

Rheologic Behavior of Epoxy Resins in the Transition Region*

PERICLES S. THEOCARIS, *Laboratory for Testing Materials, Athens National Technical University, Athens, Greece*

Synopsis

Master curves of $\log Q(t/K)$ against $\log (t/K)$ were constructed from experimental data on creep compliance, relaxation modulus, stress-optical and strain-optical coefficients of two types of epoxy resins at a series of temperatures in the transition region. The characteristic creep or relaxation time K for each temperature was defined and tabulated. The master curves were fitted to the reduced equation of the Gauss error integral form and the following characteristic parameters were calculated: Q_1 , the glassy-state parameters (creep compliance, relaxation modulus, stress-optical or strain-optical coefficients); Q_2 , the rubbery-state parameters; T_d , the distinctive temperature; K_d , the characteristic creep or relaxation time at T_d ; and the parameters h_1 and h_2 of the steepness of master curves at the transition and glassy regions, respectively. The investigation was extended to the determination of the distribution functions of mechanical and optical retardation and relaxation times $L(\log \tau)$ and $H(\log \tau)$, respectively, representing the differential contribution to instantaneous compliance, stress-optical or strain-optical coefficients associated with retardation times and instantaneous modulus, stress-optical or strain-optical coefficients associated with relaxation times.

I. Introduction

In a previous paper by the author¹ the experimental study of the viscoelastic properties of two types of epoxy polymers was undertaken. These polymers are of great importance in various applications, particularly in studying ordinary photoelasticity by transmitted light, as well as in the method of birefringent coatings for the study of the surface strain distribution of opaque models in reflected light. Creep and relaxation individual curves were plotted at various steps of temperature from the glassy up to rubbery state of these polymers. Master creep curves and master relaxation curves of these resins were constructed, representing the mechanical and optical behavior of these polymers at their transition regions. Three groups of master curves were plotted, for the creep compliance D , relaxation modulus E , and stress-optical or strain-optical coefficients C_σ and C_ϵ , respectively. The first group of curves describes the mechanical behavior of the polymers and the two last groups their optical behavior. The stress-optical or strain-optical coefficients are defined as the difference

* This research was carried out when the author held a fellowship of the National Academy of Sciences of the U. S. A.

of principal stresses or strains, respectively, in the plane of the wavefront producing a relative retardation of one wavelength per inch of thickness.

The two types of epoxy resins were (a) hot-setting epoxy resin made from Araldite liquid prepolymer (Hysol Araldite 6053) and 40% phthalic anhydrite hardener represented as H-100-40 polymer and (b) cold-setting epoxy resin made from Araldite liquid prepolymer (CIBA Araldite 6005) and 8% triethylenetetramine hardener represented as C-100-0-8 polymer. It was proved that the time-temperature superposition principle, which was proved to be valid for a great number of amorphous high polymers, holds for the creep compliance and the relaxation modulus of these two cross-linked polymers. Moreover, the validity of this principle was extended to stress-optical and strain-optical coefficients. The creep and relaxation time factors k for each master curve were determined and the equality of the k factors for mechanical and for optical creep and relaxation was established.

Creep and relaxation data embodied in constructed master curves were used in this paper to define the characteristic parameters of the polymers. The characteristic creep and relaxation time K was introduced; this corresponds to the time at which the creep or relaxation functions attain the geometric mean values of the quantities corresponding to the glassy and rubbery consistencies.² All master curves were plotted on a log-log scale, and the values of K were determined for several temperatures. Plots of $\log K$ against $1/T$, where T is the absolute temperature derived from the corresponding master curves, allow the determination of the apparent activation energy. The master curves were fitted to a reduced equation of the Gauss error integral form and the characteristic parameters of each master curve which relate the time and temperature dependence of D , E , C_σ and C_ϵ , respectively, were determined.

The time-temperature superposition principle together with the Gauss error integral representation appear to constitute a general method for condensed representation of mechanical and optical properties of these polymers in the transition region.

Distribution functions of retardation and relaxation times were calculated and compared. Similarities in the responses to mechanical and optical distribution functions are discussed.

II. Experimental Results

Master composite curves corresponding to an arbitrary reference temperature of 25°C. were constructed previously¹ by using creep and relaxation individual curves at several steps of temperatures and by applying the time-temperature superposition principle. These curves were plotted in the form of $Q(t/k)$ versus $\log(t/k)$, where $Q(t/k)$ represents in turn one of the quantities: creep compliance D , stress-optical C_σ , or strain-optical C_ϵ coefficients (for creep tests) relaxation modulus E , and stress-optical C_σ , or strain-optical C_ϵ coefficients (for relaxation tests). The quantity k , which is a time factor which is a function of temperature

alone, expresses the amount of shift of the experimental curves at different temperatures required in order to obtain the corresponding master composite curves, and it is determined completely if the reference temperature T_0 is fixed.

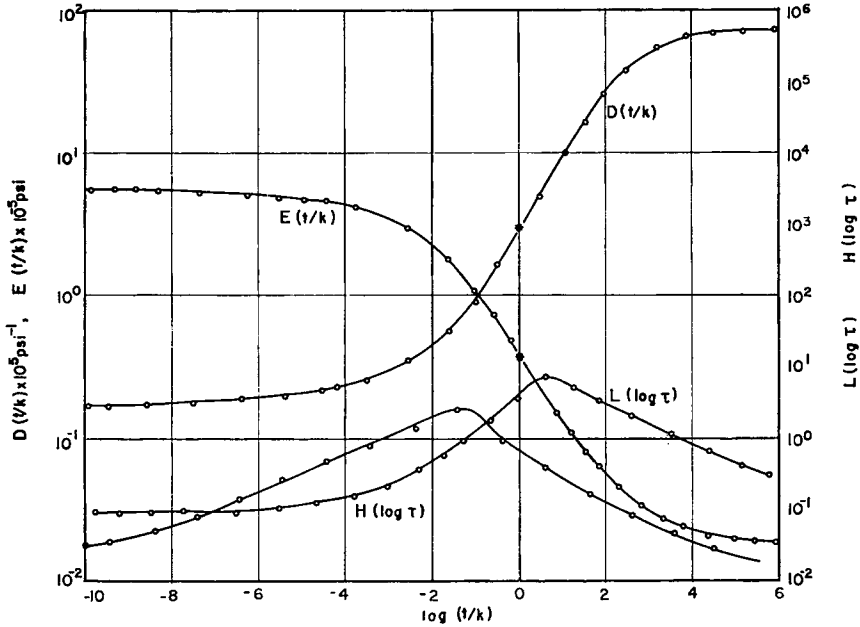


Fig. 1. Master creep compliance curve, master relaxation modulus curve and their distributions of retardation and relaxation times for H-100-40 epoxy resin.

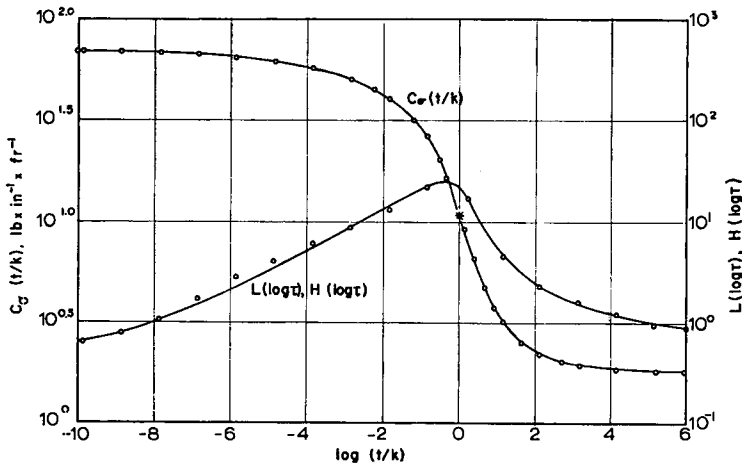


Fig. 2. Master creep and relaxation stress-optical coefficient curves and their distributions of retardation and relaxation times for H-100-40 epoxy resin.

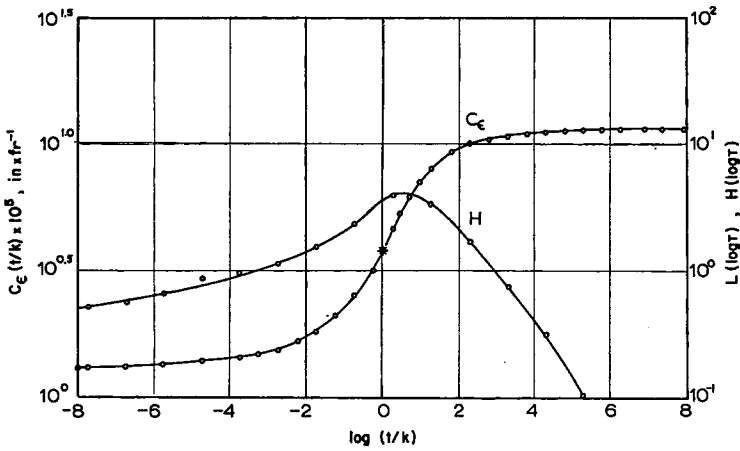


Fig. 3. Master creep and relaxation strain-optical coefficient curves and their distributions of retardation and relaxation times for H-100-40 epoxy resin.

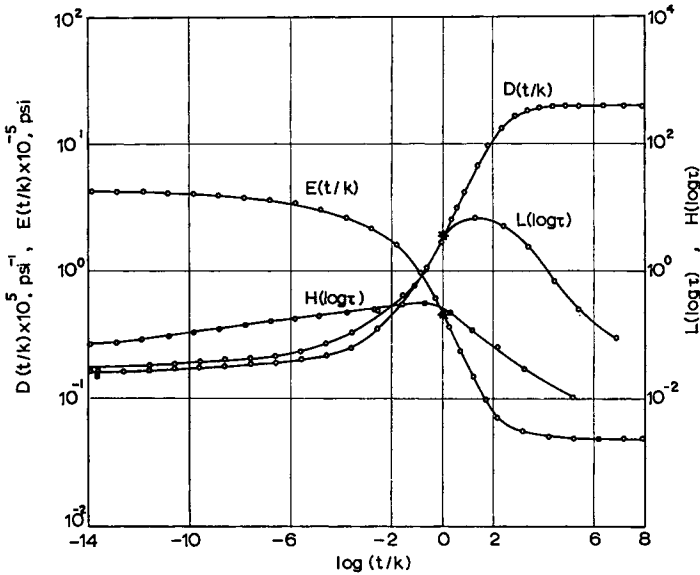


Fig. 4. Master creep compliance curve, master relaxation modulus curve and their distributions of retardation and relaxation times for C-100-0-8 epoxy resin.

Instead of the arbitrary definition of the reference temperature T_0 and the time factor k , Tobolsky and co-workers² have introduced a new quantity K , called the characteristic creep or relaxation time at each temperature. This quantity is defined as the time required to the function $Q(t)$ at any temperature to attain the geometric mean value of the function $Q_{1,2}(t)$, characteristic of the glassy and rubbery consistencies. The previously plotted master composite curves in the form of $Q(t/k)$ against $\log (t/k)$ are

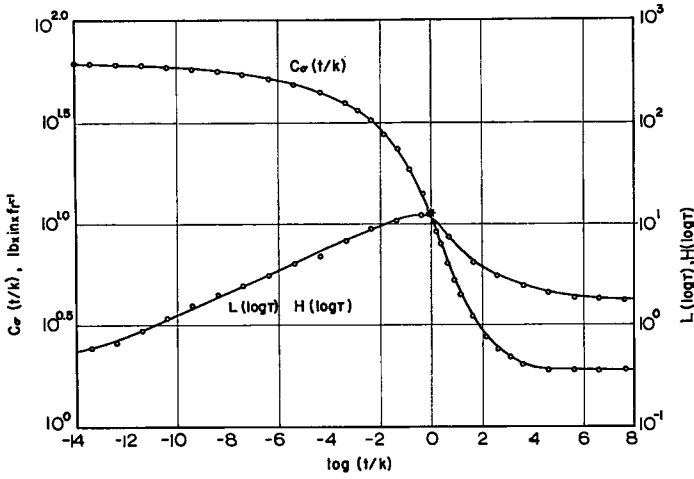


Fig. 5. Master creep and relaxation stress optical coefficient curves and their distributions of retardation and relaxation times for C-100-0-8 epoxy resin.

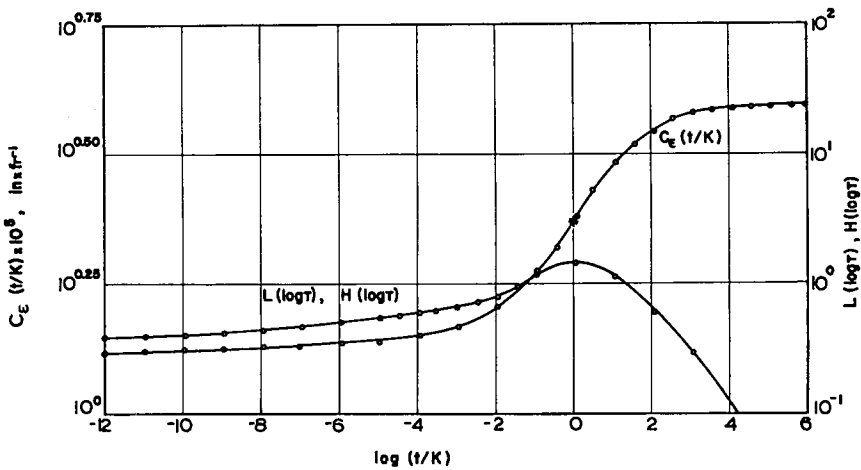


Fig. 6. Master creep and relaxation strain-optical coefficient curves and their distributions of retardation and relaxation times for C-100-0-8 epoxy resin.

in this paper plotted in the form of $\log Q(t/K)$ against $\log (t/K)$ and the origins of each log time scale were shifted in order to coincide with the defined characteristic times of each curve. The derived master curves are plotted in Figures 1-6.

Examination of Figures 1 and 4 giving curves of the creep compliance D and relaxation modulus E for both polymers shows that in logarithmic time scale the product of modulus times compliance $E(t/K) \cdot D(t/K)$ is unity in all transition-free regions and tends to unity in the transition region.

TABLE I
 Temperature Dependence of Characteristic Creep and Relaxation Times K in Minutes and of Apparent Activation Energy for H-100-40 Epoxy Resin
 in Kcal

Temp. t , °C.	$\log K_c$	$\log K_r$	ΔH_{act}	$\log K_{c\sigma}$	$\log K_{r\sigma}$	ΔH_σ	$\log K_{ce}$	$\log K_{re}$	ΔH_e
25	-9.60	9.43	-106.12	10.37	9.84	-127.34	-8.76	-8.75	-121.00
30	-8.37	8.20	-92.64	9.14	8.58	-99.56	-7.53	-7.49	-92.85
35	-7.38	7.20	-81.41	8.20	7.66	-78.35	-6.59	-6.52	-75.75
40	-6.42	6.23	-72.08	7.33	6.64	-68.98	-5.75	-5.62	-65.70
50	-5.08	4.85	-64.78	5.95	5.34	-59.48	-4.48	-4.42	-49.00
60	-3.69	3.40	-70.81	4.59	3.98	-70.06	-3.28	-3.15	-60.98
70	-2.12	1.89	-87.28	3.09	2.44	-87.90	-1.95	-1.70	-80.90
75	-1.10	1.05	—	2.04	1.52	—	-1.16	-0.90	—
80	-0.02	-0.03	-103.15	0.97	0.49	-105.82	-0.08	0.23	-100.96
85	1.06	-0.91	-112.22	-0.33	—	-113.37	1.05	—	-111.65
90	2.08	-1.95	-122.00	-1.33	-1.60	-122.34	2.02	2.15	-124.06
100	4.20	-4.07	-140.15	-3.45	-3.81	-138.78	4.14	4.39	-144.70

TABLE II
 Temperature Dependence of Characteristic Creep and Relaxation Times K in Minutes and of Apparent Activation Energy for C-100-8 Epoxy Resin
 in Kcal

Temp. t , °C.	$\log K_c$	$\log K_r$	ΔH_{act}	$\log K_{cr}$	$\log K_{cr}$	$\log K_{cr}$	ΔH_g	$\log K_{ce}$	$\log K_{re}$	ΔH_e
25	-11.61	11.81	-128.00	14.36	14.38	-135.35	-11.92	-12.15	-153.40	
30	-10.45	10.30	-91.40	12.71	12.93	-101.45	-10.23	-10.37	-112.00	
35	—	9.46	-68.46	—	—	-74.46	—	-9.39	-80.82	
40	-9.00	8.74	-59.46	10.98	11.13	-62.95	-8.43	-8.56	-65.32	
50	-7.82	7.59	-45.52	9.86	10.11	-40.05	-7.10	-7.39	-42.30	
60	-6.73	6.38	-59.46	9.00	9.20	-43.90	-6.14	-6.59	-42.85	
70	-5.46	5.12	-67.16	8.11	8.11	-56.00	-5.23	-5.74	-43.90	
80	-4.19	3.66	-76.50	7.14	7.09	-64.95	-4.40	-4.85	-51.29	
90	-2.87	2.47	-85.32	5.93	5.95	-76.48	-3.49	-3.90	-57.60	
95	—	1.71	-88.50	—	5.10	-85.28	—	-3.36	-64.76	
100	-1.49	—	-94.52	4.49	—	-91.89	-2.52	-2.79	-72.06	
105	—	0.43	-100.90	—	3.77	-105.25	-2.02	-2.05	-81.48	
110	-0.16	-0.29	-110.75	2.98	3.05	-120.88	-1.56	-1.43	-97.31	
115	1.05	-1.09	-121.00	1.42	1.23	-133.15	-0.54	-0.65	-118.80	
120	2.35	-2.01	-139.65	0.02	0.08	-149.00	0.30	0.18	-131.24	
125	3.20	-3.07	-159.40	-0.86	-1.12	-163.80	1.14	1.40	-151.68	
130	4.64	-4.40	-191.45	-2.25	-2.71	-182.20	2.28	2.90	-173.64	
135	6.39	—	-231.10	-3.20	—	-199.44	3.73	—	-189.10	

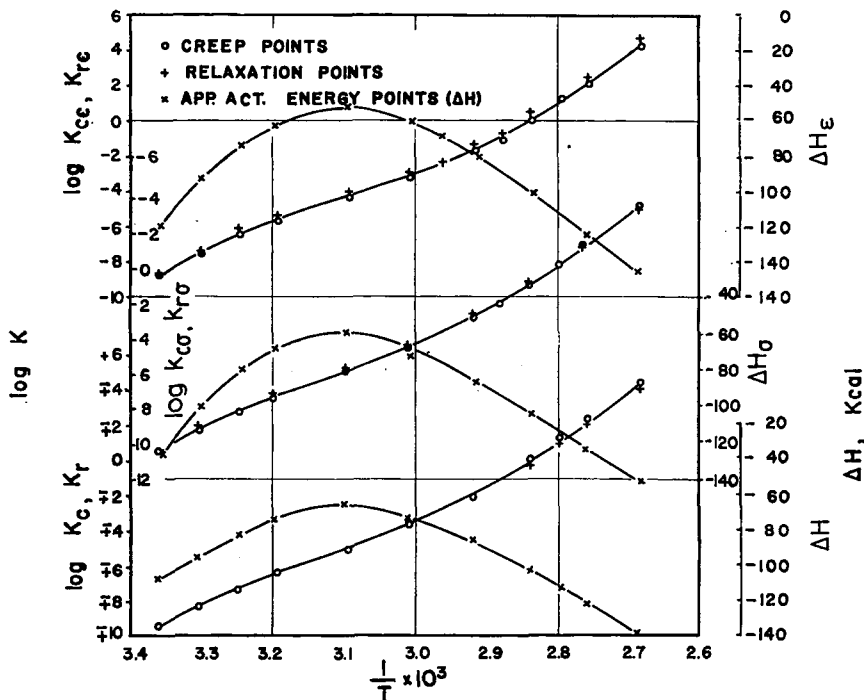


Fig. 7. Temperature dependence of characteristic (O) creep and (+) relaxation times and of (X) apparent activation energy for H-100-40 epoxy resin.

Since both creep compliance and relaxation modulus have finite long time limits neither polymer shows a Newtonian flow and the viscosity η can be assumed to tend to infinity.

We denote by K_c and K_r the characteristic times derived from creep and relaxation curves and K_{cs} , K_{rs} and K_{ce} , K_{re} the characteristic times for creep and relaxation stress-optical and strain-optical coefficients, respectively. The values of these coefficients at various temperatures are tabulated in Tables I and II. The equality of the various K_c and K_r can be derived from these values.

Plots of $\log K$ against $1/T$, where T is the absolute temperature, derived from the various master curves are shown in Figures 7 and 8. In the same figures is shown the dependence of the apparent activation energy ΔH_{act} for the two types of epoxy resins as it is calculated by the Arrhenius equation or its reciprocal form. The Arrhenius equation was used for the calculation of the variation of the apparent activation energy in creep D curves as well as in all C_e curves while its reciprocal form used for the corresponding relaxation E curves and all C_r curves. These two forms are expressed by eq. (1)

$$\Delta H_{act} = \pm 2.303R[d \log K/d(1/T)] \quad (1)$$

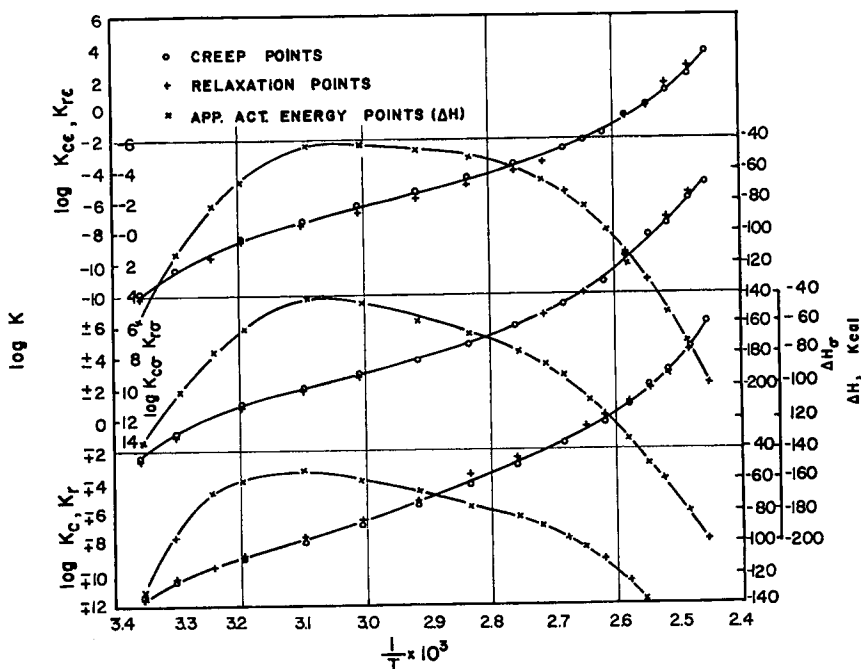


Fig. 8. Temperature dependence of characteristic (O) creep and (+) relaxation times and of (X) apparent activation energy for C-100-0-8 epoxy resin.

where R is the gas constant, K the characteristic creep or relaxation time, T the absolute temperature, and the minus sign corresponds to Arrhenius relation.

In all cases ΔH_{act} passes through a definite maximum defining the distinctive temperature T_d for each polymer and the corresponding distinctive creep and relaxation time K_d . The values of ΔH_{act} for various values of $1/T$ are given also in Tables I and II. The distinctive temperature T_d for both epoxy resins was found to be approximately 50°C . It is also worthwhile noting that these maxima have the same values for both types of epoxy resins and for all characteristic quantities examined.

The values of the parameters characterizing the viscoelastic properties of the two types of epoxy resins are listed in Table III. These parameters are the glassy-state parameters Q_1 , the rubbery-state parameters Q_2 , $\log K_d$, corresponding to the distinctive temperature T_d and the slope h , which is related to the negative slope n of the corresponding master curves $\log Q_{c,r}(t/K)$ versus $\log (t/K)$ at the value of $\log (t/K)$ for which $\log Q_{c,r}(t/K)$ attains the mean value of the two extreme consistencies.

III. Analytical Expression of the Various Master Curves

It was shown by Tobolsky and co-workers^{2,3} that the composite creep and relaxation curves of various amorphous polymers in their respective

TABLE III
Parameters of Reduced Equation for Viscoelastic Behavior of Two Types of Epoxy Resins

	$\log Q_1$	$\log Q_2$	$\log Q_{\sigma_1}$	$\log Q_{\sigma_2}$	$\log Q_{\sigma_1}$	$\log Q_{\sigma_2}$	$\log Q_{\epsilon_1}$	$\log Q_{\epsilon_2}$	$T_d,$ $^{\circ}\text{K.}$	$\log K_d$	$\log K_{de}$	$\log K_{de}$	h_g	h_t
	Epoxy Resin H-100-40													
Creep	1.18	1.97	1.85	0.17	0.11	1.10	325°	-4.75	-5.87	-4.26	0.331 ^a	0.760 ^a		
Relaxation	0.72	2.70	1.85	0.25	0.11	1.06	325°	-4.58	-5.34	-4.25	0.360 ^b	0.920 ^b		
	Epoxy Resin C-100-0-8													
Creep	1.20	1.31	1.80	0.28	0.15	0.60	324°	-7.51	-9.86	-6.82	0.279 ^a	0.761 ^a		
Relaxation	0.65	2.70	1.83	0.30	0.18	0.58	324°	-9.71	-8.88	-7.05	0.269 ^b	0.918 ^b		

^a Values of h_g and h_t correspond to D curves and C_{ϵ} creep and relaxation curves.

^b Values of h_g and h_t correspond to E curves and C_{σ} creep and relaxation curves.

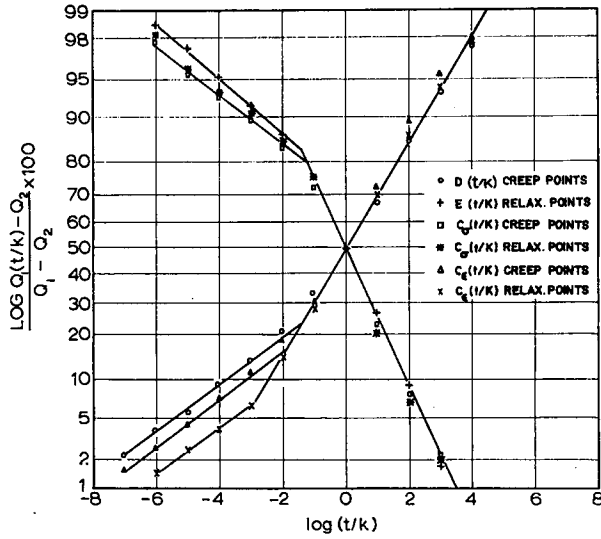


Fig. 9. Master creep and relaxation curves for H-100-40 epoxy resin on normal probability graph paper.

transition regions could be adequately reproduced by an equation of the Gauss error integral form:

$$\log Q(t/K) = [(\log Q_1 + \log Q_2)/2] - [(\log Q_1 - \log Q_2)/2] \operatorname{erf}(h \log t/K)$$

where

$$\operatorname{erf} x = 2\pi^{1/2} \int_0^x e^{-u^2} du \quad (2)$$

is the error integral and h is the adjustable parameter of the Gauss error curve. This could be obtained from an examination of the various master curves. It is apparent that if the negative derivative of each master curve is plotted against the log of temperature divided by the characteristic time K , the resulting curve is composed of two branches, each of which approximates a Gauss error curve with different parameter h .

The quantities $1/2(\log Q_1 + \log Q_2)$ for the two types of epoxy resins were readily determined from the corresponding master curves at their inflection points. Since all master curves tend to an asymptotic value in their rubbery states, the values of $\log Q_2$ can be determined. From the values of $\log Q_2$ and the ordinates at the corresponding inflection points, the values of $\log Q_1$ can be determined; an immediate check could be made by observing whether the corresponding master curves approach asymptotically these glassy limits. When the corresponding $\log Q_2$ are determined, the values of $1/2(\log Q_1 - \log Q_2)$ are found.

For the evaluation of the parameters h , we plotted on normal probability paper the curves of A versus $\log(t/K)$, where

$$A = \log Q_{c,r}(t/K) - \log Q_2 / \log Q_1 - \log Q_2 \times 100 \quad (3)$$

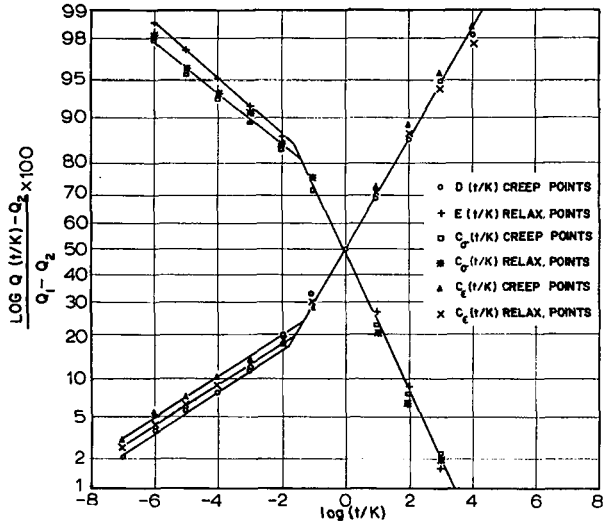


Fig. 10. Master creep and relaxation curves for C-100-0-8 epoxy resin on normal probability graph paper.

These plots are shown in Figures 9 and 10 for both types of epoxy resins. Each curve in these plots is formed by two distinctive straight lines with different slopes to which correspond different values of the parameter h . The one parameter (h_g) is related to the behavior of the polymer at the glassy state and its validity extends approximately up to the distinctive temperature T_d . The other parameter (h_t) is valid for the rubbery state and the transition region. This means that the predominating deformation mechanism in which creep or relaxation processes can occur in the glassy state is characteristically different from the deformation mechanism at the transition and partly the rubbery regions. Indeed, the deformation mechanism at the glassy state is due to deformation of primary crosslinking bonds, behaving purely elastically, while in the transition region, slipping of secondary crossbonds contributes mainly to the deformation of the polymer. It is also noteworthy that the values of all h_t and h_g are approximately the same at the various creep and relaxation A curves of each epoxy resin. These values are determined from one of the following relations

$$h = 1.645/I_1 - I_{50} = 1.645/I_{50} - I_{99} = 0.946/I_9 - I_{50} =$$

$$0.946/I_{50} - I_{91} = 0.477/I_{25} - I_{50} = 0.477/I_{50} - I_{75}$$

where I_1 denotes the intercept on the abscissa at 1% ordinate, etc. The parameters h_t and h_g for the two epoxy resins are given in Table III.

IV. Distribution Functions of Retardation and Relaxation Times

The functions $L(\log \tau)$ and $H(\log \tau)$ expressing the distribution functions of retardation or relaxation times in terms of the argument $\log \tau$ are re-

lated to the function $L(\tau)$ and $H(\tau)$, respectively, by means of the relations.

$$L(\log \tau) = 2.303\tau L(\tau)$$

and

$$H(\log \tau) = 2.303\tau H(\tau)$$

where $L(\tau)$ and $H(\tau)$ express the distributions of retardation or relaxation times.

The first approximations for the functions $L(\log \tau)$ or $H(\log \tau)$ are:

$$L'(\log \tau) = -2.303 [Q_c(t/u) d \log Q_c(t/u) / d \log t]_{t=\tau} \quad (4)$$

$$H'(\log \tau) = -2.303 [Q_c(t/u) d \log Q_r(t/u) / d \log t]_{t=\tau} \quad (5)$$

Since we are concerned only with the distribution of retardation or relaxation times related to the transition regions and corresponding to the portion of total distribution containing small retardation or relaxation times, we obtain the first approximations of the function $L(\log \tau)$ or $H(\log \tau)$ if we subtract the corresponding glassy-state parameters from all values of $Q_{c,r}(t/K)$. This subtraction corresponds to the exclusion from the distributions of retardation or relaxation times, which are assumed to have a bimodal distribution, of the one mode which corresponds to the glassy-state parameter and which contains a set of very long retardation or relaxation times, depending on the molecular weight of the polymer. The detailed shapes of the distribution functions are thus known throughout the region of time scale in which the consistencies change from those of a soft rubber to those of a hard glass. These functions are plotted in Figures 1-6, together with the corresponding master curves.

The shape of the distribution curves given by their first approximations is such, that, when they are used to recompute the respective functions $Q_{c,r}(t/K)$, they give a fairly good overall fit and they are especially good in the low time ranges corresponding to glassy-state characteristics. Therefore, a second-order approximation, yielding a further improvement in the distribution functions, was not felt to be necessary.

Examination of the various distribution curves shows that: (a) all curves possess a distinctive maximum in the vicinity of the characteristic creep or relaxation times; (b) for the distribution function curves corresponding to creep compliance and relaxation modulus, these curves are symmetric with respect to the ordinate passing through $\log(t/K) = 0$; (c) all other respective creep and relaxation distribution function curves present approximately the same shape and maximum value.

The results presented in this paper were obtained in the course of research sponsored by the National Academy of Sciences-National Research Council under the Scientific Research Project TA-01-101-4006 and the National Science Foundation under the Scientific Project NSF-G 8188 at the Division of Engineering of Brown University during the academic year 1958-59.

References

1. Theocaris, P. S., *Rheol. Acta*, **2**, No. 2, 92 (1962).
2. Bischoff, J., E. Catsiff, and A. V. Tobolsky, *J. Am. Chem. Soc.*, **74**, 3378 (1952).
3. Catsiff, E., and A. V. Tobolsky, *J. Appl. Phys.*, **25** 1092 (1954).

Résumé

Les courbes maîtresses de $\log Q(t/k)$ en fonction de $\log (t/K)$ ont été tracées à partir des données expérimentales concernant la rétraction, le module de relaxation, les coefficients de traction optique et de tension optique de deux types de résines époxy pour une série de températures dans la région de transition. Le temps caractéristique K de rétraction ou relaxation pour chaque température a été défini et classifié. Les courbes principales ont été ramenées à l'équation réduite de la forme intégrale de l'erreur de Gauss et les paramètres caractéristiques suivants ont été calculés: Q_1 , les paramètres de l'état vitreux (la rétraction, le module d'élasticité, les coefficients de tension et de traction optiques), Q_2 , les paramètres de l'état-caoutchouteux; T_d , la température "distinctive"; K_d , le temps caractéristique de rétraction ou le temps de relaxation à T_d ; et les paramètres h_i et h_o des degrés d'inclinaison de la courbe principale respectivement dans les régions de transition et de vitrification. Les recherches ont été étendues à la détermination des fonctions de distribution des temps de retard et de relaxation mécanique et optique $L(\log \tau)$ et $H(\log \tau)$ respectivement, représentant la contribution différentielle à la compliance instantanée, aux coefficients optiques de traction et de tension associés aux temps de retard, au module instantané et aux coefficients de traction et de tension associés au temps de relaxation.

Zusammenfassung

Aus Versuchsergebnissen über die Kriechfunktion, den Relaxationsmodul, die spannungsoptischen und verformungsoptischen Koeffizienten von zwei Epoxyharztypen bei einer Reihe von Temperaturen im Umwandlungsbereich wurde ein Einheitsdiagramm für $\log Q(t/K)$ gegen $\log (t/K)$ gezeichnet. Die charakteristische Kriech- oder Relaxationszeit K wurde für jede Temperatur definiert und tabelliert. Die Einheitskurven wurden der reduzierten Gleichung des Gauss'schen Fehlerintegrals angepasst und die folgenden charakteristischen Parameter berechnet: Q_1 , die Parameter für die Glaszustand (Kriechfunktion, Relaxationsmodul, spannungsoptische oder verformungsoptische Koeffizienten); Q_2 , die Parameter für den Kautschukzustand; T_d die charakteristische Temperatur; K_d die charakteristische Relaxationszeit bei T_d und die Parameter h_i und h_o für die Steilheit der Einheitskurven im Umwandlungs- bzw. Glasbereich. Die Untersuchung wurde auf die Bestimmung der Verteilungsfunktion für mechanische und optische Verzögerungs- und Relaxationszeiten, $L(\log \tau)$ bzw. $H(\log \tau)$, ausgedehnt, die der differentiellen Beitrag zur momentanen Nachgiebigkeit, zu den spannungsoptischen oder verformungsoptischen Koeffizienten in Verknüpfung mit der Retardationszeit und zum momentanen Modul, zu den spannungsoptischen oder verformungsoptischen Koeffizienten in Verbindung mit der Relaxationszeit angeben.

Received October 8, 1962