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Influence of physical aging and side group on the free volume of epoxy resins probed by positron

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Abstract

The effect of physical aging and side group on the free volume has been studied by positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimeter (DSC) for a series of epoxy resins cured separately with novolac resin and esterified novolac resins, that is, the hydroxyl group of phenol novolac resin was placed by a CH_3COO-group, a CH_3CH_2 CH_2COO- and a C_6H_5 CH_2COO-group, which were named EP, EPA, EPB and EPP, respectively. Positron experimental results show that the side group plays an important role in determining free volume properties of epoxy resins, i.e. the stronger the cross-linking of curing agent, the smaller the free volume. This is confirmed by DSC measurement. On the other hand, the free volume relaxation properties were investigated by the Kolrausch–Williams–Watt (KWW), the single exponential and the double exponential functions in aging course for all samples, respectively. We found that *ortho*-positronium (*o*-Ps) intensity decreased with increasing aging time, which meant that the free volume diminished resulting from the formation of the local order structure due to the chain segmental rearrangement. The relaxation time constants of both τ and the parameter β have been calculated, which indicated that the order of relaxation rate of free volume characterized by τ^{-1} measured by PALS was the same as the enthalpy relaxation rate characterized by $\partial \Delta H/\partial(\log t)$ measured by DSC.

Keywords: Epoxy resin; Physical aging; Free volume relaxation

1. Introduction

Epoxy resins have been widely studied due to having many industrial applications, including microelectronic packing materials and advanced composites, aerospace structural composites, adhesives, lightweight composite infrastructures, and performance sporting goods [1–4]. In each of these applications, exposure to a humid or moist environment is anticipated. Being hydrophilic in nature, epoxy resin can absorb water from surroundings. This absorbed moisture can not only deteriorate the thermal and mechanical properties of the resins, such as a decreased thermal stability [5]; a decrease in yield strength, a change of the yield/deformation mechanisms [6–8]; moisture induced swelling and swelling stresses [9,10]; the creation of microcracks and crazes [11], but also initiate corrosion of the substrate metal, delaminate the coating and destroy the adhesion between the binder and enhanced materials [12]. Clearly, one would like to control or inhibit moisture absorption to prevent these undesirable events from taking place.

To control the moisture uptake in epoxy resins, the transport mechanisms must be understood. Although it has been illustrated that free volume [13–15] and polarity [16] are the two intrinsic factors that determine the absorption and transport of moisture, and that the relationships between water sorption and indirect measurements of polymer free volume, such as specific volume and mechanical properties, have been found [17], it is not very clear because of a lack of experimental methods to accurately quantify this parameter. For example, the free volume concept attempts to describe the openness of the topology in terms of the delocalized, unoccupied volume, and several theories attempt to relate the transport behavior to the free volume content. However, one cannot directly measure the free volume, so these theories are difficult to critically test and refine. In recent years, positron annihilation lifetime spectroscopy (PALS)

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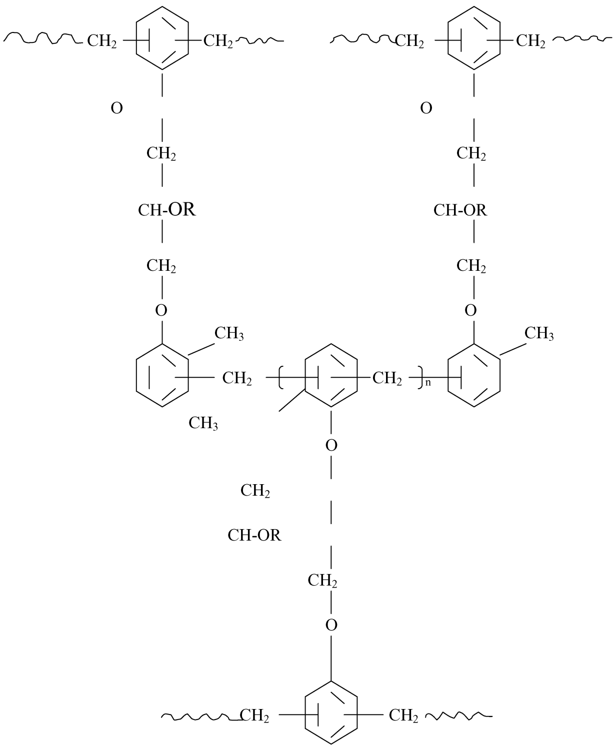
has emerged as a new microanalytical probe, which is capable of directly probing the size and content of free volume in polymers. PALS is widely used in the characterization of free volume of polymers [18–22]. On the other hand, it is noteworthy that the curing agent plays an important role in determining the structure of epoxy resin, which affects the water absorption and diffusion in epoxy resins. It is well known that physical aging affects the properties of epoxy resins owing to the changes in the molecular conformation occurrence and in the free volume. The time-dependent changes in the specific volume, free volume and enthalpy are of essential importance in physical aging for polymer engineering, since they are accompanied by changes in static and dynamic moduli, yield stress, elongation to break, fracture toughness, fatigue failure, impact strength. In this work, PALS and differential scanning calorimeter (DSC) were used to investigate the effect of the curing agent with different side group and physical aging on the free volume properties in cured epoxy resins.

2. Experimental

Novolac(H-1, hydroxyl equivalent:107 g eq.$^{-1}$) and *o*-cresol(2-methyl phenol) novolac epoxy resin (epoxy equivalent: 200–300 g eq.$^{-1}$) were supplied by Tohto kasei and Sumitomo in Japan. A series of epoxy resins were cured separately with esterified phenol novolac resin and phenol novolac resin, that is, the hydroxyl group of phenol novolac resin was replaced by a CH_3COO-group, a $CH_3CH_2CH_2COO$-group, and a $C_6H_5CH_2COO$-group. These cured resins were named EP, EPA, EPB and EPP, respectively. A detailed description of the curing can be found elsewhere [23]. The chemical structures of the cured resins are shown in Fig. 1.



For EP: R=H, EPA:R=CH_3CO

EPB:R=$CH_3CH_2CH_2CO$ EPP:R=$C_6H_5CH_2CO$

Fig. 1. Chemical structure of cured epoxy resins.

Thermal properties of epoxy resins were measured using a Seteram DSC 92 (France) at a heating rate of 10 °C/min under an atmosphere of nitrogen and the glass transition temperature was defined as the inflection temperature in the DSC scan.

Epoxy resin samples were separately heated to 493, 455, 416 and 430 K above their glass transition temperature T_g (higher than 35 K) for 10 min to erase any previous thermomechanical history, and then quenched in liquid nitrogen. A large number of the same samples for EP, EPA, EPB and EPP were physically aged at below their glass transition temperature (less than 30 K) for different aging times in air, respectively. The aged samples were quenched in liquid nitrogen before starting the positron lifetime measurements. Positron annihilation lifetime measurements were carried out using a conventional fast–fast coincident spectrometer at room temperature. A 20 μCi ^{22}Na positron source sealed between aluminum foils (0.8 mg/cm^2) was placed between two identical pieces of samples. A million counts were collected for each spectrum in about 1.5 h. The time resolution of the system was found to be a sum of two Gaussians with $(\mathrm{FWHM})_1 = 265$ ps(90%) and $(\mathrm{FWHM})_2 = 250$ ps(10%). It is noted that each aged sample was used only for one measurement of positron annihilation lifetime, which avoids any artifact due to the buildup of charge. In order to ensure the precise measurement of positron lifetime, samples always was placed at the same place on the probe marked every time.

3. Results and discussion

All the positron lifetime spectra were resolved into three or four components using PATFIT [24] after the background and the positron source correction were subtracted. Invariably, three lifetime components fit resulted in better χ^2 values and standard deviations compared to four-component fit. Hence, the positron lifetime spectra measured were fitted to three components. The shortest-lived component and the intermediate component are attribution to the self-annihilation of *para*-positronium (*p*-Ps) and the positron annihilation, respectively. The longest-lived component (τ_3 and I_3) results from the pick-off annihilation of *ortho*-positronium (*o*-Ps) in the free volume holes. Because only the *o*-Ps component is significantly sensitive to the change in the free volume, we pay special attention to the variations of the *o*-Ps annihilating parameters.

Table 1 shows the fractional free volume and radius of free volume hole for four kinds of unaged epoxy resins. Where R is the radius of the free volume hole calculated using formula in Ref. [18] and f is the relative fractional free volume calculated by $f = (4/3)\pi R^3 I_3$. From Table 1, it is clear that the fractional free volume of EP is much less than that of the esterified systems, and that the fractional free volume of EPB is the biggest among four kinds of epoxy resins. This fact indicates that there is stronger cross-linking owing to the hydroxyl group, which results in a compact structure caused by the strong molecular interaction induced by hydroxyl group in EP. Though the polarities of the ester functional groups and chemical structures of the networks are very similar among the esterified systems, the flexibilities of these cured resins are rather different. The flexibility of the side group of EPB is the best. The flexible side group reduces the packing density of chains, which brings about an increase in the free volume. This is well in agreement with the results measured by DSC and density measurement at room temperature as shown in Table 2. Combining Table 1 with Table 2, we can see that the lower the density of the cured resin, the lower the glass transition temperature and the bigger the fractional free volume. The T_g of EP is the highest, however, the T_g of the esterified systems is much lower than that of EP. Two factors, including the polarity and the internal plasticity of the side group, influence the value of T_g, that is, the higher the polarity of the side group the higher the T_g [25], and the more flexible the lower the glass transition temperature because the side group can act as the internal plasticizer of the network and greatly reduces the T_g.

Glass polymers are known to have changes with time in their physical properties and microstructure when annealed at temperature close to, but below their glass transition temperature. The aging mechanism results from two causes: (1) is assigned to intrinsic phenomena associated with changes of the molecular conformation that occur within the relaxation times; and (2) depends on the distance to the equilibrium state of the samples, i.e. a process that is driven by the excess free volume present in the system. This means that at given aging temperature, the rate of free volume relaxation is determined by the segmental mobility. In order to examine further the influence of side group on the microstructure and the free volume, aging experiments were performed for all samples. Figs. 2 and 3 show the variations of *o*-Ps lifetime and intensity as a function of aging time.

Table 1
Relative fractional free volume measured by PALS for unaged epoxy resins

Materials	EP	EPA	EPB	EPP
f (%)	7.32	9.32	14.03	10.07
R (nm)	0.1012	0.1182	0.1348	0.1244

Table 2
Glass transition temperature measured by DSC and density of unaged samples

	EP	EPA	EPB	EPP
ρ (g cm^{-3})	1.2174	1.2094	1.1772	1.2024
T_g (K)	457	418	381	399

From the results shown in Fig. 2, we find that the variations of the *o*-Ps lifetimes are very small except for EPP during from 0 to 40 h and for EP during 0–20 h, respectively. The decrease in τ_3 is also observed in other polymers [18,26,27], which is not clear and needs to be studied further.

On the other hand, physical aging appears to have a greater effect on the intensity than the lifetime of the *o*-Ps component. The *o*-Ps intensity shows a continuous decrease and reaches its lowest value finally for all samples as shown in Fig. 3, which indicates that the free volume concentration and fractional free volume decrease during physical aging, here we assume that I_3 is proportional to the number of the free volume holes. A similar phenomenon has been observed, such as polycarbonate [28–30], poly(ethylene terephthalate) [27,31], polystyrene [32,33], polyethylene [34], and poly(chlorotrifluoroethylene) [26,35]. The decreasing free volume with increasing aging time causes the gradual densification of the samples, which is confirmed by density increasing with an increasing aging time [36]. In Ref. [36], Mukherjee and Jabarin also reported that the decrease in free volume causes the polymer to become more

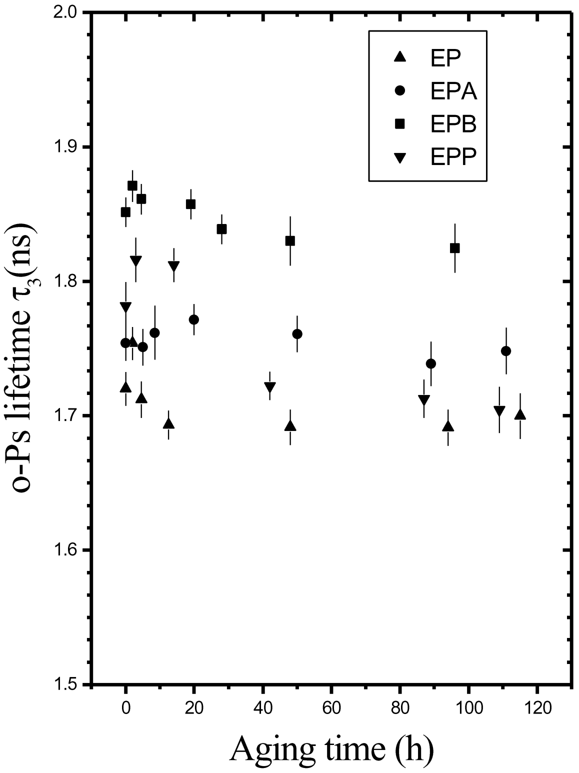


Fig. 2. Aging time dependence of *o*-Ps lifetime.

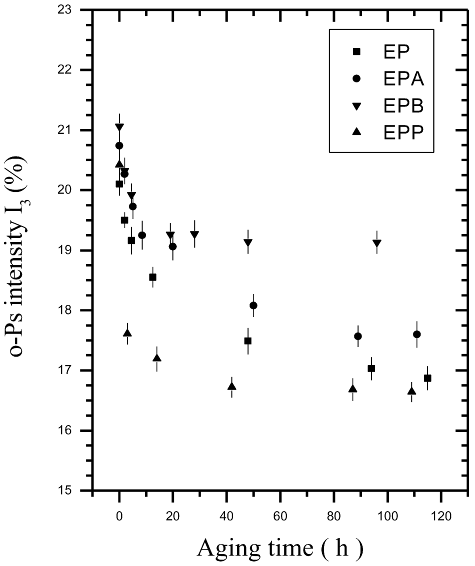


Fig. 3. Aging time dependence of *o*-Ps intensity.

compact and results in an increase in the yield stress with increasing aging time. Yeh, Geil and other authors have reported the formation of local ordered domains within glassy materials during aging and these domains have been observed to grow with aging time [37,38]. As mentioned above, we think that maybe the decrease in the free volume is due to the formation of local ordered domains. It is to be noted that the effect of positron irradiation on the *o*-Ps intensity can be neglected because both the collecting time of each spectrum is about 1.5 h far less than aging time and that each sample is used only for one measurement, which avoid prolonged exposure to the positron source. Therefore, the decrease in I_3 mainly stem from the structural relaxation and the segmental rearrangement. This is demonstrated by the measurement of the glass transition temperature as a function of aging temperature as shown in Table 3.

From Table 3, we observe an increase in T_g after physical aging. This phenomenon has been observed in literature [27, 39]. In fact, since the polymer molecules are in a nonequilibrium state, there exists a thermodynamic potential or drive force for them to approach their equilibrium by undergoing conformation rearrangement. The conformation changes during the aging have been observed by Ito [40] and Tant [41]. Because physical aging does not alter the molecular weight of the polymer, the decrease in I_3 in aged material could be due to fewer free sites made available by the motion of chain segments or particular groups. As mentioned above, we conclude that the decrease of free volume stems from the structural relaxation and conformation arrangement. This conclusion is supported by the work of Bubeck et al. [42] and Cangialosi [30].

Table 3
Aging time dependence of the glass transition temperatures

	Glass transition temperature (K) measured by DSC			
Aging time (h)	EP	EPA	EPB	EPP
0	457	418	381	399
5	460	420	385	402
20	460	420	385	402

Polymers exhibit relaxation phenomena in the glass state were commonly described by some nonlinear response functions, such as single exponential, double additive exponential [29,31,33,35] and Williams–Watt–Kohlrausch model (WWK) [29,31,33,35,43]. The functions are given as follows:

Single exponential fit

$$\phi(t) = A\exp[-t/\tau] + C \tag{1}$$

Double-additive exponential fit

$$\phi(t) = A\exp[-t/\tau_1] + B\exp[-t/\tau_2] + C \tag{2}$$

KWW fit

$$\phi(t) = A\exp[-(t/t)]^{\beta} \qquad 0 < \beta \leq 1 \tag{3}$$

where τ_1, τ_2 and τ is the relaxation time constants and A, B, C and β are positive constants. The equilibrium relaxation function $\phi(t)$ of the free volume can be evaluated using the relation

$$\phi(t) = \frac{I_3(t) - I_{3f}(\mathrm{eq})}{I_{3i}(t=0) - I_{3f}(\mathrm{eq})} \tag{4}$$

where $I_3(t)$ is the value of I_3 at any setting up aging time t, I_{3f} (eq) is the equilibrium value as aging time $t \to \infty$, I_{3i} is the equilibrium value at $t = 0$ prior to aging. The free volume relaxation function $\phi(t)$ can be calculated in terms of Eq. (4). Eq. (3) can be rewritten as follows

$$\ln[-\ln\phi(t)] = \beta\ln t - \beta\ln\tau_0 \tag{5}$$

Thus, a straight line is expected between $\ln(-\ln\phi(t))$ and $\ln t$ as shown in Fig. 4. A least-squares fitting program is used to calculate the relaxation time constants of both τ_0 and

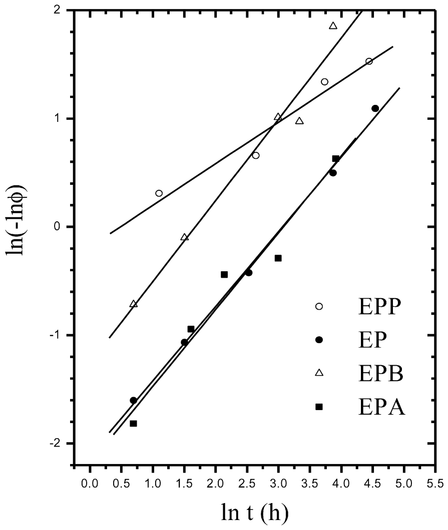


Fig. 4. Aging time dependence of relaxation function $\phi(t)$.

β. A summary of fitted parameters for the above three models is given in Table 4.

From Table 4, we find that the double exponential fit gives a poor fit and that no stable solution is available, which will be studied further. Comparison of results of three fitting procedures leads to the conclusion that the KWW fit provides the best description of the relaxation process. Single exponential and KWW fits give a better result than double-exponential fit suggesting that the relaxation phenomenon arises from the cooperative segmental motion of the polymeric chains, since there are no double bond units in their molecular structure. It is evident that the values of both β and τ are the lowest in EPP compared to other samples. The small values of β and τ imply that a larger number of chain segments are involved in the relaxation process owing to the existence of the flexible side groups and larger free volume for EPP. Because the relaxation rate depends on both the free volume frozen by quenching in liquid nitrogen and the segmental mobility of the chain that attributed to the side group flexibility and the interaction between the main chain and side chain. This is consistent with the glass transition temperature measurement, which is confirmed by enthalpy relaxation determined from DSC data as shown in Fig. 5. Enthalpy relaxation rate is frequently used to characterize the relaxation kinetics in various materials [44–46]. From Fig. 5, it is clear that the relaxation rate of the enthalpy relaxation defined as $\partial(\Delta H)/\partial(\log t)$ [47] has an order: EPP > EPB > EPA > EP. This fact indicates the flexibility of the side group and hydrogen band that lows the relaxation rate play important role. A high level of free volume leads to a high driving force for relaxation. The linear variation of ΔH with aging time has been observed in literatures [48–50]. The relaxation rates of the free volume and enthalpy are shown in Table 5.

From Table 5, we can see that the order of free volume relaxation rate characterized by τ^{-1} is: EPP > EPB > EPA > EP, which is the same as the enthalpy relaxation rate characterized by $\partial(\Delta H)/\partial(\log t)$. According to the Struik model [30]

$$\ln \tau = \ln \tau_0 + \Delta G/KT - \gamma(V_\mathrm{f} - V_{\mathrm{f}\infty}) \tag{6}$$

and to the Kovacs equation [51]

$$\tau = K_0^{-1}\exp(1/f) \tag{7}$$

where ΔG is the activation energy, τ_0 is a preexponential fact, γ is a constant, K is the Boltzmann constant, V_f is the actual free volume and $V_{f\infty}$ is the equilibrium free volume, f is the fractional free volume and K_0^{-1} is a constant, we conclude that an increasing relaxation time is due to a decrease in the excess free volume at fixed aging temperature [30]. This result indicates that the free volume is very important in determining relaxation behavior, which reveals that the flexibility of the side group has strong effect on the aging process due to the effect of the flexibility of the side group on the free volume. Owing to the interaction between chains, the molecular chains pack more tightly, which results in the decrease of free volume and in having the longest relaxation time.

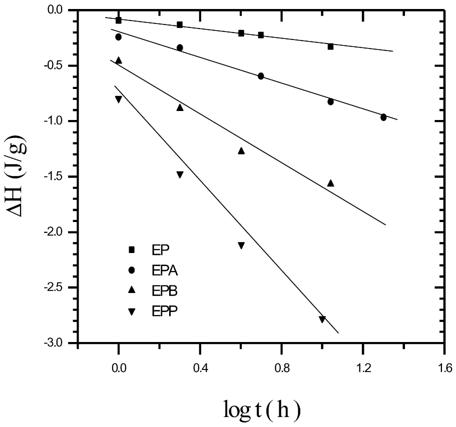


Fig. 5. Aging time dependence of enthalpy relaxation.

Table 4
Relaxation parameters of samples used in this study

	1-exp fit		2-exp fit			KWW fit		
	τ_1	R^2	τ_1	τ_2	R^2	τ	β	R^2
EP	25.20	0.986	4.39	37.70	–	22.32	0.68 ± 0.09	0.992
EPA	20.57	0.941	2.63	–	–	21.68	0.71 ± 0.01	0.981
EPB	5.96	0.993	4.82	–	–	5.41	0.75 ± 0.03	0.995
EPP	17.49	0.996	17.49	17.49	–	1.62	0.38 ± 0.06	0.997

4. Conclusion

The PALS and DSC are used to study the effect of the curing agent on the microstructures of epoxy resins EP, EPA, EPB and EPP in physical aging process. The experimental results indicate that the flexibility of the side group can greatly influence the free volume of the cured epoxy resins. The higher the flexibility of the side group, the lower value the relaxation time constant and the faster the relaxation rate. The relaxation rate of the free volume measured by PALS shows the order: EPP > EPB > EPA > EP, which is the same as the enthalpy relaxation rate measured by DSC. These results reveal that the hydroxyl group in EP plays an important role, i.e. enhancing the cross-linking density. On the other hand, from the dependence of the free volume concentration on the aging time, we found that the free volume diminishes with increasing aging time resulting from the formation of local

Table 5
Relaxation rates of the free volume and enthalpy

Sample	EP	EPA	EPB	EPP
τ_0^{-1} (h^{-1})	0.045	0.046	0.185	0.617
$\partial\Delta H/\partial\log t$	0.23	0.56	1.06	1.98

ordered structure induced by the structural relaxation and the conformation rearrangement.

Acknowledgements

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