

MECHANICAL RELAXATION TIME OF A TWO-COMPONENT EPOXY NETWORK-LiClO₄ POLYMER ELECTROLYTE*

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ABSTRACT

The mechanical relaxation time of a two-component epoxy network-LiClO₄ system as a polymer electrolyte was investigated. The network is composed of diglycidyl ether of polyethylene glycol (DGEPEG) and triglycidyl ether of glycerol (TGEG), wherein LiClO₄ was incorporated and acts as both the ionic carrier and the curing catalyst. As the relaxation time is informative to the segmental mobility, which is known to be essential for ionic conductivity, the average relaxation times of the specimens were determined through master curve construction. Experimental results showed that the salt concentration, molecular weight of PEG in DGEPEG and DGEPEG/TGEG ratio have profound effect on the relaxation time of the specimen. Among these factors, the former reinforces the network chains, leading to lengthen the relaxation time, whereas the latter two are in favour of the chain flexibility and show an opposite effect. The findings was rationalized in terms of the free volume concept.

INTRODUCTION

Over the past decade, much interest has been focused on polyethylene oxide (PEO) as a polymer host capable of dissolving a range of inorganic salts, because the system is expected to be applicable as an electrolyte to solid state batteries and electrochemical devices^[1]. While the PEO-alkali metal salt system is among the most highly conductive ($\sim 10^{-3}$ – 10^{-4} S/cm) at 100 °C in solid polymer electrolytes, the high degree of crystallinity of the PEO system at room temperature interferes with the ion transport and results in the ionic conductivity to a level too low to meet the requirement of an electrolyte used in room temperature rechargeable lithium batteries ($\sim 10^{-5}$ S/cm). A variety of approaches has been adopted to overcome the difficulty arising from crystallinity, e. g., by copolymerizing with monomers other than ethylene oxide (EO) to hinder the long EO sequences from forming so as to inhibit the ability of crystallizing, by grafting non-crystallizable short EO segment or polyethylene glycol (PEG, a low molecular weight analogue of PEO) onto the main chain of a non-crystalline polymer having active groups to connect the PEG group, and by making the PEG structure crosslinked through chemical or radiation method^[2, 3]. Recently we have synthesized a two-component epoxy network system composed of diglycidyl ether of polyethylene glycol (DGEPEG) and triglycidyl ether of glycerol (TGEG), wherein the lithium perchlorate was incorporated. This system has a peculiarity

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Received November 16, 1991

that not merely can the lithium perchlorate provide ionic carriers but also catalyse the crosslinking reaction of the epoxy groups without adding an usual curing catalyst. Because of the presence of three dimensional networks and more salvation active units being contained in the system, this two-component epoxy system features mechanically strong and electrically highly conductive ($\sim 10^{-5}$ S/cm)^[4].

It has been widely recognized that the ionic conductivity of a polymer electrolyte is governed by the product of the number of ionic carriers and their mobility, and that the latter is closely concerned with the segmental motion of the host polymer^[5]. Since it is known that the reciprocal of the relaxation time is informative to characterize the backbone motion of a network^[6], the effects of salt concentration, PEG chain length between crosslinks and the ratio of DGEPEG to TGEPEG on relaxation time would inevitably influence the conductivity. However, it is impossible to evaluate this value directly by means of a simple experimental way, such as dynamic mechanical analysis, stress relaxation, etc. As in the case of the conventional dynamic mechanical method, the available frequency ranges only over 2 — 3 orders of magnitude, which is too narrow to construct a storage modulus or loss modulus curve involving the whole process of the transition, from which the relaxation time during transition could be obtained. A similar condition will be encountered if stress relaxation method is used, because an extremely long time is needed for evaluating the value of relaxation time. Nevertheless, according to the temperature-time equivalence principle^[8], it is possible, e. g., using dynamic mechanical method, to construct a master curve over a wide frequency range of ca. 10 or more orders of magnitude at a definite temperature by shifting storage modulus isotherms at different temperatures, and calculate the average of relaxation times at the definite temperature from the curve. In the present work, such a method was adopted in an attempt to obtain the average of relaxation times and then explore the effect of salt concentration, PEG chain length between crosslinks and the ratio of DGEPEG/TGEPEG on the molecular motion of this system through mechanical relaxation time. Besides, the results obtained were discussed in terms of the free-volume concept.

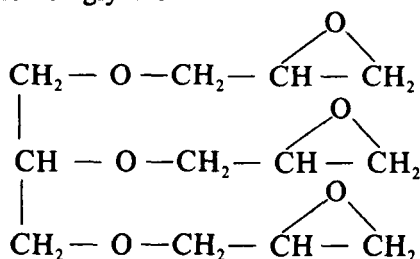
EXPERIMENTAL

Materials and sample preparation

Two precursors, diglycidyl ether of polyethylene glycol



and triglycidyl ether of glycerol



were synthesized by a two-step reaction, i. e. PEG's with different molecular weight or glycerol were combined with epichlorohydrin by using boron trifluoride etherate as a catalyst, and then dehydrochlorinated with sodium aluminate to form the desired DGEPEG and TGEG. Three series of epoxy network-based electrolyte films were prepared by mixing thoroughly the two precursors at 60 °C in different proportions and then curing the mixture in the presence of different amounts of lithium perchlorate according to three different predetermined curing schedules in order to ensure complete cure of each specimen of the series. Details of the preparative method have been reported elsewhere^[4, 7].

Methods of measurement

Dynamic mechanical properties of the specimens were examined on a Toyo Baldwin Rheovibron viscoelastometer (Model DDV-II-E) at a heating rate of 2 °C /min. The effective dimension of the specimens was 30 × 4 × 0.2 mm. Storage modulus, loss modulus and loss tangent values were measured at 3.5, 11, 35 and 110 Hz at temperatures ranging from -70 to +50 °C.

A Perkin-Elmer (Model DSC-2C) differential scanning calorimeter was used to measure the thermal behaviour of the specimens at a heating rate of 20 K/min. The midpoint of the baseline shift was defined as the glass transition temperature, which is designated as $T_{g(DSC)}$.

RESULTS AND DISCUSSION

Master curve construction

The storage modulus E' isotherms of the three series (A, B and C) of specimens (see Table 1) at different temperatures were superposed to construct master curves based on the time-temperature equivalence principle. Firstly the peak temperature of the loss tangent at 11 Hz was chosen as a reference temperature for each specimen, which was also granted to be the glass transition temperature and expressed in latter sections as $T_{g(DDV)}$. The modulus isotherm at $T_{g(DDV)}$ was then used as a reference and the horizontal shift on the logarithmic axis was applied to make the modulus isotherms at other temperatures join onto the reference isotherm as smoothly as possible. As a representative, Fig. 1 shows the frequency-temperature superposition for a two-component epoxy network (DGEPEG/TGEG = 3 : 2) specimen containing 3 wt.% of LiClO₄. Even though no vertical shift correction was applied, the superposition seemed to be successful as evidenced by the shape of the master curve. The curve shows three characteristic zones. The material is glassy with E' values ca. 10^9 Pa at higher frequencies. The transition zone is characterized by an abrupt drop of the storage modulus, resulting in a plateau represented by E' values as low as ca. 10^6 Pa at lower frequencies. The latter zone is typical of the crosslinked nature of the specimen in the rubbery state. Equally successful frequency-temperature superposition were also achieved for most other specimens. The amount of shift is defined as $\log a_T$, where a_T is equal to the ratio of mechanical relaxation time at temperature T (τ_T) to that at $T_{g(DDV)}$ (τ_{T_g})^[8].

Fig. 2 shows the Arrhenius plots of the minus shift factor, $-\log a_T$

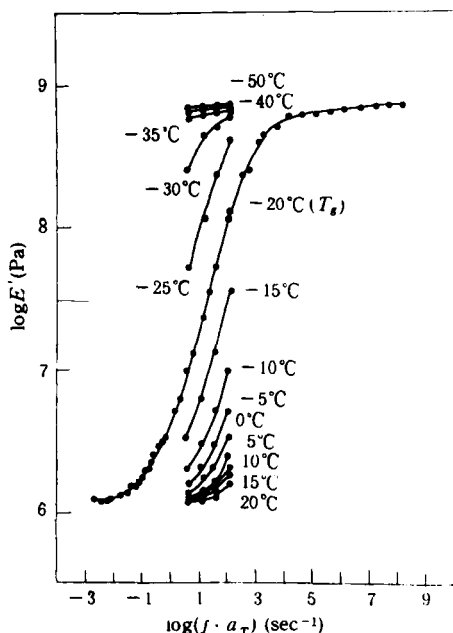
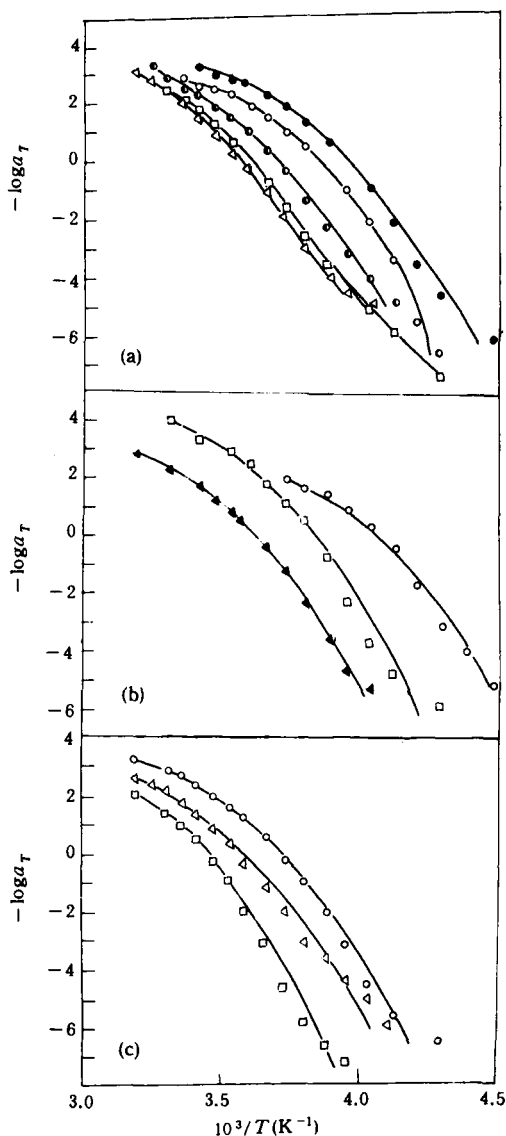


Fig. 1 Frequency dependence of the storage modulus isotherms and their master curve constructed with $T_g(\text{DDV}) = -20^\circ\text{C}$ for specimen A_1 (LiClO_4 : 3 wt. %)

Fig. 2 Arrhenius plots of minus shift factor against $1/T$ for three series of specimens.
(a) series A, LiClO_4 content (wt. %): (●) 3%; (○) 5%; (◐) 10%; (Δ) 15%; (□) 20%.
(b) series B, PEG MW: (▲) PEG (200); (□) PEG (1000); (○) PEG (2000).
(c) series C, DGEPEG/TGEG ratio, (□) 2:3, (Δ) 1:1; (○) 3:2



against the reciprocal temperature, whereas Fig. 3 exhibits the iso-free-volume plots of $-\log a_T$ vs. reduced temperature, $(T - T_g)$. As shown in the figures, the Arrhenius plots are non-linear, and are separated from each other depending on the salt concentration, PEG MW, and DGEPEG/TGEG ratio. On the other hand, all the $-\log a_T$ values are basically located on a common curved line in the iso-free-volume plots even though somewhat scattered at low temperature region. The scattering could be attributed to the error accumulation on the shift factor by the graphic construction of the master curve. Besides, as shown in Fig. 3(a), another reason for the scatter of data points especially in the glassy state is that the modulus is salt concentration dependent. In spite of the scattering of data, the above results still clearly indicate that the transition of the specimens is of WLF type.

In an attempt to evaluate the relaxation time of the specimens, an alternative

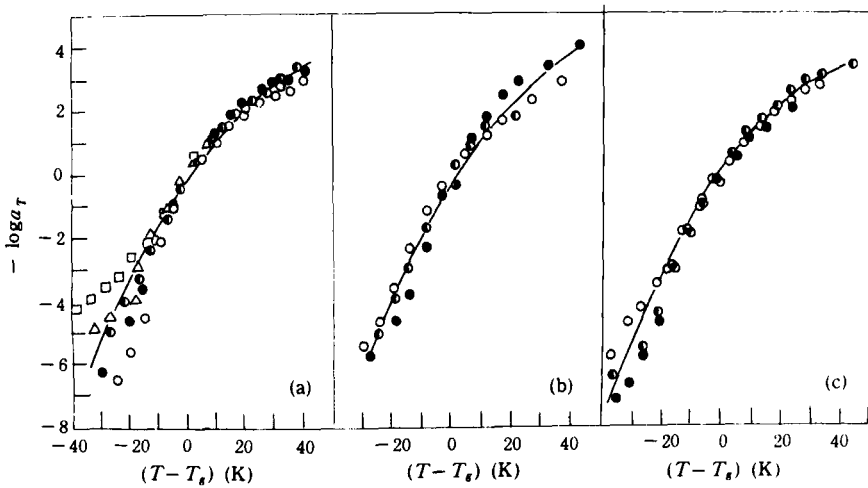


Fig. 3 Iso-free-volume plots of $-\log a_T$ vs. $(T - T_g)$ for three series of specimens. (a) series A, LiClO₄ content (wt. %). (●) 3%; (◐) 5%; (○) 10%; (Δ) 15%; (□) 20%. (b) series B, PEG MW. (○) PEG (200); (●) PEG (1000) (◐) PEG (2000); (c) series C, DGEPEG / TEGEG ratio. (●) 2:3, (◐) 1:1, (○) 3:2

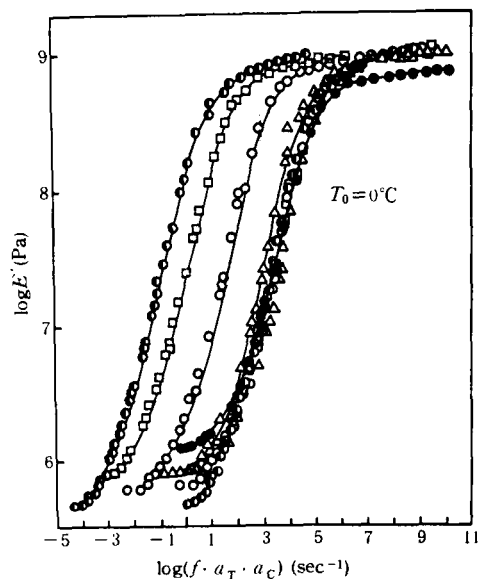


Fig. 4 Storage modulus master curve constructed by frequency-temperature superpositions for series A specimens at $T_0 = 0^\circ\text{C}$, from which their respective relaxation time, $\log \tau_C$ during transition were evaluated. Besides, the double superposed (frequency-temperature and frequency-concentration) master curve derived by taking the master curve for A_1 as a reference is also shown. LiClO₄ content (wt. %): (●) 3%; (Δ) 5% (○) 10% (□) 15% (◐) 20%.

way of master curve construction was adopted. Instead of taking the T_g of each specimen, a common reference temperature T_0 was selected, whereat the change in E' of the modulus isotherm segments for all the specimens of this series was large enough to make the superposition possible. By taking specimens of series A as an example, the master curves constructed by reference to $T_0 = 0^\circ\text{C}$, approximately the $T_{g(\text{DDV})}$ of specimen A_3 , are displayed in Fig. 4. For each curve three characteristic zones are distinguishable. The master curves are displaced progressively to lower frequencies as the salt concentration is increased. It is known that at the inflection point of the E' curve (or in the midway of transition there exists the following relationship between the angular frequency ω and the relaxation time τ [8].

$$\tau = 1/\omega \tag{1}$$

Therefore, the average of the relaxation times of the specimen could be evaluated.

Effect of salt concentration

The characteristics of the network specimens used in this work are tabulated in Table 1. It should be noted that all the specimens are non-crystalline in nature since no melting endotherm is discernible in their DSC thermograms, even if some precursors, e. g., DGEPEG (1000) or DGEPEG (2000) are crystallizable. The value in the parenthesis denotes the molecular weight of the PEG segment in the respective DGEPEG.

From Table 1, it is noted that the glass transition temperature, expressed either by T_g (DDV) or by T_g (DSC), is increased monotonically with increasing LiClO_4 concentration. All the T_g values measured by DDV are considerably higher than those measured by DSC, for the former is examined in the dynamic condition. However, both values have the same upward tendency as the salt concentration is increased. The effect of salt concentration on T_g is believed to be caused by the occurrence of the dipole-cation interaction between the oxygen atoms in polyether segments and lithium ions. This type of interaction is a true form of ionic bonding and acts as ionic crosslinks. It increases the cohesive energy of the network, thus reducing the free volume fraction of the system. Consequently, it is natural that the mobility of the PEG chains in the network is inhibited or the length of the moving segments is shortened^[9], causing a reinforcing effect on the network and an increased glass transition temperature.

Table 1 Characteristics of two-component epoxy network- LiClO_4 system

No	DGEPEG/TGEG wt. /wt.	PEG MW in DGEPEG	LiClO_4 wt. %	T_g (DDV) ($^{\circ}\text{C}$)	T_g (DSC) ($^{\circ}\text{C}$)
A ₁ ^(a)	3:2	1000	3	-20.2	-40.3
A ₂	3:2	1000	5	-15.0	-37.5
A ₃	3:2	1000	10	-2.9	-34.2
A ₄	3:2	1000	15	6.8	-26.3
A ₅	3:2	1000	20	12.5	-24.5
B ₁ ^(b)	3:2	200	10	3.5	-23.1
B ₂	3:2	1000	10	-12.0	-38.2
B ₃	3:2	2000	10	-26.7	-39.7
C ₁ ^(c)	2:3	1000	10	16.0	-12.9
C ₂	1:1	1000	10	7.0	-21.9
C ₃	3:2	1000	10	-4.0	-33.9

(a) Cure schedule: 70 $^{\circ}\text{C}$, 48h; 80 $^{\circ}\text{C}$, 1h; 100 $^{\circ}\text{C}$, 4h; 120 $^{\circ}\text{C}$, 2.5h.

(b) Cure schedule: 80 $^{\circ}\text{C}$, 1h; 100 $^{\circ}\text{C}$, 2h; 110 $^{\circ}\text{C}$, 2h; 120 $^{\circ}\text{C}$ 3h.

(c) Cure schedule: 90 $^{\circ}\text{C}$, 1h; 100 $^{\circ}\text{C}$, 2h; 110 $^{\circ}\text{C}$, 2h; 120 $^{\circ}\text{C}$, 6h.

A WLF type treatment of the A series specimen was made by plotting $-1/\log a_T$ vs. $1/(T - T_g)$ according to the following WLF equation^[13]

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (2)$$

The yielded WLF parameters C_1 and C_2 are barely comparable with the so-called universal value ($C_1 = 17.4$, $C_2 = 51.6$)^[10] as shown in Fig. 5. The values of C_1 and C_2 exhibit somewhat salt concentration dependence and increase with

increasing salt concentration just like the results obtained by Eissenberg for the stress relaxation study of ion-containing polymers in the solid state^[11].

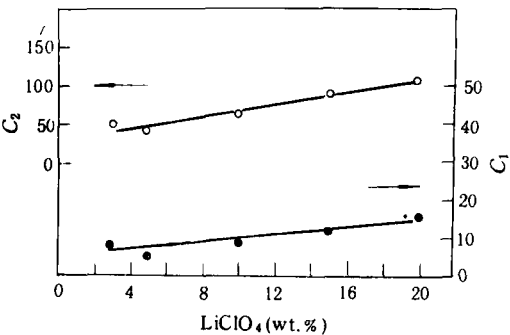


Fig. 5 The WLF parameters C_1 and C_2 as a function of salt content for series A specimens. The values were evaluated by choosing T_g (DDV) as a reference temperature.

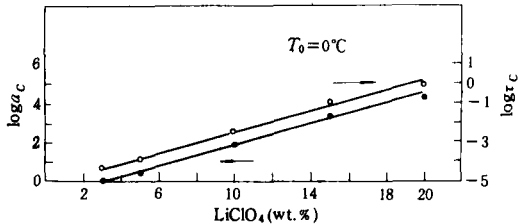


Fig. 6 Variation of the logarithmic relaxation time, $\log \tau_c$ and the concentration shift factor, $\log a_c$ with the LiClO_4 content at $T_0 = 0^\circ\text{C}$

For this series of specimens, the evaluated values of the average relaxation times of the specimens by the above mentioned method and equation (1) are denoted by τ_c , and plotted against salt concentration c in Fig.6. The correlation between them is linear and can be written as

$$\log \tau_c = -5.08 + 0.262c \tag{3}$$

with a correlation factor $r=0.991$.

It is worthy to note that on studying the dynamic mechanical properties of a polyether based polyurethane network-sodium tetraphenylborate system polymer electrolyte, Killis et al. ^[12] have performed a frequency-concentration superposition of the master curves at a common reference temperature T_0 for different salt content specimens. They found that the concentration shift factor $\log a_c$ is a linear function of the salt concentration. In the present work, the same superposition was carried out by taking the master curve for specimen A₁ (LiClO_4 , 3 wt.%) as reference. The superposition achieved in Fig. 4 is rather successful especially near the transition zone. In the glassy and rubbery zones, however, the superposition is not so successful because of the salt concentration dependence of the modulus in both zones. As the figure shows, the higher the salt concentration, the higher the E' in the glassy state and the lower the E' in the rubbery state.

Thus the constructed double-superposed master curve gives the dependence of the storage modulus on the double-reduced frequency $f^* = f \cdot a_T \cdot a_c$ at 0°C . By plotting $\log a_c$ against concentration c , their relationship is also linear as shown in Fig. 6, and can be expressed in the following form with $r=0.997$

$$\log a_c = -0.773 + 0.262c \tag{4}$$

where c is the salt concentration in weight percent.

On comparing these two lines expressed by Eqs. 3 and 4, it is noted that they are completely in parallel with each other, and that the difference between these two equations equals -4.31 , just the same as the value of $\log \tau_c$ for 3% salt content specimen A₁ determined by the inflection point method. It is not surprising, because by definition^[12], a_c equals τ_c / τ_{cR} , the ratio of the average relaxation

times at concentration c to that at reference concentration c_R , so the difference between these two equations should be $\log \tau_{cR}$, the logarithmic relaxation time of the reference specimen, in the present case, the $\log \tau_c$ of the reference specimen A_1 .

Therefore, both equations 3 and 4 are essentially equivalent. However, it seems that the direct use of the relaxation time might be more simple and unambiguous to examining the effect of salt concentration or other factors on the mechanical relaxation of the system.

It should be noted that the effect of salt concentration on the relaxation time is tremendous. From the above equation it is clear, that $d \log \tau_c / dc = 0.262$, i. e. about 1.8-fold increase in relaxation time per 1% increase in salt content. There-

fore, while the increase in salt concentration is beneficial to provide more ionic carriers and raise the ionic conductivity, the adverse effect of prolonging the relaxation time or hindering the segmental motion might possibly result in a depression of conductivity if the salt content is in excess.

Effect of molecular weight of PEG in DGEPEG

The construction of the master curves by choosing T_g (DDV) as reference temperature for series B specimen were also performed. Their WLF parameters C_1 and C_2 are in the range of ca. 10 and 60 respectively, and are nearly independent of the molecular weight of PEG in DGEPEG, taking the master curve for B_3 as a reference is also shown. (Δ) PEG (200), ($\square$) PEG (1000), ($\circ$) PEG (2000) (MW)_{PEG}. In order to investigate whether the (MW)_{PEG} have any influence on the relaxation time, the master curves for specimens with different (MW)_{PEG} are shown in Fig. 7, where a common reference temperature $T_0 = -7^\circ\text{C}$ was selected for the same reason stated above. The master curves are displaced progressively to higher frequencies as the (MW)_{PEG} is increased. By using the same procedure adopted in the above section, the average relaxation time, τ_M , during the transition for each specimen was evaluated and plotted as a function of (MW)_{PEG} as shown in Fig. 8. A linear correlation was also obtained and could be characterized by the equation ($r=0.998$)

$$\log \tau_M = 0.177 - 2.3 \times 10^{-3} (MW)_{\text{PEG}} \quad (5)$$

In Fig. 7 the double superposed (frequency-temperature and frequency (MW)_{PEG}) master curve constructed by taking the master curve for B_3 as reference is also shown. The relationship between shift factor, $\log a_M$ and (MW)_{PEG} is also linear as exhibited in Fig. 8.

The equation (5) clearly indicates that the effect of increasing (MW)_{PEG} upon the relaxation time follows a trend opposite to that exhibited by increasing salt concentration. This is because the (MW)_{PEG} determines the chain length between

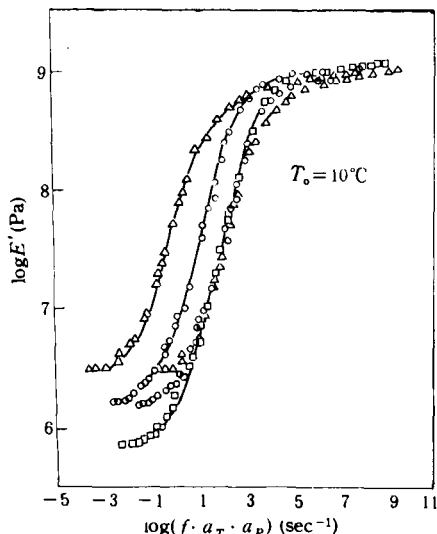


Fig. 7 Storage modulus master curves constructed by frequency-temperature superpositions for series B specimens at $T_0 = -7^\circ\text{C}$, from which their respective relaxation time, $\log \tau_M$ during transition were evaluated. Besides, the double superposed (frequency-temperature and frequency-(MW)_{PEG}) master curve derived by taking the master curve for B_3 as a reference is also shown. (Δ) PEG (200), ($\square$) PEG (1000), ($\circ$) PEG (2000) (MW)_{PEG}.

crosslinks. Obviously, the chain would be more flexible if it is longer, as the restriction imposed by crosslinks is lowered. Thus, the longer the chain or the higher the $(MW)_{PEG}$, the easier the chain movement. As a result, this plasticizer-like action of the longer PEG segment gives higher free volume fraction and lowers both the T_g (see Table 1) and the average relaxation times. Therefore, the increase in $(MW)_{PEG}$ is advantageous to the conductivity of this epoxy network electrolyte system.

However, the above expectation is only valid in the lower MW range as used in the present work. If the chain length of PEG segment between crosslinks is long enough to allow the chain to crystallize, the ionic conductivity would drop dramatically. Besides, the increase in $(MW)_{PEG}$ will give rise to other harmful effects such as incomplete ring closing during the epoxidation of PEG and the low reactivity during the cure of the system^[7].

Effect of DGEPEG/TGEG ratio

The experimental results show higher T_g for the specimens rich in TGEG (see Table 1, series C). It might be expected that higher proportion of TGEG in the system would result in a denser crosslinking density, less mobile network chains and depressed free volume fraction because of its three functionality of TGEG. The master curves for this series of specimen are shown in Fig. 9. In this case, 10 °C was chosen as the reference temperature. As the proportion of TGEG increases the master curves are displaced progressively to the lower frequencies. The average relaxation time, τ_p during the transition for each specimen was evaluated and plotted against the percentage of DGEPEG (1000) content, P_{DGEPEG} (Fig. 10). Their correlation is also linear and can be expressed as

$$\log \tau_p = 2.44 - 0.1 P_{DGEPEG} \tag{6}$$

with a correlative factor equals 0.993.

The double superposition (frequency-temperature and frequency-DGEPEG/TGEG ratio) of master curves of this series of specimens by taking C_3 as a reference is also performed (Fig. 9). As shown in Fig. 10, a linear plot of $\log a_p$ against the percentage DGEPEG(1000) content is also obtained.

Again, the equation shows a negative slope. Thereby the increase in the proportion of DGEPEG lowers the relaxation time and favours the segmental mobility. However, on considering the mechanical strength of the system, an excessive high proportion in DGEPEG/TGEG ratio would yield a product too low in strength. Thus to keep an adequate proportion between these two precursors is a matter of importance.

To sum up, the preceding findings indicate that all the three factors, i. e. salt concentration, molecular weight of PEG in DGEPEG and the DGEPEG proportion in DEGPEG/TGEG ratio have profound influence on the average relaxation times, which in turn affect the ionic conductivity of the system. Among the

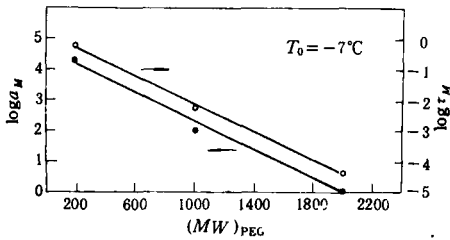


Fig. 8 Variation of the logarithmic relaxation $\log \tau_M$ and the $(MW)_{PEG}$ shift factor, $\log a_M$ with the MW of PEG in DGEPEG.

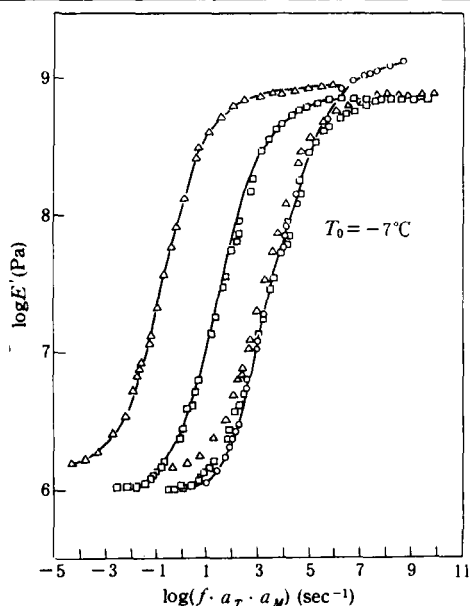


Fig. 9 Storage modulus master curves constructed by frequency-temperature superpositions for series C specimens at $T_0 = 10^\circ\text{C}$, from which their respective relaxation time, $\log \tau_P$ during transition were evaluated. Besides, the double superposed (frequency-temperature and frequency-DGEPEG/TGEG ratio) master curve derived by taking the master curve for C₃ as a reference is also shown.

DGEPEG/TGEG ratio, (Δ) 2:3, ($\circ$) 1:1, ($\square$) 3:2.

factors, the former reinforces the network chains, leading to prolong the relaxation time. On the contrary, the latter two have plasticizer-like action and show an opposite effect. Based on the free volume concept, all the effect arising from these factors could be attributed to the change in the free volume. The argument is evidenced by the fact that from Fig. 3(a), (b) and (c), wherein the iso-free-volume plots of $-\log a_T$ are illustrated, all the three curves could be coincided with each other. As has been stated above, $-\log a_T = -\log \tau_T + \log \tau_{T_g}$, where the last term has a logarithmic value around -1.9 ± 0.1 sec for all the specimens studied and thus can practically be regarded as a constant. The result indicates that the relaxation time at the glass transition temperature is the same irrespective of the formulation or structure of the specimen. As a matter of fact, if T_g of each specimen is selected instead of a common reference temperature T_0 , only one universal master curve of $\log E'$ against logarithmic frequency could be obtained independently of the salt concentration, $(MW)_{PEG}$, or DEGPEG proportion in DGEPEG/TGEG ratio, as the free-volume change due to above effects has been automatically taken into account in this case. In other words, it might be stated that during glass transition the specimen is in the "iso-relaxation-time state". In fact, this statement could easily be deduced from the so-called "iso-viscous state" concept proposed early by Boyer and Spencer^[14] for characterizing the glass transition. Therefore, the $-\log a_T$ is in fact an alternative expression of the segmental mobility. The coincidence of the curves means that in the iso-free-volume state, all the specimen have the same segmental mobility. As a consequence, a polymer with a low T_g would possess a high segmental mobility at any temperature T above T_g and thus a high

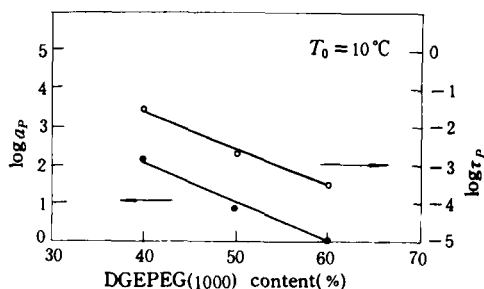


Fig. 10 Variation of the logarithmic relaxation time, $\log \tau_P$ and the DGEPEG/TGEG ratio shift factor $\log a_P$ with the percentage DGEPEG (1000) content at $T_0 = 10^\circ\text{C}$.

ionic conductivity. To be a useful solid polymer electrolyte, however, an adequate mechanical strength at least capable of self-supporting should be maintained. Thereby a compromise between T_g and the strength of the specimen must be taken into consideration. A detailed investigation on the correlation between the mechanical relaxation and ionic conductivity of this system will soon be published elsewhere.

Keywords:

Polymer solid electrolyte, Mechanical relaxation time, Segmental mobility, Two-component epoxy network-LiClO₄ complex.

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