QUALITY ASSURANCE PROCEDURES FOR V378A MATRIX RESIN*

Charles L. Hamermesh and Paul J. Dynes
Rockwell International Science Center

A characterization methodology has been developed on which to base quality assurance procedures for U.S. Polymeric V378A bismaleimide matrix resin. Chemical composition was established by partition reverse-phase and size exclusion liquid chromatography. Cure rheology behavior was quantitatively characterized by dynamic viscoelastic analysis using the parallel-plate technique. The overall cure process was characterized by differential scanning calorimetry. The sensitivity of the procedures was evaluated by studying the effects of ambient out-time on the chemical and behavorial properties of the resin.

INTRODUCTION

The use of composites in aerospace applications has grown substantially in recent years and it appears that this upsurge will continue into the foreseeable future. Composites, however, are only useful if their performance is both reliable and reproducible. With the state-of-the-art composite materials, the epoxy resins, a considerable effort was undertaken a number of years ago to define the chemical nature and behavior of such material so that quality of composites could be assured.

Bismaleimides, although not new, are being reexamined as potential candidates for the next generation of matrix resins for intermediate temperature usage in the 450-505 K (350-450°F) range. As a class, bismaleimides show generally higher cured glass transition temperatures and less environmental sensitivity than state-of-the-art epoxies. They have suffered, however, from too much brittleness and difficult processibility.

These problems have been alleviated to a large degree in V378A, a modified bismaleimide developed by U.S. Polymeric (ref. 1). This system possesses the easy processibility characteristics of epoxies but shows improved retention of mechanical properties at 450 K (350°F) under moisture saturation conditions. Its rapid development and testing in primary aircraft structures have prompted the need for a characterization methodology upon which to base quality assurance procedures. V378A, like most matrix resins, with the exceptions of the PMR type systems developed by the Government owned laboratories, is a proprietary formulation. Thus, the specific composition and exact nature of the ingredients which make up the system are not likely to be divulged by its owners beyond such general descriptions as "a formulation of a modified bismaleimide and at least two volatile components." As

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this paper shows, this need not be a deterrent to the development of the characterization procedures for quality assurance of the material. With a good understanding of the underlying chemistry of bismaleimide resins and the inferences which can be drawn as to the general nature and purpose of the volatile components, a strong base can be established for the characterization of such a system despite its proprietary nature and without jeopardizing the rights of its owner.

SYMBOLS

G^*	dynamic shear modulus, N/m^2 (dynes/cm^2)
G'	storage shear modulus, N/m^2 (dynes/cm^2)
G''	loss shear modulus, N/m^2 (dynes/cm^2)
ω	oscillating shear frequency rad/s
η^*	dynamic viscosity, $N.s/m^2$ (poise)
E_a	activation energy, J/mole (kcal/mole)
dH/dT	differential heat input, J/s (mcal/s)
ΔH	heat of polymerization, J/g (cal/g)
ϕ	heating rate, K/min
T_{OS}	DSC exotherm onset temperature, K
T_{IP}	DSC exotherm inflection temperature, K
T_{EXO}	DSC exotherm peak temperature, K

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The primary goal of the liquid chromatographic study was to develop a quantitative procedure capable of separating the primary ingredients present in V378A resin. These included the major resin, which is composed of several fractions, and the two volatile components in the formulation.

The liquid chromatography method chosen was a partition reverse-phase separation utilizing a water/acetonitrile solvent gradient. This type of analysis has proven to be the most successful for prepolymer resins containing a broad range of component polarities and oligomer molecular weights. Detection of components was made by ultraviolet spectrophotometry. A detection wavelength of 200 nm was chosen to enhance the analysis of Volatile Component 2 in the resin. In order to completely dissolve the resin for analysis a minimum of 25% dimethylformamide in tetrahydrofuran was required. A summary of the chromatographic conditions used for the analysis of V378A resin is given in table 1.

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The separation of V378A resin using this procedure is shown in figure 1. A total of approximately eighteen components are resolved. Eight of these have been identified as belonging to one of the three major ingredients of V378A resin. Identification was based on peak elution times verified by spiking of V378A resin with individual ingredients. The liquid chromatographic separations of the three major components of V378A resin are shown in figure 2.

Although a large number of components are separated by the partition liquid chromatographic technique, it was found that the acetonitrile or tetrahydrofuran insoluble fractions of V378A resin did not elute during the water/acetonitrile solvent gradient. Moreover, the fractions soluble in tetrahydrofuran or acetonitrile gave the same chromatographic peaks and peak area distibutions as did totally solubilized samples. The V378A resin system thus appears to be comprised of two fractions. One is of relatively low molecular weight consisting of the two volatile components and bismaleimide resin oligomers. The insoluble fraction is presumably composed of products formed by reactions among these starting ingredients.

Characterization of the insoluble fraction of V378A resin was made by size exclusion liquid chromatography. With tetrahydrofuran as solvent, the once solubilized resin remains in solution during size exclusion analysis. The experimental details of this technique are given in table 2. The size exclusion separation of V378A resin is shown in figure 3. The first and therefore highest molecular weight component to elute was determined to correspond to the insoluble fraction of the resin not detected by partition liquid chromatography. The remaining ingredients, however, are not resolved as well as with the partition method. Partition and size exclusion liquid chromatography thus complement each other and together provide the means for a comprehensive analysis of the chemical constituents of V378A resin.

CURE RHEOLOGY

The rheological behavior of V378A neat resin during cure was studied with the Rheometrics Visco-Elastic Tester. The experimental conditions used to analyze the resin are given in table 3. The instrument calculates the dynamic shear modulus G* and its two components, the dynamic storage or elastic modulus G' and the dynamic loss or viscous modulus G". A dynamic viscosity is defined from the dynamic modulus as, $n* = G*/\omega$, where ω is the oscillatory shear frequency. The variation in the dynamic viscoelastic properties of V378A resin during a 2 K/min heating cycle is plotted in figure 4.

Several factors critical to a matrix resin's processibility can be derived from these data. One is the initial value of the dynamic viscosity. V378A has a room tempertaure value of ~ 6×10^2 N·s/m^2 (6×10^3 poise) which imparts satisfactory drape in the prepreg. Resin dynamic viscosity decreases with increasing temperature until around 383 K where it reaches a minimum of ~ 5×10^{-1} N·s/m^2 (5 poise). Above this temperature, polymerization reactions bring about a rapid rise in dynamic viscosity. At a specific temperature the shear storage and loss moduli are equal. This midway point between viscous liquid behavior and solid state elastic response has been found to correlate with resin gelation as measured by standards methods (ref. 2).

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The dynamic viscosity profiles for several cure cycle heating rates are shown in figure 5. Faster heating rates tend to reduce the minimum dynamic viscosity reached during cure. This effect can be of value for controlling the amount of flow desired during processing. The temperatures at which gelation occurs for four heating rates are given in table 4. By analogy to differential scanning calorimetry, the dependence of the temperature at gelation on heating rate can be plotted in a modified Arrhenius equation (ref. 3). The data are plotted in figure 6 where a good fit to the Arrhenius equation is found. An activation energy to gelation of 89.5 J/mole (21.4 kcal/mole) is calculated from the slope of the curve.

The rheological behavior of V378A resin was also explored under isothermal cure conditions. The dynamic viscoelastic properties of V378A resin at 393 K are shown in figure 7. Initially, the resin displays a very low viscosity with almost no elastic character (G' ≈ 0). At longer times G' increases rapidly and surpasses G". Again gelation is associated wih the crossover of the two dynamic moduli. The gel times determined by this method are given in table 5 for several temperatures. These data are plotted in figure 8 according to the Arrhenius equation. A linear relationship is found and from the slope of the curve an activation energy of 89.7 J/mole (21.4 kcal/mole) to gelation is derived.

DIFFERENTIAL SCANNING CALORIMETRY

The differential scanning calorimetry (DSC) behavior of V378A resin is shown in figure 9 for a heating rate of 1.25 K/min. Curing is characterized by two exotherms. The major exotherm is centered at 415 K (142°C) while a second much smaller one occurs about 70 K higher. The major exotherm is related to reactions involving Volatile Component 1. The exotherm at higher temperature appears to result primarily from additional polymerization of bismaleimide groups.

Several DSC parameters were evaluated for quality assurance purposes. They include the reaction onset temperature T_{OS}, the peak inflection temperature T_{IP}, the peak exotherm temperature T_{EXO} and the heats of polymerization ΔH associated with the two reaction exotherms. A summary of such data for four heating rate experiments is given in table 6.

Heats of polymerization were not sufficiently reproducible to use as quality assurance parameters. The characteristic thermogram temperatures, however, can be determined more precisely. The peak exotherm temperature T_{EXO}, in particular, is very reproducible. The inflection point temperature T_{IP} was also investigated, as it has been show to coincide with gelation in epoxy resin systems (ref. 3). The heating rate dependence of T_{IP} and T_{EXO} are plotted in figure 10 according to the modified Arrhenius relation discussed previously. Linear relationships are obtained which define activation energies of 78.9 J/mole (18.7 kcal/mole), 69.1 J/mole (16.5 kcal/mole) from T_{EXO} and T_{IP}, respectively. The inflection point temperature data in table 6 are in fairly good agreement with the rheologically determined gel temperatures given in table 4. Experimentally, gel times determined from rheological data are more accurate and reproducible than can be derived from DSC measurements.

RESIN OUT-TIME EVALUATION

It was of interest to examine the effects of ambient aging on the properties of V378A neat resin. Film samples of resin were exposed to 296 K and 30-60% RH conditions for periods up to three weeks. At ambient the resin loses its tack within one day. It has, however, a twenty-one day recommended out-time in terms of processibility.

Partition liquid chromatographic analysis of resin aging revealed only one significant change to be taking place. The concentration of Volatile Component 1 decreases as shown in figure 11. The decrease in Volatile Component 1 occurs as a result of both B-staging and evaporation. Weight loss measurements indicate approximately one-third loss due to evaporation and the remainder cause by resin advancement. Evidence of resin advancement is shown by size exclusion chromatography in figure 12 where the concentration of early eluting highr molecular weight species increases with resin aging.

Two rheological tests were used to characterize the effects of ambient aging on V378A resin. They were a linear 2 K/min heating rate cure and a 398 K isothermal gel time test. The results of the 2 K/min cure cycle experiments are shown in figure 13. The dynamic viscosity profiles show a significant increase with ambient aging time. A plot of the gel times determined from the isothermal rheology data are plotted in figure 14. For short aging times the gel time increases and then drops markedly around the fourth day of aging.

DSC is a sensitive tool for analyzing the effect of aging on V378A resin. Thermograms for resin aged up to 20 days are plotted in figure 15. The primary result of out-time is a reduction in the major DSC exotherm which is associated with the reactions of Volatile Component 1. The smaller high temperature exotherm appears to be unaffected by ambient aging. The major exotherm has a slight shoulder located at 370-390 K. After about 1 week of aging, this shoulder begins to resolve itself into a new exotherm peak centered near 395 K. These changes are indicative of a resin in which more than one path of cure is available. In such cases, the cure temperature and kinetic parameters of the various reaction paths control which path predominates.

REFERENCES

1. McKague, L: V378A Polymide Resin - A New Composite Matrix for the 80's. Proceedings of ASTM Symposium on Composites for Extreme Environments, Bal Harbour, FL, November 11, 1980.

2. Tung, M.C.; Dynes, P.J: Relationship Between Viscoelastic Properties and Gelation in Thermosetting Systems. J. Appl. Polym. Sci., 27, 569 (1982).

3. Carpenter, J.F: Instrumental Techniques for Developing Epoxy Cure Cycles. Proceedings of 21st National SAMPE Symposium and Exhibition, Los Angeles, CA, April 6-8, 1976.

Table 1

Experimental Conditions for Separation of
U.S. Polymeric V378A Resin by Partition
Liquid Chromatography

Column:	Spectra-Physics Sperisorb 10 ODS
Solvent:	Baker Liquid Chromatographic Water Burdick and Jackson Acetonitrile
Gradient:	10-80% CH_3CH/H_2O, Linear in 50 min
Flow:	Ultraviolet at 200 nm
Sample:	10 ul of a 1.5 mg/ml solution in 25/75 DMF/THF

Table 2

Experimental Conditions for Separation of
U.S. Polymeric V378A Resin by Size
Exclusion Chromatography

Column:	Waters Associates μ-Styragel 1 (500A) + 2 (100A)
Solvent:	Burdick and Jackson Tetrahydrofuran (Unstabilized UV Grade
Flow:	1 ml/min
Detection:	Ultraviolet at 254 nm
Sample:	100 ul of a 2 mg/ml solution in 25/75 DMF/THF

Table 3

Rheometrics Visco-Elastic Tester
Experimental Parameters

Geometry	25 mm Parallel plates
Frequency	10 rad/s
Gap	0.5 mm
Percent Strain	< 10%
Environment	Dry nitrogen

Table 4

Variation in Temperature at
Gelation According to G'=G"
Criterion of U.S. Polymeric
V378A Resin

ϕ K/min	$T (G' = G")$ K
2	401
3	408
4	412
5	415

Table 5

Variation in Time to Gelation
According to G'=G" Criterion
of U.S. Polymeric V378A Resin

Temperature K	Gel Time min
388	18.6
393	11.3
398	8.2
413	3.2

Table 6

Differential Scanning Calorimetry Analysis
of U.S. Polymeric V378A Resin

ϕ K/min	T_{OS}	T_{IP} K	T_{EXO}	ΔH_1	ΔH_2 J/g
1.25	363	388	402	235	18
2.50	345	403	415	214	15
5.00	366	418	429	264	10
10.0	367	429	442	205	10
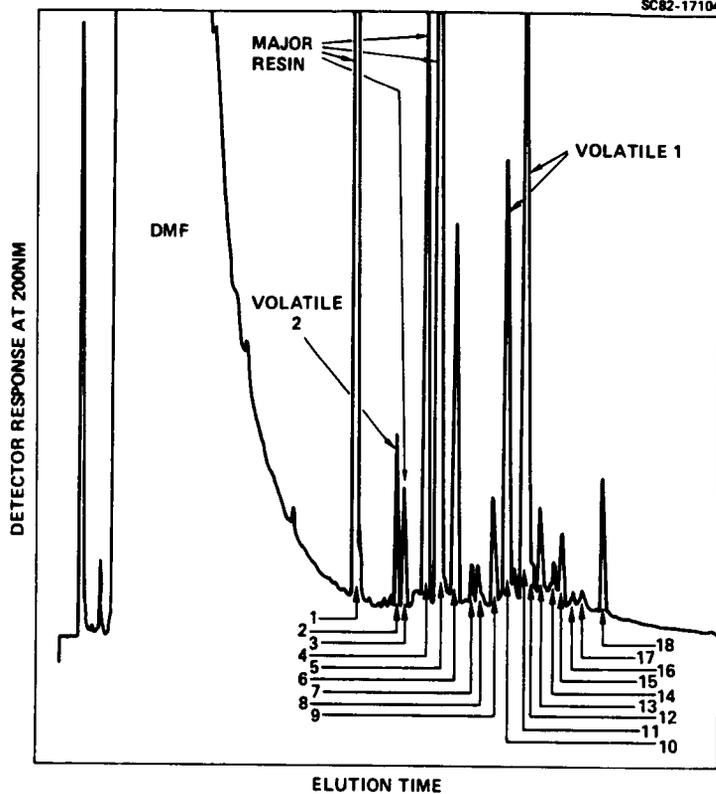
Figure 1.
Partition liquid chromatographic analysis of U.S. Polymeric V378A resin.
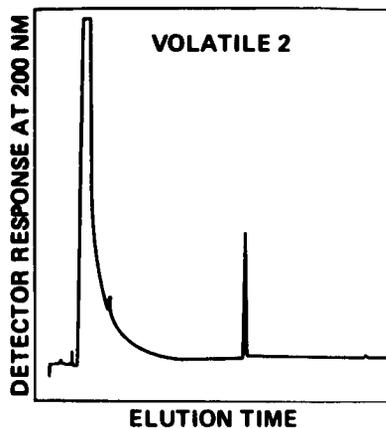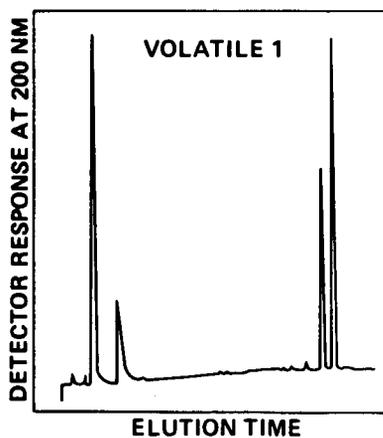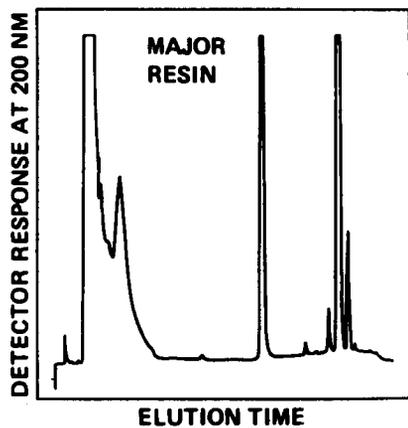
Figure 2.   Partition liquid chromatographic analysis of U.S. Polymeric V378A resin ingredients.

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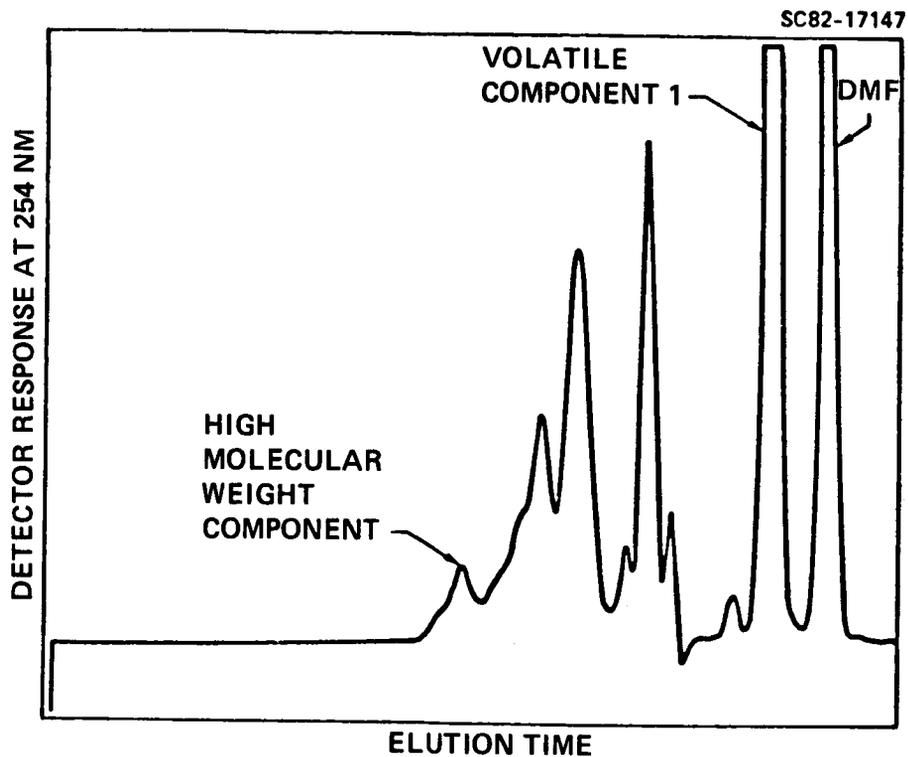
Figure 3. Size exclusion liquid chromatographic analysis of U.S. Polymeric V378A resin.
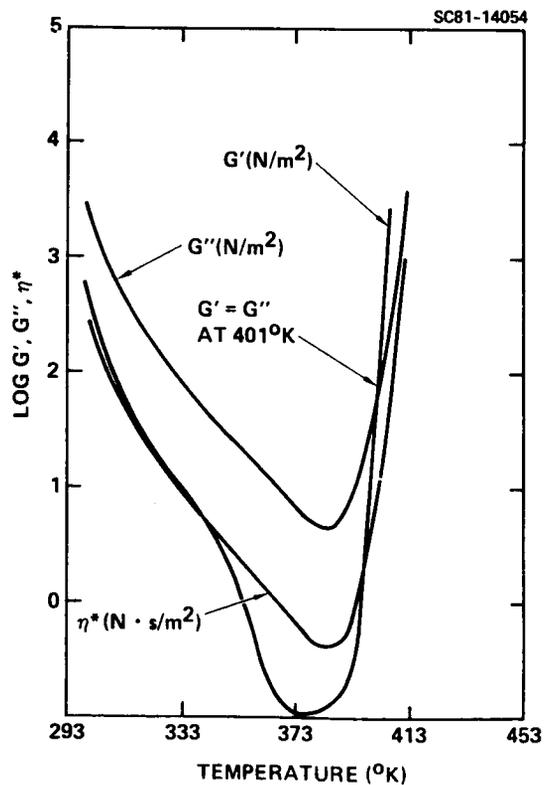
Figure 4.
Dynamic viscoelastic behavior of
U.S. Polymeric V378A resin at a
2 K/min heating rate.
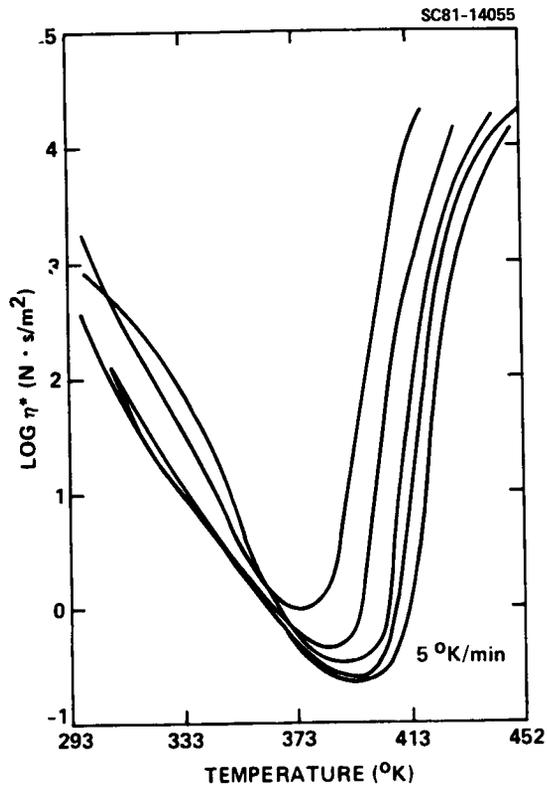
Figure 5.
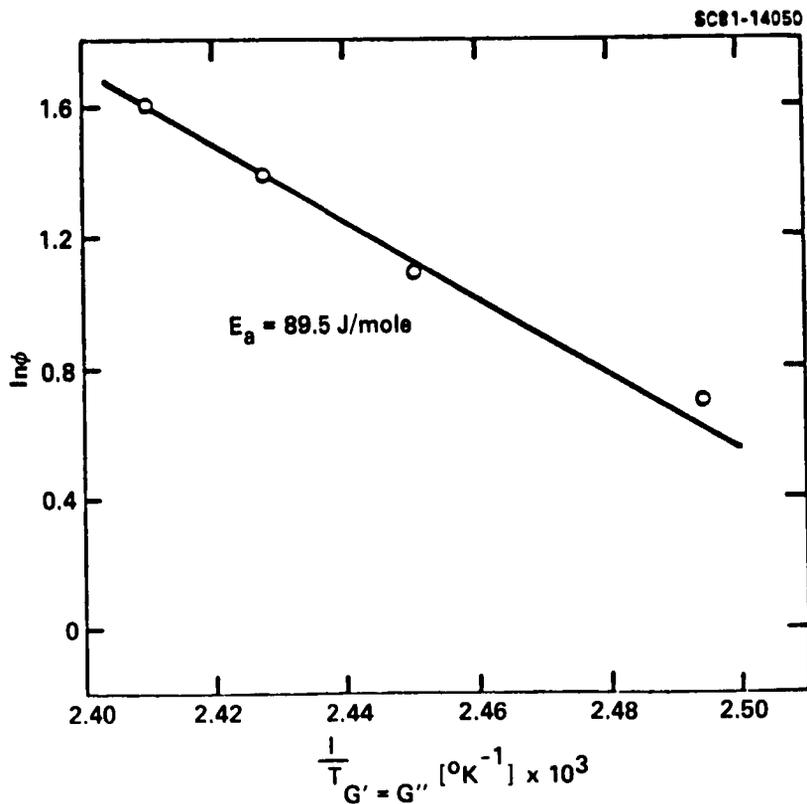Effect of heating rate on the cure rheology of U.S. Polymeric V378A resin.

Figure 6.
Dependence of the dynamic moduli crossover temperature with heating rate for the cure of U.S. Polymeric V378A resin.

SC81-14053
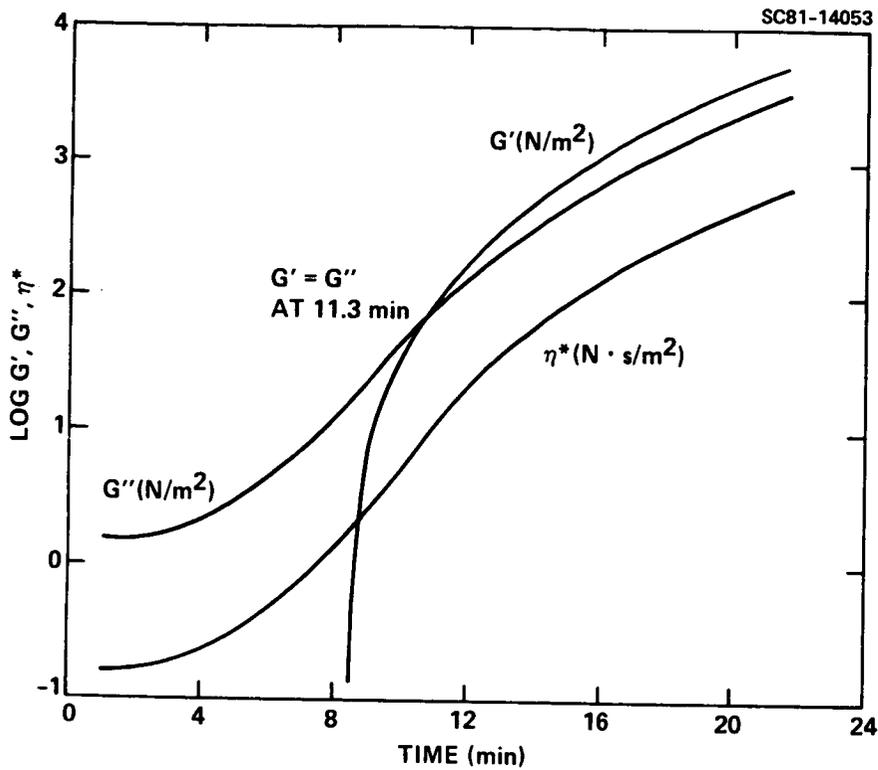
Figure 7.
Dynamic viscoelastic
behavior of U.S. Polymeric
V378A resin at 393 K.

SC81-14051
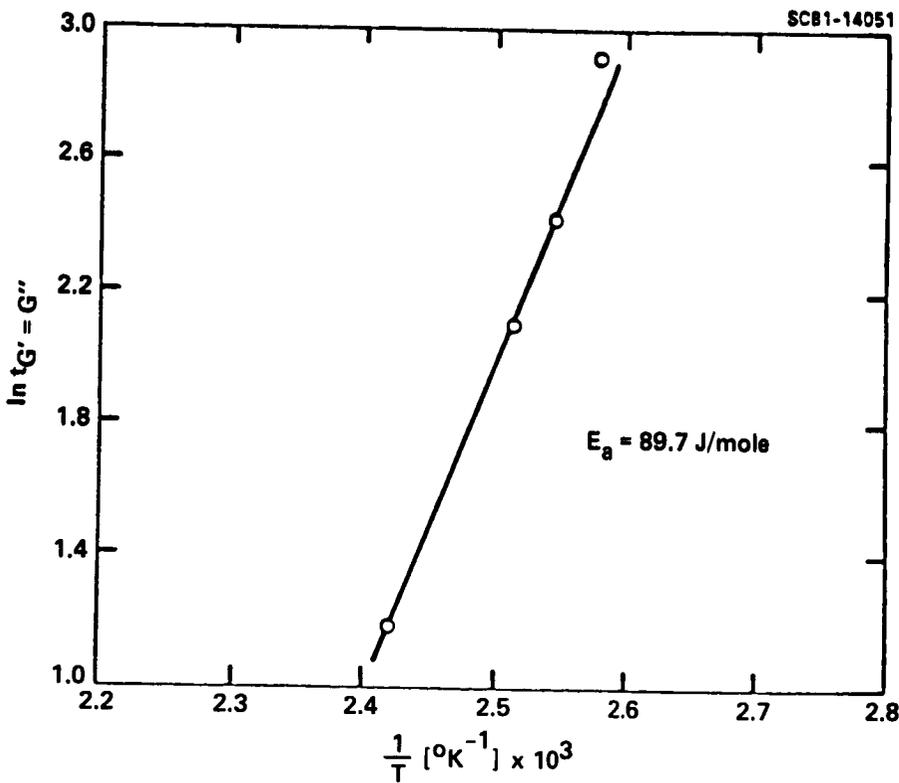
Figure 8.
Dependence of the dynamic
moduli crossover time with
isothermal cure temperature
for U.S. Polymeric V378A
resin.

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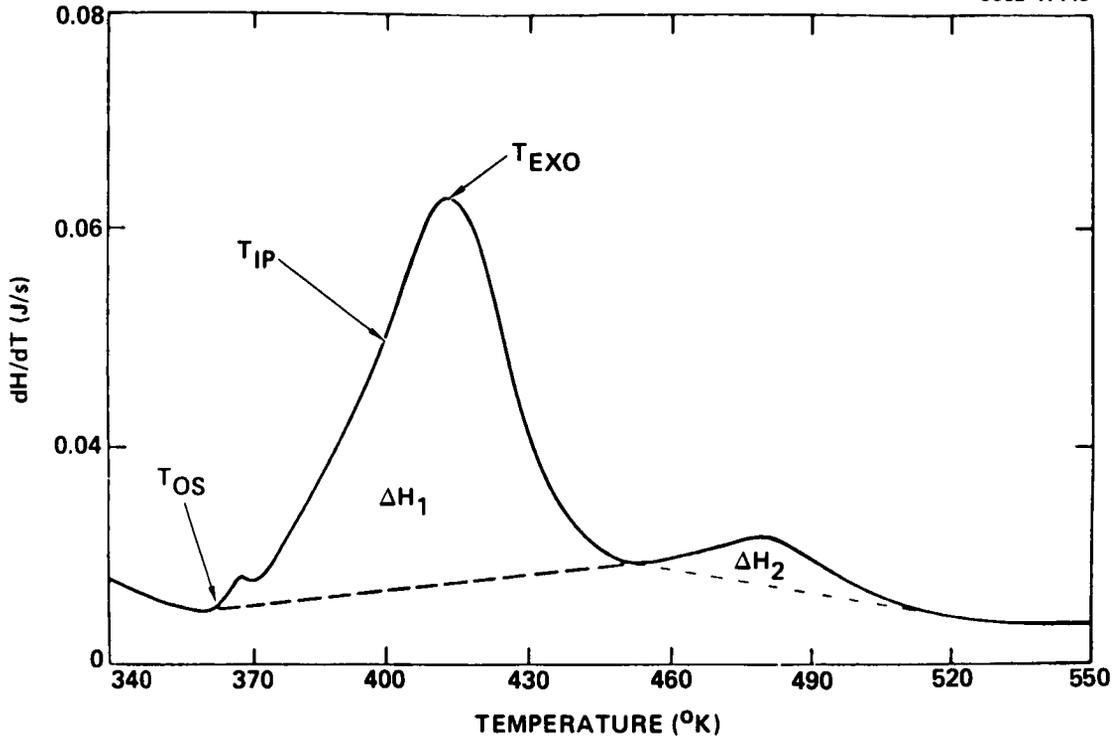
Figure 9. DSC thermogram for the curing of U.S. Polymeric V378A resin.
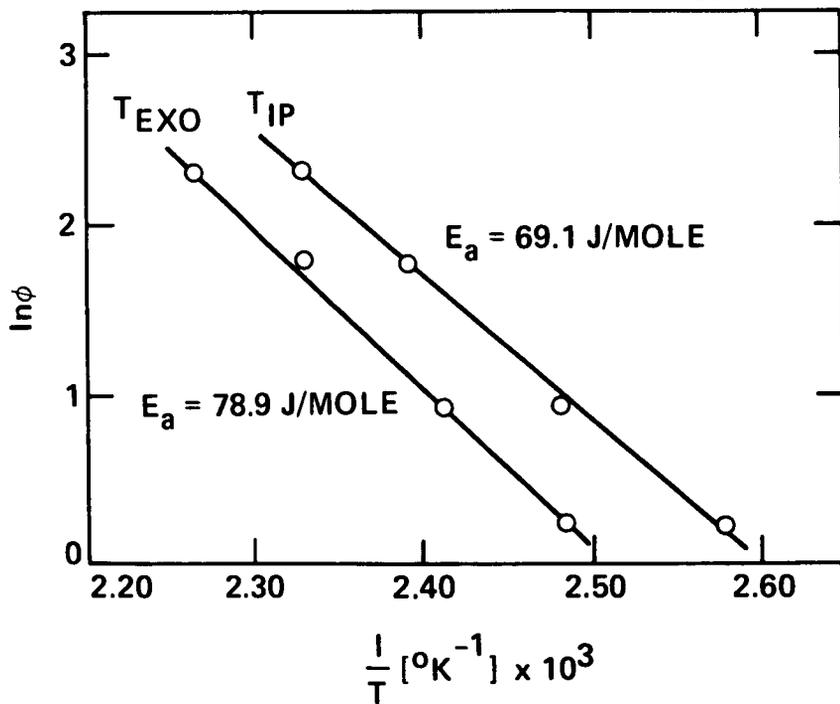
Figure 10.
Dependence of DSC exotherm
peak and inflection point
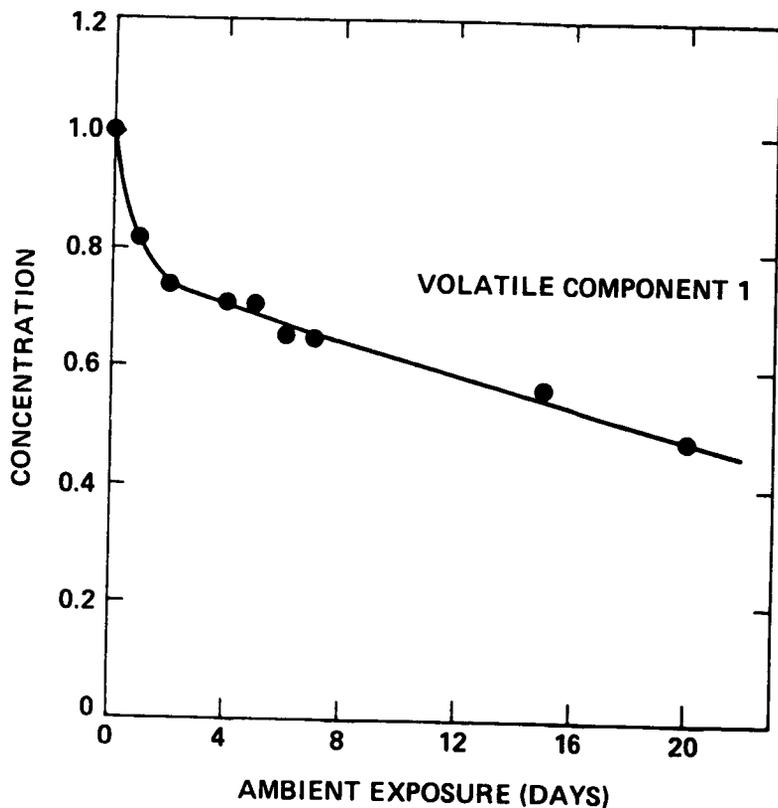temperature with heating
rate for U.S. Polymeric
V378A resin.

Figure 11.
Effect of ambient aging on the concentration of Volatile Component 1 in U.S. Polymeric V378A resin.
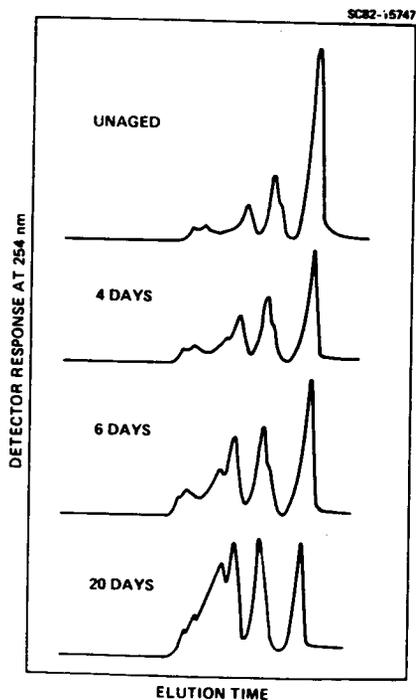

Figure 12.
Effect of ambient aging on the size exclusion liquid chromatographic separation of U.S. Polymeric V378A resin.
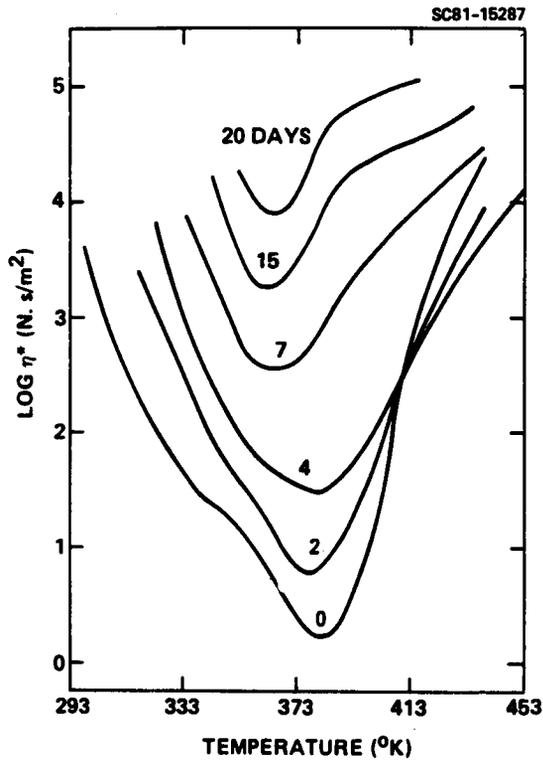
SC81-15287

Figure 13.
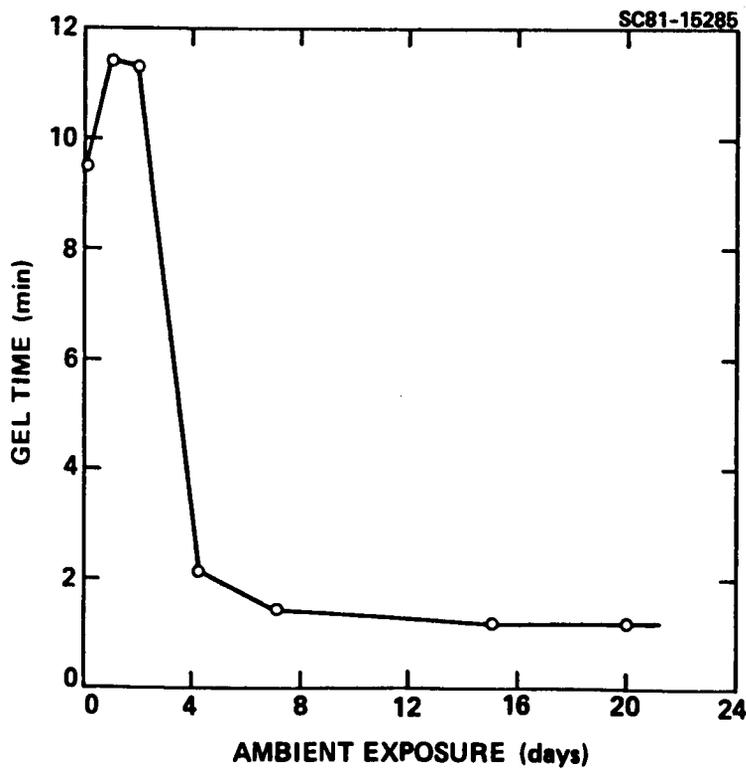Effect of ambient aging on the cure rheology of U.S. Polymeric V378A resin.

(Graph: LOG η^* (N. s/m^2) vs TEMPERATURE ($^\circ$K), with curves labeled 20 DAYS, 15, 7, 4, 2, 0)

SC81-15285

Figure 14.
Effect of ambient aging on the time of gelation at 398K for U.S. Polymeric V378A resin.

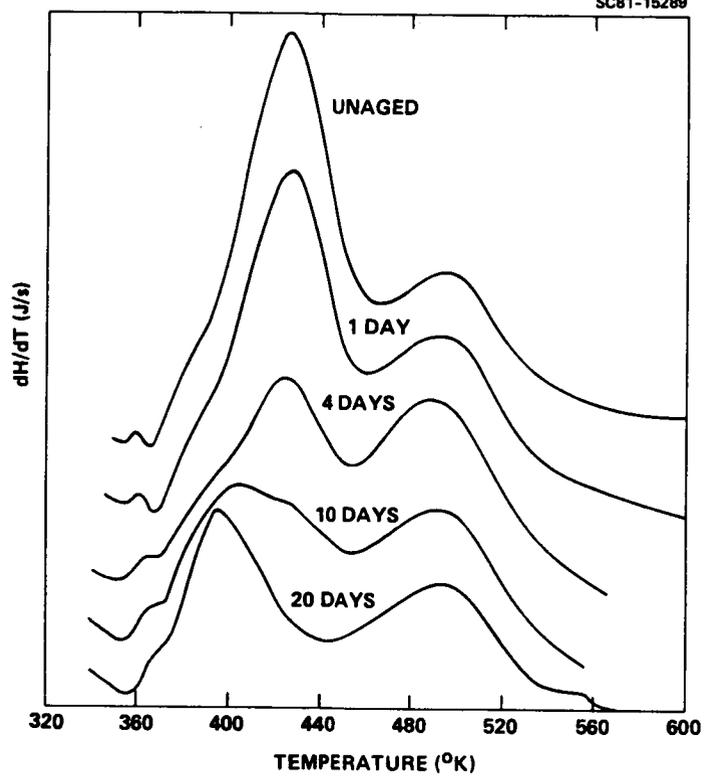(Graph: GEL TIME (min) vs AMBIENT EXPOSURE (days))

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Figure 15.   Ambient aging effect on the DSC behavior
of U.S. Polymeric V378A resin.