Journal of Chromatography, 316 (1984) 343–358
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 530

THERMOSET RESIN MICROSTRUCTURE BY GEL-PERMEATION CHROMATOGRAPHY: AN ANHYDRIDE-CURED EPOXY

DELMAR C. TIMM*, WIE M. TIAN and BARRY J. LARSON
Chemical Engineering Department, University of Nebraska, Lincoln, NE 68588-0126 (U.S.A.)
and
RICHARD D. SUDDUTH
Brunswick Corporation, Defense Division, Lincoln, NE 68504 (U.S.A.)

SUMMARY

Gel-permeation chromatography was used to characterize at the molecular level the extract fraction leached from cured, thermoset epoxy resin matrixes within filament wound E-glass composites. Monomer concentrations defined the extent of reaction. Oligomeric population density distributions, coupled with step-growth, kinetic reaction theory, defined cross-link average molecular weight. Cross-link architecture was confirmed via measurements by dynamic mechanical spectroscopy of the complex moduli. The average size of macromolecules within the network structure was also estimated. Our research demonstrates that gel-permeation chromatography is an effective technique for the characterization of network structures within thermoset resins.

INTRODUCTION

Gel-permeation chromatography (size-exclusion chromatography) is an effective method for the molecular characterization of thermoplastic resins. Population density distributions of constituent macromolecules and molar concentrations for unreacted monomeric species reflect intrinsic kinetic mechanisms. Kinetic reaction mechanisms show that most chain-growth and step-growth resins are comprised of molecular distributions whose most prolific species are oligomers, including dimers, trimers, etc., even at high extents of reaction. Within a thermoset resin's molecular labyrinth, oligomeric molecules exist that are not attached to the network structure. These materials may be leached, as has been shown in studies of resin swelling. Chromatography provides a powerful, analytical tool for the molecular characterization of the extract fraction.

Timm and co-workers[1,2] studied a chain-growth polymerization in which 1,2-polybutadiene was crosslinked via *tert.*-butylstyrene. Oligomeric molar distributions were consistent with kinetic theory, reflecting the molecular weight of the 1,2-polybutadiene formulated. Molecular estimates of cross-link average molecular weight were confirmed through the theory of rubber elasticity, as modified by Niel-

0021-9673/84/$03.00 © 1984 Elsevier Science Publishers B.V.

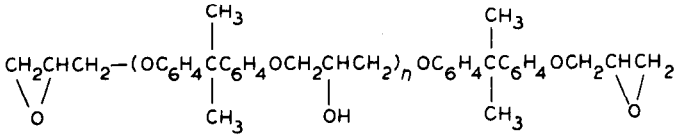
sen[3]. The number average molecular weight for the oligomeric fraction was proportional to the average molecular weight of the cross-links. The proportionality constant reflected termination by combination.

Current research demonstrates that molecular analyses of extracts from anhydride-cured epoxy resins accurately predict molecular structure within the resin matrix. Interpretation of molecular data can yield information that currently is possible only through distinct caracterization procedures. For example, infrared analysis tracks functional groups; the complex modulus yields cross-link average molecular weight; and compressive stress-strain phenomena yield mechanical properties, including yield points and postyield stress. Inasmuch as molecular architecture determines mechanical performance, data from a chromatogram will correlate such diverse observations. Furthermore, since a variance in a cure changes molecular distributions within the matrix, analyses of chromatograms provide information for quality control applications and contain definitive data descriptive of the extent of cure.

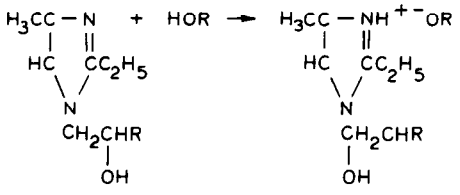
GEL-PERMEATION CHROMATOGRAPHY

Reagents

The epoxy resin was formulated from industrial grade reagents,including diglycidyl ether of bisphenol A (DGEBA). The dominant molecule is at $n=0$, but oligomers at $n > 0$ are present:



The co-monomer was methyltetrahydrophthalic anhydride. The initiator–catalyst, 2-ethyl-4-methylimidazole (EMI24), is known to react with the oxirane[4] via its primary hydrogen. A bis-adduct subsequently forms via an alkoxide ion, forming an activated intermediate. In the present formulation, alcohol and acid groups provide reactive hydrogen sites, which form ionic intermediates, including



In dry formulations, oxirane and anhydride rates of reaction are essentially equal, but in a wet medium, epoxide consumption exceeds that for the anhydride. Water may result in a shift in chemical equilibrium and/or catalyst selectivity. Coupled with anhydride hydrolysis, increased acidity may contribute to an increased polyether formation rate. Acids not only catalyze this competing reaction, but will cause ester bonds within the epoxy resin to be subject to hydrolysis[5].

Polymerization mechanism

The model descriptive of the kinetic mechanism is similar to that for *tert.*-amines[6–8].

$$A_jC + A \overset{k_1}{\rightarrow} A_jAC \overset{K_1}{\rightleftarrows} A_jA + C$$

$$A_jAC + E \overset{k_2}{\rightarrow} A_{j+1}C \overset{K_2}{\rightleftarrows} A_{j+1} + C$$

$$A_jAC + A_k \overset{k_2}{\rightarrow} A_{j+k}C \overset{K_2}{\rightleftarrows} A_{j+k} + C$$

$$A_jAC + A_kA \overset{k_2}{\rightarrow} A_{j+k}AC \overset{K_2}{\rightleftarrows} A_{j+k}A + C$$

$$j,k = 1, 2, 3 \ldots.$$

The bis-adduct of an alcohol on a macromolecule of degree of polymerization j is A_jC and that for an acid is A_jAC. Monomeric anhydride and oxirane are A and E, respectively. The monomers are devoid of reactive hydrogen sites and are thus distinctly different from polymeric molecules. During the development of macromolecules, an anhydride A reacts with an alcohol–catalyst complex A_jC, producing an acid adduct, A_jAC, which then dissociates reversibly. Oxirane groups, supplied via monomeric DGEBA and by pendant epoxides on macromolecules A_k and A_kA, react with acid adducts to generate hydroxyl sites. This is represented by the last three expressions. Chain branches and, ultimately, crosslinks are formed by these macromolecular combinations. The reaction sequence accounts for changes in functional acid groups; macromolecules will develop complex isomers that contain multiple reactive hydrogen sites, but their explicit descriptions are not intended. Chromatographic analysis identifies a molecule by its molecular weight. A model constraint is that every macromolecule contains at least one oxirane.

Population density distributions

Chemical equilibrium constraints provide

$$(A_jC) = K_1A_jC$$
$$(A_jAC) = K_2(A_jA)C$$

The symbols are now understood to be expressions of molar concentrations. The catalyst concentration is C; a polymeric molecule, A_j, is of degree of polymerization j and contains a hydroxyl site. The molecule A_jA contains a carboxyl group. Conservation laws for batch polymerizations yield

$$\mathrm{d}(A_jC)/\mathrm{d}t = -k_1(A_jC)A + k_2 \sum_{i=1}^{j/2} \{(A_{j-i}AC)[A_i + A_iA]\} + k_2(A_{j-1}AC)E$$

$$\mathrm{d}(A_jAC)/\mathrm{d}t = k_1(A_jC)A - k_2(A_jAC)[E + A_{\mathrm{TOT}} + A_{\mathrm{TOT}}A] = 0$$

The several rate expressions in the first differential equation are: (1) a bis-adduct of an alcohol on a macromolecule of degree of polymerization j reacts with monomeric anhydride; (2) bimolecular combinations of two smaller polymeric species, one of which contains an acid adduct and the second an oxirane, form an alcohol–catalyst complex of degree of polymerization j; and (3) a monomeric oxirane reacts within an ionic acid intermediate. In the second differential equation, rate expressions are: (1) a bis-adduct of an alcohol couples with an anhydride and (2) an acid complex reacts with all molecules that contain an oxirane, including monomeric, oligomeric, and polymeric species. The variables $A_{TOT} = \Sigma A_i$ and $A_{TOT}A = \Sigma A_iA$ are cumulative molar concentrations. The acid complex is further assumed to be an activated intermediate; thus the rate of change in concentration is small compared to rates of reaction.

An experimental chromatography constraint is that all species are eluted according to molecular size. The observed response for polymeric molecules will be the sum of molecules that contain a reactive hydrogen site:

$$P_j = A_j + A_jA$$

The intent is to count molecules only once. Subject to equilibrium constraints, the assumption of an acid, activated intermediate and experimental chromatography restrictions, the following relationship describes this epoxy polymerization

$$dP_j/dt = kE(P_{j-1} - P_j) - kP_{TOT}\,P_j + k\sum_{i=1}^{j/2} P_iP_{j-i} \qquad (1)$$

where $P_0 = 0$ and $j = 1, 2, 3...$

Initially, reactive hydrogen sites are supplied via oligomers of DGEBA, $n > 0$, and by EMI24. For simplicity, their molar concentrations are lumped into one variable, $P_1(0)$. Zero initial conditions exist for $P_j(0)$ when $j > 1$. A degree of polymerization unit indexes the combined molecular weights of the oxirane monomer and anhydride where the molecular weight for the oxirane is one half that for DGEBA.

The nature of the polymerization is adequately described by eqn. 1[9]. The first term is analogous to propagation kinetics, which in the absence of competing reactions would yield a Poisson molar distribution of polymeric molecules within the matrix. The second and third rate expressions are characteristic of more traditional step-growth polymerizations, where one molecule has an equal probability of reacting with all others. Such reactions by themselves result in molar distributions that are described by exponential functions. The simultaneous occurrence of the reactions yields a more complex distribution, but one which contains these two fundamental relationships. Experimental molar distributions, P_j, provide a means via regression analysis for numerical evaluation of rate parameters within the kinetic polymerization model[9].

The kinetic model necessarily becomes more complex if water is present during the cure. Moisture effectively increases available polymerization sites; therefore, the molar concentrations of polymeric species, P_j, substantially increase, as will rates of monomer consumption. A second effect is a relative increase in the rate of competing side reactions, one of which is likely the formation of polyethers. The consequence is an imbalance in stoichiometry at the end of the cure, excess anhydride and deficient

epoxide. Reactive sites become acid groups predominantly; the reaction terminates prematurely, yielding a less developed cross-link labyrinth.

Current research emphasizes the molecular characterization of oligomeric materials leached from quality resins at high extent of reaction by gel-permeation chromatography analysis. Applications include high-performance, filament-wound composites on the space shuttle.

EXPERIMENTAL RESULTS

Formulations and the cure cycle for the resin are presented in Table I. E-glass, filament-wound composites were manufactured. Density measurements and pyrolytic tests confirmed that the resin content within specimens was 33.3% by weight, 51.3% by volume. Samples were milled for dynamic mechanical spectroscopy measurements. Chromatography specimens were initially broken, then subjected to ambient leaching until equilibrium was confirmed. For a well-cured thermoset, 1 g of composite was leached with 10 ml of tetrahydrofuran. For less-cured specimens, up to 25 ml of solvent have been used.

TABLE I

MOLECULAR CHARACTERIZATION OF THERMOSET RESINS IN E-GLASS COMPOSITES

*Formulation**		*Monomer fraction weight fraction*		*Oligomer fraction*		*Polymer fraction insoluble*	
Epoxy (g)	*Water (%)*	*Epoxy*	*Anhydride*	*Weight fraction*	M_n	*Weight fraction*	*M*
500	0	0.002	0.010	0.012	415	0.976	34,200
500	1	0.003	0.013	0.048	650	0.936	13,300
500	2	0.006	0.014	0.104	930	0.876	8800
500	3	0.011	0.019	–	1140	–	–
600	0	0.000	0.001	0.019	710	0.980	37,300
700	0	0.002	0.006	0.026	665	0.965	25,300
800	0	0.001	0.000	0.008	800	0.991	99,900
800	1	0.001	0.002	0.036	750	0.961	20,800
800	2	0.001	0.002	0.096	810	0.900	8300
800	3	0.001	0.004	0.215	1050	0.780	4900

* With 420 g anhydride, 10 g EMI24 and 8 g 3-aminopropyltriethoxysilane. Cured for 2 h at 367, 401 and 428°K for a total of 6 h.

The extract phase was subjected to analysis by gel-permeation chromatography, utilizing procedures described by Timm and Rachow[10] and Adesanya *et al.*[11] to correct for imperfect resolution. The chromatograph was equipped with two 100-Å microstyragel columns plus a single 500-Å column, manufactured by Waters Assoc. The solvent was tetrahydrofuran. A chromatogram took about 45 min at a solvent flow-rate of 0.67 ml/min. A variable sample size for injection into the chromatography ranged from 0.5 to 0.005 ml, depending on extent of cure. The instrument was equipped with a Waters R401 differential refractometer, which was oper-

ated at a "1" to "2" setting for attenuation. The combinations of solubility, sample injection volume, and attenuator setting were selected to produce a full-scale deflection at 100 mV. A series of molecularly characterized linear epoxies, polymerized from phenyl glycidyl ether and nadic methyl anhydride, were used for instrument calibration. These linear standards are of varying average molecular weights and are described by Poisson molar distributions.

The chromatograph is interfaced with a Digital LSI 11/23 microcomputer. Data interpretation includes population density distributions and average molecular weights for the oligomeric fraction plus molar concentrations for monomers contained within the resin matrix. Reactants were utilized as standards for monomer analysis. No corrections were incorporated for branching with the oligomeric fraction. Thus, reported degrees of polymerization are relative and do not reflect molecular structure effects on hydrodynamic volume. However, research in progress[9] shows that the kinetic model discussed adequately describes observed chromatographic data as a function of cure time and temperature. These data include monomer concentrations and oligomeric population density distributions. Independent observations via dynamic mechanical spectroscopy of cross-link average molecular weight agree with chromatographic estimates. Software for chromatographic analysis has been extensively tested with both step-growth and chain-growth polymers[11].

Chromatography

Chromatograms. Analysis of the extract phase produced representative chromatograms shown in Fig. 1. Material eluted prior to 35 min consists of oligomeric

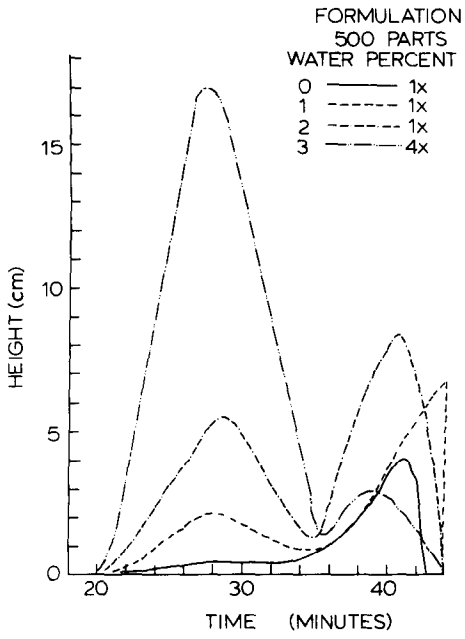


Fig. 1. Gel-permeation chromatography; chromatograms of the extract fraction for a 500-part epoxy resin.

species, the major topic of this research. The monomer DGEBA is eluted near 36 min and the anhydride near 39 min. The initiator–catalyst EMI24 initially forms a positive chromatogram and is eluted after 40 min; but upon curing, a complex series of positive and negative curves form, eluted after 40 min. These low-molecular-weight compounds may be fiber sizings and other substances leached from the E-glass, products of minor degradative side reactions that occur during the polymerization, and molecular substances related to changes in EMI24 that occur during a cure. The evaluation of the chromatogram after about 40 min is difficult and was not attempted. Such phenomena at low molecular weights are frequently encountered when utilizing size-exclusion chromatography, since the columns are basically designed and selected to separate polymeric materials. The emphasis of this research is on oligomeric fractions and monomeric species, which are eluted in a portion of the chromatogram that is highly reproducible. Although resolution is low compared to some high-performance liquid chromatography (HPLC) techniques, numerical interpretations yield repeatable results with unknowns and accurately regenerate distributions in known blends of oligomers and monomers[11].

Inspection of Fig. 1 shows that a dry formulation with 500 parts of DGEBA produced a very insoluble extract, both with respect to oligomeric and monomeric materials prior to 40 min. Data in Table I show that the resin matrix is comprised of 0.2% unreacted epoxy, 1.0% unreacted anhydride, and 1.2% oligomeric materials; 97.6% of the thermoset was insoluble.

With the addition of water to the formulation containing 500 parts of epoxy before the cure, the extract phase from the cured composite contained appreciable and increasing amounts of oligomeric species plus anhydride (Table I and Fig. 1). Oligomeric materials became increasingly soluble; extent of cross-link development within the thermoset was reduced; macromolecules became relatively small. To maintain the response on the strip-chart recorder for the chromatogram corresponding to a resin formulated with 500 parts epoxy and 3% water, the attenuator had to be positioned at a setting of 4. Thus, the response at an attenuation of 1 would be four times larger than that shown on Fig. 1. This resin is relatively uncross-linked and is very soluble during solvent leaching.

Data presented in Table I include the mass fractions for unreacted monomers, the mass fraction of soluble oligomeric molecules plus that for the insoluble network fraction. The average molecular weight for the resin, M, was calculated from the weight of oligomeric and macromolecular materials plus the molecular weight of oligomeric species, M_n:

$$M = M_n \text{ (grams oligomer + polymer)/grams oligomer} \tag{2}$$

Cumulative molar distributions, which will be discussed, are such that the oligomeric fraction dominates the total moles within the resin matrix. The average molecular weight, M, defined by eqn. 2, indicates the average size of individual molecules within the insoluble network structure. For the resin formulated with 0 parts of water, compared to that formulated with 2% water at 500 parts epoxy, the individual molecules within the network structure are nearly four times larger (34,200 compared to 8800). The network labyrinth is more macroscopic of truly global proportions for the dry resin.

species, the major topic of this research. The monomer DGEBA is eluted near 36 min and the anhydride near 39 min. The initiator–catalyst EMI24 initially forms a positive chromatogram and is eluted after 40 min; but upon curing, a complex series of positive and negative curves form, eluted after 40 min. These low-molecular-weight compounds may be fiber sizings and other substances leached from the E-glass, products of minor degradative side reactions that occur during the polymerization, and molecular substances related to changes in EMI24 that occur during a cure. The evaluation of the chromatogram after about 40 min is difficult and was not attempted. Such phenomena at low molecular weights are frequently encountered when utilizing size-exclusion chromatography, since the columns are basically designed and selected to separate polymeric materials. The emphasis of this research is on oligomeric fractions and monomeric species, which are eluted in a portion of the chromatogram that is highly reproducible. Although resolution is low compared to some high-performance liquid chromatography (HPLC) techniques, numerical interpretations yield repeatable results with unknowns and accurately regenerate distributions in known blends of oligomers and monomers[11].

Inspection of Fig. 1 shows that a dry formulation with 500 parts of DGEBA produced a very insoluble extract, both with respect to oligomeric and monomeric materials prior to 40 min. Data in Table I show that the resin matrix is comprised of 0.2% unreacted epoxy, 1.0% unreacted anhydride, and 1.2% oligomeric materials; 97.6% of the thermoset was insoluble.

With the addition of water to the formulation containing 500 parts of epoxy before the cure, the extract phase from the cured composite contained appreciable and increasing amounts of oligomeric species plus anhydride (Table I and Fig. 1). Oligomeric materials became increasingly soluble; extent of cross-link development within the thermoset was reduced; macromolecules became relatively small. To maintain the response on the strip-chart recorder for the chromatogram corresponding to a resin formulated with 500 parts epoxy and 3% water, the attenuator had to be positioned at a setting of 4. Thus, the response at an attenuation of 1 would be four times larger than that shown on Fig. 1. This resin is relatively uncross-linked and is very soluble during solvent leaching.

Data presented in Table I include the mass fractions for unreacted monomers, the mass fraction of soluble oligomeric molecules plus that for the insoluble network fraction. The average molecular weight for the resin, M, was calculated from the weight of oligomeric and macromolecular materials plus the molecular weight of oligomeric species, M_n:

$$M = M_n \text{ (grams oligomer + polymer)/grams oligomer} \tag{2}$$

Cumulative molar distributions, which will be discussed, are such that the oligomeric fraction dominates the total moles within the resin matrix. The average molecular weight, M, defined by eqn. 2, indicates the average size of individual molecules within the insoluble network structure. For the resin formulated with 0 parts of water, compared to that formulated with 2% water at 500 parts epoxy, the individual molecules within the network structure are nearly four times larger (34,200 compared to 8800). The network labyrinth is more macroscopic of truly global proportions for the dry resin.

fraction is inversely proportional to the slopes, S, of the population density distributions of Fig. 2.

$$M_n = \text{grams/mole} = M^0/S \tag{5}$$

The resin cured without water, therefore, has a lower number average molecular weight than that cured with water (Fig. 2). The number average molecular weight for the oligomeric fraction will be shown to be proportional to the cross-link average molecular weight in the insoluble thermoset resin fraction. Data stated in Table I include the number average molecular weight of the oligomeric fractions M_n for the several resins and cures. Mass fractions reported are consistent with eqn. 3.

A comparison of chromatograms and population density distributions for resins formulated with 500 parts epoxy (Figs. 1 and 2, respectively) reveals similar trends in the oligomeric fractions. As the extent of cross-linking diminishes, the chromatogram area increases. Population density distributions substantially increase in concentration, but equally important molecules become larger in size on the average (see M_n of Table I and Fig. 2). Cross-link average molecular weight within the thermoset resin also increases; the size of individual macromolecules within the thermoset fraction decreases (see column M). Therefore, the presence of water during the cure results in a less developed network structure. The mechanical performance of such resins will reflect increased ductility and reduced yield strength and post-yield strength. Shear bands will develop in a more localized region[12].

Cross-link average molecular weight. The architecture of the network structure within the resin matrix is fundamental to mechanical performance of a resin of constant chemical composition. Young's modulus reflects molecular conformational changes within the labyrinth before the onset of molecular slippage. A resin's yield stress and yield strain will be dependent on cross-link average molecular weight. Post-yield strain is a consequence of laminar flow and correlates with the global size of individual macromolecules if cross-link density is sufficiently developed[13]. As a molecule increases in size, its mean end-to-end distance increases, allowing for substantial entanglements with its nearest neighbors. In thermosets, entanglements not only form temporary knots, but a molecule can initially pass through a section where there is physically no path of escape except via bond rupture, an interpenetrating network.

The molecular development and architecture of the individual macromolecules within the resin are ultimately dependent on the kinetic polymerization mechanism. Investigations show that if at an instant during the polymerization oligomeric species are, on the average, small, their union must necessarily result in a structure that increases by a small extent. Inasmuch as such reactions form branches and ultimately cross-links and since molecular packing is dependent on cross-link size, the number average molecular weight between cross-links has the potential of being small as well. Inspection of population density distributions in Fig. 2 indicates that the resin cured in a dry medium likely produced a material with a high cross-link density. As water levels increased, resins became progressively less cross-linked. Dynamic mechanical spectroscopy is an experimental tool capable of confirming this molecular architecture[14].

DYNAMIC MECHANICAL SPECTROSCOPY

Theory of rubber elasticity

Dynamic mechanical spectroscopy provides an independent means for verification of molecular arguments describing cross-link structure. The theory of rubber elasticity states that

$$E = 3DRT/M_c \tag{6}$$

where Young's modulus in the rubber plateau is E, absolute temperature is T, specimen density is D, the gas constant is R and cross-link average molecular weight is M_c. Nielsen[3] suggested that a better fit can be achieved in resins of higher cross-link densities if correlated by

$$\log(E/3) = 6 - 2988DT/M_c \tag{7}$$

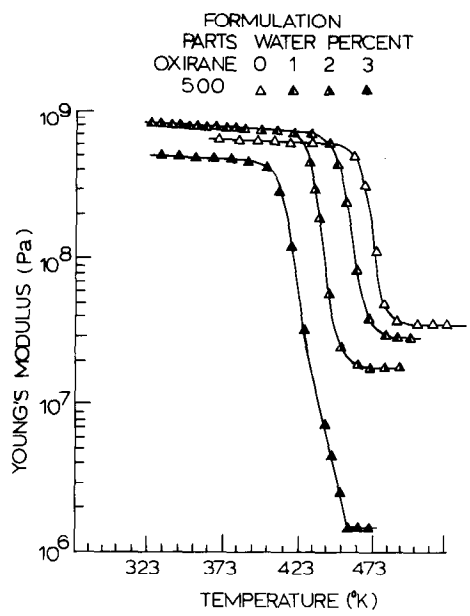
The basic concept couples microscopic structure to molecular motion and temperature. A decrease in cross-link average molecular weight will require a greater energy level for a similar level of molecular activity. Smaller chain segments between cross-link sites within a macromolecule restrict motion. The modulus E, a measure of stiffness, therefore, is a measure of this molecular activity of chain segments.

Complex modulus

The instrument utilized is a forced vibration instrument, a DuPont Mechanical Analyzer, Model 980, that operates at the system's resonance frequency. Temperature scans were made at 2°K/min. Composites were initially machined to exacting tolerances and then were mounted so that fiber was transverse to the grips. The resultant complex moduli were then corrected for fiber content, using the method suggested by Halpin-Tsai and modified by Lewis and Nielsen[15]. Resultant data for the matrix (Fig. 3) reflect relative molecular motion within the network structure which, in turn, will be dependent on cross-link average molecular weight and other factors. The glass relaxation is apparent and is accompanied by at least an order of magnitude reduction in the complex moduli. As the level of water formulated within the resin increased, the glass transition temperatures diminished as did rubber moduli. Data reported were observed for the resin formulated with 500 parts epoxy and with up to 3% water.

Comparison of these macroscopic data (Fig. 3) with molecular data (Fig. 2) reveals similar trends. As moisture increases, relaxations shift toward lower temperatures, and molecular solubility increases. In fact, extensive research is showing that both instruments are equally sensitive to subtle changes in cross-link structure[2,12,16].

Cross-link average molecular weight. Formulations explored the effect of water (0–3%) and epoxy content (500–800 parts) on the subsequent cure. Molecular analyses yielded monomer conversion, oligomeric average molecular weight, M_n, and global molecular size, M (Table I). Fig. 1–3 are representative of observations of formulations that contained up to 700 parts oxirane. Data of Fig. 4–6 are summaries of observations with a formulation containing 800 parts of DGEBA and various levels of water. The oligomeric fraction which was eluted prior to 34 min became bimodal. A competing, secondary reaction likely is producing species coupled via



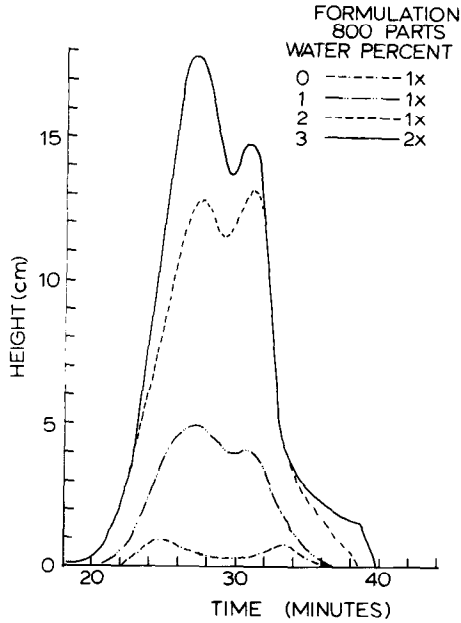
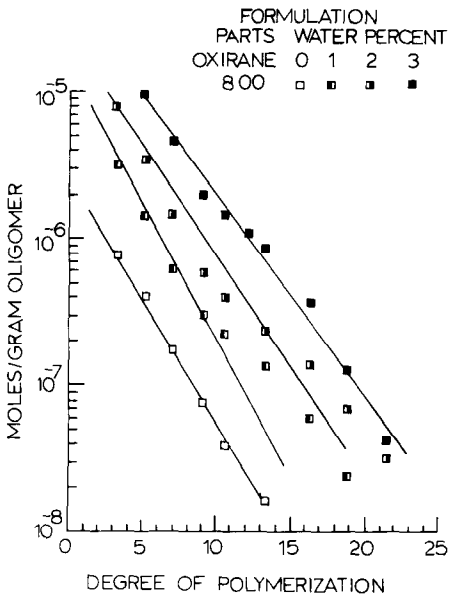


Fig. 3. Dynamic mechanical spectroscopy; complex moduli for resins formulated with 500-parts epoxy.

Fig. 4. Gel-permeation chromatography; chromatograms of the extract fraction for an 800-part epoxy resin.



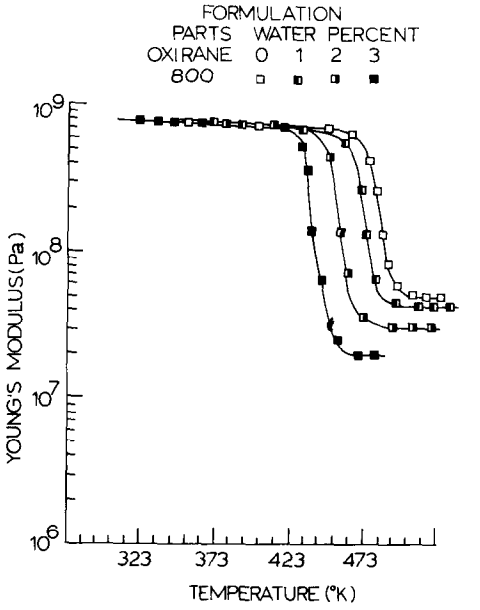


Fig. 5. Population density distributions for oligomeric fraction leached from an 800-part epoxy resin.

Fig. 6. Dynamic mechanical spectroscopy; complex moduli for resins formulated with 800-parts epoxy.

ether linkages. Comparison of Figs. 1 and 4 reveals lower levels of extractables (Table I) for both oligomeric and monomeric species, with the increased oxirane content at a constant water level. It is likely that the anhydride is partly hydrolyzed. The resultant acids can increase the relative rate of polyether formation, increasing the relative rate of DGEBA consumption.

Dynamic mechanical analyses (Fig. 6) confirm improved cross-link structure, as is apparent by higher glass transition temperatures and higher rubber moduli at a given moisture level (Fig. 3 and M_c data summarized in Table II for the several resins).

TABLE II

MACROSCOPIC CHARACTERIZATION OF THERMOSET RESINS IN E-GLASS COMPOSITES

Formulation		*Rubbery* modulus*	*Cross-link molecular weight*	*Glass transition temperature*
Epoxy (g)	*Water (%)*	$E \cdot 10^7$ *(Pa)*	M_c *(g/mole)*	T_g *(°K)*
500	0	3.6	326	415
500	1	3.0	353	400
500	2	1.8	451	381
500	3	0.14	—**	358
600	0	4.1	311	420
700	0	4.3	304	423
800	0	5.0	288	425
800	1	4.4	301	415
800	2	3.1	345	398
800	3	2.0	425	381

* Corrected for transverse fiber content[14].

** Could not be calculated by eqn. 7.

Transitions. Glass transition temperatures were evaluated at that point of intersection of the extension of the glassy modulus and a linear extrapolation of the relaxation region. Results are presented by Fig. 7. Spectroscopy observations indicate that

$$T_g = 297 + 3.66 \cdot 10^4/M_c \tag{8}$$

The molecular weight of the anhydride is 166; that for DGEBA is 340. If every functional group reacted, the link formed by the oxirane monomer and that by the anhydride would have a molecular weight of between 200 and 300. The observed molecular weights reported in Table II are consistent. Not every functional group forms a crosslink.

MICROSCOPIC/MACROSCOPIC CHARACTERIZATIONS

Independent estimates of cross-link average molecular weight have been made. Gel-permeation chromatography via molecular analysis of the leached phase yields

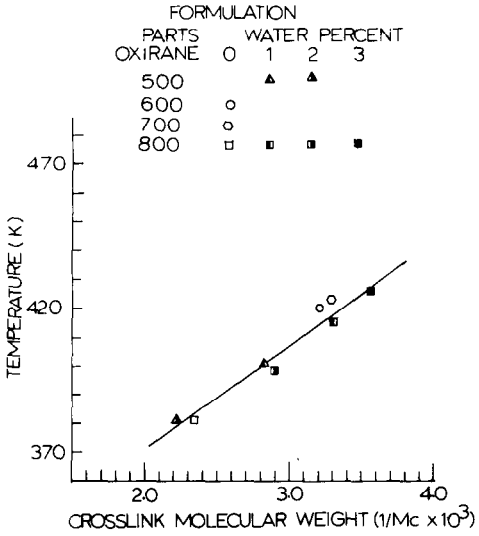


Fig. 7. Glass transition temperature dependence on cross-link average molecular weight.

the number average molecular weight for the oligomeric fraction, M_n (see Table I). Macroscopic estimates of cross-link average molecular weights observed by dynamic mechanical spectroscopy are reported as M_c in Table II. These independent, experimental observations are correlated by Fig. 8 and yield

$$M_c = kM_n^{1.0} \tag{9}$$

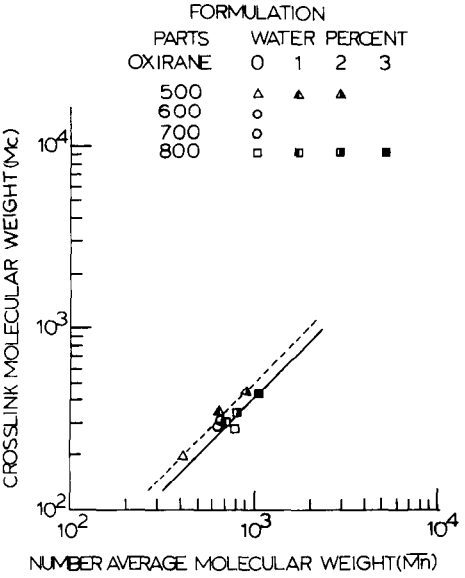


Fig. 8. Cross-link average molecular weight is correlated with oligomeric fractions number average molecular weight.

The proportionality factor k is confined by 0.4 to 0.5. Inasmuch as bimolecular combinations of polymeric molecules ultimately result in the construction of the network labyrinth, a proportionality factor of 0.5 may reflect this kinetic mechanism. A molecule reacts with a site on the network macromolecule or with an oligomeric species. The resultant pendant chain will be, on the average, half the size of the resultant oligomeric molecule. The significant factor is that oligomeric population densities via reaction kinetics are proportional to cross-link average molecular weight. Molecular analysis via gel-permeation chromatography is an effective tool for thermoset resin characterization. The region of data fit shown in Fig. 8 reflects chemical structure changes caused by the oxirane content of the resin. Dynamic mechanical spectroscopy via molecular activity is sensitive to structure changes within the chains of network macromolecules.

Quality control

Moisture. The potential for utilization of chromatography in the quality control of thermosets is excellent, though in its infancy. Multi-detectors, including traditional refractive index, infrared, ultraviolet and viscosity, coupled with developing systems[17], provide a molecular characterization tool of great diversity, yielding routine, fast, and automated analysis. A single characterization can contain information that is now available only by distinct multiple characterizations. One practical application related to anhydride-cured epoxies in the presence of moisture has been discussed. Dynamic mechanical analysis clearly shows that the cross-link structure has changed but cannot reveal why; chromatography analysis frequently can.

Fibers. Laboratory studies on neat resin castings and on filament-wound composites consistently show that neat resins cure to a greater extent than do composites with high fiber content. Studies in progress, though limited, have shown this for carbon, Kevlar 49 and glass fibers. The high surface areas of the reinforcing provide ample opportunity to alter the cure, perhaps by entering into the reaction, as with Kevlar 49, or through the introduction of proprietary sizings and other surface treatments, which may alter stoichiometric ratios of reactants. Detective work by chromatographic analysis provides an effective tool for optimizing the formulation and cure that is actually achieved, enhancing the performance of the composite material. Literature references include[18–20].

DISCUSSION

Gel-permeation chromatography is an effective tool for the molecular analysis of a thermoset resin matrix. Chromatographic data allow assessment of the actually achieved extent of cure. Variance frequently correlates with changes in mechanical performance, even in specimens that are expected to be fiber-dominated, such as filament-wound pressure vessels. Molecular analysis permits the determination of extent of cure, molecular size, and distribution of macromolecules, as well as cross-link architecture. Data also allow development of innovative strategies in order to yield better product quality through optimal design of the molecular infrastructure.

Flory[21] considered the effect of monomer conversion on step growth resins in which the primary reaction was one of random, bimolecular combinations in the presence of an excess of one of the reactants. This yields an exponential population

density distribution. The number average molecular weight was expressed in terms of extent of reaction, $p = [E(O) - E(t)]/E(O)$, and the molar concentration of the reactant in excess, $r = A(O)/E(O)$.

$$M = M^0 [1 + P]/[2r(1 - P) + 1 - r] \tag{10}$$

If a 1% error exists in the initial formulation of the two monomers, at 100% conversion, the average degree of polymerization will be reduced to about 200, a substantial effect. Competing side reactions can have an equivalent effect, resulting in an excess of one reactant at the end of the cure. Moisture not only increases the number of reactive hydrogen sites, but may increase the relative rates of competing side reactions. Side reactions that increase rates of oxirane consumption ultimately cause the anhydride to be in excess.

The average size of individual molecules (Table I) covers truly macro-species of the order of 100,000 molecular weight units. As a reference, linear fibers, made by step-growth polymerizations, are only of the order of 10,000. The molecules within a well-cured thermoset are truly macromolecules. Oligomeric fractions via chromatography analyses also provide definitive information, descriptive of the density of cross-links within these macromolecules.

Composites discussed were filament-wound and cured on a metal mandrel. The surface of a composite was exposed to high-temperature, low-relative-humidity air within an electrically heated oven during the cure. Drying of specimens surely occurred. Though final water levels are unknown, data analyses confirm that initial moisture content affected the final network structure within the resin matrix. Fibers were wound on the mandrel's circumferences at 90° to the axis for a total of seven plies. The resultant cylinder had an inner diameter of 7.0 cm and an outer diameter of 7.75 cm. Spectroscopy specimens with transverse fiber were machined from sections parallel to the axis.

ACKNOWLEDGEMENTS

Financial and technical support supplied by the Brunswick Corporation, Defense Division and the Engineering Research Center is appreciated.

GLOSSARY

A	Monomeric anhydride (M)
A_j	Polymeric alcohol (M)
A_jA	Polymeric acid (M)
A_jAC	EMI24 bis-adduct of an acid (M)
A_jC	EMI24 bis-adduct of an alcohol (M)
C	EMI24, initiator/catalyst (M)
D	Resin matrix density (g/ml)
E	Monomeric epoxide (M)
E	Young's complex moduli (Pa)
I	Intercept of oligomeric population density distribution (moles/gj)
K_1	Kinetic equilibrium constant for acid adduct (M^{-1})

k_1	Kinetic rate constant for anhydride monomer (l/moles sec)
K_2	Kinetic equilibrium constant for alcohol adduct (M^{-1})
k_2	Kinetic rate constant for epoxide monomer (l/moles sec)
M	Number average molecular weight of macromolecules (g/mole)
M_n	Number average molecular weight of oligomeric material (g/mole)
M^0	Molecular weight increment in polymer chain (g/mole)
R	Gas constant (Pa ml/°K mole)
S	Slope of population density distribution
T	Temperature (°K)
i,j,k	Degree of polymerization
TOT	Cumulative molar distribution

REFERENCES

1 A. J. Ayorinde, C. H. Lee, D. C. Timm and W. D. Humphrey, *ACS Symp. Ser.*, 245 (1983) 321.
2 D. C. Timm, A. J. Ayorinde, F. K. Huber and C. H. Lee, *Proc. Int. Rubber Conf., Moscow, U.S.S.R.*, Vol. A2, 1984, p. 66.
3 L. E. Nielsen, *J. Macromol. Sci.*, C3 (1969) 69.
4 A. Farkas and P. F. Strohm, *J. Appl. Polym. Sci.*, 12 (1968) 159.
5 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Boston, MA, 1960, pp. 423, 444.
6 E. S. Narracott, *Brit. Plast.*, 26 (1953) 120.
7 L. Shechter and J. Wynstra, *Ind. Eng. Chem.*, 48 (1956) 86.
8 Y. Tanaka, M. Tomoi and H. Kakiuchi, *J. Macromol. Sci.*, 1 (1967) 471.
9 C. C. Lai, *M.Sc. dissertation*, University of Nebraska, Love Library, Lincoln, NE, 1984.
10 D. C. Timm and J. W. Rachow, *J. Polym. Sci.*, 13 (1975) 1401.
11 B. A. Adesanya, H. C. Yen, D. C. Timm and N. C. Plass, *ACS Symp. Ser.*, 245 (1984) 113.
12 D. C. Timm, A. J. Ayorinde and R. F. Foral, *7th European Polymer Network Conference, Manchester, U.K., 1984, Polymer*, (1984) submitted for publication.
13 H. S. Kaufman and J. J. Falcetta, *Introduction to Polymer Science and Technology, SPE Textbook*, Wiley, New York, 1977, p. 330.
14 L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1 and 2, 1974.
15 T. B. Lewis and L. E. Nielsen, *J. Appl. Polym. Sci.*, 14 (1970) 1449.
16 D. C. Timm, A. J. Ayorinde, C. H. Lee and L. F. Steele, *Polym. Eng. Sci.*, 24 (1984) 930.
17 N. Watanabe, *J. Chromatogr.*, 316 (1984) 495.
18 G. F. Sykes, G. F. Burks and J. B. Nelson, *Nat. SAMPE Symp. Exhib. Proc.*, 22 (1977) 350.
19 L. C. Wang, D. C. Timm, N. C. Plass and W. D. Humphrey, *Second Int. Conf. Reactive Processing of Polymers, Proc.*, 1 (1982) 70.
20 H. L. Price, *Second Int. Conf. Reactive Processing of Polymers, Proc.*, 1 (1982) 202.
21 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, p. 92.