boric acid McCauley and Lien[6b] have shown that hexamethylbenzene is a stronger base than any of the other methylbenzenes.

**Association Ratio.**—A study was made to determine the nature of the association of chloroform with several aromatic compounds, namely, mesitylene, *p*-xylene, toluene, benzene, bromobenzene and chlorobenzene. This was done calorimetrically by determining the concentration at which maximum heat evolution per mole of solution is obtained when the liquids are mixed. Plots of the heats of mixing per mole of solution *versus* the mole % of chloroform are shown in Fig. 3. The symmetrical shape of the curves indicates that association between chloroform and an aromatic compound occurs in a one-to-one ratio.

Andrews and Keefer[4] have shown that a silver ion adds to an aromatic molecule in a one to one ratio and, to a smaller extent, in a two to one ratio. The present investigation shows no evidence for hydrogen bond formation of two chloroform molecules with a single aromatic molecule. This lack of evidence may be due in part to a lack of sensitivity of the method, rather than to the complete absence of such association. This would be true particularly for the weak electron donors which give broad heat of mixing–composition curves, making the location of the peaks more difficult. It may be concluded, however, that if there is association of chloroform to aromatic compound in two to one ratio, it must exist to an extent appreciably smaller than that of one to one ratio.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# Elastoviscous Properties of Amorphous Polymers in the Transition Region. I

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Experimental data on the stress–relaxation modulus $E_{r,T}(t)$ of a GR-S gum vulcanizate at a series of temperatures in the transition region are presented, and a "master curve" of log $Q(t/K)$ *versus* log $(t/K)$ is thereby constructed. The characteristic relaxation time, $K$, for each temperature is defined and tabulated. A distinctive temperature, $T_d$, is observed at which the activation energy for $K$ is a maximum. Analytical expressions are given which describe the GR-S master-curve with great accuracy. The same analytical procedure can be successfully applied to data previously obtained for polymethyl methacrylate. A reduced equation is proposed which describes the time and temperature dependence of $Q(t/K)$ in the transition region for both polymers.

## Introduction

It has been shown previously that for a given amorphous polymer, the stress relaxation curves determined at different temperatures may be made to coincide by a translation along the logarithmic time axis.[1] This makes possible the construction of a composite stress relaxation curve or "master curve" valid over an extended time scale at any given temperature. The master curve can be conveniently plotted in the form of log $E_{r,T_0}(t)$ *versus* log $(t)$, where $E_{r,T}(t)$, the relaxation modulus at a temperature $T$, is the stress per unit strain in a sample maintained at a constant small strain for a time, $t$. When plotted in this form a master curve for a given polymer is also valid at any other temperature by simply shifting the origin of the log time axis.

From the master curve $E_{r,T}(t)$ and from the amount of shift of the log time scale at each temperature a new function $Q(t/K)$ may be defined as

$$E_{r,T}(t) = Q(t/K) \qquad (1)$$

In equation (1) $K$ is a function of temperature alone which will be more explicitly defined subsequently, and $t$ has the same numerical value on both sides of the equation. The function $Q(t/K)$ is a universal function of $t/K$ which is valid at all temperatures, and may therefore be called the universal master relaxation curve for a given polymer.

An analytical or graphical representation of $Q(t/K)$ together with an analytical expression or tabulation of $K$ as a function of $T$ are a complete representation of the viscoelastic properties of an amorphous polymer at all times and temperatures in the range of strains where the Boltzmann superposition principle applies. They can be used in principle to calculate any other property such as dynamic modulus.

In a previous paper, it was shown that the viscoelastic behavior of amorphous polymers can be classified into three distinct regions: a glassy region ($E_{r,T}(t) \sim 10^{10.5}$ dynes/cm.$^2$) where the mechanical properties depend on previous thermal history, a transition region where the relaxation modulus lies approximately between $10^7$ dynes/cm.$^2$ and $10^{10.5}$ dynes/cm.$^2$ and is independent of thermal history and of the molecular weight of the polymer, and a rubbery region where the relaxation modulus is less than $10^7$ to $10^{7.5}$ dynes/cm.$^2$ and depends on the molecular weight of the polymer and on the presence or absence of cross links.[2]

In this paper new experimental data for $E_{r,T}(t)$ of a GR-S gum vulcanizate at a series of temperatures in the transition region are presented. The GR-S vulcanizate used is identical with that used and previously described.[1] A master curve is constructed, an analytical formulation of $Q(t/K)$ is given, and the $K$ values at different temperatures are tabulated. The results are compared with those previ-

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(1) A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3 (1945). See also J. D. Ferry, THIS JOURNAL, **72**, 3746 (1950).

(2) A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.*, in press.

ously obtained for polymethyl methacrylate and striking similarities between the behavior of these two apparently very different polymers are discussed.

## Experimental Results for a GR-S Gum Vulcanizate

The apparatus used in this investigation was a modification of the instrument described by McLoughlin.[3] Stress was measured by means of a Schaevitz differential transformer mounted on a spring dynamometer; the transformer output was fed into a Brown Electronik Recording Potentiometer. Temperatures in the range between −33 and −64° were maintained to an accuracy of 0.1-0.2°. The accuracy of the measured absolute moduli was primarily determined by the temperature control, and was approximately 10%. This accuracy was satisfactory considering the tremendous variation of modulus with temperature. In order to keep the stress in an easily measured range, the constant strain applied at different temperatures was varied between 0.3 and 18% according to the initial value of the modulus.

Figure 1 shows the stress-relaxation curves at various temperatures, plotted as log $E_{r,T}(t)$ *versus* log $t$. Duplicate points are shown on the curve at −49.5° to indicate the reproducibility of the data.

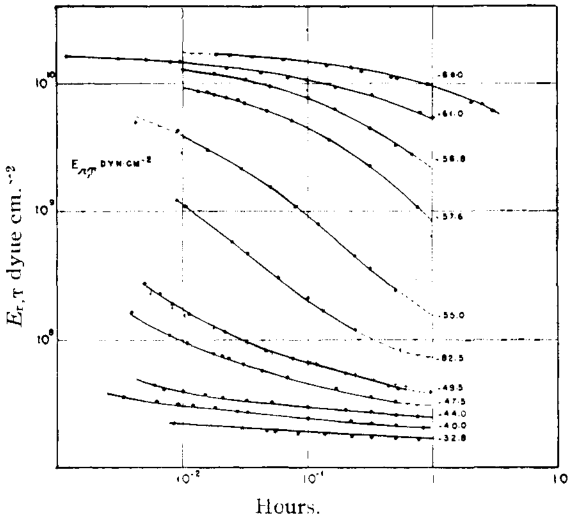

Fig. 1.—log $E_{r,T}(t)$ *versus* log ($t$) for GR-S gum stock.

**Master Curve and Definition of the Characteristic Relaxation Time $K$.**—In order to construct the master curve one may select an arbitary reference temperature and slide the plots of $E_{r,T}(t)$ at other temperatures along the log time scale until they superpose with the relaxation curve at the reference temperature $T_0$. The time scale of the master curve obtained in this way will be the time scale of the reference temperature $T_0$. The relation between the relaxation modulus $E_{r,T}(t)$ at temperature $T$ and the relaxation modulus $E_{r,T_0}(t)$ at temperature $T_0$ will then be

$$E_{r,T}(\kappa t) = E_{r,T_0}(t) \qquad (1a)$$

In equation (1a) $\kappa$ is a function of temperature alone which is completely determined if $T_0$ is given.[2] At first it is necessary to choose the reference temperature $T_0$ arbitrarily in order to construct the master curve. Once this is done, however, it is desirable to find a less arbitrary definition of $T_0$ and $\kappa$ particularly when different polymers are being compared.

This can be achieved as follows: the master curve of log $E_{r,T}(t)$ *versus* log $t$ in the transition region generally passes through an inflection point. We can define a new quantity, $K$, at any temperature as the time (in hours) required to attain this inflection point, so that $t/K = 1$ at the inflection point at all temperatures. $K$ has the dimensions of time whereas $\kappa$ was a dimensionless quantity.[2] The values of $K$ and $\kappa$ differ by the same numerical factor at all temperatures.

Table I gives the value of $K$ in hours for GR-S at the temperatures used to obtain the relaxation curves shown in Fig. 1. The quantity $K$ may be regarded as a *characteristic relaxation time* at each temperature.

TABLE I

TEMPERATURE DEPENDENCE OF CHARACTERISTIC RELAXATION TIME $K$ IN HOURS FOR GR-S AND POLYMETHYL METHACRYLATE

| GR-S Temp., °C. | GR-S log $K$ | Polymethyl methacrylate Temp., °C. | Polymethyl methacrylate log $K$ |
|---|---|---|---|
| −64.0 | 2.2 | 40 | 6.60 |
| −61.0 | 1.40 | 60 | 4.50 |
| −58.8 | 0.70 | 80 | 3.60 |
| −57.6 | .20 | 92 | 3.15 |
| −55.0 | −0.82 | 100 | 2.20 |
| −52.5 | −1.66 | 110 | 0.00 |
| −49.5 | −2.78 | 112 | −1.85 |
| −47.5 | −3.32 | 115 | −3.10 |
| −44.0 | −4.7 | 120 | −4.30 |
| −40.0 | −5.5 | 125 | −5.70 |
| −32.8 | −6.1 | | |

The universal master relaxation curve $Q(t/K)$ defined in equation (1) may now be introduced. The plot of log $Q(t/K)$ *versus* log $(t/K)$ for GR-S gum stock where $K$ is defined as above is shown in Fig. 2. The points shown on this graph are taken from the original data at the eleven different temperatures shown in Fig. 1. The experimental times were divided by the $K$ values given in Table I and then were plotted in Fig. 2.

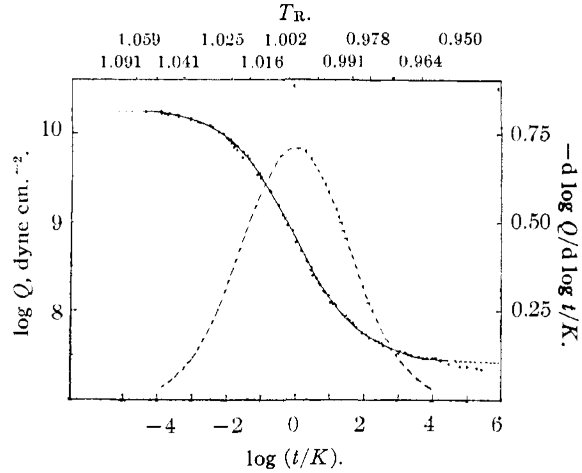

Fig. 2.—log $Q(t/K)$ *versus* log $(t/K)$ for GR-S; also −d log $Q(t/K)$/d log $(t/K)$ for GR-S.

In Fig. 2 there is also shown a plot of −d log $Q(t/K)$/d log $(t/K)$ *versus* log $(t/K)$. The maximum value of this plot obviously corresponds to the inflection point of the universal master curve.

**Definition of the Distinctive Temperature.**—The temperature dependence of $K$ for other polymers has previously been expressed by the Arrhenius relation $K = A \exp(H_{\text{act}}/RT)$.[4,5] The apparent activation energy is obtained from the relation

$$H_{\text{act}} = 2.303\, R \frac{\text{d} \log K}{\text{d}\,(1/T)} \qquad (2)$$

For polyisobutylene the value of $H_{\text{act}}$ was found to be approximately constant at high temperatures, increasing markedly however as the temperature is lowered toward the glass transition ("second-order transition") temperature.[4,5] For polymethyl methacrylate the apparent activation energy was found to go through a definite maximum.[2,3] This was also found to be the case with GR-S.

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[3] J. R. McLoughlin, Ph.D. Thesis, Princeton University, 1951.

[4] R. D. Andrews, N. Hofman-Bang and A. V. Tobolsky, *J. Polymer Sci.*, **3**, 669 (1948).

[5] G. M. Brown and A. V. Tobolsky, *ibid.*, **6**, 165 (1951).

In Fig. 3 is shown a plot of log $K$ *versus* $1/T$ and also a plot of $H_{\text{act}}$ (defined by equation 2) against $1/T$. The $H_{\text{act}}$ *versus* $1/T$ curve goes through a definite maximum at a certain temperature. (The plot of $H_{\text{act}}$ *versus* $T$ goes through a maximum at the same temperature.) This unambiguously defined temperature may be regarded as a distinctive temperature for each polymer and will be denoted by $T_{\text{d}}$. For the GR-S gum vulcanizate, the distinctive temperature $T_{\text{d}}$ is approximately −53°. This may be compared with the reported value of −61° for GR-S polymer for the "second-order transition" temperature obtained from the apparent discontinuity in heat capacity.[6]

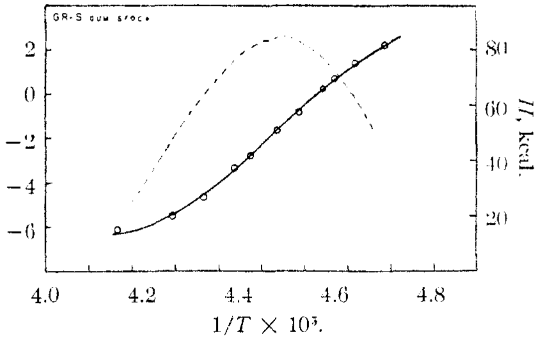

Fig. 3.—log $K$ *versus* $1/T$ for GR-S; also $H$ *versus* $1/T$ for GR-S.

**Analytical Expression for $Q(t/K)$ for GR-S.**—Seeking an empirical expression to fit the experimental results for $Q(t/K)$, we noticed that the negative derivative of the master curve approximated a Gauss error curve, *i.e.*

$$-\frac{\mathrm{d}\log Q(t/K)}{\mathrm{d}\log(t/K)} = A\exp\{-[h\log(t/K)]^2\} \qquad (3)$$

where $A$ and $h$ are the adjustable parameters of the Gauss error curve. Upon integrating (3) one obtains

$$A\int_{-\infty}^{\infty}\exp\{-[h\log(t/K)]^2\}\,\mathrm{d}\log(t/K) = \log E_1 - \log E_2 \qquad (4)$$

where $E_1$ and $E_2$ are the limiting values of the modulus at both ends of the transition region; *i.e.*, $E_1$ is the "glassy" modulus ($10^{10.24}$ dynes/cm.$^2$ for GR-S) and $E_2$ is the "rubbery modulus ($10^{7.44}$ dynes/cm.$^2$ for the GR-S gum vulcanizate). By evaluating the definite integral in equation (4) one obtains

$$A = \frac{h}{\pi^{1/2}}(\log E_1 - \log E_2) \qquad (5)$$

The equation of the master curve therefore is

$$\log Q(t/K) = \log E_2 + \frac{\log E_1 - \log E_2}{\pi^{1/2}}\int_{h\log t/K}^{\infty} e^{-x^2}\,\mathrm{d}x \qquad (6)$$

Equation (6) can be readily transformed into the more easily handled equation (7)

$$\log Q(t/K) = \frac{\log E_1 + \log E_2}{2} - \frac{\log E_1 - \log E_2}{2}\left[\frac{2}{\pi^{1/2}}\int_0^{h\log t/K} e^{-x^2}\,\mathrm{d}x\right] \qquad (7)$$

The quantity within the brackets is the tabulated probability integral.

The quantities $h$ and $\log E_1 - \log E_2$ were evaluated from the slope and intercept of a plot of

$$\log\left[-\frac{\mathrm{d}\log Q(t/K)}{\mathrm{d}\log(t/K)}\right] \textit{ versus } \log(t/K)^2$$

(This graph is not shown in the paper.) For the GR-S gum vulcanizate $h$ = 0.45 and $\log E_1 - \log E_2 = 2.80$. The excellent fit of equation (7) to the experimental points of the master curve is shown by the full curve of Fig. 2. This curve was obtained from equation (7) by taking $h$ = 0.45, $\log E_1 = 10.24$ and $\log E_2 = 7.44$. The agreement, as can be seen from Fig. 2 is excellent for temperatures ranging from −64 to −40°. Some deviation occurs at higher temperatures.

It is clear from equation (7) that when $t/K = 1$, $\log Q(t/K) = (\log E_1 + \log E_2)/2$. This, of course, means that $\log Q(t/K) = (\log E_1 + \log E_2)/2$ at the inflection point of the master curve if equation (6) is valid. However, this may also be used as an alternate way to define the characteristic relaxation time $K$, particularly in polymers where the inflection point on the master curve is not sharply defined. In other words, $K$ may be defined at any temperature as the time in hours required for $\log E_{\text{r,T}}(t)$ to attain the value $(\log E_1 + \log E_2)/2$.

**Analytical Expression for $Q(t/K)$ for Polymethyl Methacrylate.**—The method used for GR-S is also applicable to the previously obtained[2,3] master curve for polymethyl methacrylate. As shown in Fig. 4, the equation

$$\log Q(t/K) = 8.85 - 1.5\left[\frac{2}{\pi^{1/2}}\int_0^{0.31\log t/K} e^{-x^2}\,\mathrm{d}x\right] \qquad (8)$$

expresses the experimental results for polymethyl methacrylate quite accurately in the temperature range between 60 and 125°.

The $\kappa$ values for polymethyl methacrylate used in reference 2 were calculated from equation (1a), using as the reference temperature $T_0$ = 110°. Fortuitously this definition of $\kappa$ leads to a scale factor of unity for converting $\kappa$ values to $K$ values; this is because $E_{\text{r},383}(t)$ is exactly at the inflection point of the relaxation curve after 1 hr. Thus the table of $\kappa$ for polymethyl methacrylate given in reference 2 need only have the heading changed to conform to the definition of $K$ in this paper. The distinctive temperature $T_{\text{d}}$ for polymethyl methacrylate was reported as 111°.[3,7]

**Variation of the Characteristic Relaxation Time $K$ with Temperature.**—If a reduced equation for elastoviscous behavior of polymers were found to be valid, one might expect that the distinctive temperatures $T_{\text{d}}$ of various polymers would be corresponding temperatures. It would therefore be very interesting to compare the values of the mean relaxation times $K_{\text{d}}$ of various polymers at their respective distinctive temperatures.

In the case of GR-S, ($T_{\text{d}}$ = −53°), log $K_{\text{d}}$ is about −1.5. In the case of polymethyl methacrylate, ($T_{\text{d}}$ = 111°), log $K_{\text{d}}$ = −1.5 within the limit of accuracy of our measurements. This coincidence is obviously interesting and values of $K_{\text{d}}$ for

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(6) R. H. Wiley, G. M. Brauer and A. R. Bennett, *ibid.*, **5**, 609 (1950).

(7) The "second-order transition" temperature for polymethyl methacrylate was reported as 105° by S. Loshaek, 312th meeting, American Physical Society, Columbus, O., March 22, 1952.

other polymers should soon decide whether it is accidental.

In order to compare the temperature dependence of the mean relaxation time $K$ for both polymers, it seemed advisable to introduce a reduced temperature, $T_R = T/T_d$, and a reduced characteristic relaxation time $K_R = K/K_d$. A complete description of each polymer can then be provided by presenting the master curve, and along with the master curve a graphical presentation of the variation of log $K_R$ with $T_R$. This latter was achieved in Figs. 2 and 4 by considering the abscissa of the master curves as a log $K_R$ scale and indicating along the upper border of the graph the values of reduced temperature $T_R$ that correspond to the experimentally observed values of log $K_R$.

The $T_R$ keys shown in Figs. 2 and 4 for GR-S and polymethyl methacrylate are not identical. This is perhaps to be expected since the master curves themselves are not identical.

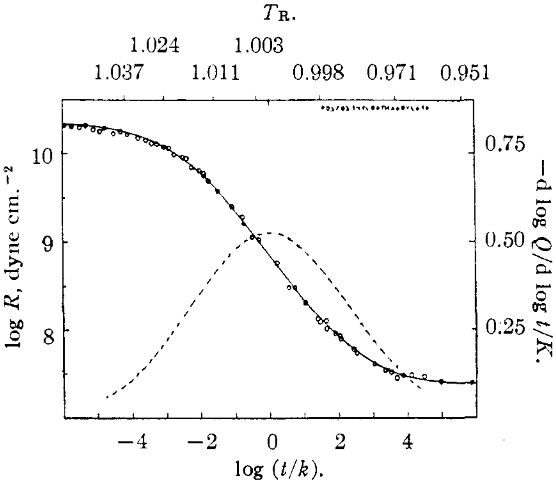

Fig. 4.—log $Q(t/K)$ *versus* log $(t/K)$ for polymethyl methacrylate; also −d log $Q(t/K)$/d log $(t/K)$ for polymethyl methacrylate.

**Reduced Equation for Viscoelastic Behavior of GR-S and Polymethyl Methacrylate.**—The master curves for stress relaxation of GR-S and polymethyl methacrylate could be made practically identical if one were to plot

$$[\log Q(t/K) - \log (E_1E_2)^{1/2}]/[\log(E_1/E_2)^{1/2}]$$

as a function of $h \log t/K$ as can be seen by inspection of equation (7).

It is reasonable to speculate about the result of placing the $T_R$ keys for the two polymers on such a reduced master curve. Since the abscissa of the reduced master curve is $h \log (t/K)$, the $T_R$ keys can be compared by plotting $h \log K_R$ *versus* $T_R$. As can be seen from Fig. 5, such a plot gives the same curve for both polymers. This means that the same $T_R$ key applies to both polymers on the reduced master curve. A reduced equation which applies for both can therefore be written

$$\frac{\log Q(t/K) - {}^1/_2 \log E_1E_2}{{}^1/_2 \log (E_1/E_2)} = -\frac{2}{\pi^{1/2}}\int^{\log y} \exp(-x^2)\mathrm{d}x \quad (9)$$

where $y = (t/K)^h = (t_R/K_R)^h$ and $t_R = t/K_d$.

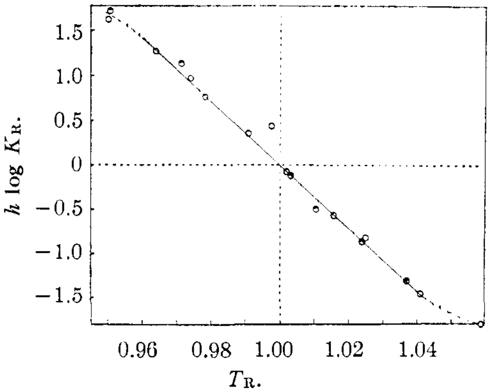

Fig. 5.—$h$ log $K_R$ *versus* $T_R$ for GR-S and polymethyl methacrylate: ○, GR-S; ●, polymethyl methacrylate.

In the region $0.95 < T_R < 1.05$, $K_R$ may be approximated by

$$h \log K_R = -36(T_R - 1) \quad (10)$$

Additional experimental data on other amorphous polymers will be necessary to test the generality of equations (9) and (10).

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