Melt Viscosity at Glass Transition Temperature for Some Epoxide Oligomers

INTRODUCTION

The diglycidyl ether of bisphenol-A (DGEBA), one of the epoxide oligomers, is usually manufactured by the direct addition of epichlorohydrin to bisphenol-A in the presence of sodium hydride, which is called the conventional process or the solvent-finished process. Another process, the advancement or fusion process, involves the reaction of low-molecular-weight DGEBA with bisphenol-A in order to advance the molecular weight.[1] Both types of DGEBA oligomers are described in the same structural formula (Table I).[2-4]

The viscoelastic behavior around the glass transition temperature (T_g) is difficult to measure for both polymers and oligomers. The direct current (dc) conductivity, on the other hand, can be measured over wide temperature ranges including T_g.[3,5] This article focuses on the analysis of the relationship between the melt viscosity and the dc conductivity for some advancement-type DGEBA oligomers, in order to understand the viscosity behavior at the T_g for the oligomer in terms of the difference between polymer and oligomer.[6-8]

EXPERIMENTAL

Materials

The DGEBA oligomers used in this study were Epikote 1001F, 1002F, and 1004F (Yuka Shell Epoxy), which were manufactured by the advancement process. The $\bar{M}_w$'s for three oligomers are from 1969 to 3606. The characteristics of the samples are summarized in Table I.

Measurements

Viscosity and the dc conduction measurements were performed in the same manner as described before.[3,4]

The T_g was measured using a DuPont 9900 differential scanning calorimeter (DSC). The temperature scan was at a rate of 20°C/min. The T_g was determined as the in-tersection point of the baseline and the transition line in the heat flow vs. temperature curve. There are several measuring methods of T_g. Although the T_g value slightly varies depending on the type of measurement, the DSC method was used for determining the T_g of the epoxide oligomer at the point of consistency with the results of previous studies.[3-5]

RESULTS AND DISCUSSION

Temperature Dependences of Melt Viscosity and Conductivity

In a previous study,[4] the temperature dependencies of the melt viscosity (η) and the dc conductivity (σ) for the conventional-type DGEBA oligomer were found to be governed by the following Williams–Landel–Ferry (WLF) equations.[9]

$$\log \frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \tag{1}$$

where $\eta(T)$ is the melt viscosity at temperature T ($T_g \leq T \leq T_g + 100°C$), and C_1 and C_2 are parameters.

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1''(T - T_g)}{C_2'' + T - T_g} \tag{2}$$

where $\sigma(T)$ is the dc conductivity at T ($T_g \leq T \leq T_g + 100°C$), and C_1'' and C_2'' are parameters.

The temperature dependencies of η and σ for three advancement-type DGEBA oligomers were investigated in terms of the WLF equation. The temperature dependencies of η and σ are plotted for two advancement-type oligomers, Epikote 1001F and 1002F, in Figures 1 and 2, respectively. The WLF equation was found to be applicable to the temperature dependencies of both η and σ for Epikote 1001F and 1002F. Similar behavior was also observed for the other DGEBA oligomer, Epikote 1004F. The best-fit WLF parameters are summarized in Table I.

Table I   Properties and WLF Parameters for Advancement-Type DGEBA Oligomers

| DGEBA Oligomer[a] | T_g (°C) | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | WLF Parameters | | | | | |
| | | | | Viscosity | | Conductivity | | | |
				C_1	C_2	C_1''	C_2''	k	C_1''/C_1
Epikote 1001F	31	1696	1.78	14.10	49.2	12.24	50.8	0.86	0.87
Epikote 1002F	42	2111	1.79	14.13	50.7	11.63	51.3	0.82	0.82
Epikote 1004F	57	3606	1.98	14.94	43.2	9.71	46.8	0.63	0.65

[a]
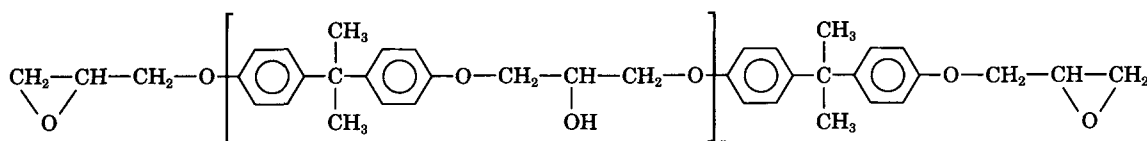
Comparison of Melt Viscosity with Conductivity

Log-log plots of melt viscosity (η) vs. dc conductivity (σ) for three advancement-type oligomers are shown in Figure 3. A linear relationship is observed for each log-log plot in Figure 3, which provides the following experimental relationship between $\eta(T)$ and $\sigma(T)$:

$$\sigma(T)[\eta(T)]^k = \text{const.} \tag{3}$$

where k is an exponent ($0.63 \leq k \leq 0.86$). This is the same relationship obtained for the conventional-type DGEBA oligomers in a previous study.[4] If Eq. (3) is valid at the T_g of the oligomer, the following relations are obtained:

$$\sigma(T)[\eta(T)]^k = \sigma(T_g)[\eta(T_g)]^k \tag{4}$$

$$\log \sigma(T) + k \log \eta(T) = \log \sigma(T_g) + k \log \eta(T_g) \tag{5}$$

According to the free volume theory,[9] on the other hand, the WLF C_2 parameter is determined by the characteristics of an oligomer or a host oligomer matrix only, as described below.

$$C_2 = f_g/\alpha_f \tag{6}$$

where f_g is the free volume fraction at the T_g and α_f is the thermal expansion coefficient of the free volume. The C_2 parameters for η and σ are expected to have the same
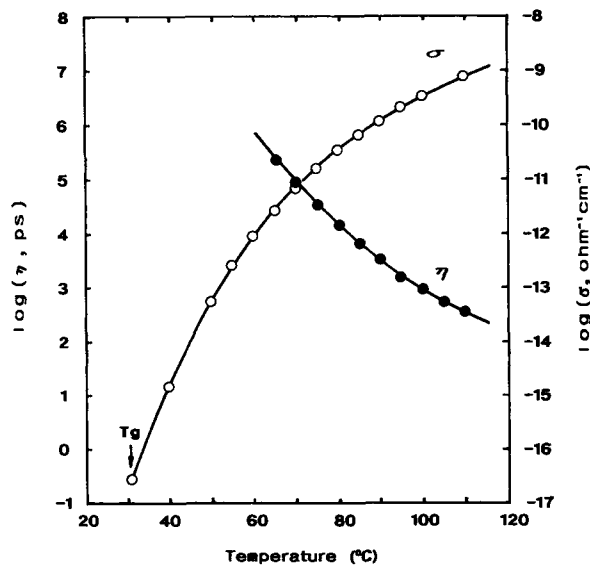
Figure 1   Temperature dependence of melt viscosity η and dc conductivity σ for Epikote 1001F: (●) η and (○) σ.
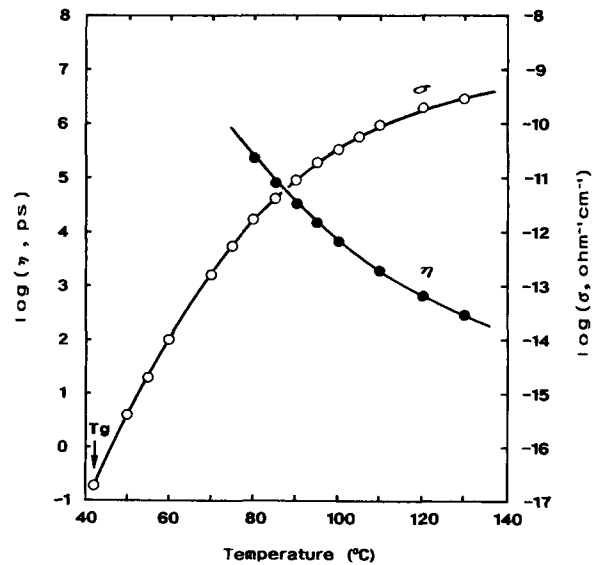
Figure 2   Temperature dependence of melt viscosity η and dc conductivity σ for Epikote 1002F: (●) η and (○) σ.
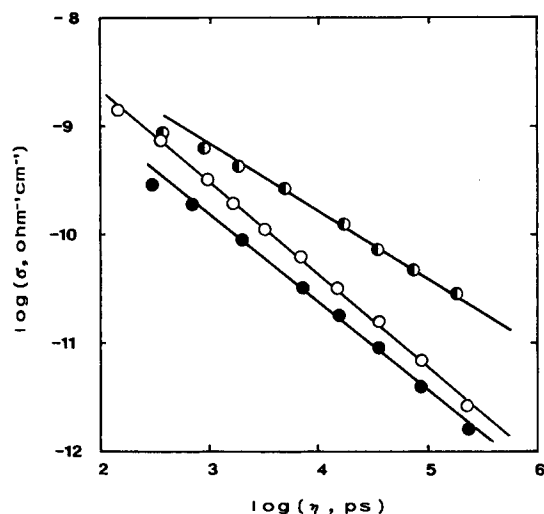
Figure 3 Relationship between log η and log σ for the advancement-type DGEBA oligomers: (O) Epikote 1001F, (●) Epikote 1002F, and (◐) Epikote 1004F.

value for the same oligomer or host oligomer. Table I shows that the value of C_2'' is almost equal to that of C_2 for three advancement-type oligomers. When the C_2'' parameter for σ has the same value as C_2 for η, dividing Eq. (2) by Eq. (1) gives the following simple relationship:

$$\log[\eta(T)/\eta(T_g)]/\log[\sigma(T)/\sigma(T_g)] = -C_1/C_1'' \quad (7)$$

Equation (7) becomes

$$\log \sigma(T) - \log \sigma(T_g)$$

$$= -(C_1''/C_1)[\log \eta(T) - \log \eta(T_g)] \quad (8)$$

$$\log \sigma(T) + (C_1''/C_1)\log \eta(T)$$

$$= \log \sigma(T_g) + (C_1''/C_1)\log \eta(T_g) \quad (9)$$

These rearrangements show that Eq. (9), which is obtained from the analysis of the temperature dependencies for σ and η, respectively, has the same form as Eq. (5), which is experimentally derived from the direct comparison of σ and η for the epoxide oligomer. Table I shows that the coefficient k in Eq. (5) has almost the same value as C_1''/C_1 for three advancement-type oligomers, which supports the above discussion.
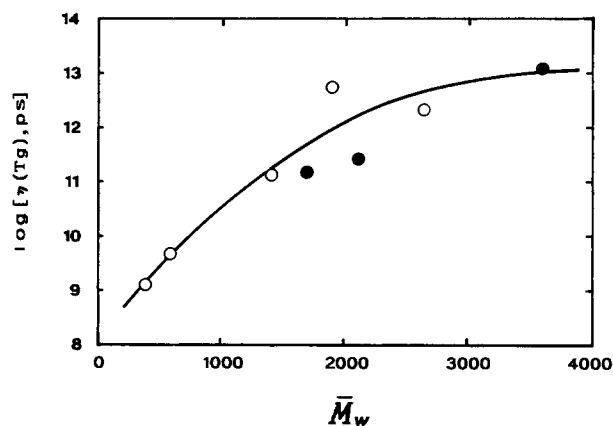
Melt Viscosity at T_g

Generally, the WLF equation is valid in the temperature range from T_g to $T_g + 100°C$. Equation (3) is also considered to be valid at the T_g of the oligomer judging from the WLF-type temperature dependence for σ and η of the oligomer. The melt viscosity at the T_g, $\eta(T_g)$, is difficult to measure. The dc conductivity at the T_g, $\sigma(T_g)$, can be

actually measured for the DGEBA oligomer (Figs. 1 and 2), so that $\eta(T_g)$ is calculated from $\sigma(T_g)$ using Eq. (4), which describes the relationship between $\eta(T_g)$ and $\sigma(T_g)$. Although both η and σ were measured for the conventional-type DGEBA oligomer in a previous study,[4] the estimation of $\eta(T_g)$ was not discussed. In Figure 4 the relationship between the calculated $\eta(T_g)$ and $\bar{M}_w$ is plotted for three advancement-type DGEBA oligomers ($1969 \le \bar{M}_w \le 3606$) along with that for the conventional types ($388 \le \bar{M}_w \le 2640$). Figure 4 indicates that the $\eta(T_g)$ value of the DGEBA oligomer increases from 10^9 to 10^{13} P with the increase in $\bar{M}_w$ and appears to saturate at around 10^{13} P for high $\bar{M}_w$ oligomers ($\bar{M}_w > $ ca. 3000).

The glass transition of a polymer or an oligomer is regarded as the state in which the free volume fraction is around 0.025, which means that the melt viscosity is not always a constant at the T_g. The melt viscosity at the T_g is said to be around 10^{13} P for many polymers having some degree of molecular entanglement.[10] An oligomer, especially the DGEBA having a rigid structure, is considered to have little molecular entanglement. Figure 4 shows that the melt viscosity at the T_g, $\eta(T_g)$, depends on the $\bar{M}_w$ for the DGEBA oligomer ($388 \le \bar{M}_w \le 3606$) and appears to be similar for the oligomer in a higher $\bar{M}_w$ region ($\bar{M}_w > $ ca. 3000). A polymer has a larger $\bar{M}_w$ than that of an oligomer. The behavior of $\eta(T_g)$ for a polymer is roughly predicted from the $\bar{M}_w$ dependence of $\eta(T_g)$ for the DGEBA oligomer. The finding for the epoxide oligomer in Figure 4 implies that the $\eta(T_g)$ for a high $\bar{M}_w$ polymer essentially depends on the characteristics of the polymer as well as for a low $\bar{M}_w$ epoxide oligomer, and the influence of $\bar{M}_w$ on the $\eta(T_g)$ becomes small for the polymer having a higher $\bar{M}_w$ than the epoxide oligomer. The long molecular chain (the large molecular weight and the entanglement) is considered to narrow the difference in the melt viscosity at the T_g between many polymers which have different $\bar{M}_w$'s and chemical structures.

An oligomer has a $\bar{M}_w$ between a monomer and a polymer. The study of the DGEBA oligomers having various

Figure 4 Relationship between melt viscosity at T_g $\eta(T_g)$ and $\bar{M}_w$ for DGEBA oligomers: (●) advancement-type oligomer and (O) conventional-type oligomer.

$\bar{M}_w$'s reveals that the melt viscosity at the T_g, which is said to be similar for many polymers, clearly depends on the $\bar{M}_w$ for the epoxide oligomers. Investigation of the difference between the oligomer and the polymer may provide useful information, from a different point of view, for better understanding of the viscoelastic behavior of the polymer.

CONCLUSIONS

The melt viscosity (η) at the glass transition temperature (T_g) for an epoxide oligomer was estimated from the direct current conductivity (σ), which was actually measured at the T_g, through the linear relationship between log η and log σ. The η value at the T_g for the DGEBA oligomer increases from 10^9 to 10^{13} P with the increase in the weight average molecular weight ($\bar{M}_w$) ($388 \leq T_g \leq 3606$) and appears to saturate at around 10^{13} P for a high $\bar{M}_w$ oligomer ($\bar{M}_w > $ ca. 3000). This finding for the epoxide oligomer implies that the melt viscosity at the T_g for a high $\bar{M}_w$ polymer essentially depends on the characteristics of the polymer as well as for a low $\bar{M}_w$ epoxide oligomer. The long molecular chain (the large molecular weight and the entanglement) is considered to narrow the difference in the melt viscosity at the T_g between many polymers which have different $\bar{M}_w$'s and chemical structures.

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