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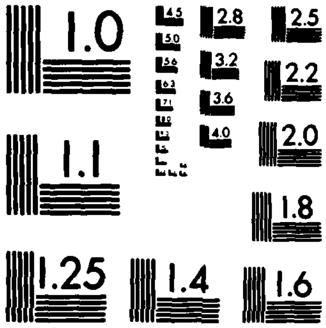
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REPORT DOCUMENTATION PAGE

REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

SECURITY CLASSIFICATION

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release, distribution unlimited

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5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 86-0695

NAME OF PERFORMING ORGANIZATION
Institute of Polymer Science
University of Akron

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Air Force Office of Scientific Research

ADDRESS *(City, State and ZIP Code)*
Akron, Ohio 44325

7b. ADDRESS *(City, State and ZIP Code)*
Building 410
Bolling AFB, D. C. 20332-6448

NAME OF FUNDING/SPONSORING ORGANIZATION
Air Force Office of Scientific Research

8b. OFFICE SYMBOL *(If applicable)*
NC

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F49620-83-C-0032

ADDRESS *(City, State and ZIP Code)*
Building 410
Bolling AFB, D. C. 20332-6448

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61102F	2303	A3	

TITLE *(Include Security Classification)* Time-Dependent Response and Fracture of Cross-linked Polymer (U)

PERSONAL AUTHOR(S)
F. N. Kelley, M. Morton, D. Plazek

TYPE OF REPORT
Final

13b. TIME COVERED
FROM Jan '83 TO Dec '86

14. DATE OF REPORT *(Yr., Mo., Day)*
1986 DEC.

15. PAGE COUNT
36

SUPPLEMENTARY NOTATION

COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Synthesis, Cross-Linked, Polymers, Molecular, Epoxy Matrix, Resin

ABSTRACT *(Continue on reverse if necessary and identify by block number)*

This study was concerned with the synthesis, preparation and characterization of cross-linked polymers, and their time-dependent fracture behavior. Emphasis was given to well-defined polymer network structures of two types: 1) end-linked terminally functional liquid polymers having nearly uniform or deliberately distributed initial chain lengths, and 2) model glassy networks in which the network topology was varied with respect to chain length per cross-link, and network defects such as dangling ends and soluble fraction.

Fracture measurements have validated the relationship $G_{1c} = kM_c^{1/2}$, where G_{1c} is the strain energy release rate, k is a material constant and M_c is the molecular mass of a network chain.

Also, a model rubber-toughened resin was developed by dispersing well-characterized rubber particles, made separately from the matrix, into an epoxy matrix resin. Thermally stable poly(n-butyl acrylate) based particles, crosslinked and functionalized, had their size and size distribution controlled by the polymerization method. (see over)

DISTRIBUTION/AVAILABILITY OF ABSTRACT
CLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

NAME OF RESPONSIBLE INDIVIDUAL
Dr. Donald R. Ulrich

22b. TELEPHONE NUMBER *(Include Area Code)*
202-767-4960

22c. OFFICE SYMBOL
NC

19. Abstract

Differences were observed in the fracture energies of the individual matrix resins containing different rubber particle sizes and particle reactivity.

The model composite fracture energies display maxima when plotted against weight percent particles. A theoretical model for rubber toughening by Kunz-Douglass, et al. was examined, but this model was shown to be inadequate in predicting the composite fracture energy dependence on constituent properties, as well as in predicting the correct functional form.

AFOSR-TR- 86-0695

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I. STATUS OF RESEARCH

This report covers the results generated in our research over the past three years on the relationships of the strength of cross-linked polymers to their local segmental mobility, molecular networks and microphase structure. Significant to our findings are the direct relationships established between features of the fracture process above and below the glassy transition temperature, T_g. We have altered the network topology and, through a model rubber-toughened epoxy, have demonstrated some key aspects of the toughening mechanisms. Control of the processes which occur at the crack tip, in particular the size and energy dissipative character of the inelastically deformed zone, is key to these approaches. The quantitative characterization of structure resulting from chemical and process manipulations through the use of model material systems constitutes a main thrust of the work. Correlations of structure with properties such as the characteristic fracture energy were achieved in quantitative form for the average network chain molecular mass (1).

A. Glassy Thermosetting Networks

Studies were undertaken of three significant local structural variations in epoxy polymers:

1. Average length of the primary network chain;
2. Concentration of non-functional bis-phenol A type oligomers embedded in the fully cured network; and
3. Rubber particle modification in which concentration, mean diameter and reactivity with the epoxy matrix were precisely controlled.

In each case materials produced were characterized as to cure level (cross-link density), glassy transition temperature and, most importantly, their viscoelastic response. Creep compliance measurements taken by Professor Plazek at the University of Pittsburgh complement the studies in a very close collaborative effort.

Fracture investigations using single-edge notched and double torsion tests at a wide range of temperatures above and below T_g were completed on over 60 distinct material systems.

In measurements above T_g ($\sim T_g + 40^\circ C$), the epoxy networks display rather normal rubberlike behavior. Equilibrium moduli correspond unusually well with systematic variation in average molecular weight of the terminally functional prepolymer when stoichiometric ratios of reactants were employed. Fracture energies at "threshold" ($T_g + 100^\circ C$) and slow extension rates displayed an approximate $M_c^{\frac{1}{2}}$ dependence, as predicted by theory. In fact, this dependence persisted even at non-threshold conditions.

The work conducted during the past year has shown that as glasses, the epoxies exhibited unstable fracture. The initiation fracture energies did not display a simple M_c dependence; however, the arrest values showed a strong $M_c^{\frac{1}{2}}$ relationship, as shown in Figure 1. Furthermore, the arrest values exhibited threshold-like characteristics, i.e., a lower, limiting value, and temperature independence. The presence of a highly constrained yielded zone at the sharp arrest crack tip was suggested by the data. The stress on this zone was found to be a constant function of the bulk yield stress. The diameter of the zone was determined to be dependent on $M_c^{\frac{1}{2}}$.

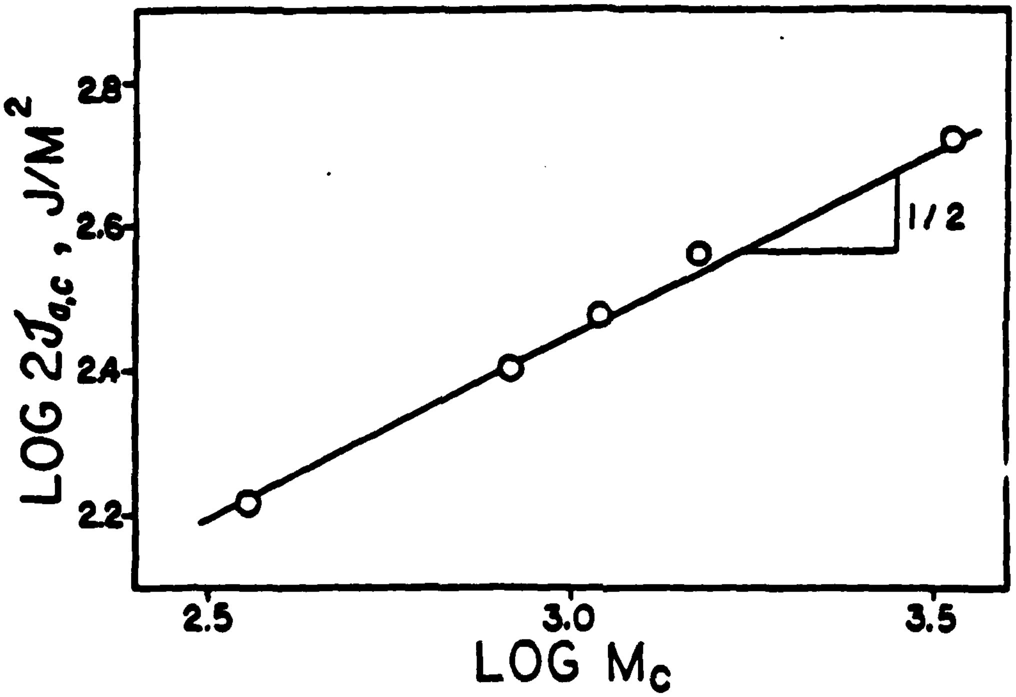


Figure 1. Log-log plot of average arrest (and stable) fracture energies versus M_c. A line of 1/2 slope is drawn through the points.

The bulk yield stress was found to be independent of M_c, as was the glassy modulus. The modulus, however, was determined to be influenced by those segmental molecular motions responsible for the β-relaxation in the tan δ-temperature spectrum.

The control which we exercised over network structure has permitted us to show topological dependencies of the fracture energy which have not been observed previous to this work. For example, in preliminary studies, it has been shown that the presence of increased quantities of a non-functional EPON 828 (Shell) in a cured epoxy network decreases the fracture energy of constant cross-link density of the matrix. Viscoelastic measurements on these materials are underway at the University of Pittsburgh to determine if the nonfunctional material (soluble fraction) affects energy dissipation in the bulk sample in such a way that it might similarly affect the material in the plastically deformed zone at the crack tip.

Finally, a large number of material variations have been studied using a unique model of a rubber toughened epoxy resin. Rubbery particles of a reasonably high T_g have been produced by emulsion as well as suspension polymerization methods. Butyl acrylate cross-linked with a dimethacrylate has been produced as spherical particles and dispersed in an epoxy matrix by special methods developed in our laboratories. In some instances a glycidal containing comonomer was included to provide reactive sites on the surfaces of the rubbery particles. Systematic fracture studies were conducted in which the material variables of mean diameter, concentration, reactivity and cross-link level of the materials were controlled. Fracture energy differences on the order of 20 times were observed when comparing some formulations with the unmodified epoxy network at the same T_g-T_{test}. This work examined some of the purported quantitative theories of rubber toughening such as those by Kunz-Douglas et al. (2) and and Kinloch et al. (3, 4).

B. Model Rubbery Networks -- Effect of Cross-link Distribution

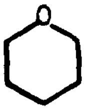
1. Preparation of α,ω-dihydroxypolyisoprene by lithioacetal initiators

During the past contract year, work has continued on the synthesis of α,ω-dihydroxypolyisoprene of near monodisperse molecular weight, as a precursor of near-uniform elastic networks. As stated previously, it was planned to prepare a series of such polymers, varying in molecular weight from 1000 to 10,000, and to end-link them into networks by means of a triisocyanate, as described before (5). Thus, by using either a single variety of the dihydroxypolyisoprene or a mixture of 2 or more species to form the network, it should be possible to determine the effect of both cross-link density and of cross-link distribution on the viscoelastic and fracture properties of rubber networks.

In this work, a new type of organolithium initiator was used, which had a lithium atom at one end and an acetal group at the other, i.e., ethyl 6-lithiohexyl acetaldehyde. This initiator, which had first (6) been used to polymerize butadiene, is also known to work for isoprene. It has the advantage of being a monolithium initiator, so that the resulting polyisoprenyl lithium can be converted to a hydroxy-terminated polymer by treatment with ethylene oxide (and water) without encountering the strong association and gelation effects of the dialkoxy-polyisoprenes obtained by use of a dilithium initiator. Then the second hydroxy end-group is generated by hydrolysis of the acetal end-group.

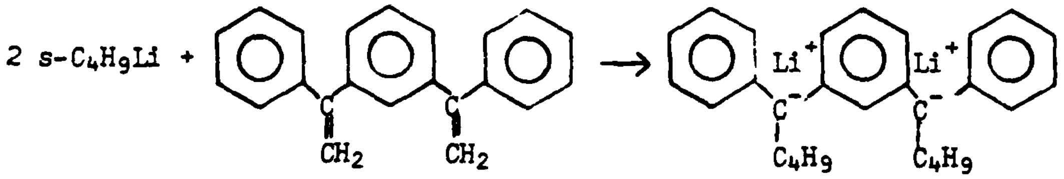
The first results of the use of this initiator showed that it was possible to obtain an apparently narrow molecular weight distribution in the final product (α,ω-dihydroxypolyisoprene), i.e., $M_w/M_n = 1.08$. However, the molecular weight was much higher than predicted, e.g., 20,100 instead of the predicted 10,000, indicating some loss of initiator by side reaction (or due to limited solubility of the initiator). Although the hydroxyl functionality of this polymer, as measured by acetic anhydride method, was 1.9, attempts to "chain extend" the difunctional polymer with TDI (toluene diisocyanate) were of limited success, showing that the polymer chains were not difunctional to any great extent.

At this stage of the work, there was a hiatus of several months, during which a replacement was sought for K. Suzuki, who returned to Japan at the end of February, 1985. Hence this project was not started again until the summer months, when the services of M. Alsamarraie became available.

Since it had been found that the above-mentioned initiator, ethyl 6-lithiohexyl acetaldehyde, showed signs of solubility difficulties in hydrocarbon solvents, it was thought best to try another variety, of the same type, which had also previously (2) been shown to work, i.e., 2-(6-lithio-n-hexoxy)tetrahydropyran, [$Li(CH_2)_6$-O– ]. This initiator was used to polymerize isoprene at 0°C in cyclohexane solution, without any solubility problems, and the polymer was converted to the dihydroxypolyisoprene by treatment first with ethylene oxide followed by hydrolysis of both the lithium alkoxide and the acetal end-groups. In this way it was found possible to prepare a polymer of M.W. = 1100 and M_w/M_n of 1.11. Although this is a promising result, considering that the predicted mol. wt. was 1000, no functionality data are available at the time of writing, and hence no chain extension results can be given.

2. Possible preparation of α,ω-dihydroxypolyisoprene by use of a new dilithium initiator derived from 1,3-bis(phenyl ethynyl) benzene

It has been shown very recently (7, 8) that a very clean reaction can be obtained between s-butyl lithium and 1,3-bis(phenyl ethenyl) benzene (also known as DDPE, "double diphenylethylene") leading to a dilithium initiator which is very soluble in hydrocarbon solvents. The reaction is shown below:



It is interesting to note that it is this meta-substituted central benzene ring which leads to higher reaction rate, and better solubility of the product. Since the formation of this dilithium initiator does not involve filtration problems (previously found in reactions with lithium metal), and since this initiator has been shown (8) to polymerize butadiene without the aid of polar solvents, to predictable molecular weights of narrow MWD, it shows promise in this project as well, and will be investigated when the work is renewed.

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(Subcontract to the University of Pittsburgh)

C. Cure Shrinkage and Creep Response of Glassy Networks

During the three year period from the beginning of 1983 to the end of 1985, studies were carried out on a series of epoxy resins with different network chain lengths on

1) Physical properties during curing:
    a) the volume shrinkage reflecting the degree of cure;
    b) the shear viscosity·
    c) the viscoelastic response;
    d) the fictive temperature; and
    e) the gel fraction

2) Physical properties after curing:
    a) thermal contraction coefficients;
    b) glass temperatures;
    c) creep behavior above and below T_g

In the search for the governing factors determining fracture toughness it is necessary to know if the curing conditions influence the nature of the cured epoxy resin. It is also necessary to determine if a complete cure has been achieved. The measurement of properties during curing must be made to obtain this knowledge. Since fracture is known to usually be determined by dissipation processes,[1-7] the viscoelastic behavior (the time dependent mechanical response) must play a role. Valid correlations must be made at corresponding temperatures since the temperature has a strong influence in determining the rate of molecular response. It must be noted that the effect of temperature is principally through the establishment of the density, since molecular crowding is the dominating factor in determining the rate of irreversible processes in polymers.[8,9]

Measurements on elastomers in the past have clearly shown that the viscoelastic dissipation of energy correlates with their fracture toughness.[9,10] The results presented below in combination with those of our collaborators at the Polymer Science Institute of the University of Akron show that at equal temperatures above T_g (i.e. constant $T-T_g$) epoxy resins with greater values of the viscoelastic retardation spectrum at reciprocal retardation times which are equal to the rate of tearing show greater fracture toughness. Therefore viscoelastic measurements yield results that allow the prediction or ordering of the fracture toughness of materials above T_g.

However, epoxy resins are usually used at temperatures below T_g and the variables determining fracture toughness and the corresponding states of polymeric glasses at these lower temperatures have yet to be ascertained. Since materials at temperatures below their glass temperatures are not at thermodynamic equilibrium, their state, determined by their thermal history, must be identified before their properties can be rationalized. It is widely recognized that a glass's density is an important variable in determining its viscoelastic response. The value of its density incessantly increases toward its equilibrium value. At temperatures below T_g-40°C, the contraction called physical aging is so slow that density equilibrium is not achieved in a millenium. This physical aging slows down most viscoelastic processes and glasses inevitably become more brittle.

The results obtained on the changing physical properties during the curing of the epoxy resins will be described. The behavior of the fully cured resins at temperatures equal to or above their T_g will be presented.

MATERIALS AND INSTRUMENTATION

The epoxy resins and crosslinking agents are those studied by our collaborators LeMay, Swetlin and Kelley[7,11,12] The Shell Epon Resins 828, 1001, 1002, 1004, and 1007 have been characterized at the University of Akron by the above mentioned colleagues. The characterization information provided to us along with the materials at the University of Akron by the above mentioned colleagues. The characterization information provided to us along with the materials including the same stocks of 4,4'-methylene dianiline (MDA) and 4,4'diamino diphenyl sulfone (DDS) is shown in Table I. All samples have been cured with stoichiometric amounts of reactants.

Three principal pieces of equipment have been utilized in these investigations.

1) A pressurized volume dilatometer.

This bellows dilatometer is a modified version of that of Zoller et al.[13] It was designed and constructed under the direction of N. Wackenhut here at the University of Pittsburgh.

2 Fictive temperatures T_f were measured with a Perkin Elmer Differential Scanning Calorimeter DSC-II.

3. Creep and recovery measurements which yielded viscosities and recoverable steady state compliance J_e were carried out with a frictionless magnetic bearing torsional creep apparatus.[14] Mechanical characterization of the fully cured resins above and below the glass temperature was also accomplished with this instrument. Measurements were carried out in a nitrogen atmosphere after drying in situo in vacuo.

Properties During Curing

In a previous paper the volume shrinkage which occurs the during curing of Epon 1001/DDS has been presented along with the increase in the fictive temperature of Epon 828 cured with methylene diamiline MDA at four curing temperatures between 40 and 100°C. The rise in viscosity followed by the decrease in the equilibrium compliance Je as functions of the curing time at about 143°C for some of the resins cured with DDS was reported. Times to the point of incipient gelation at the same temperature were determined.

The shrinkage of the 828 resin as it reacts with a stoichiometric ratio of DDS in a two stage cure is presented in Figure 1. The reaction mixture was first heated to 147°C where it was held for 40 hours. During this time a 7.6% decrease was incurred. The curing temperature was then increased to 216°C for 24 hours where an additional 0.9% of shrinkage occurred. A subsequent heating to 247°C showed no further decrease in volume indicating that the reaction had reached completion at 216°Cr.

The specific volume history data of the curing 828/DDS are cross-plotted in Figurge 2 where the specific volume is shown as a function of temperature. The volume of the reactant mixture is seen to increase linearly as the temperature is increased to 147°C. A slight overshoot was incurred before a constant temperature was achieved. The deceleration of the rate of reaction at 147°C occurred because the fictive temperature reached the reaction temperature. This can be seen by extrapolating the straight line segment found between 190° and 220°C temperature just before the step up in temperature. The final cooling indicates as glass temperature for the fully cured material $T_g(\infty)$ of 204°C with a cooling rate of 5° per minute.

The sigmoidal curve between 170° and 200°C with an inflection point at 185° is the consequence of fact that the material was a densified (aged) glass at 147° before it was heated.

The specific volume-temperature cooling curves obtained on the fully cured 828, 1001, 1004 and 1007/DDS resins shown in Fig. 3. The systematic decrease in specific volume with increasing cross-linking density is clearly depicted as the increase in T_g with crosslink density. However, it is surprising to see that the fully curev epoxies with lower crosslink densities and therefore presumable looser molecular networks (e.g. 1004 & 1007/DDS) have lower segmental mobilities at higher specific volume Resulating in a departure from equilibrium volume at the lower densities. Class temperature and expansion coefficients just above and below T_g for these fully cured systems are listed in Table II.

Creep Behavior of Fully Cured Epoxy Resins Above T_g

The shear creep compliance curves J(t) (cm^2/dyne) of Epons 828, 1001, 1002, 1004, and 1007 fully cured with stoichiometric amounts of DDS were determined at several temperatures near and above T_g. Illustrative results are shown in Figure 1 where reduced creep compliance curves $J_p(t) = J(t)\, T\rho/T_o\rho_o$ determined on Epon 1007 at seven temperatures between 99.8° and 127.3°C are presented. A single dispersion extending from the glassy level slightly above 10^{-10} cm^2/dyne up to a form rubbery level close to 10^{-7} cm^2dyne is indicated.

These compliance curves are reduced to a reference temperature, T_o, of 100.7°C in Figure 2 to yield a curve extending over ten decades of time. This test of time temperature equivalence is eminently successful. In fact, it can be added that, in spite of the deviations from thermo-rheological simplicity that have been observed in the behavior of linear amorphous polymers [15-18], we have yet to encounter a molecular network polymer that didn't exhibit satisfactory reduction within experimental uncertainty.[19-20]

All of the reduced shear compliance J(t) curves of the epoxy resins studied, Epon 828, 1001, 1002, 1004, and 1007/DDS are shown in Fig. 3 as functions of the reduced time, t/a_t, in a double logarithmic plot. This comparison plot was constructed by arbitrarily requiring all of the reduced curves to cross at a compliance level of $\mathrm{Log}J_r(t) = 8.5$. The resulting positions represent the response of the different epoxy resins at specific temperatures T_o to which are 205°, 130°, 118.6°, 110.7°, and 100.7°C for the DDS crosslinked 828, 100k, 1002, 1004, and 1007 respectively. The fictive temperatures T_f measured by means of a differential scanning calorimeter, DSC at a heating rate of 20°C/min, immediately following cooling at a rate of 80°C/min through the glass temperatures, T_g. With the exception of the 828/DDS resin, the comparison T_o's average 3°C lower than the T_f's. The results obtained on the 828/DDS cured resins are less reliable than those found on the other materials. This lack of reliability is believed to be due to the occurrence of thermal degradation at the higher temperature of measurement.

The DSC determinations of the T_f's were made by James LeMay at the University of Akron. The fact that the equilibrium compliance J_e increases uniformly from the 828 to the 1007 resins is to be expected on the basis of the kinetic theory of rubberlike theory since the concentration of network chains decrease in the same order.

At all temperatures it is seen (Fig. 3) that the order of densities is primarily determined by the density of crosslinks. However, the epoxy networks with the lower crosslink densities and lower specific densities surprisingly display lower glassy compliance J_g values.

The most loosely crosslinked network Epon 1007/DDS has the lowest J_g and the most tightly crosslinked network (828/DDS) has the greatest J_g. The J_g's and the T_g's dilatometrically determined are presented in Table II.

The time-scale shift actors a_T that were determined in the reduction of the creep compliance curves to obtain the reduced curves shown in Fig. 6 are presented in Fig. 7. The logarithms of a_T are plotted as a function of the reciprocal absolute temperature. The temperature dependence of the epoxy resin with the tighest network density appears to be Arrhenius while the looser networks exhibit shift factor data that generate curves that suggest free volume dominance. This pattern of behavior has been reported previously.[21] These temperature dependence data can be fitted to the Vogel, Tamman, Hesse and Fulcher VTHF equation[8].

$$a_T = A \exp C/(T-T_\infty).$$

The parameters obtained for the curves are presented in Table III. For the chosen reference temperatures T_o, $A = \exp C/T_o-T_\infty)$.

Retardation Spectra

The viscoelastic retardation spectra $L(\ln \tau)$ have been calculated from the $J_p(t)$ curves presented in Figure 6. Iterative computer calculations were necessary to obtain optimized values of $L(\ln \tau)$[22] which are shown in Figure 8. The temperature of presentation of the L's were chosen to match the positions of the observed maxima. These reference temperatures T_0' are only slightly different from the T_o valves obtained from the common compliance criterium used in preparing Fig. 6. The systematic variation in $L(\ln \tau)$ is clear. The short time linear variation of Log L with log τ/a_T were τ is the retardation time is virtually common to all of the epoxy samples. The slope of the linear variation is 1/3 which indicates the dominance of Andrade creep in the corresponding region of the time scale. Andrade creep is recognized as a strain $\alpha(t)$ which is linear with the cube root of time under condition of constant stress, σ_o, dyne/cm^2.

$$J(t) \equiv \frac{\alpha(t)}{\sigma_o} = J_A + \beta t^{1/3}$$

The characterizing parameters J_A which here we identify as J_g and β are listed in Table I for most of the resins studied. The functionality of L (Ln τ) when Andrade creep is observed is [23]

$$L(\ln\tau) = 0.247\beta\tau^{1/3}$$

Beyond the Andrade creep region the various resins exhibit a fairly symmetrical maximum in Log L which increases in magnitude with the increase in the molecular weight per crosslinked unit, i.e. the length of the molecular network strands. The looser molecular networks, not unexpectedly, are capable of dissipating greater amounts of mechanical energy into heat. The increasing peaks in Log L clearly indicate that the fracture energy should show a corresponding increase and it does[24].

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TABLE I

Epoxy Resin Properties

Material*	M_n g/mole	n	T_g °C	f	Soluble Fraction % (wt/wt)
Epon 828	380	0.14	-14	2.0	0.3
Epon 1001F	996	2.31	31	1.9	1.3
Epon 1002F	1342	3.52	40	1.8	1.9
Epon 1004F	1450	4.85	56	1.7	2.8
Epon 1007F	2600		70	1.4	9.0

*Suffix F is Shell's indication for fusion being involved in their process.

M_n- the number average molecular weight.

n- the average number of repeat units in the resin molecule as shown below.

f- functionality determined by chemical analysis.

Soluble Fraction of resin completely cured with stoichmetric amount of DDS.

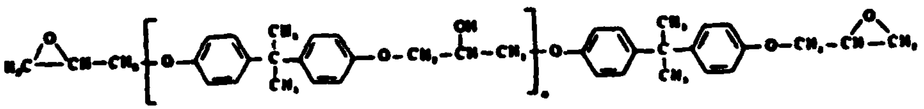


TABLE II

Thermal Parameters for Fully Cured Epoxy Resins

EPON/DDS	T_f °C [a]	T_g °C [b]	T_o °C [c]	T_o' °C [d]	Density at T_g, g/cm³ [e]	$\alpha_{vol,g} \times 10^4$ [e]	$\alpha_{vol,r} \times 10^4$ [e]
828/DDS	212	204	205	201	1.184	2.8	5.5
1001/DDS	132	127	130	130	1.183	1.8	4.3
1002/DDS	121	—	118.6	—	—	—	—
1004/DDS	113	112	110.8	111	1.171	2.2	5.3
1007/DDS	105	101	100.7	101.1	1.163	2.6	5.8

a. Measured using DSC by LeMay, University of Akron; heating rate was 10°/min following cooling at 80°/min.

b. Determined from specific volume vs. temperature plot obtained by dilatometric measurements; cooling rate = 5°/min.

c. Reference temperatures which make creep compliance curves meet at logJ(t) = -8.5 (See Fig. 6). Reference system was 1001/DDS.

d. Reference temperatures which match the peaks on the retardation time scale. Reference system was EPON 1001/DDS.

e. Densities and volumetric thermal expansion coefficients below $T_g(\alpha_{vol,g})$ and above T_g $(\alpha_{vol,r})$, determined from dilatometric measurements.

TABLE III

Mechanical and Temperature Dependence Parameters

EPON /DDS	$J_g \times 10^{10}$ [a] cm²/dyne	$\beta \times 10^{11}$ [a]	log A [b]	C [b]	T_∞ °C [b]	$\Delta = T_g - T_\infty$ [b]	log J_e [c] cm²/dyne
828/DDS	1.82	6.96	−4.7	157,000	−273.2	478	−8.05
1001 /DDS	1.36	4.20	−19.3	2218	80	50	−7.64
1004/DDS	1.32	2.87	−21.0	2420	60.8	50	−7.39
1007 /DDS	1.18	2.22	−20.6	2360	50.7	50	−7.10

a. Andrade equation parameters for $T = T_o$. See Equation 2 and TABLE II .

b. VTHF equation parameters for $T = T_o$. See Equation 1 and TABLE II .

c. Equilibrium Creep compliance; $\log J_e = -7.53$ for EPON 1002/DDS

LEGENDS

Figure 1

The curing history of a stoichiometric ratio of the epoxy resin Epon 828 and 4.4' diamino diphenyl sulphone followed by the devrease in specific volume with time at several temperatures.

Figure 2

Specific volume of Epon 828/DDS reacting stoichiometric mixture versus temperature T. Data cross-plotted from Fig. 1.

Figure 3

Cooling curves for the fully cured epoxy system 828, 1001, 1004, and 1007/DDS slowing the decrease in volume with decreasing temperatures at a rate of cooling at 5°/min.

Figure 4

Reduced shear creep compliance surves J_p (t), cm^2/dyne, determined on Epon 1007/DDS for seven temperatures, as indicated, presented logarithmically as functions of logarithmic time, t, sec.

Figure 5

Reduced shear creep compliance curves $J_p(t)$ of Epon 1007/DDS shifted to superimpose upon the response measurement the reference temperature of 1007.°D shown logarithmically versus the logarithm of the reduced time, t/a_T .

Figure 6

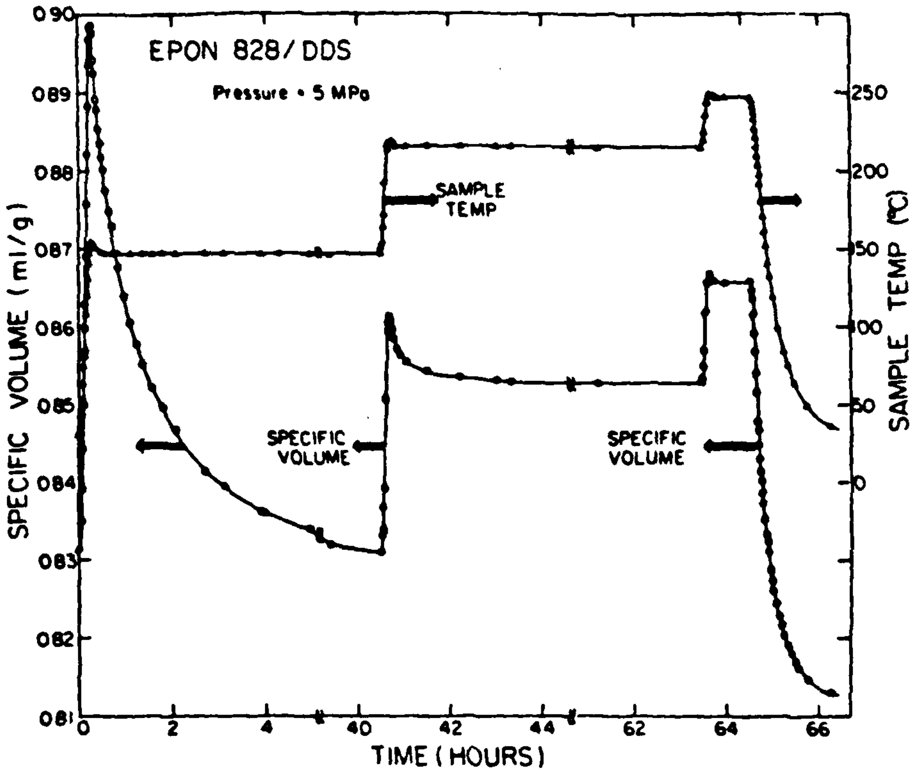
Comparison of reduced shear creep compliance curves of Epon 828, 1001, 1002, 1004, & 1007/DDS plotted logarithmically against the time at the reference temperatures indicated which are close to the respective T_g's.

Figure 7

Log a_T plotted as functions of the reciprocal absolute temperature T/K for the four indicated epoxy resins which were obtained from the reduction process used in producing the curves in Fig. 3.

Figure 8

Logarithmic presentation of the retardation spectra $L(\ln \tau)$ versus the logarithm of the reduced retardation time τ/a_T of four fully cured epoxy resins, as indicated. Temperatures at which the specra are shown were chosen to match the times at the maxima.



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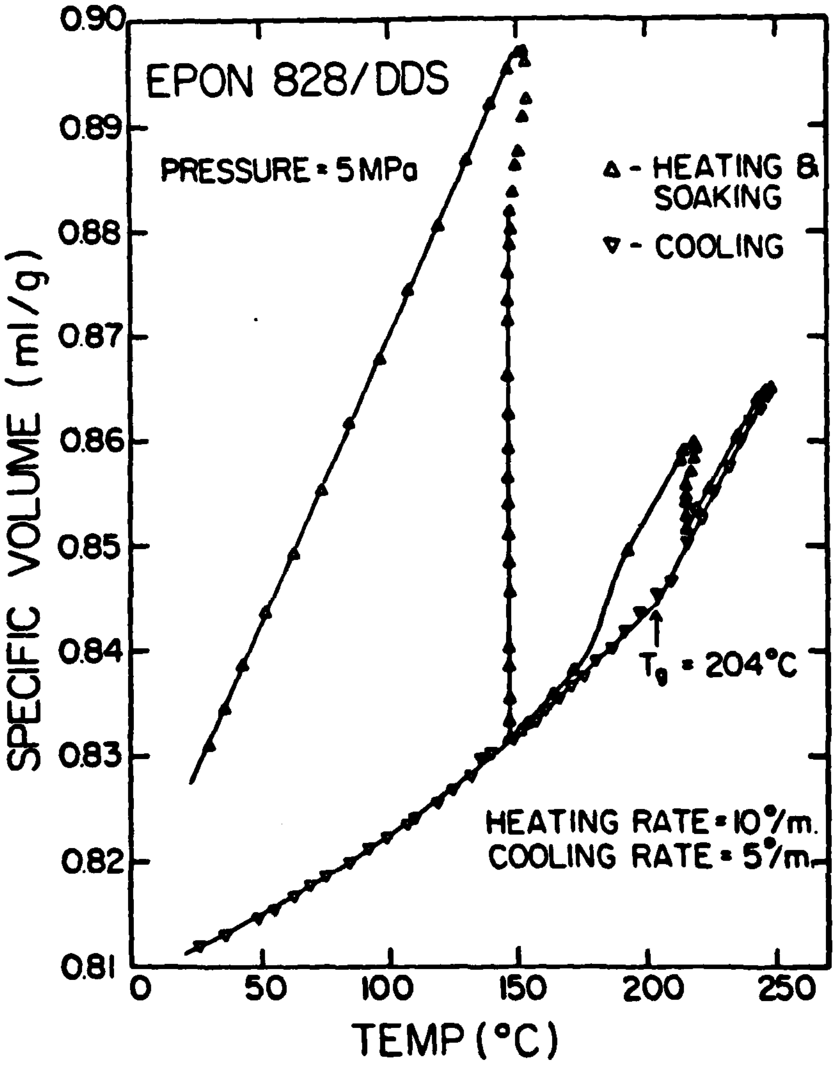

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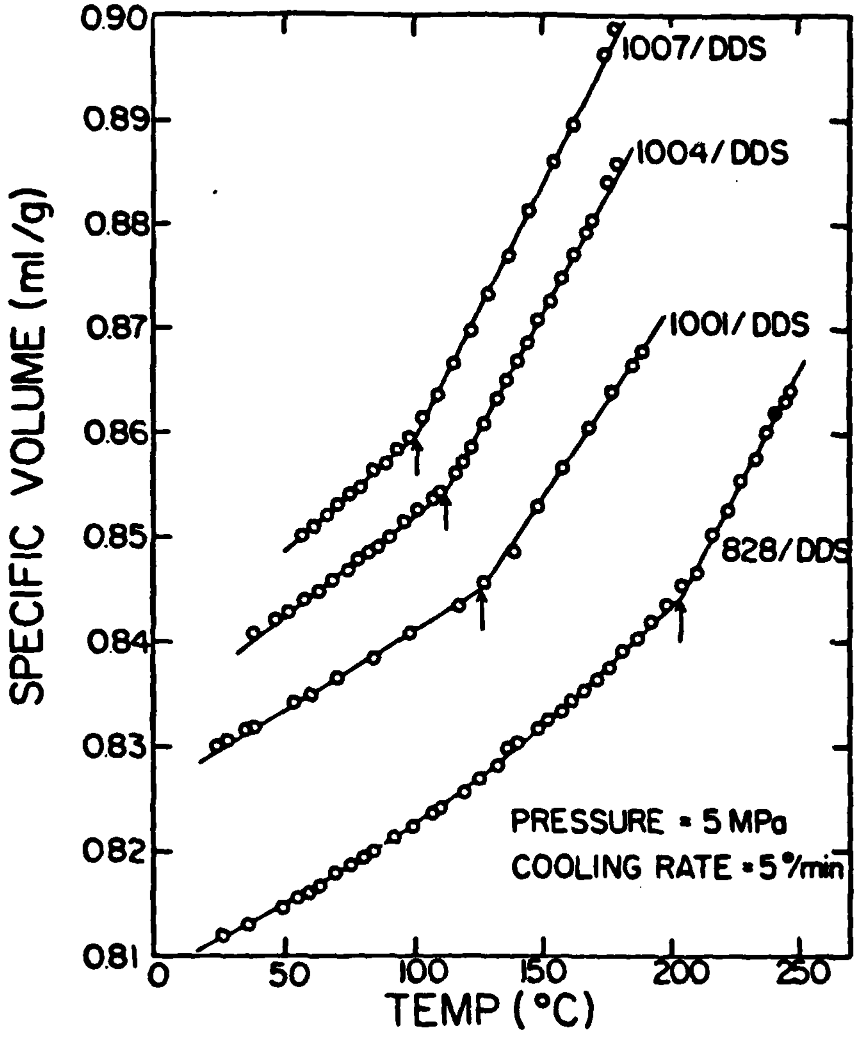

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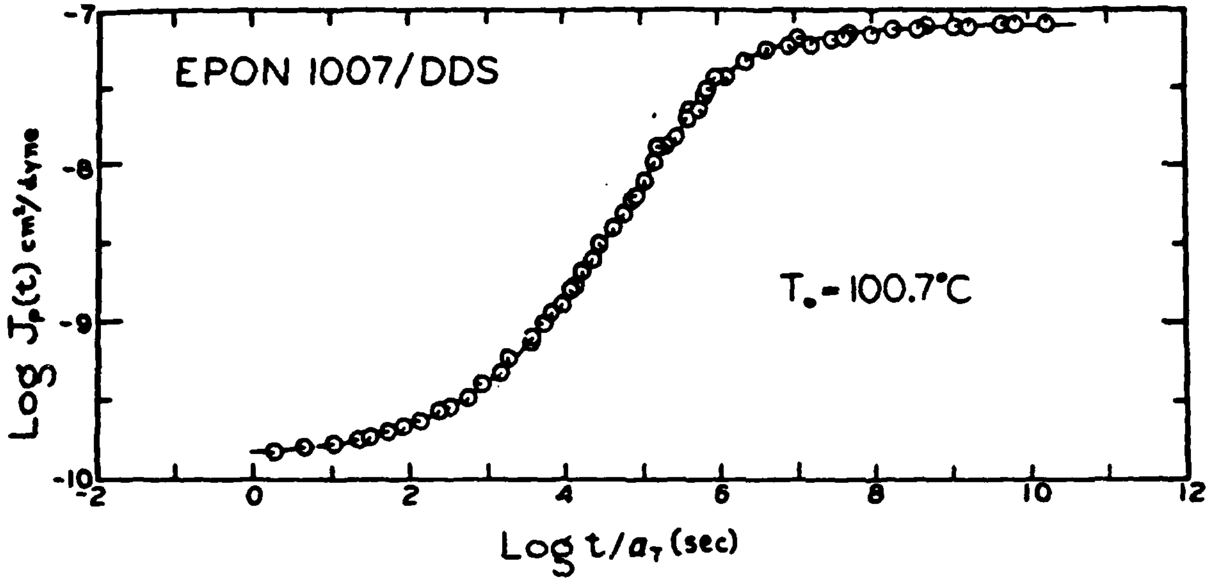

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Reduced shear creep compliance curves $J_p(t)$ of Epon 1007/DDS shifted to superimpose upon the response measurement the reference temperature of 1007.°D shown logarithmically versus the logarithm of the reduced time, t/a_T .

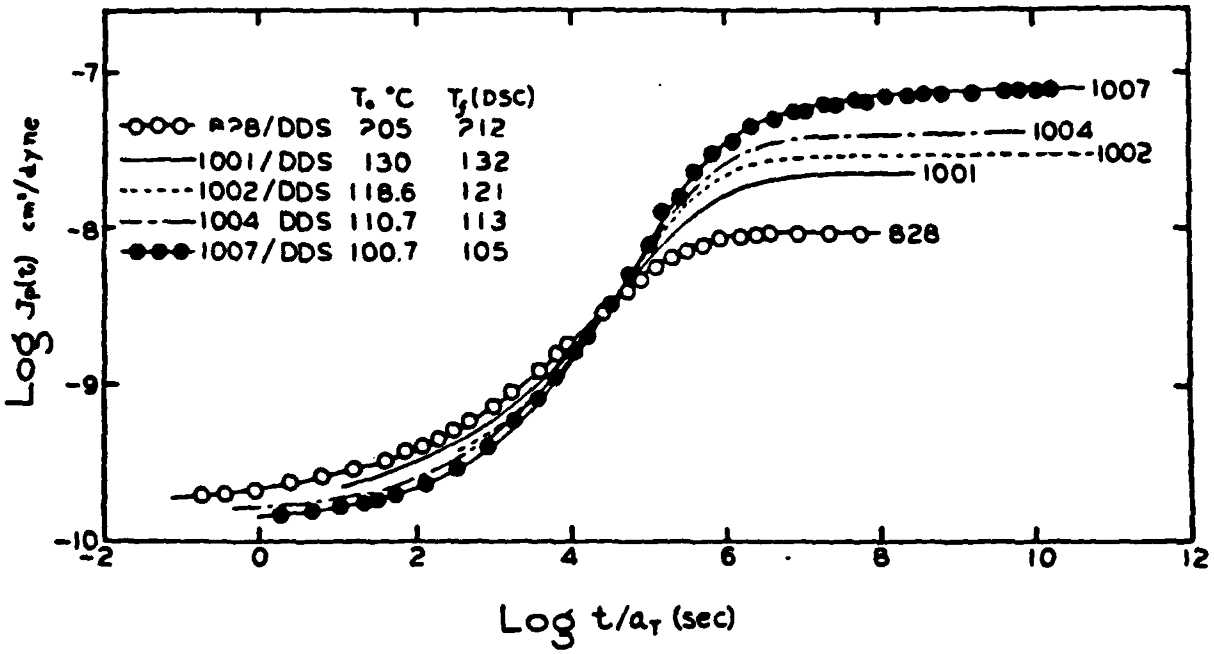

Figure 6

Comparison of reduced shear creep compliance curves of Epon 828, 1001, 1002, 1004, & 1007/DDS plotted logarithmically against the time at the reference temperatures indicated which are close to the respective T_g's.

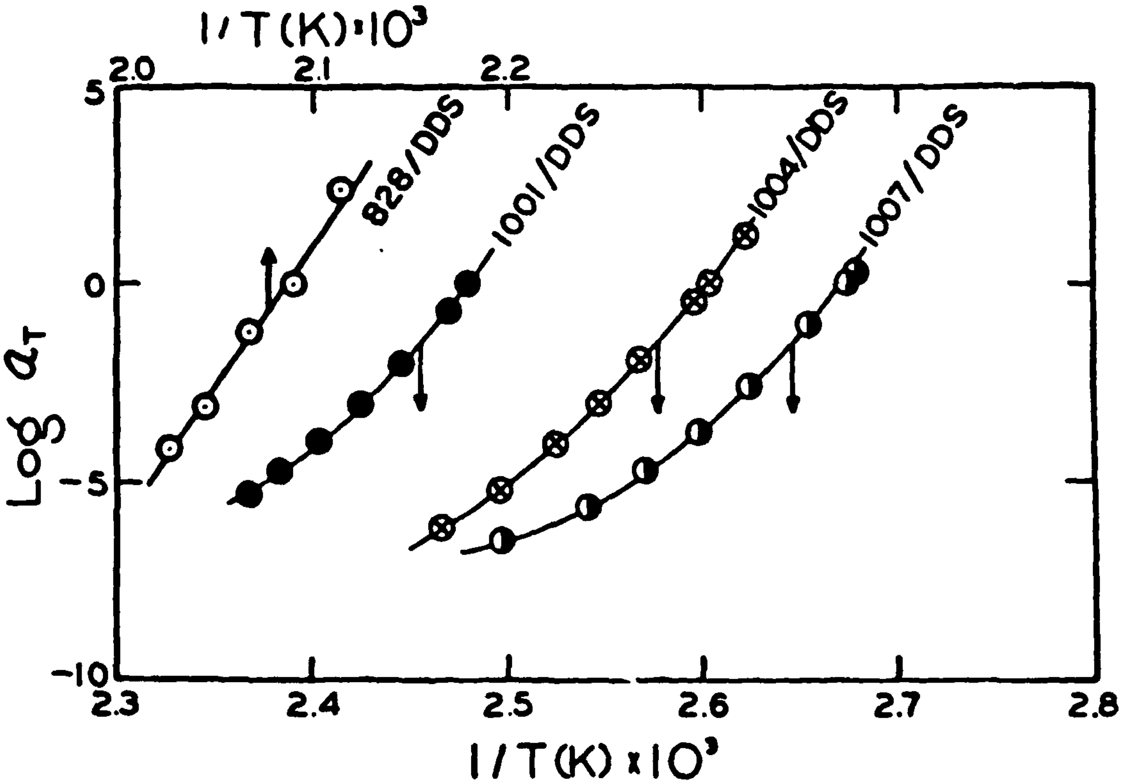

Figure 7

Log a_T plotted as functions of the reciprocal absolute temperature T/K for the four indicated epoxy resins which were obtained from the reduction process used in producing the curves in Fig. 3.

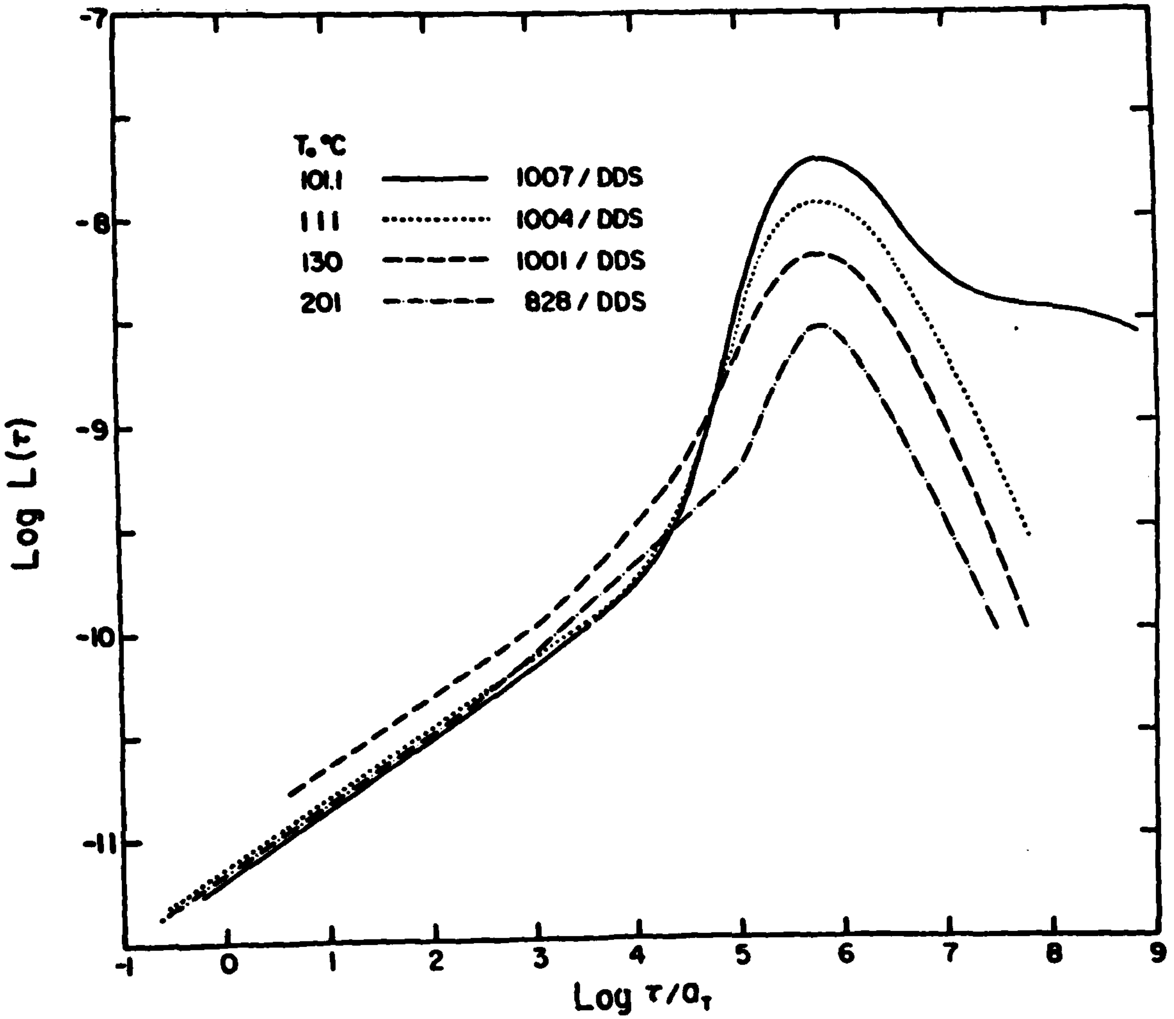

Figure 8

Logarithmic presentation of the retardation spectra L(ln τ) versus the logarithm of the reduced retardation time τ/a_T of four fully cured epoxy resins, as indicated. Temperatures at which the specra are shown were chosen to match the times at the maxima.

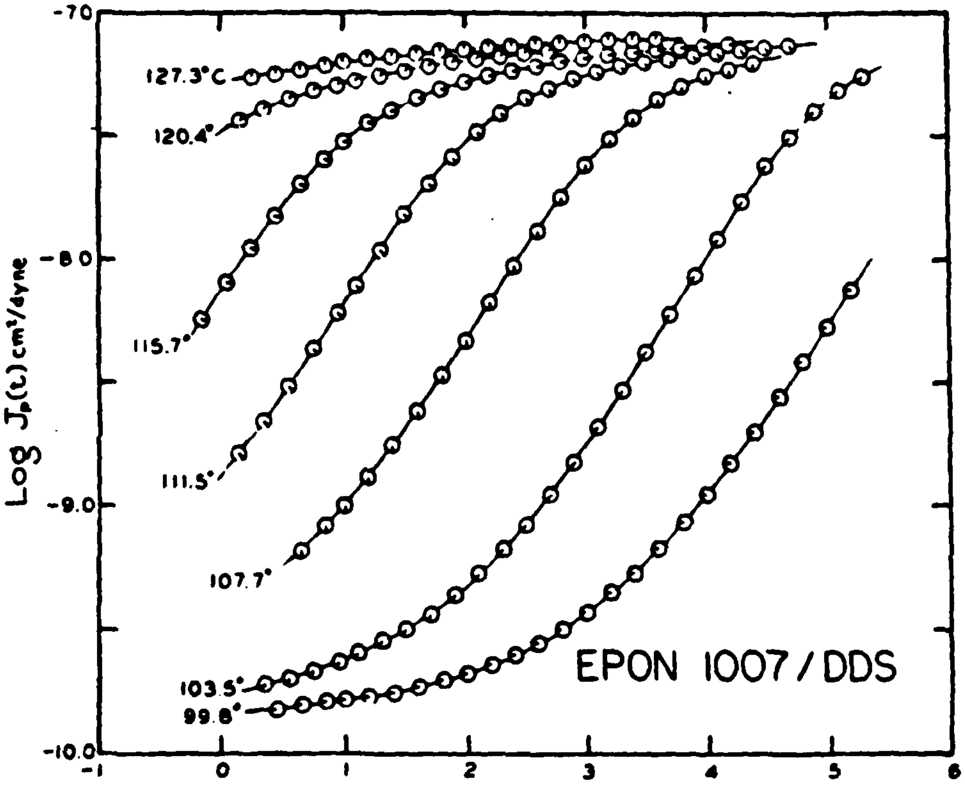

Figure 4

Reduced shear creep compliance surves J_p (t), cm^2/dyne, determined on Epon 1007/DDS for seven temperatures, as indicated, presented logarithmically as functions of logarithmic time, t, sec.

APPENDICES

A. Cumulative List of Publications

F. N. Kelley, B. J. Swetlin, D. Trainor, "Structure-Property Relationships in Composite Matrix Resins," IUPAC Macromolecules, H. Benoit and P. Rempp, editors, Pergamon Press, Oxford and New York, 1982.

F. N. Kelley and L.-J. Su, "Time-Dependent Fracture of Elastomeric Network Polymers," Proceedings IUPAC MACRO 82, Amherst, MA, July, 1982.

F. N. Kelley and D. Trainor, "Model Inhomogeneous Glassy Network Polymers," Polymer Bulletin, 7, 369 (1982).

D. J. Plazek, F. N. Kelley, E. von Meerwall and L. Su, "Viscoelasticity and Tearing Energy of Fluorinated Hydrocarbon Elastomers," Rubber Chem. Technol., 56, 866 (1983).

J. LeMay, B. Swetlin and F. N. Kelley, "Characterization and Properties of Some Epoxy-Amine Networks," Proceedings of the Division of Organic Coatings and Plastics Chemistry, ACS, Seattle Meeting, March, 1983.

E. von Meerwall, D. Shook, K. J. Min and F. N. Kelley, "Self-Diffusion of C_6F_6 in Filled Rubber Polymers," J. Appl. Phys. 56, 9 (1984).

E. von Meerwall, D. Shook, K. J. Min and F. N. Kelley, "Effect of Filler Particles on the Diffusion of Penetrants in Polymers," Bull Am. Phys. Soc., 29/3, 243 (1984).

J. LeMay and F. N. Kelley, "Structure and Ultimate Properties of Epoxy Networks," book chapter, Advances in Polymer Science Vols. 78/79: Epoxy Resins and Composites, K. Dusek, editor, Springer Heidelberg/Berlin/New York, Vol. IV, (1986).

R. G. Stacer, L. Yanyo and F. N. Kelley, "Observations on the Tearing of Elastomers," Rubber Chem. Technol., May/June, Vol. 59, 1985.

R. G. Stacer and F. N. Kelley, "Criteria for Unstable Tearing of Elastomers," Rubber Chem. Technol., Vol. 58, No. 5, p. 924 (1985).

E. von Meerwall, D. Thompson and F. N. Kelley, "Adaptive Modelling of Tear Energy in Filled Rubber Networks," J. Material Sci., 21, 1801 (1986).

B. Degrees Awarded

Ph.D.

1. "Effect of Viscoelastic Properties and Molecular Parameters on Time-Dependent Fracture of Polymer Networks" -- Long-Ji Su (1984)
2. "Fracture of Model Inhomogeneous Networks" -- Donna R. Trainor (1984).
3. "Fracture of Highly Cross-linked Epoxy Networks" -- Brian J. Swetlin (1984)
4. "The Influence of Molecular Structure on the Mechanical Behavior of Highly Cross-linked Epoxy Networks" -- James D. LeMay (1985).

M.S.

1. "Secondary Plateau in the Tear Energy Master Curve of a Polyurethane" -- Robert H. E. Seiple (1985)

C. List of Professional Personnel Associated with the Research Effort

1. Prof. F. N. Kelley
2. Prof. M. Morton
3. Prof. E. von Meerwall
4. Prof. D. Plazek

D. Papers Presented (by F. N. Kelley) at Meetings and Conferences, Seminars

Invited Main Lecturer, IUPAC Symposium on Macromolecules, Strasbourg, France, "Structure-Property Relationships in Composite Matrix Resins," July, 1981.

Hercules Research Laboratory Seminar Speaker. "Fracture in Glassy Network Polymers," Wilmington, Delaware, November, 1981.

Industrial Technology Research Institute, Hsin-Chu, Taiwan. "Epoxy Structure and Fracture Behavior" and Advances in Polymer Science and Engineering in the U. S.," January, 1982.

General Electric Research Laboratories, invited research seminar, "Structure and Fracture of Densely Cross-linked Polymers," May, 1982.

Akron Polymer Conference on Fracture of Polymers and Composites, "Time and Temperature Effects on the Fracture of Polymer Networks," Akron, Ohio, May, 1982.

Gordon Research Conference on Structural Polymer Characteristics, "Fracture of Epoxy Networks" (presented by Brian Swetlin), Plymouth, New Hampshire, June, 1982.

Gordon Research Conference on Adhesion, "Model Glassy Inhomogeneous Networks," New Hampton, New Hampshire, August, 1982.

Gordon Research Conference on Thermosetting Polymers, "Effect of Structure on the Mechanical Behavior of Epoxy Resins" (presented by J. D. LeMay), New London, New Hampshire, June 1985.

Ohio State University, Chemical Engineering Seminar, "Preparation and Properties of a Model Rubber-Toughened Epoxy," February, 1986.

Gordon Research Conference on Thermosetting Polymers, "Toughening of Structural Resins," New London, New Hampshire (June 1986).

E. Consultative and Advisory Functions to Other Laboratories and Agencies

a. Doctoral graduate student under this grant, Kenneth Ptak, expected to graduate in January, 1987, is now employed as a visiting scientist at the Air Force Materials Laboratory, WPAB, under an on-site contract.

b. Four visits have been made to AFML, Wright-Patterson AFB, Ohio. Two seminars given, one leading to the employment of K. Ptak (April, 1986).

c. One visit by Dr. T. Helminiak, AFML, to University of Akron for technical interchange on February 27, 1986.

d. One visit by F. Kelley to NASA Langley to give review of thermoset work and discuss future program activities (May 1986).

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