Temperature dependence of the zero-shear melt viscosity of oligomeric epoxy resins

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(Received 15 March 1983)

The melt viscosities of a homologous series of five epoxy resins based on bisphenol A and epichlorohydrin have been measured over a wide range of temperatures. It is shown that the temperature dependence of the zero-shear viscosity can be well described by the three-parameter Vogel equation. The Vogel parameters B and T_0 were found to increase with increasing glass transition temperature, T_g, of the resin, while the ratios B/T_g and T_0/T_g remained approximately constant. This constancy of the reduced Vogel parameters implies that T_g can be used as a corresponding states parameter to superimpose the viscosity–temperature data of all five resins onto a single master curve. The existence of such a master curve is of practical use, as it enables melt viscosities of epoxy resins to be predicted over a fairly extensive temperature range from only two quantities, viz. the value of T_g and one single viscosity value at a given temperature.

INTRODUCTION

The flow properties of polymer melts are of great practical importance in both polymer characterization and polymer processing. Accordingly, for a wide variety of polymers a very large amount of data are to be found relating the shear viscosity to molecular parameters (molecular weight, molecular weight distribution, branching) and processing parameters such as shear rate (or shear stress) and temperature. For epoxy resins, however, only a limited amount of melt viscosity data exist. In the past, these materials were mainly processed via the solution state and, therefore, solution viscosities have been frequently used for the viscosity characterization. At present, however, epoxy resins are increasingly being processed via the molten state (for example, in powder coating formulations) and this has led to a growing interest in the melt viscosities of epoxy resins at processing temperatures.

In this article we report zero-shear melt viscosity data for a number of oligomeric epoxy resins over a wide range of temperatures. The data are presented in the form of a master curve by using the glass transition temperature T_g of the resins as a corresponding states parameter. With this master curve, it is possible to calculate the viscosity–temperature dependence of an epoxy resin knowing only two quantities, the value of T_g and one single viscosity value at a given temperature.

EFFECT OF TEMPERATURE ON VISCOSITY

The zero-shear viscosity of polymeric liquids is highly dependent upon temperature. For amorphous polymers it may increase by a factor of 10^{13} when the glass transition is approached from a suitably high processing temperature. So far, no single equation is known that can adequately describe the temperature dependence of

viscosity over such a wide range. The several theoretical and semi-empirical equations proposed adequately describe viscosity–temperature dependencies in different, relatively narrow, temperature regions only.

At temperatures well above T_g ($T > T_g$ + approx. 200 K) the temperature dependence of viscosity can be represented by the Arrhenius equation, based on the Eyring hole theory of liquids[1]:

$$\eta = Z \, e^{E/RT} \qquad (1)$$

in which η is the zero-shear viscosity, Z a constant, E the activation energy for viscous flow, R the universal gas constant and T the absolute temperature. The value of the activation energy is generally in the range between 20 and 200 kJ mol^{-1} and depends on the chemical structure of the polymer. This Arrhenius type of temperature dependence, however, fails in the neighbourhood of the glass transition temperature T_g. Plots of log η versus $1/T$ are, in general, markedly non-linear in the region T_g to T_g + approx. 100K. The apparent activation energy is not a constant but is itself strongly temperature-dependent and increases as the temperature decreases[2].

In the temperature region near T_g ($T < T_g$ + approx. 100K), the temperature dependence of the zero-shear viscosity may be represented by the Vogel equation:

$$\log \eta = \log A + \frac{B}{T - T_0} \qquad (2)$$

in which A, B and T_0 are constants. Equation (2) is equivalent to the well known WLF equation[2,3] which is based upon the concept of free volume. At very high temperatures ($T \gg T_0$) the Vogel equation approaches the Arrhenius equation, which implies that the Vogel parameter B is related to the constant activation energy for

viscous flow E by $E = 2.3RB$. The values observed for the parameter T_0 are usually some 50K lower than the T_g values. As to the molecular interpretation of the Vogel parameters, the work of Miller is of particular importance. According to Miller T_0 is the temperature at which the conformational entropy, associated with rotational isomerization about main-chain bonds, becomes zero[4] and B is related to the intramolecular energy barriers to rotation about these bonds[4,5]. The Vogel parameter A is primarily governed by the molecular weight of the polymer[6].

Besides the equations (1) and (2), several others have been proposed. These will not be discussed here, as they do not fit the experimental data as well as equation (2) and/or because they are much more complicated. An excellent literature review covering a number of the equations is given by Kumar[7].

More recently, several new attempts have been made to derive a universal equation describing the temperature dependence of viscosity of polymeric and non-polymeric liquids over the whole range of temperatures. The most successful of these approaches have utilized the glass transition temperature T_g as a normalization or corresponding states parameter and have used the temperature ratio T/T_g rather than a temperature difference such as $T - T_g$ as a reduced temperature scale. Magill and Li[8], for instance, have found empirically a single master curve for a total of seven polymeric and non-polymeric liquids by plotting the logarithm of the viscosity ratio $\eta(T)/\eta(1.24T_g)$ against T/T_g. This master curve covers the temperature range up to $T = 2.5T_g$; at low temperatures the curve is markedly non-linear corresponding to equation (2), while at very high temperatures the curve can be approximated by a straight line corresponding to equation (1). Van Krevelen and Hoftijzer[9] have since analysed more than ten polymeric liquids using essentially the same plotting procedure. They found that in the temperature region near T_g ($T < 1.2T_g$), the temperature dependence of viscosity could be described by a single curve for all polymers. At higher temperatures, however, the curves of the various polymers followed completely different paths.

In the present paper the glass transition temperature T_g is also used as a corresponding states parameter to obtain a master curve for the viscosity–temperature data of epoxy resins.

EXPERIMENTAL

Material characterization

The samples used in this study were commercially available epoxy resins: EPIKOTE 828, 1001, 1004, 1007 and 1009, all manufactured by Shell. The resins are prepared by reacting diphenylolpropane (bisphenol A) with epichlorohydrin under the catalytic influence of alkali.

The idealized structure of the resins is as follows:
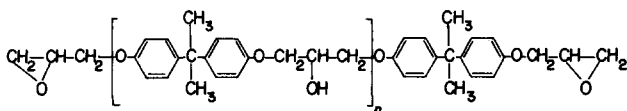
The resins are liquid or solid at room temperature depending on the value of n in the formula. For EPIKOTE 828, a liquid grade, the value of n is about 0.1. The other four resins are solid grades, n varying from

about 2 for EPIKOTE 1001 to about 12 for EPIKOTE 1009. Some other characteristic properties of the resins are summarized in *Table 1*.

Viscosity measurements

Because of the limitations of the various instruments, more than one had to be used.

The viscosities of the liquid resin were measured between 0° and 80°C with an Epprecht viscosimeter (Couette type). The measurements were performed over a range of shear rates so as to produce reliable data for the zero-shear viscosity. The temperature variations during the measurements were less than $\pm 0.1°C$.

The viscosities of the solid resins were measured with a Weissenberg rheogoniometer, model R 16, using the cone-and-plate arrangement in the rotational or steady shearing mode. The platen diameter was 2.5 cm and the cone angle 1° 58'. All measurements were performed in a nitrogen atmosphere. The resin specimen, in the form of flakes or powder, was placed at the centre of the lower platen (the cone), which had been preheated to the required test temperature. During the melting of the specimen the upper platen was lowered slowly to the correct gap setting and excess resin removed from the platens. The measurements were started when the test temperature was reached again. All measurements were carried out with increasing values of the shear rate. For each shear rate at least three shear stress–time traces were recorded. The average of the individual shear stress values at equilibrium was used for the calculation of the viscosity. At high shear rates problems were sometimes encountered by the sample shearing out, as indicated by a continuously decreasing shear stress with time. Such measurements, however, were rejected. The measurements were performed in the temperature range between $T_g + 15°C$ and $T_g + 120°C$, the upper limit being fixed by thermal instability effects. Owing to the rather poor temperature control of the rheogoniometer, the test temperatures were only accurate to within $\pm 0.5°C$. Mainly as a result of temperature errors the reported viscosity values at temperatures close to T_g are only accurate to within $\pm 25\%$, in contrast to the viscosity values at temperatures far removed from T_g, which are accurate to within $\pm 5\%$.

Because of these experimental difficulties, several additional measurements were taken with an Instron capillary rheometer to check the validity of the rheogoniometer data. The capillary used here had the following dimensions: diameter 0.8 mm, length-to-diameter ratio 40 and entry angle $= 90°$. No corrections were made for end effects and non-parabolic flow profiles.

Table 1 Some characteristic properties of the resin samples used in this study

Sample	Solution viscosity at 25°C* (Pa s)	Epoxy molecular mass (kg kEq^{-1})	$\bar{M}_n$[†]	T_g (K)
EPIKOTE 828	–	189	376	258
EPIKOTE 1001	0.143	491	875	303
EPIKOTE 1004	0.52	885	1495	323
EPIKOTE 1007	1.90	1932	2355	343
EPIKOTE 1009	7.87	2913	3020	352

* 40 wt% solution in butyldioxitol
[†] Calculated from end group analysis data

Figure 1 shows the viscosity–shear stress dependence of EPIKOTE 1004 at two temperatures obtained with the two different techniques. It is clear that there is a very good quantitative agreement between the rheogoniometer and capillary rheometry data, in spite of the experimental difficulties. Furthermore, *Figure 1* clearly illustrates that the molten resin exhibits Newtonian behaviour up to relatively high shear stresses or shear rates. Non-Newtonian behaviour, in fact, starts at shear stresses of about 10^4 Pa or higher. All the viscosity data presented in this paper were collected at shear stress values well below 10^4 Pa and thus can be considered as zero-shear or Newtonian viscosities. Similar data showing the Newtonian behaviour of epoxy resins up to very high shear rates (stresses) were reported by Aleman[10,11].

Glass transition measurements

The T_g values of the resin samples were measured with a Perkin-Elmer differential scanning calorimeter, model DSC-2. The samples, varying in mass from 10 to 15 mg, were run in standard aluminium sample pans with an empty pan as the reference. All scanning in the instrument was conducted under an atmosphere of helium. The temperature calibration of the instrument was carried out at a heating rate of 20°C min^{-1} using pure substances with well known transition temperatures, such as cyclohexane and indium.

In order to eliminate thermal history effects the samples were first preheated at 150°C for 1 min, thereafter quickly cooled (320°C min^{-1}) below T_g and then scanned immediately at a rate of 20°C min^{-1} to detect the glass transition. *Figure 2* shows the thermograms thus obtained for two of the samples. As can be seen, the glass transitions are visible as pure baseline shifts. For the sake of reproducibility, the T_g values were taken as the point of intersection of the extrapolated baseline at the low-temperature end and the tangent to the curve at the inflection point. The T_g values thus obtained were reproducible to within 1°C. The results are included in the last column of *Table 1*.

Figure 2 Typical thermograms of the glass transition range for epoxy resins: curve A, EPIKOTE 828; and curve B, EPIKOTE 1004
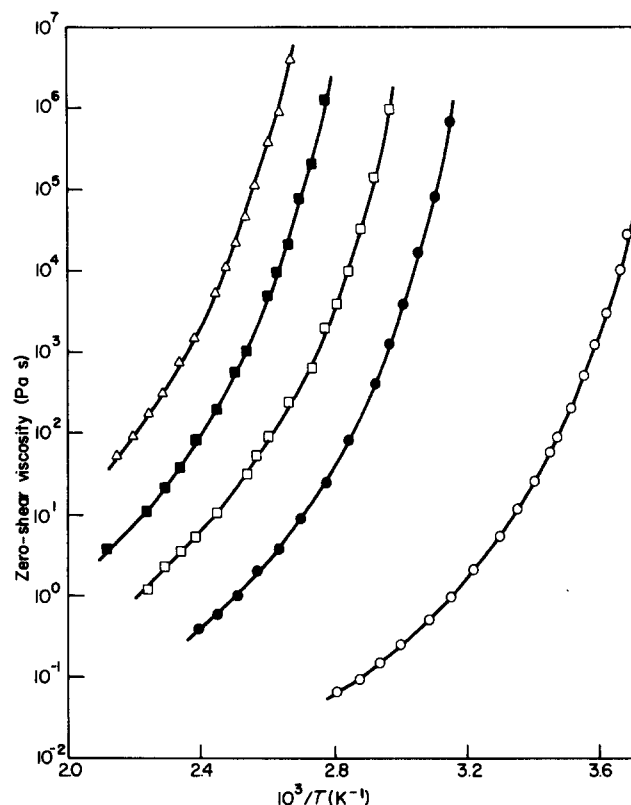
Figure 3 Effect of temperature on the zero-shear melt viscosity of epoxy resins: EPIKOTE 828 (O), EPIKOTE 1001 (●), EPIKOTE 1004 (□), EPIKOTE 1007 (■), EPIKOTE 1009 (△)

RESULTS AND DISCUSSION

Figure 3 shows the viscosity–temperature data of the epoxy resins. For all resins the plots of log η *versus* $1/T$ are markedly non-linear, i.e. the Arrhenius type of temperature dependence is not obeyed over wide intervals of temperature. The apparent activation energy for viscous flow E, calculated from the equation

$$E = R \frac{d(\ln \eta)}{d(T^{-1})} \tag{3}$$

is, therefore, not a constant but strongly temperature-dependent. In the case of EPIKOTE 1004, for instance, E varies from about 100 kJ mol^{-1} at relatively high temperatures (125°–175°C) to about 400 kJ mol^{-1} at low temperatures (60°–70°C). These high values illustrate that the melt viscosity of epoxy resins is extremely sensitive to
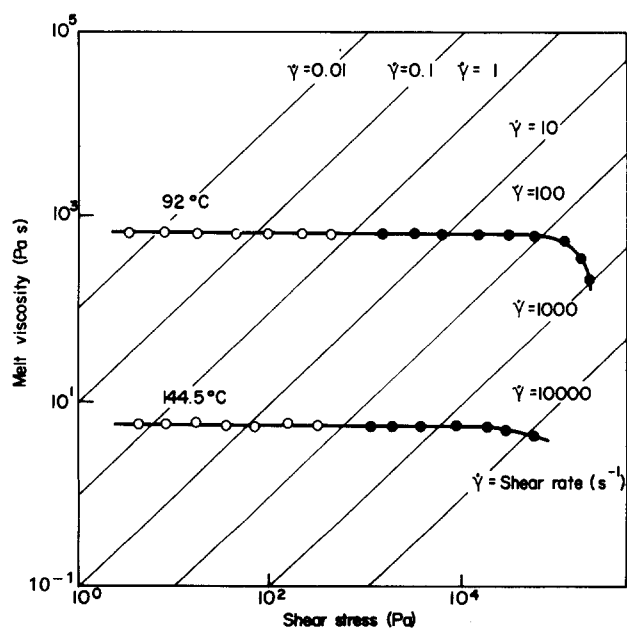

Figure 1 Effect of shear stress on the melt viscosity of EPIKOTE 1004 at two temperature levels: rheogoniometer data (O) and capillary rheometry data (●)
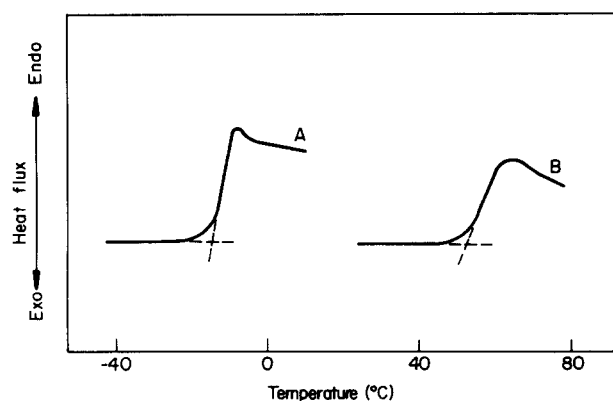
temperature changes over the whole temperature range studied. At low temperatures (say 15°C above T_g) a temperature change of 1°C changes the resin viscosity by 50%. Constant, temperature-independent flow activation energies were recently reported by Aleman[11]; his results, however, are based on a limited number of viscosity data in a relatively narrow temperature interval.

The temperature dependence of the melt viscosity of epoxy resins can be well represented by the Vogel equation. *Figure 3* shows the good agreement between the fitted Vogel equations, represented by the drawn curves, and the experimental data for all five resins. Only at very low temperatures are considerable deviations found (up to 25%). For the calculation of the parameters of the Vogel equation, a sequential simplex computer program[12] for solving minimization problems was used. The temperature function was minimized in all cases, as the deviations of the experimental data from the Vogel equation are more likely due to temperature errors than to viscosity errors. The values obtained for the Vogel parameters are given in *Table 2*.

The accuracy with which the Vogel parameters are obtained is rather poor, because these parameters are asymptotes of the Vogel equation far outside the experimental region. The parameters A and B are particularly sensitive to the actual experimental data (number and accuracy of data points) and result in an uncertainty in A and B of about $\pm 25\%$ and $\pm 25K$. Nevertheless, it follows from *Table 2* that all the three Vogel parameters increase with increasing glass transition temperature (given in *Table 1*) and, moreover, that the ratios B/T_g and T_0/T_g are approximately constant for the five resins. This constancy of B/T_g and T_0/T_g implies that plots of $\log \eta$ versus T/T_g (or T_g/T) only differ in vertical position and thus can be reduced to one single master curve by applying a vertical shift. *Figure 4* shows such a master curve obtained by plotting $\log[\eta(T)/\eta(1.2T_g)]$ versus T_g/T. The vertical shift factor was arbitrarily chosen as $\eta(1.2T_g)$; the plots thus obtained are similar to those proposed by van Krevelen and Hoftijzer[9] and also by Magill and Li[8]. The calculated curve has the following form:

$$\log \frac{\eta(T)}{\eta(1.2T_g)} = \log 38 \times 10^{-6} + \frac{1.38}{(T/T_g - 0.89)} \quad (4)$$

The master curve fits all experimental data reasonably well. As expected, the deviations are greatest at the high viscosity end.

The existence of such a master curve is of the utmost practical importance since knowledge of only two quantities, for instance the value of T_g and one viscosity at a given temperature, or two viscosities at different temperatures, is now sufficient for the calculation of viscosities of both liquid and molten solid epoxy resins over a fairly extensive temperature range.

Table 2 Vogel parameters of resin samples

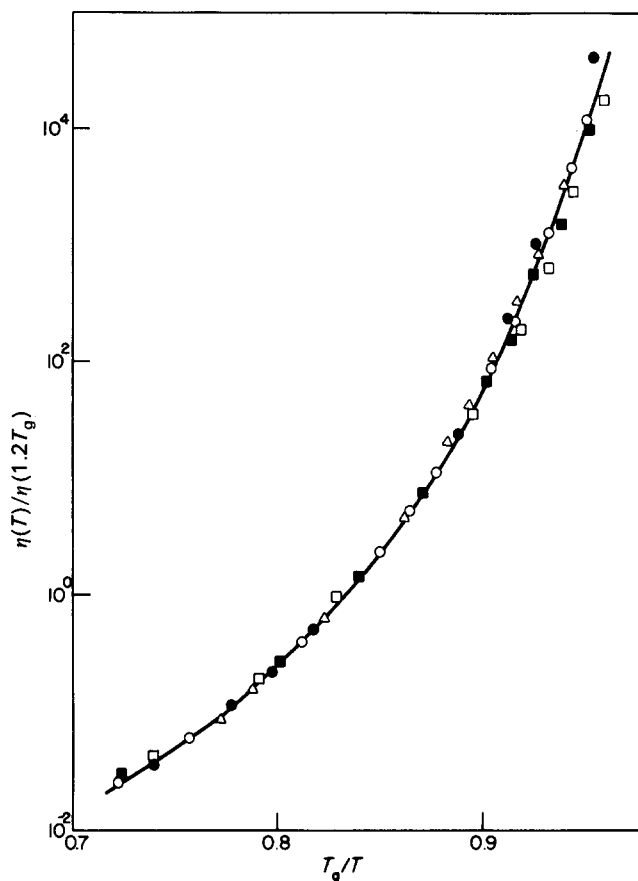| Sample	$A \times 10^3$ (Pa s)	B (K)	T_0 (K)	B/T_g	T_0/T_g
EPIKOTE 828	1.2	339	231	1.31	0.89
EPIKOTE 1001	0.75	393	273	1.30	0.90
EPIKOTE 1004	2.2	467	282	1.45	0.88
EPIKOTE 1007	6.2	471	303	1.37	0.88
EPIKOTE 1009	18	539	310	1.53	0.88

Figure 4 Master curve for the temperature dependence of zero-shear viscosity of epoxy resins (see *Figure 3* for symbols)

CONCLUSIONS

The following conclusions can be drawn from the present study of the melt viscosities of a homologous series of five epoxy resins over a wide range of temperatures.

The temperature dependence of the zero-shear melt viscosity of epoxy resin homologues can be adequately described by the three-parameter Vogel equation; the Vogel parameters B and T_0 are found to increase with increasing glass transition temperature T_g such that the ratios B/T_g and T_0/T_g are approximately constant.

With the use of the glass transition temperature as a corresponding states parameter, it is possible to super-impose the (zero-shear) viscosity–temperature data of the resins in the form of a single master curve. Melt viscosities of epoxy resins at different temperatures can now easily be predicted from the knowledge of only two quantities, viz. the value of T_g and one single viscosity value at a given temperature.

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