the purity of the starting materials. Appendix I contains the proton magnetic resonance spectra of each of the four compounds (E, M, D and T) at low (60 MHz) and high (300 on 360 MHz) field which confirm the structure and purity in each case. The monoaryl system (M) is easily oxidized in air and pure material required three distillations at 0.5 torr/80-90°C, m.p. 63-65°C; lit.[3], 64.5°. Two sources of the diaryl diamine (D) were available. The Fairfield Chemical Co. material was found to be of excellent purity (m.p. 85-86°; lit.[4], 82-83°). The Synmet Inc. batch of D was grossly the correct material but contained colored impurities and had a low melting point (80-82°). The spectral data on T indicated it was of high purity (m.p. 106-108°) but a previous chromatographic analysis showed minor impurities were present. This material was used without further purification.

The infrared spectra were also examined for each of the compounds and found to confirm the structures. Figure 1 contains a portion of the infrared spectrum and the gel permeation chromatogram of EPON/825 (E). The infrared in this case shows the presence of a small amount of OH group which is characteristic of a small amount of the dimer of E usually[5] present in this product. This impurity is important since it affects the epoxy equivalents of the resin. The gel permeation chromatogram indicates a relative area of 0.9% for the dimer. This translates into an epoxy equivalent weight of 170.2±.2 vs. 170.0 for the pure material. All experiments used 170 as the epoxide equivalent weight of the EPON/825 batch which was the same for all runs.
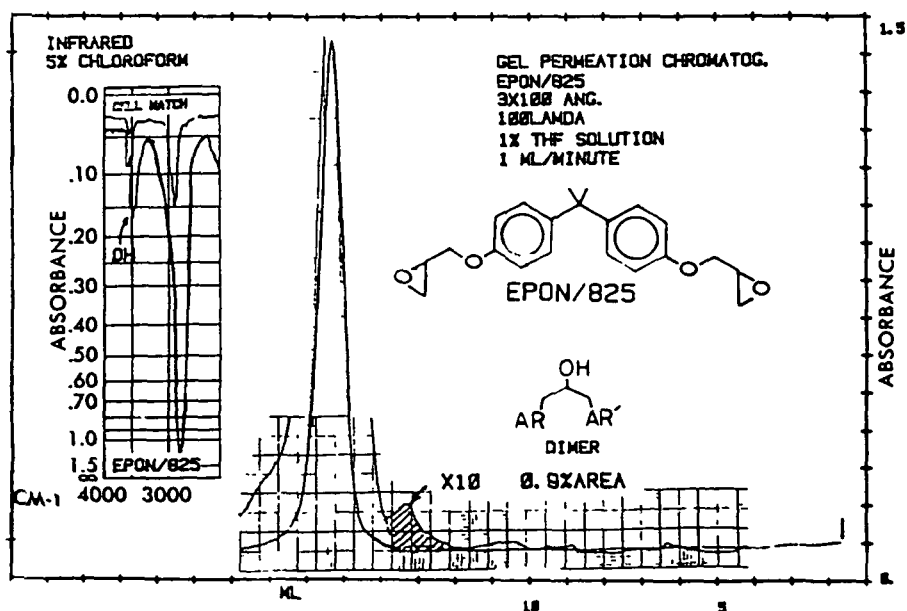

FIGURE 1.

Kinetic determinations were by differential scanning calorimetry
(DSC) with a DuPont 1090 system. Figure 2 shows the principal observables
with this equipment. The polymerization reaction is exothermic and the
heat released by the reaction can be measured by integration (Figure 1,
upper) of the DSC peak (Figure 1, lower). Melting transitions and glass
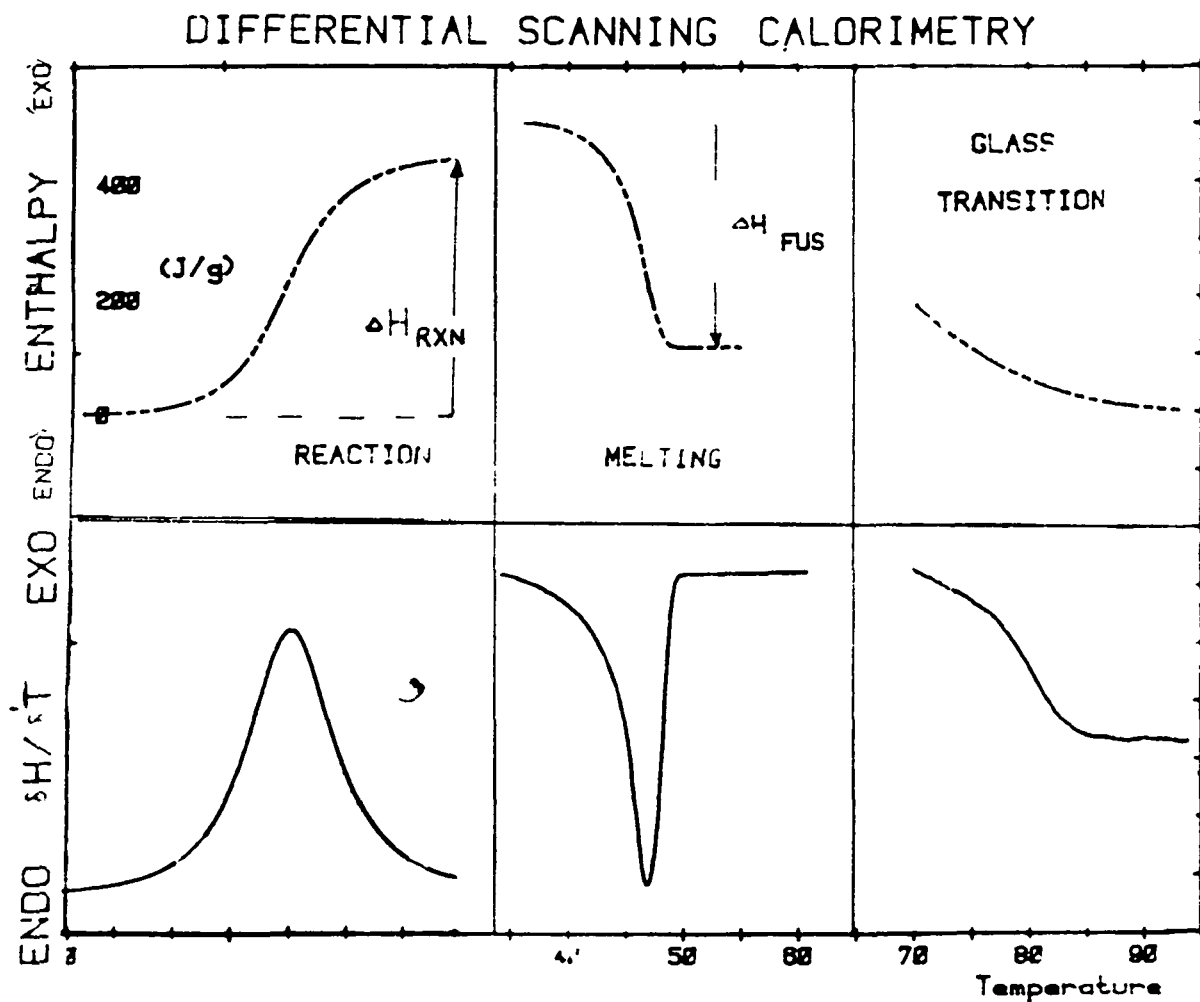transition temperatures are also revealed by this method.

DIFFERENTIAL SCANNING CALORIMETRY

FIGURE 2.

Kinetic samples were prepared by dissolving 2 mmolar equivalents
(4 epoxy mequivalents) of E and 1 mmolar equivalent (4-H mequivalents)
of diamine (M, D or T) in 1 to 1.5 g of methylene chloride. Only T
presented any solubility difficulties and at least 1.5 g of solvent was
required to obtain a homogeneous solution in this case. Constant aliquots
(usually 25 microliters) were added to tared DSC pans. Most (90%) of the
solvent evaporated in 1 hour at room temperature and 3 of a particular
sample set were heated at 103° for ca. 1 hour to complete evaporation.
The residual weights of resin mixture obtained in this way were generally
within a 1% range. The average residual weights were taken as constants
for the remaining samples prepared from the same original solution. The
rate of reaction at room temperature was shown to be slow during the first
two hours for all three systems. However, the monoaryl system (M) does
begin to react at an appreciable rate after a few hours at 25°. Kinetic

samples, prepared in this way, were heated for variable times in ovens regulated to ± 1° C. Temperature calibration was to the DSC through a common thermocouple also to ± 1° C.

Table 1 gives the average heats of reaction at zero reaction time for each of the variable diamines used in this study. The average deviations (± A) are within the 2.5% typically reported[6] in the literature for similar systems. The range (R) is, however, large enough to make small extents of reaction (short reaction times) difficult to determine. All DSC runs were heated at 10°/min unless otherwise specified.

Table 1

Heats of Reaction (Q_0), Average Deviations (A) and Deviation Ranges (R)
N Determination of 2E:1M, 2E:1D, 2E:1T

Resin [a]	Q_0 (J/g) [b]	A	R	N
2E:1M	434	10	26	4
2E:1D	371	8	32	10
2E:1T	321	8	32	8

a) 2 moles E to 1 mole diamine. b) At zero time, DSC heat rate 10°/min.

III. Results

Figure 3 represents the simplest method of kinetic determination in these systems which is the batch version. In this method, a sample of the resin mixture of known weight is simply heated for a time, quenched and subjected to a standard DSC scan. The integrated area (ΔQ) divided by the appropriate Q_0 (Table 1) can be taken to measure the Fraction cure (F) or percent cure (Fx100) as shown.
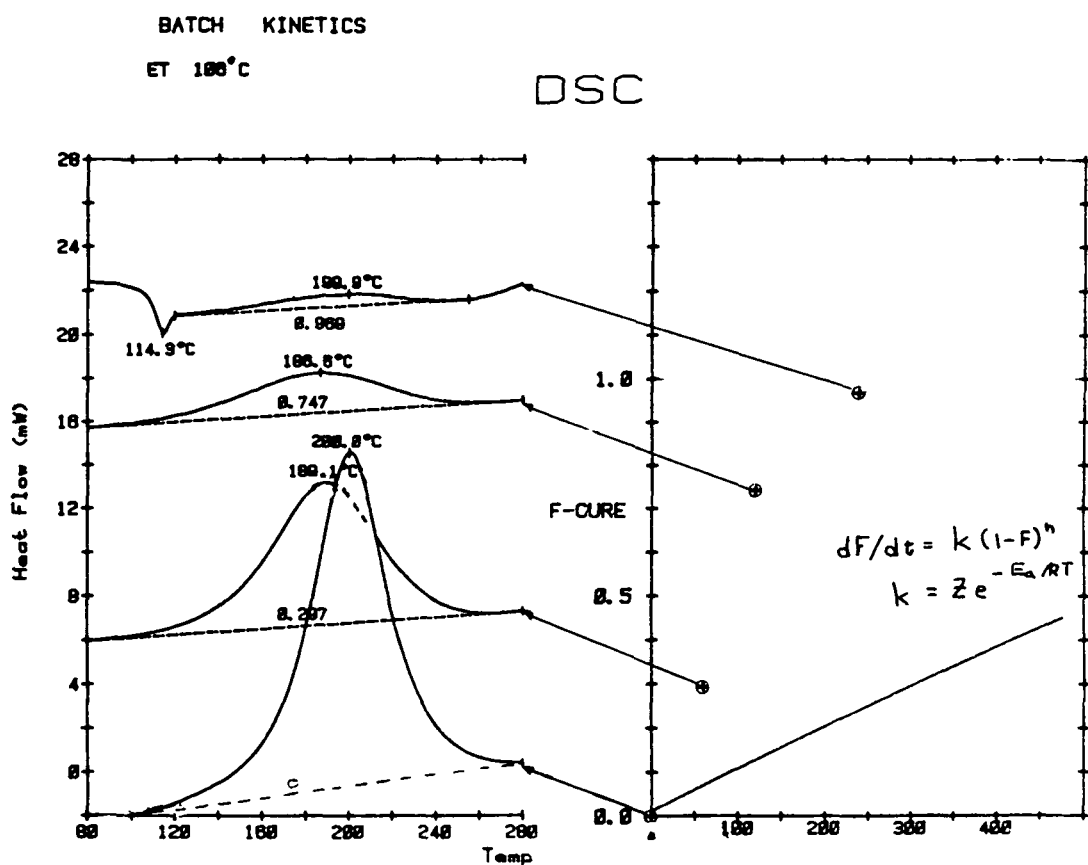
BATCH KINETICS

ET 180°C

DSC

FIGURE 3.

A second method of analysis of a DSC scan is a least squares fit of the shape of the DSC exotherm to equation (1) (Borchardt-Daniels analysis[7]).

(1) $dF/dt = (1-F)^n \cdot Z \cdot \exp\left[-Ea/RT\right]$.

Here (equation 1), dF/dt is the normalized DSC scan measurement, F is fraction cure (conversion), Z is an Arrhenius frequency factor and Ea is the corresponding activation energy. The inset of Figure 3 shows the predicted F - time curve using this (1) analysis of the zero time DSC scan.

The assumption of the Borchardt-Daniels method is that no change
in mechanism occurs during the cure reaction. The very large discre-
pancy between the predicted F - time and the pointwise batch cure is
suggestive of an autocatalytic change in the mechanism as the reaction
proceeds. The same implication is suggested by the decrease in the
temperature of the maximum rate of the batch samples of Figure 3.

Figure 4 shows the variation in the predicted cure rates by the
Borchardt-Daniels fits to each of the first three batch samples of
Figure 3. As expected, the activation energy is reduced with the
temperature of maximum heat flow. The reaction order (n) also changes
significantly, further indications of autocatalysis during the first
75% in apparent conversion. A plausible explanation of the apparent
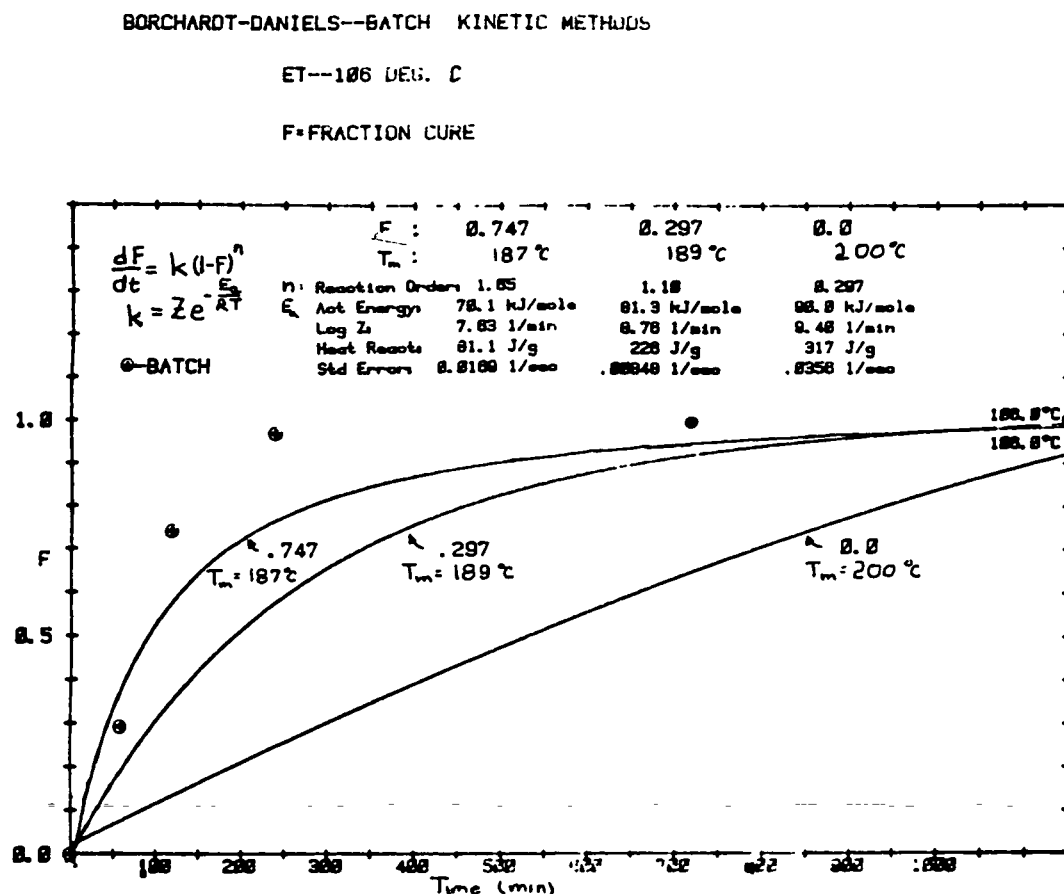autocatalysis is shown in Scheme II.

BORCHARDT-DANIELS--BATCH KINETIC METHODS

ET--106 DEG. C

F=FRACTION CURE

FIGURE 4.

Scheme II

$$R\text{-}NH_2 \; + \; CH_2\text{-}CH\text{-}Ar \longrightarrow R\text{-}\overset{\oplus}{N}H_2\text{-}CH_2\text{-}\overset{O^\ominus}{CH}\text{-}Ar$$

(zwitter ion Z)

$$(Z) \longrightarrow R\text{-}NH\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}Ar$$

(R'-OH)

Catalysis:

$$R'\text{-}OH \; + \; CH_2\text{-}CH\text{-}Ar \longrightarrow \left[R'\text{-}OH \cdots O\diagup^{CH_2}_{CH\text{-}Ar} \right]$$

(Catalytic Intermediate, I)

$$R\text{-}NH_2 \; + \; (I) \longrightarrow \left[R\text{-}OH \cdots \overset{\ominus}{O}\text{-}CH_2\text{-}CHAr\text{-}\overset{\oplus}{N}H_2\text{-}R \right]$$

(II)

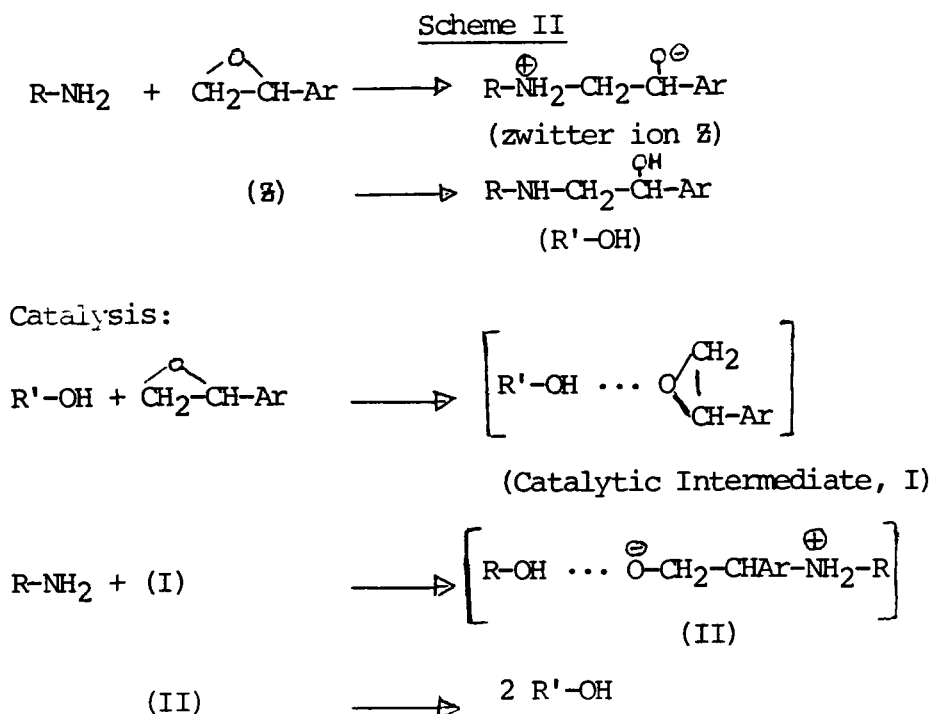$$(II) \longrightarrow 2 \; R'\text{-}OH$$

Figure 5 shows an example of the isothermal heat flow method for following the cure reaction. In this method, the kinetic sample is quickly brought to a temperature of appreciable reaction rate and held constant while the heat flow is recorded. The shape of the heat flow (reaction rate) curve at the top is indicative of an autocatalysis in that the reaction rate increases for a time before it begins to decrease. The lower portion shows the agreement between the batch data and the normalized integration of the peak at the top. As is evident, the agreement is good for the integrated curve at 107° and the batch data at 106°. The 101.7° curve gives a calibration of the sensitivity of this system to change in oven or isothermal temperature.

Figure 6 shows isothermal heat flow measurements which confirm the gross features of the catalysis that are depicted in Scheme II. The heat flow peak in the upper right is a portion of that shown in Figure 5. A system undergoing simple reaction should show a monotonous decrease in rate as starting material is consumed, like the peak shape shown for the ET system after pretreatment at 106° to 75% apparent cure (Figure 5, middle, right). The lower pair of curves of Figure 6 were obtained for a comparable sample of the ET system with 1.1 equivalents of triethylene glycol as an additive. The temperature of maximum rate of the diol sample is reduced to 186° without prior heat treatment and the form of the isothermal rate curve shows almost no increase after reaching reaction temperature (107°).
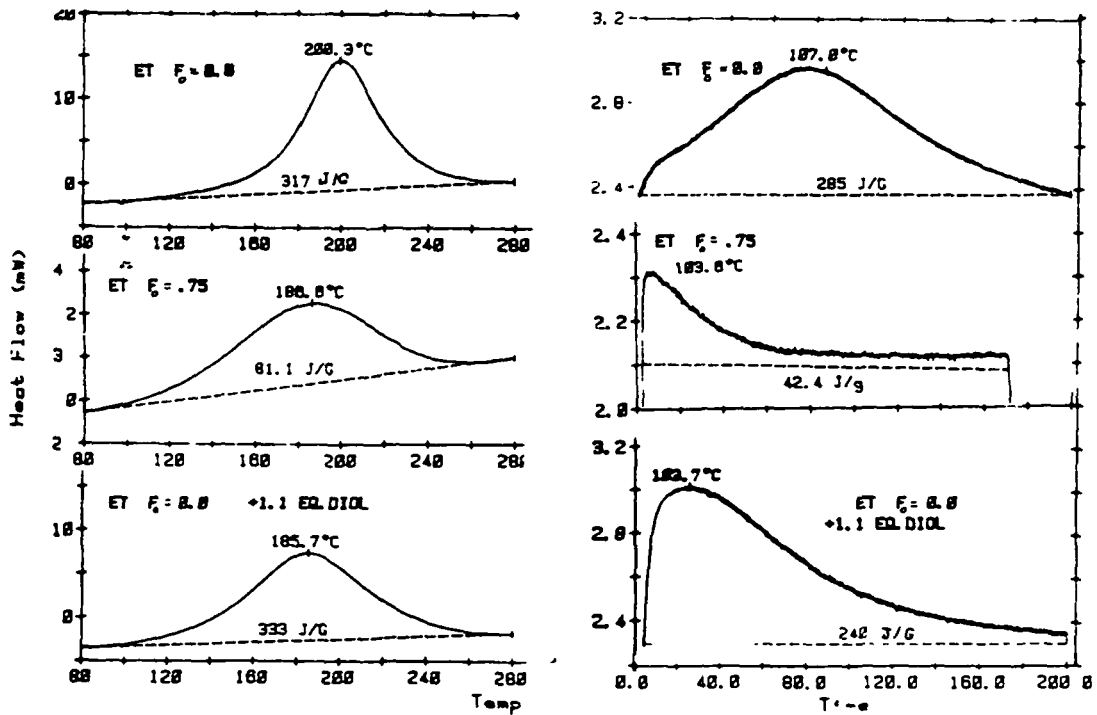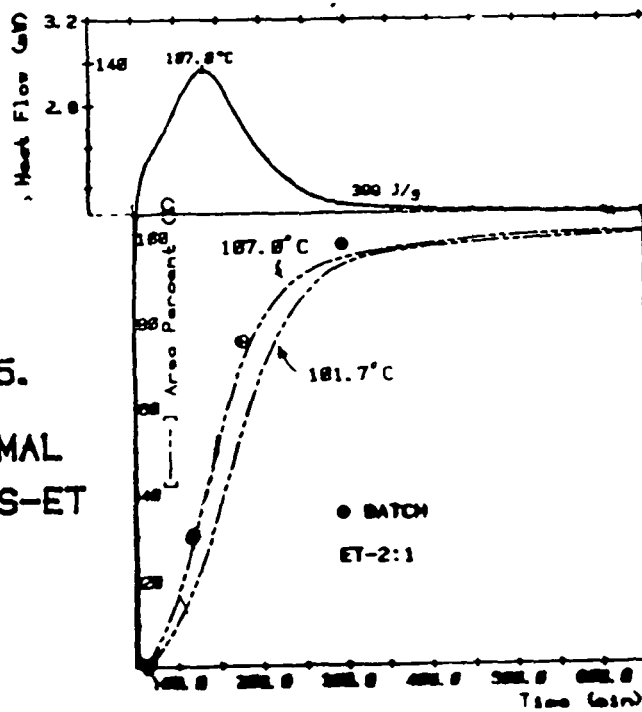
FIGURE 5.

ISOTHERMAL
KINETICS-ET

FIGURE 6.   AUTOCATALYSIS

Figure 7 (middle portion) allows a comparison of the integrated
rates of the three present systems (EM, ED and ET) at comparable tem-
peratures (103-107° C). The upper and lower curves are similar to that
for ET (Figure 5) and indicate autocatalysis is common to all three
systems. These data, together with literature precedent[8], make it clear
that all three of the present epoxy systems are subject to an auto-
catalytic stage like that depicted as Scheme II. The catalysis is turned
off when the mobility of the subgroups in the resin matrix becomes
slow. This accounts for the increase in the temperature of maximum
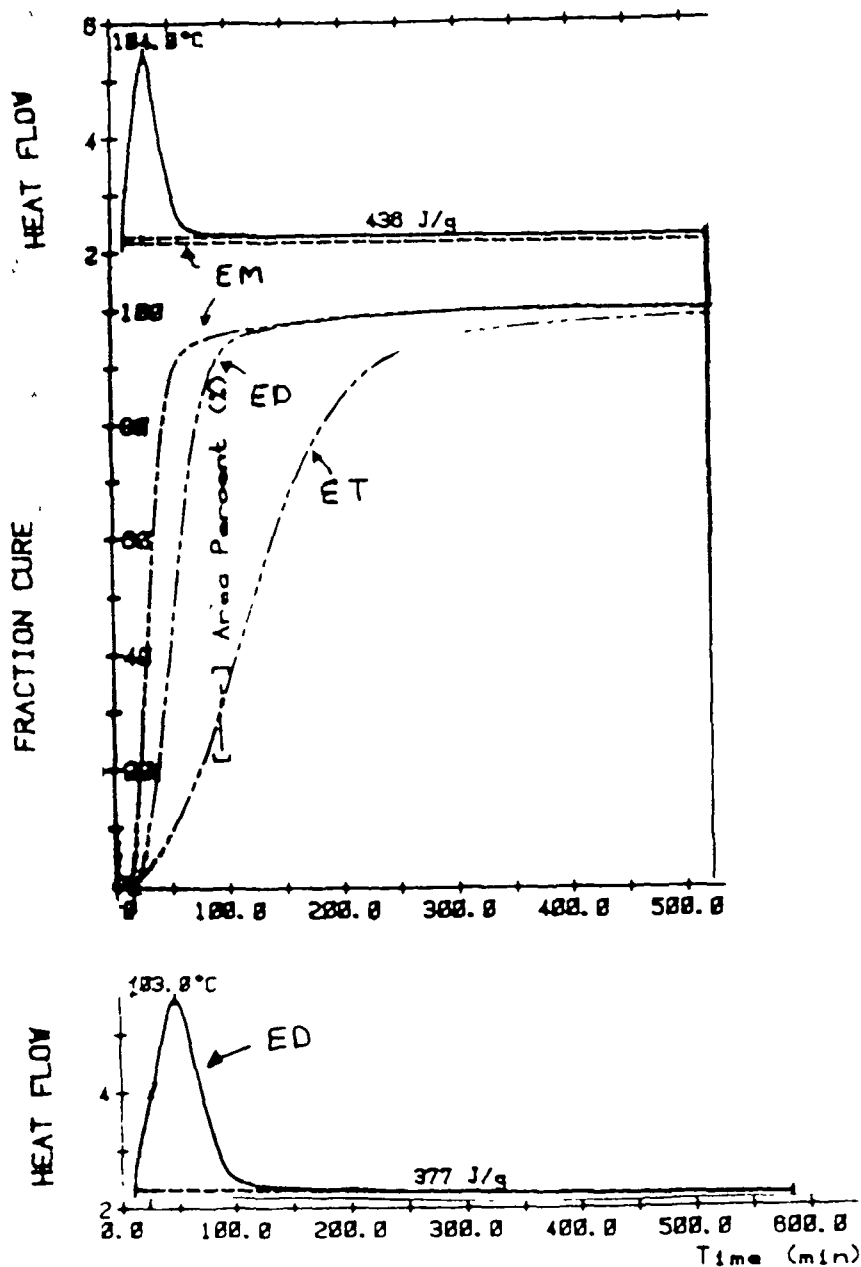rate during the last observable stages of the ~100° cure (e.g. Fig. 3).

FIGURE 7.

Figure 8 shows the DSC curves of each of the three resin systems obtained from a 103-107° cure temperature and at relatively long cure times after the reaction exotherm appears to have ceased. The sharply peaked endothermic transitions are like melting transitions but are ascribed to enthalpy relaxation[9] which differs only in the nature of initial state. That is, these sharply peaked transitions do correspond to the change from an ordered to a disordered state but do not require crystallinity in the ordered state. For our purposes, the results of this figure suggest the first important point whereby tests responding to structure variation, separated from cure, could be made. The slowly changing nature of the cure process in this temperature range and the similarity in transition temperatures suggest that it should be possible to prepare specimens of the three structurally different resins with identical transition temperature. Tests of toughness of these specimens would at least be on resins of constant transition temperature and "complete" cure insofar as exothermal behavior is concerned. Results of such tests could be very interesting.
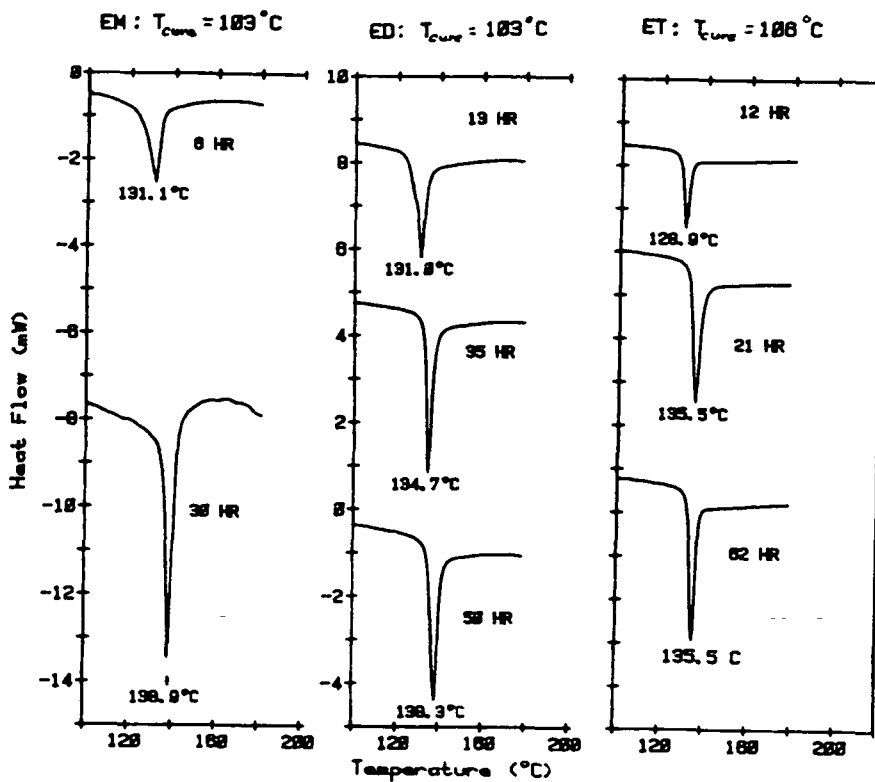

FIGURE 8.

Figure 9 is a composite of the types of measurements which were made
on the EM resin system. It shows that the features already discussed
for the ET system are present in the EM system as well. It shows, in
addition, the effects of subjecting the resins to a second higher cure
temperature after the cure at ca. 103° C is apparently complete. The
isothermal method reveals an appreciable amount of additional heat flow
at the higher second temperature which can be used to further quantify
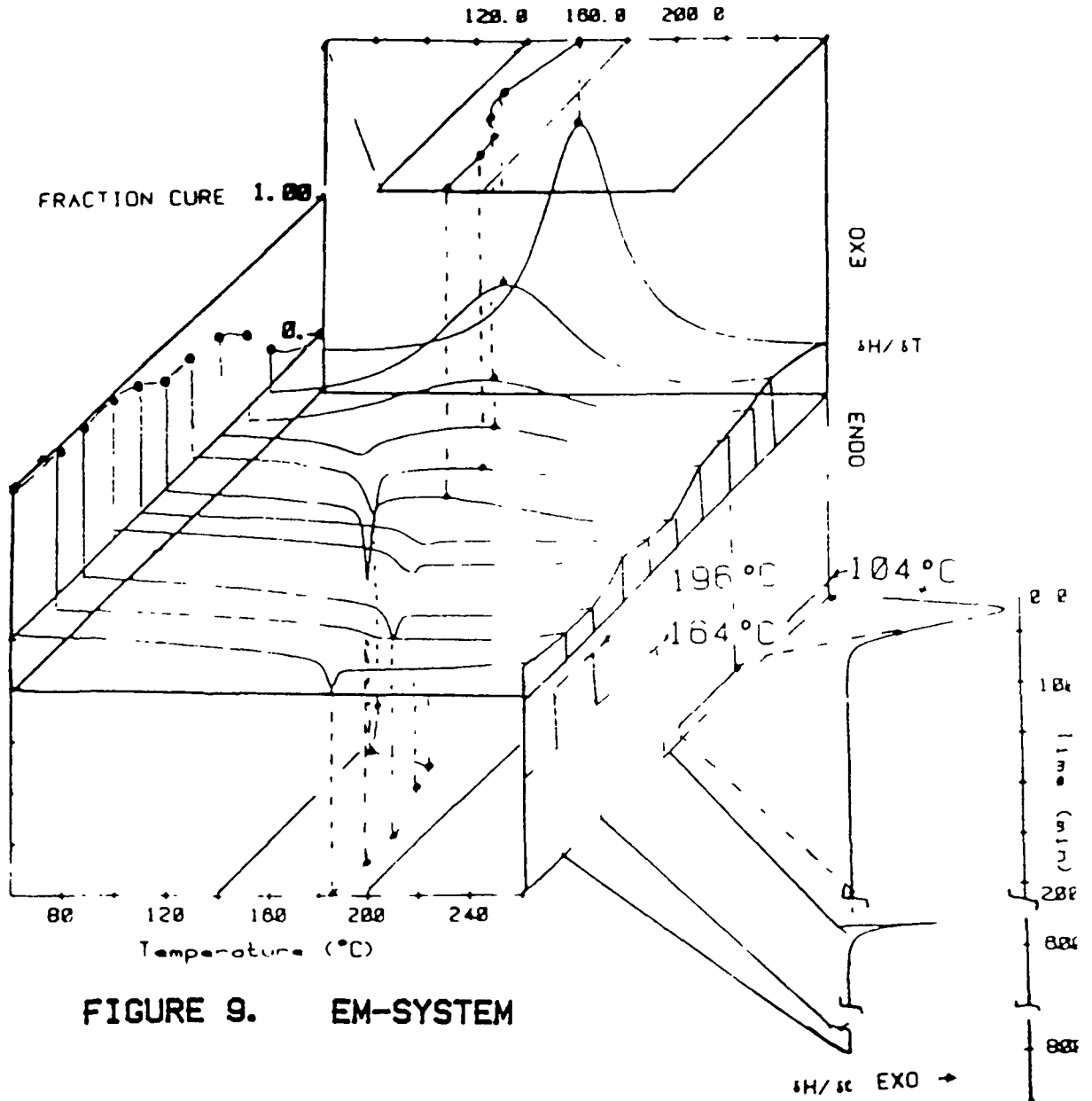the systems.

FIGURE 9.   EM-SYSTEM

Figure 10 gives a more detailed view of the measureable heat flow
for the EM system. The upper portions show the isothermal exotherm mea-
sured at temperatures of 103° C for the first 9 hours, 164.4° C for the
next 200 minutes and 196.7° C for the final hour. The lower portion
shows the integral of the 103° exotherm normalized for the first 9 hours
and compared to batch samples at the same temperature. The agreement
between the integral and batch methods is quite good. However, the
observed exotherms at the higher temperatures clearly show that the batch
method gives an apparent cure which is too high. The (+) points mark
the F (fraction cure) values after correction for the higher temperature
exotherm measurements. The dotted curves below the 164.4° isotherm and
the 196.7° isotherm show the integrals of the corresponding exotherms
after approximate normalization to the total measureable heat evolution.
Corresponding determinations with the ET and ED systems show corres-
ponding exotherms at 150-164° but no measureable heat evolution at a
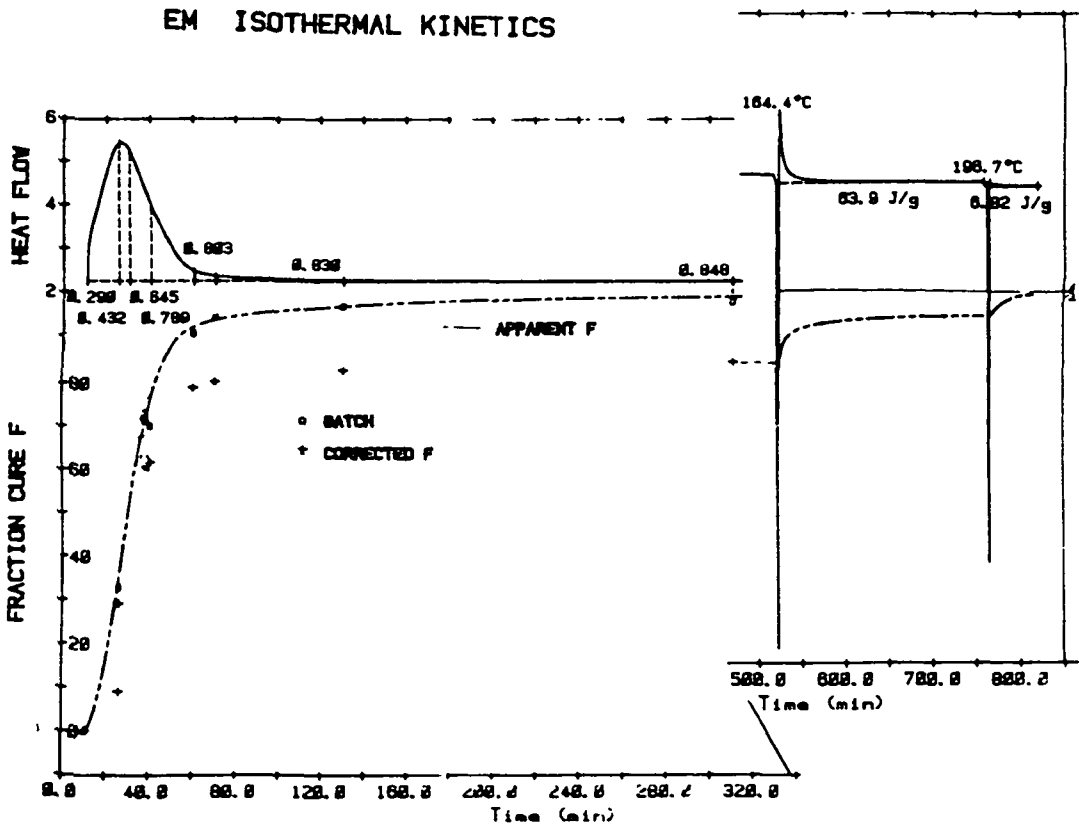higher temperature (175°).

FIGURE 10.

Figure 11 shows the glass transitions of the resins obtained from the three systems after a long-term cure at 164° C. The ED and ET systems show an apparently constant glass transition temperature after 7 hours and 17 hours respectively. The ultimate glass transition temperatures (151° C and 157° respectively) for these two sytems are well below the final cure temperature (164°). The results for the ED and ET systems indicate that it should be possible to prepare specimens of these two matrix resins at "complete" cure as defined by the absence of a measureable exotherm at a higher temperature and no change in glass temperature on extended reaction time at the final (164°) cure temperature.

FIGURE 11.

FINAL CURE 164°C
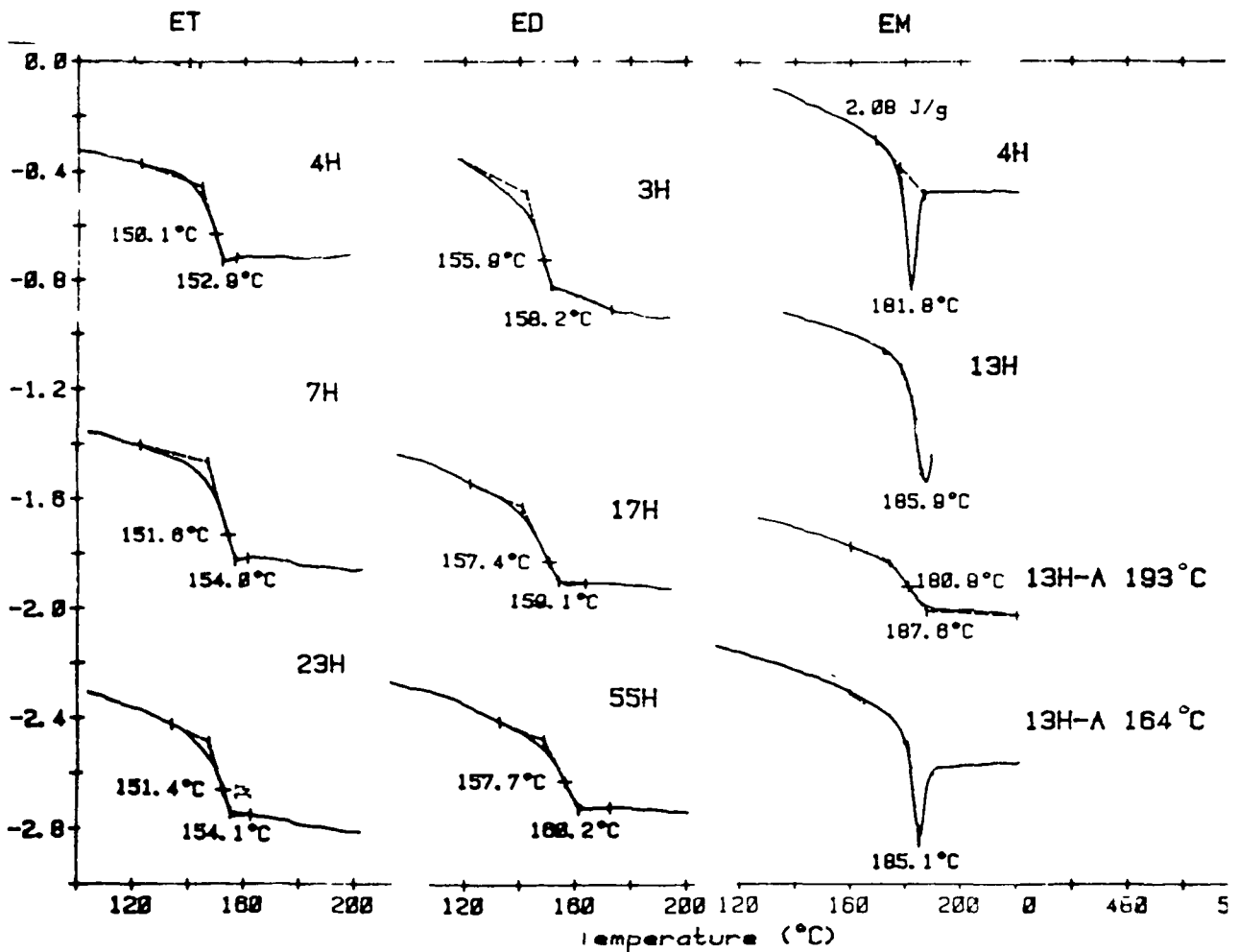
The results of Figure 11 for the EM system are more involved. The
transition temperature in this case is above the final cure temperature
(164° C). The sharply peaked exotherm is again indicative of the enthalpy
relaxation[9] observed for all three systems at the lower cure temperature
(103-107°, Figure 8). The curve marked 13H-A is from the identical
sample that gave the 13H curve except that the sample was annealed for
10 minutes at 193° and cooled quickly. The curve marked 13H-A2 was
treated in an identical fashion to 13H-A and then re-annealed at 164°
for 24 hours. These observations are a demonstration of the enthalpy
relaxation phenomenon which is generally known[9] to be a characteristic
of such epoxy systems.

The enthalpy relaxation phenomenon is especially important for the
present purposes because it demonstrates that these systems exist in
two states which may have different mechanical properties. Furthermore
the present results demonstrate the possibility of producing specimens
at comparably "complete" cures in each of the two (ordered and dis-
ordered) states for all three resin systems.

Finally, Figure 12 shows the results of thermogravimetric analysis
of each of the three resin systems in air with a heat rate of 10°/min.
These results show a modest increase in thermal stability on going
from the monoaryl (M) to the triaryl (T) system. This observation is
mildly surprising since thermal degradation would be expected to begin
in the side chain groups derived from the epoxy unit which was held
constant in these studies. The increased thermal stability might offer
advantages for rocket applications.

FIGURE 12.

THERMOGRAVIMETRIC ANALYSIS
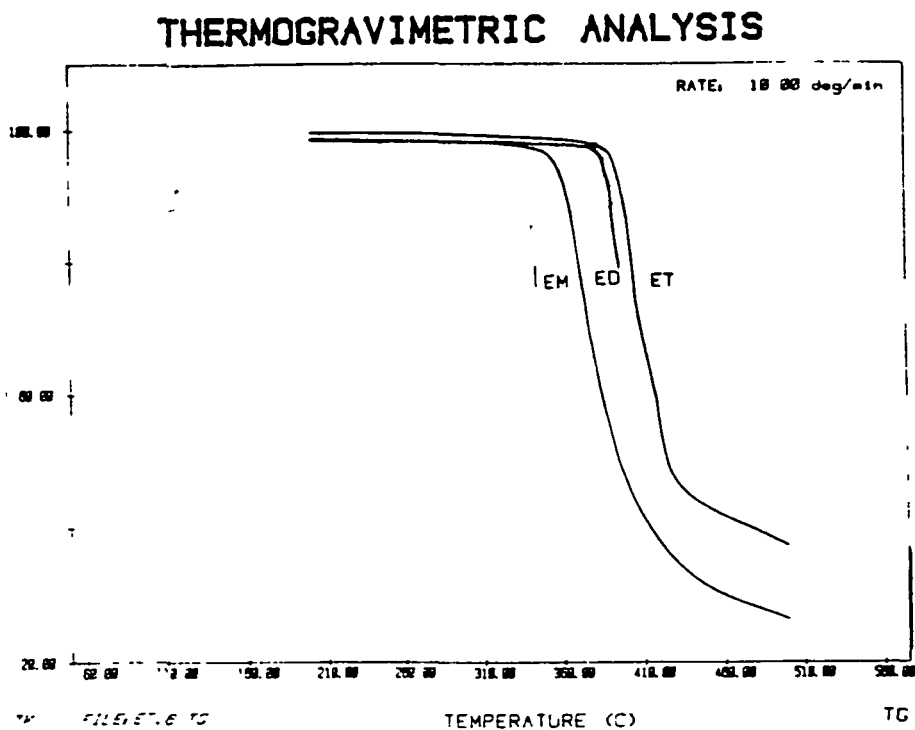
IV. Discussion

The present results provide the suggestion of three sets of conditions under which toughness test specimens might be prepared such that the diamine structural variation effects can be isolated. They are, first, after complete apparent cure at a temperature near 103° C. These specimens could possibly be made so that they show identical enthalpy relaxation peak temperatures. Second, the three-resin system could be prepared at complete cure at a final-cure temperature near 164° C. Complete cure in this case would be defined as no additional exotherm at higher temperature and no change in observed glass transition temperature on extended cure times. Finally, the latter specimens could be induced to populate their more stable states by annealing them for 24 hours at temperatures 10° below their glass transition temperatures. These conditions are summarized in Table II.

Table II

Conditions for Preparation of Comparable Specimens of EM, ED and ET Matrix Resins

| Resin	T_1 °C	Time (hr.)	T_g °C	T_2 °C	Time (hr.)	T_g °C	T_A °C[c]
EM	103	30	138.9	164	23± 6	180[a]	170
ED	103	50	138.3	164	23± 6	157[b]	147
ET	106	40	135.5	164	17	151[b]	141

a) Specimens must be annealed at 190° for 10-15 min. to be free of enthalpy relaxation.

b) Specimens without enthalpy relaxation.

c) Temperature of annealment for 24 hours producing the stable states of the resins that will show the characteristic sharp enthalpy relaxation transition peak.

It should be mentioned in closing that the present results apply to the milligram scale of sampling. Technical problems remain in translating these results to the 100-gram scale necessary for mechanical specimens. Some of these problems relate to the fact that all of the materials here are solids and must be melted in order to obtain the resin mixture. Some attention to cure rates in the 60-70° C range is needed. Also, the degree of overheating by the exothermic reaction in a large sample requires some attention.
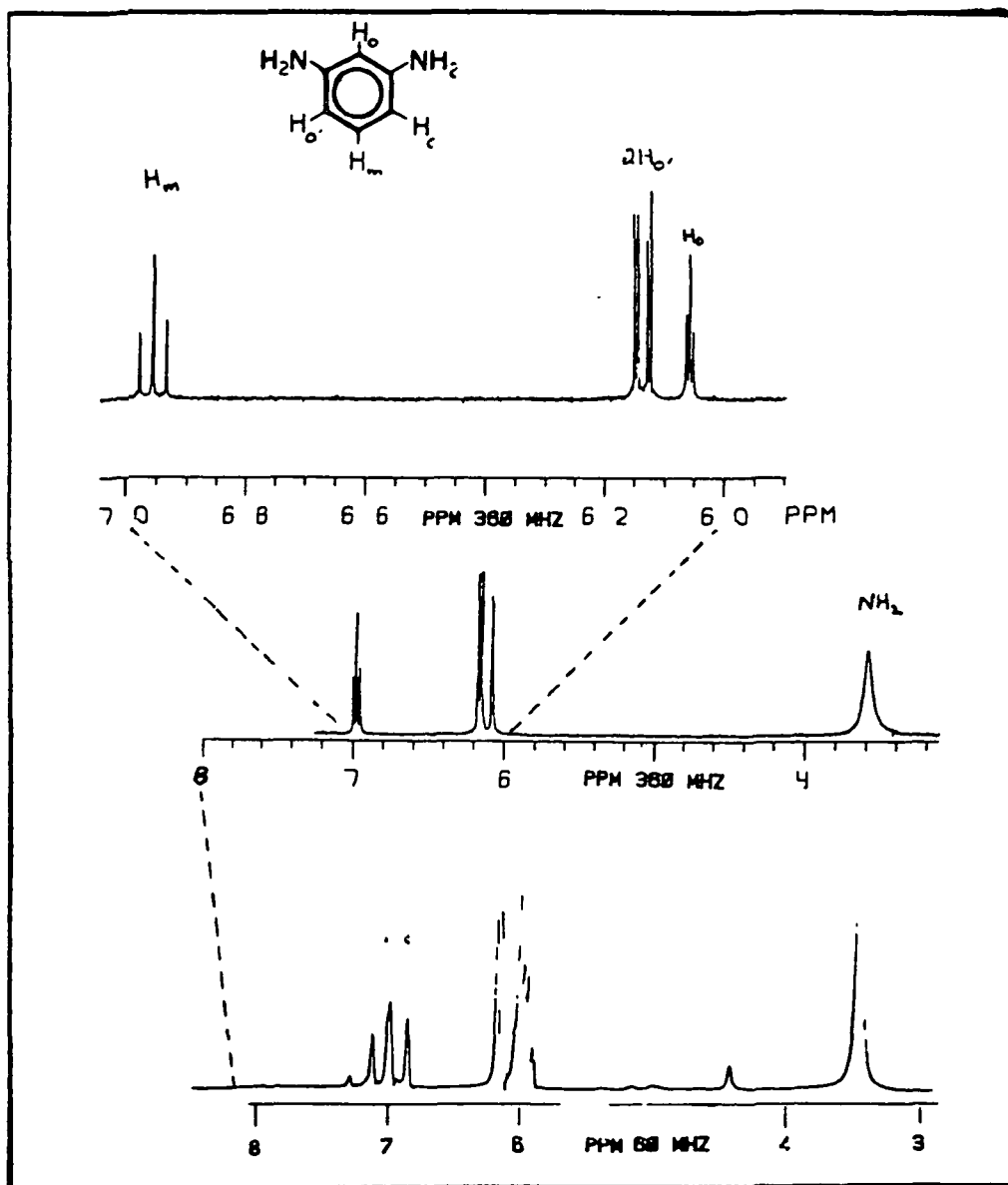
V. References

1. Martin T. Goosey, "Plastics for Electronics", Elsevier Applied Science Publishers, New York, 1985, pp. 99-135.

2. The chemical nomenclature of E, M, D and T is problematic, being consistent in neither time nor convention. The epoxide (E) is usually referred to as the bis-glycidyl diether of bisphenol A. Diamine M is m-phenylenediamine or 1,3-benzenediamine. Diamine D is 3 - [(3-aminophenyl)methyl] benzenamine or 3,3'-diaminodiphenyl-methane. Diamine T is listed in Chemical Abstracts under 3,3'- [1,3-phenylenebis(oxy)] bis-benzenamine.

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EPON/825
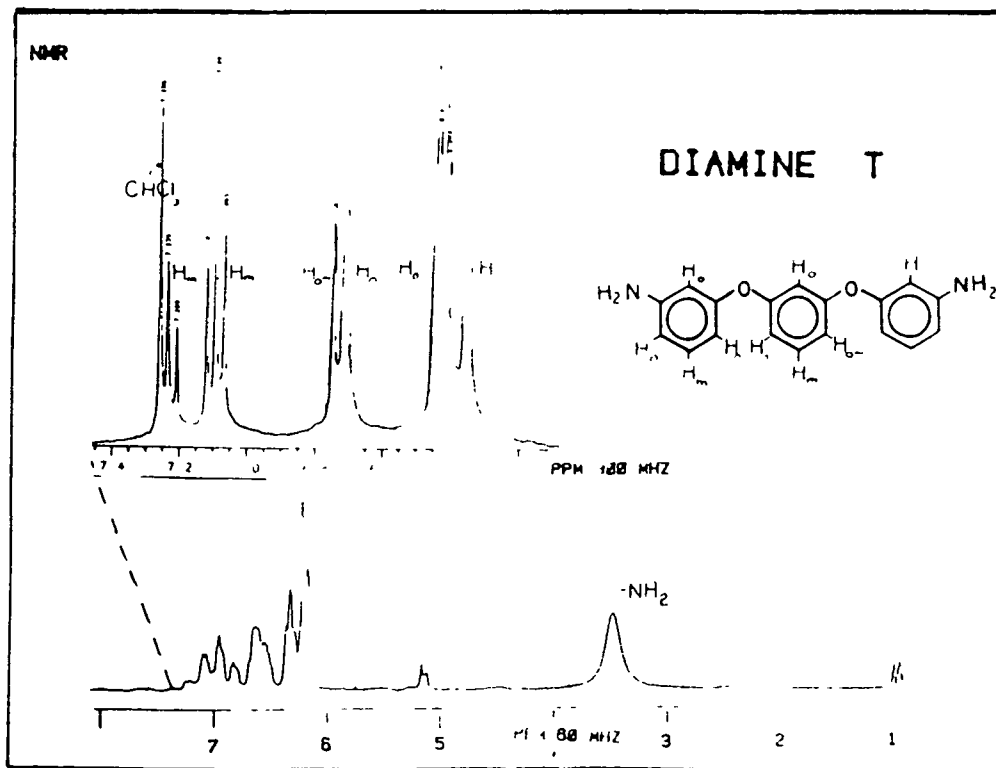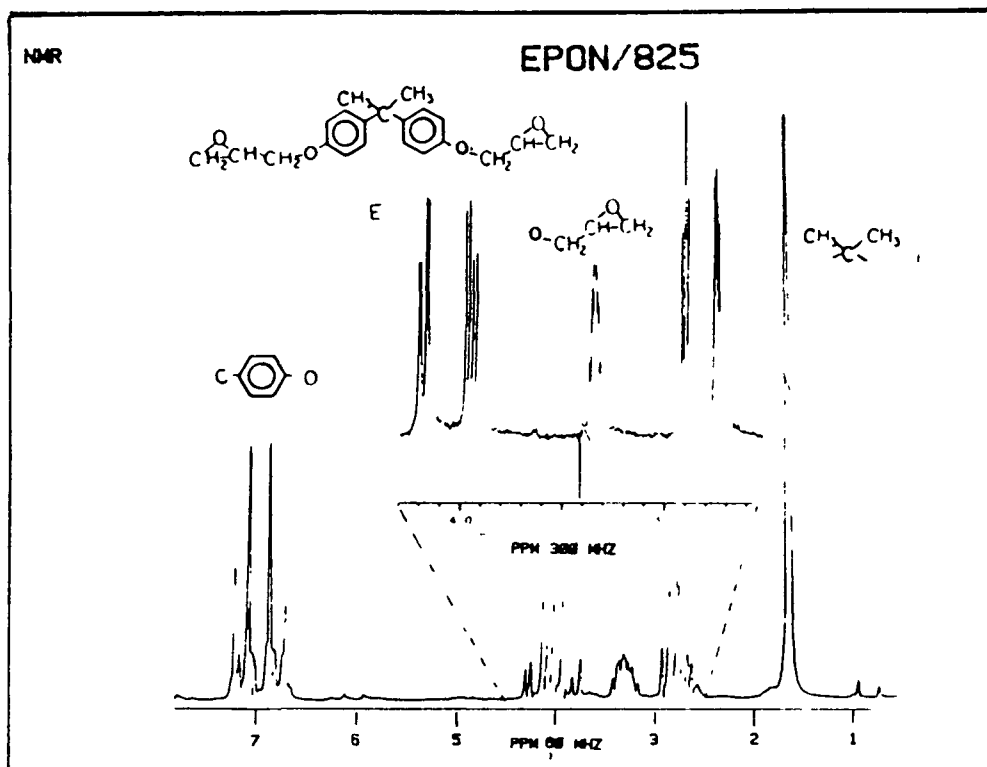
DIAMINE T

PROTON MAGNETIC RESONANCE SPECTRA

DIAMINE D