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Positron annihilation lifetime spectroscopy study on the structural relaxation of phenylmethylsiloxane-modified epoxy hybrids at different aging temperatures

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HIGHLIGHTS

- The cured network conformations of DGEBA–PMSE hybrids were studied using DMA.
- The structural relaxation behaviours of DGEBA–PMSE hybrids were studied using PALS.
- The cured DGEBA–PMSE hybrids were interpenetrating polymer networks (IPNs).
- PALS studies provided a quantitative demonstration of relaxation behaviours.
- Double additive exponential model effectively predicted the relaxation times of hybrids.

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ABSTRACT

The cured network conformations and structural relaxation behaviours of the diglycidyl ether of bisphenol A (DGEBA)-methylhexahydrophthalic anhydride (MHHPA) modified with phenylmethylsiloxane-modified epoxy (PMSE) at different aging temperatures were studied using dynamic mechanical analysis (DMA) and positron annihilation lifetime spectroscopy (PALS). The DMA results revealed that the cured PMSE network can insert into the cured DGEBA network to form interpenetrating polymer networks (IPNs). The structural relaxation behaviours of DGEBA–PMSE-0.4 produced using DGEBA, PMSE, and MHHPA at a ratio of 0.6:0.4:1 by equivalent weight were studied using PALS at 150 °C and 55 °C. The aging-induced free volume relaxation parameters of DGEBA–PMSE-0.4 at 150 °C and 55 °C were investigated using the double additive exponential model and the Kohlrausch–Williams–Watts exponential model. For double additive exponential model, only one relaxation time (ζ) of 584.5 h was found at 150 °C; By contrast, there were two separate relaxation times of 37.4 h (ζ_1) and 753.6 h (ζ_2) at 55 °C. The ζ_1 of the IPNs hybrid can be attributed to the network relaxation of PMSE, and the ζ_2 can be attributed to the network relaxation of DGEBA at 55 °C. The results suggested the double additive exponential model can effectively predict DGEBA–PMSE hybrid relaxation behaviours.

1. Introduction

Thermosetting epoxy resins, such as those made of cycloaliphatic polymers or the diglycidyl ether of bisphenol A (DGEBA), are generally used as photo-electronic packaging materials thanks to their high optical transmittance as well as their effectiveness as barriers and their adhesive properties. However, these optical epoxy resins exhibit evolving properties that change significantly with thermal and/or UV exposure to become yellow and brittle. Polydimethylsiloxane-modified epoxy resins have been developed to increase toughness as well as optical and thermal stability. However, because polysiloxanes are immiscible with epoxy resins due to the differences in molecular polarity and flexibility, obtaining a homogeneous and optically transparent polydimethylsiloxane -modified epoxy hybrid is still something of a challenge [1–3].

We have previously described the use of a thermal curing process for the fabrication of a transparent hybrid based on DGEBA and phenylmethylsiloxane-modified epoxy (PMSE) [4].

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The DGEBA–PMSE hybrids show better optical thermal stability than the DGEBA–MHHPA hybrids. However, thermal aging at 150 °C leads to a stiffening of the material, causing lightout decay of the light emitting diodes (LEDs) encapsulated by the DGEBA–PMSE hybrids. Studies of the resin using transmission electron microscopy (TEM) provided a qualitative indication that the conformational rearrangement was associated with thermal aging behaviour.

The thermal aging of thermosetting polymers has been studied extensively [5–8] and several models have been developed to describe this behaviour [9–11]. In recent years, positron annihilation lifetime spectroscopy (PALS) has been used in many structural relaxation studies to monitor the free volume changes that take place during aging. Additionally, semi-empirical models have been developed to investigate the relaxation parameters [12–14]. However, few PALS studies have focused on the conformational rearrangement of nanohybrid materials and the characteristics of structural relaxation during the aging process at different temperatures.

The objective of the study described herein was to investigate the cured network conformation of DGEBA–PMSE hybrids and to understand in quantitative terms the structural relaxation characteristics at different aging temperatures. DMA and PALS were used to gain insights into the cured network conformation and the conformational rearrangement processes that take place in thermal aging, to identify the changes in the free volume radius and fraction, and to elucidate and quantify the various key structural parameters and their relationships.

2. Experimental

2.1. Materials

DGEBA with an epoxide equivalent weight of 190 g/eq. was obtained from Eclat Applied Technology Co. Ltd. (Taoyang County, Taiwan). (Phenylmethylsiloxane-co-dimethylsiloxane)-glycidyl ether terminated copolymer (also called phenylmethylsiloxane-modified epoxy, PMSE), with an epoxide equivalent weight of 680 g/eq., was obtained from Grand Tek Advance Material Science Co. Ltd. (Taipei, Taiwan). Its structure is shown in Scheme 1. Methylhexahydrophthalic anhydride (MHHPA) was obtained from Eclat Applied Technology Co. Ltd. Quaternary phosphonium bromide (U-cat 5003) was obtained from San-Apro Ltd. (Tokyo, Japan) and was used to accelerate the epoxy and anhydride curing process. Activated carbon was purchased from Showa Co. (Tokyo, Japan) and was used to purify the PMSE.

2.2. Purification of the PMSE

The PMSE was light yellow, with an initial yellowness index of 10.91 (measured using an SA2000 spectrophotometer; Nippon Denshoku Industries Co., Ltd., Tokyo, Japan). The PMSE was placed in a round-bottomed flask and 3 g of activated carbon was added per 100 g of PMSE. The mixture was stirred for 24 h and then filtered through a 0.2 mm polytetrafluoroethylene membrane (Whatman Inc., New Jersey, NJ, USA) to remove the activated carbon. Each batch of PMSE was purified three times. The purified PMSE was then placed in a vacuum oven at 80–100 °C under reduced pressure to remove the water. The yellowness index of the purified PMSE was 1.24.

2.3. Preparation of cured plate samples

In this study, we used materials with two different DGEBA–PMSE hybrids. DGEBA–PMSE-0.2 was produced using a DGEBA:PMSE:MHHPA equivalent weight ratio of 0.8:0.2:1, and DGEBA–PMSE-0.4 was produced using a DGEBA:PMSE:MHHPA equivalent weight ratio of 0.6:0.4:1. For comparison, DGEBA–MHHPA and PMSE–MHHPA were prepared as reference materials using an equivalent weight ratio of 1:1. The catalyst (U-cat 5003) was used at a concentration of 0.5% by weight of the total solution in each case. For each preparation, the catalyst was first dissolved in MHHPA at 50 °C for 60 min in a beaker, followed by the addition of the DGEBA and PMSE and stirring of the mixture at room temperature until a homogeneous solution was formed. Bubbles were removed from the solution using a vacuum pump and the solution was then cast in a mould made from two pieces of glass separated by a piece of silicone rubber 3 mm thick that formed a seal between them. After the sample had been fully cured, the two pieces of glass were removed to reveal a transparent plate sample with dimensions 40 mm × 40 mm × 3 mm.

2.4. Analysis of the dynamic mechanical properties using DMA

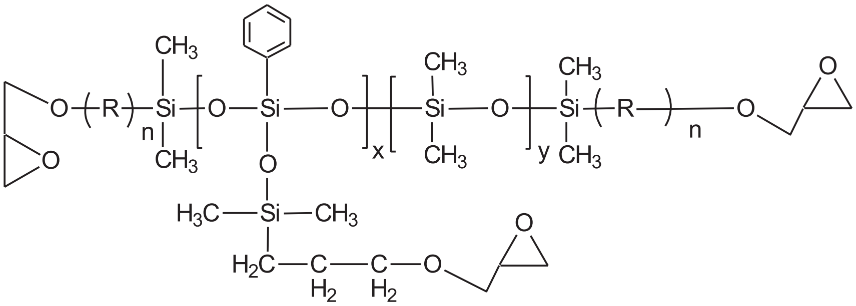
The dynamic mechanical properties of the cured samples were measured between −100 °C and 280 °C at a heating rate of 5 °C min^{-1} and a fixed frequency of 1 Hz, using a Q800 instrument (TA Instruments, Inc., New Castle, DE, USA).

2.5. Experimental thermal aging process

The cured plate samples were placed in a programmable oven at the selected thermal aging temperature and the properties of the resins were measured after 0, 96, 240, 480, 720 and 960 h. Five samples were used for each test interval.

2.6. Positron annihilation lifetime measurements [15–18].

The free volumes in the samples were measured using a PALS instrument (Ortec, Oak Ridge, Tennessee, USA). A conventional



Scheme 1. (Phenylmethylsiloxane-co-dimethylsiloxane)-glycidyl ether terminated copolymer (PMSE).

fast–fast coincidence spectrometer with a time resolution of 250 ps was used for the PALS measurements. The 15 μCi ^{22}Na positron source was placed in an envelope of Kapton foil (6 μm thick) and then sandwiched with DGEBA–PMSE-0.2, DGEBA–PMSE-0.4 and DGEBA–MHHPA samples of 3 mm thickness. One million counts were recorded for each PALS spectrum over a typical acquisition period of 3–5 h. The PATFIT-88 program was used for the conventional analysis and the PALS spectra were analysed for lifetime components (ζ_1, ζ_2, and ζ_3) and intensities (I_1, I_2, and I_3). Source correction terms were determined from the data analysis of each spectrum. Continuous lifetime distributions were obtained using the MELT computer program, which uses the maximum entropy method and does not require a reference spectrum to deconvolute positron annihilation lifetime spectra.

3. Results and discussion

3.1. Investigation of the cured network conformation of DGEBA–PMSE hybrids using DMA

The logarithmic storage modulus (E′) and the loss modulus (E″) measured as functions of temperatures are shown in Figs. 1 and 2, respectively. The value of E′ for the PMSE–MHHPA at room temperature was about two orders of magnitude lower than the values for the DGEBA–PMSE hybrids and DGEBA–MHHPA. This shows that the rigid network of the cured DGEBA can be toughened through the incorporation of the flexible cured PMSE network. E′ for each material decreased sharply for higher temperatures at which the E″ reached its maximum value. The temperature of the peak of the E″ curve was defined as the glass transition temperature T_g. This transition is a consequence of the massive cooperative chain motions and is also called the α transition. Fig. 2 shows a single α transition peak for DGEBA–PMSE-0.2 and DGEBA–PMSE-0.4. The presence of such a single transition peak implies the absence of macro phase separation in the DGEBA–PMSE hybrids. The relaxation characteristics of the two DGEBA–PMSE hybrids and of the materials prepared for comparison as reference materials are summarised in Table 1. Both T_g and the peak intensity reduced as the amount of PMSE increased because of the incorporation of the longer flexible siloxane chains of PMSE. The crosslink density (ν) was calculated from the E′ at $T = T_g + 30$ °C assuming rubber-like elasticity using $\nu = E'/3RT$, where R is the gas constant and T is the absolute temperature [19,20]. It is important to note that the crosslink density values for DGEBA–PMSE-0.2 and DGEBA–PMSE-0.4 were higher than for DGEBA–MHHPA, despite the presence of longer and flexible siloxane chains in PMSE. This implies that the relatively long dimethyl- and phenyl-substituted siloxane chains of the PMSE cured network can be inserted into the cured DGEBA network to form well distributed physical entanglements. This is in agreement with our previous morphological study of DGEBA–PMSE-0.2 and DGEBA–PMSE-0.4, which showed that DGEBA–PMSE hybrids were homogeneous [14]. Furthermore, the widths of the E″ peaks at half maximum for the α transition of DGEBA–PMSE-0.2 and DGEBA–PMSE-0.4 were wider than those for DGEBA–MHHPA and PMSE–MHHPA. We attribute this to the higher number of physical entanglements formed between the DGEBA cured network and the PMSE cured network, leading to a slower relaxation process.

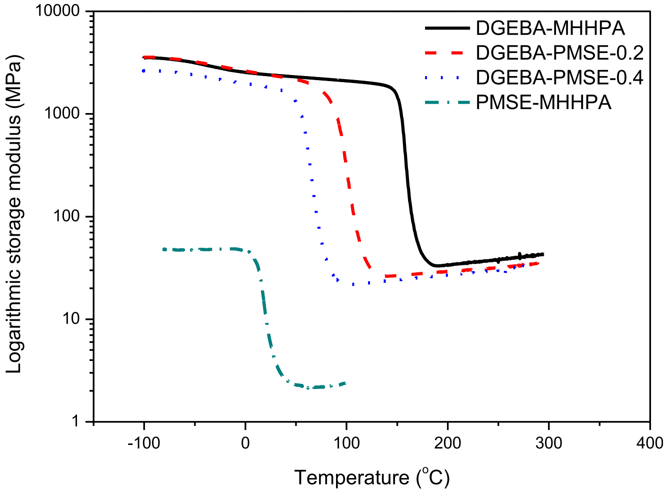


Fig. 1. Logarithmic storage modulus E′ of the DGEBA–PMSE hybrids, DGEBA–MMHPA and PMSE–MHHPA.

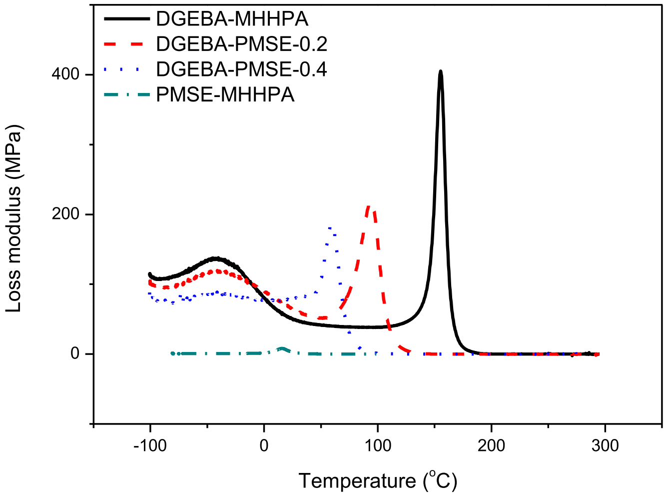


Fig. 2. Loss modulus E″ of the DGEBA–PMSE hybrids, DGEBA–MHHPA and PMSE–MHHPA.

3.2. Characteristics of β transition of DGEBA–PMSE hybrids

At lower temperatures (−25 to −45 °C), another well defined transition peak can be observed for the loss modulus curves of DGEBA–PMSE-0.2 and DGEBA–PMSE-0.4; the temperature of this peak is defined as the β transition temperature (T_β) [21]. A small decrease in the storage modulus was found to correspond to this transition, as shown in Fig. 1. The motion processes responsible for the relaxation in crosslinked epoxy resins have received considerable attention, with the β transition attributed to the local or pendant group motion [22]. The addition of a plasticiser or a flexible curing agent usually influences the relaxation behaviour in two ways. First, it leads to a remarkable depression of T_g, and second it gives rise to a decrease in the β peak intensity and a shift in T_β to a lower temperature [23–26].

The β relaxation characteristics determined in our study for the DGEBA–PMSE hybrids and the DGEBA–MHHPA are listed in Table 2. Interestingly, the T_β, the E″ peak height, and the width of the β transition for DGEBA–PMSE hybrids remain similar to those for DGEBA–MHHPA, even for the hybrid with the larger fraction of PMSE. By contrast, the area under the β transition peak shows a dramatic decrease for the increased amounts of PMSE in the DGEBA–PMSE hybrids. Because the area under the β transition peak usually represents the relaxation strength, which in turn determines the activation barrier for the transition, these phenomena can imply that the β relaxation behaviour of the hybrid composites is due to the local motion of the cured DGEBA networks and that

Table 1
The α relaxation characteristics of the DGEBA–PMSE hybrids, DGEBA–MMHPA and PMSE–MHHPA.

	T_g (°C)[a]	Intensity (MPa)[b]	Width (°C)[c]	Storage modulus E′ (MPa) at 25 °C	Storage modulus E′ (MPa) at Tg + 30 °C	Crosslink density ($\nu \times 10^3$) (mol m^{-3})
DGEBA–MHHPA	155.3	405.2	11.1	2166.7	33.8	3.1
DGEBA–PMSE-0.2	95.4	216.5	15.0	2172.8	30.4	3.3
DGEBA–PMSE-0.4	55.6	180.5	20.4	1802.2	28.6	3.5
PMSE–MHHPA	15.6	8.0	14.0	5.7	2.4	0.3

[a] α transition peak temperature.
[b] α transition peak intensity.
[c] α transition width at half peak.

Table 2
The β relaxation characteristics of the DGEBA–PMSE hybrids and DGEBA–MHHPA.

	T_β (°C)[a]	Intensity (MPa)[b]	Width (°C)[c]	Area (MPa·min)[d]
DGEBA–MHHPA	−34.6	130.0	93.0	622.1
DGEBA–PMSE-0.2	−35.6	116.9	116.5	540.0
DGEBA–PMSE-0.4	−38.3	117.3	92.2	119.3

[a] β transition peak temperature.
[b] β transition peak intensity.
[c] β transition width at half peak.
[d] β transition area.

the flexible cured PMSE networks contribute to the local motion and decrease the barrier to β relaxation [27]. The unique β relaxation features of the DGEBA–PMSE hybrids indicate that PMSE and DGEBA can form individual cured networks and that IPNs are formed when the flexible PMSE cured network is inserted into the rigid DGEBA network.

3.3. Free volume analysis of the DGEBA–PMSE hybrids

Molecular conformation rearrangement is usually associated with structural relaxation behaviour [28]. The mechanism involved in the structural relaxation of thermosetting polymers is related to the rigidity of the molecular chain, the physical entanglement, and the free volume in the polymers. In recent years, PALS has been widely used as a microanalytical method for the quantitative characterisation of the free volume in a wide variety of polymers [29,30]. PALS experiments have helped to clarify the relationship between the size and the fraction of the free volume in a polymer and its chain dynamics and have revealed the crucial role that the free volume size and concentration play in structural relaxation.

The long-lived lifetime component ζ_3 and its intensity I_3 associated with *ortho*-Positronium (*o*–Ps) pick off annihilation were the focus of this study. The free volume parameters for the DGEBA–PMSE hybrids and DGEBA–MHHPA are summarised in Table 3. As expected, the rigid glassy cured DGEBA network exhibits a relatively short free volume radius and a relatively low fractional free volume. Compared to the properties of DGEBA–MHHPA, the free volume parameters for the DGEBA–PMSE hybrids increased monotonically as the content of the cured PMSE network increased. Because the chemical structures for DGEBA–PMSE-0.2 and DGEBA–PMSE-0.4 are similar, the o–Ps intensity can be interpreted as an indicator of the number density of the nanoholes in the hybrids. Thus, while the two hybrids are thoroughly homogeneous at the macroscale, they exhibit a larger number of nanoholes that are also of larger size. The properties of DGEBA and PMSE, including the chain stiffness and the polarity, are different [14]; this results in the penetration by the flexible cured PMSE network into the rigid cured DGEBA network and the formation of looser heterogeneous IPN morphologies at the nanoscale.

Table 3
Free volume radii and fractional free volumes of the DGEBA–PMSE hybrids and DGEBA–MHHPA.

	o–Ps lifetime ζ_3 (ns)	o–Ps intensity I_3 (%)	Free volume radius R (Å)	Fractional free volume FFV (%)
DGEBA–MHHPA	1.8216	25.1212	2.6857	3.6693
DGEBA–PMSE-0.2	1.8873	28.5537	2.7498	4.4761
DGEBA–PMSE-0.4	1.9843	31.9211	2.8409	5.5185

3.4. Structural relaxation behaviour of DGEBA–PMSE-0.4 at different temperatures

Physical aging mechanisms are influenced by the rigidity of the molecule chains, the molecular conformation, the entanglement and the free volume [31,32]. It was therefore necessary to understand the structural relaxation behaviour in the DGEBA–PMSE hybrids at different aging temperatures.

The lifetime probability density function [33] PDF $(\zeta) = \lambda^2 \alpha(\lambda)$, was determined as a function of the o–Ps lifetime for the thermal aging using the MELT program; the PDF (ζ) of DGEBA–PMSE-0.4 at 150 °C is shown in Fig. 3. The full width at half maximum becomes dramatically narrower after 480 h of thermal aging, and then narrows more gently over the following 240 h. However, the peak o–Ps lifetime decreases only slightly over that period, indicating that the aging of DGEBA–PMSE-0.4 at 150 °C is a physical aging process and that the cured networks in the DGEBA–PMSE-0.4 can be rearranged to give a more compact conformation.

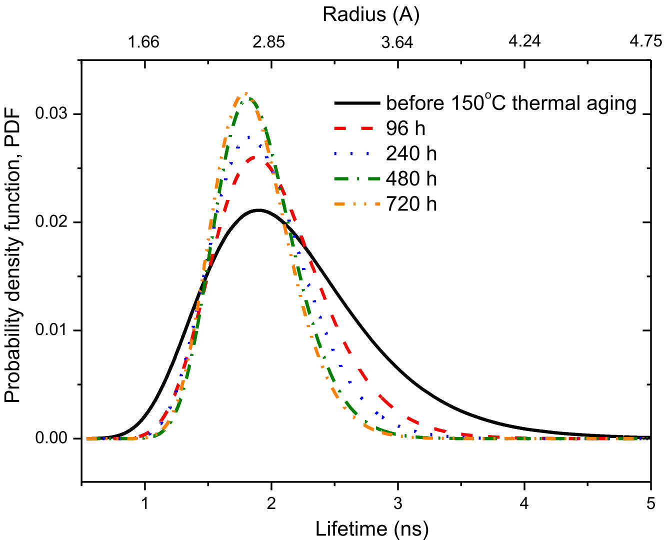


Fig. 3. Probability density function for the o–Ps lifetime of the DGEBA–PMSE-0.4 thermally aged at 150 °C.

We then investigated thermal aging at the T_g of DGEBA–PMSE-0.4 (55.6 °C). Unlike the aging at 150 °C that resulted in the monotonic narrowing of the PDF (ζ), aging at 55 °C led to the gradual broadening of the PDF (ζ) (Fig. 4). This implies that a complex mechanism was involved in the physical aging process at 55 °C. The differences between the thermal aging temperatures and the individual T_g values for the cured DGEBA and PMSE networks significantly influenced the structural relaxation behaviour of the DGEBA–PMSE-0.4. For thermal aging at 150 °C, the temperature is high enough to induce cooperative motion in the cured PMSE and DGEBA networks and a more densely packed conformation results. For thermal aging at 55 °C, the PMSE molecule may be in a rubbery state but the DGEBA molecules are in a glassy state. Because the most likely structural relaxation for the DGEBA cured network in the glassy state is a π flip of the phenylene groups and the trans–gauche isomerisation of the methylene groups in the backbones [31], such a glassy network may restrict free spatial motion in the cured PMSE network. However, the cured PMSE molecules in the rubbery state can undergo chain motion and serve as plasticisers, increasing the local mobility of the cured DGEBA.

We also calculated the changes in the free volume radius and the fractional free volume for DGEBA–PMSE-0.4 aging at 150 °C and 55 °C; these are shown in Fig. 5 (a) and (b). At 150 °C, the free volume radius of the hybrid decreased by 5.8% after 720 h, while the fractional free volume showed a much larger decrease of 25.4%. At 55 °C, the free volume radius of the hybrid only decreased by 2.4% after 960 h, while the fractional free volume increased by 6.7%. This confirms that DGEBA–PMSE-0.4 is very thermally stable and that the conformational changes are caused by physical aging.

3.5. *Structural relaxation time of DGEBA–PMSE-0.4 at different temperatures*

Polymers that exhibit structural relaxation phenomena are commonly described using nonlinear model functions [34], such as the single exponential, the double additive exponential model, and the Kohlrausch–Williams–Watts exponential model (KWW exponential model).

The single exponential fit model is given by

$$\varphi(t) = A\exp\left(-t/\zeta\right) + C. \tag{1}$$

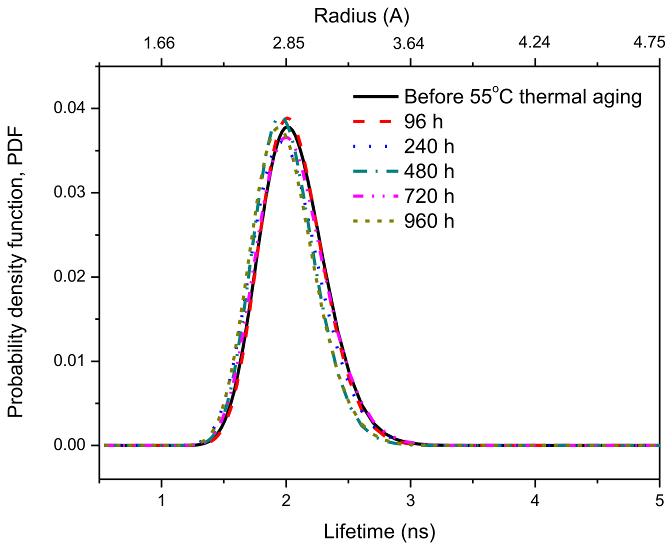


Fig. 4. Probability density function for the o–Ps lifetime of DGEBA–PMSE-0.4 thermally aged at 55 °C.

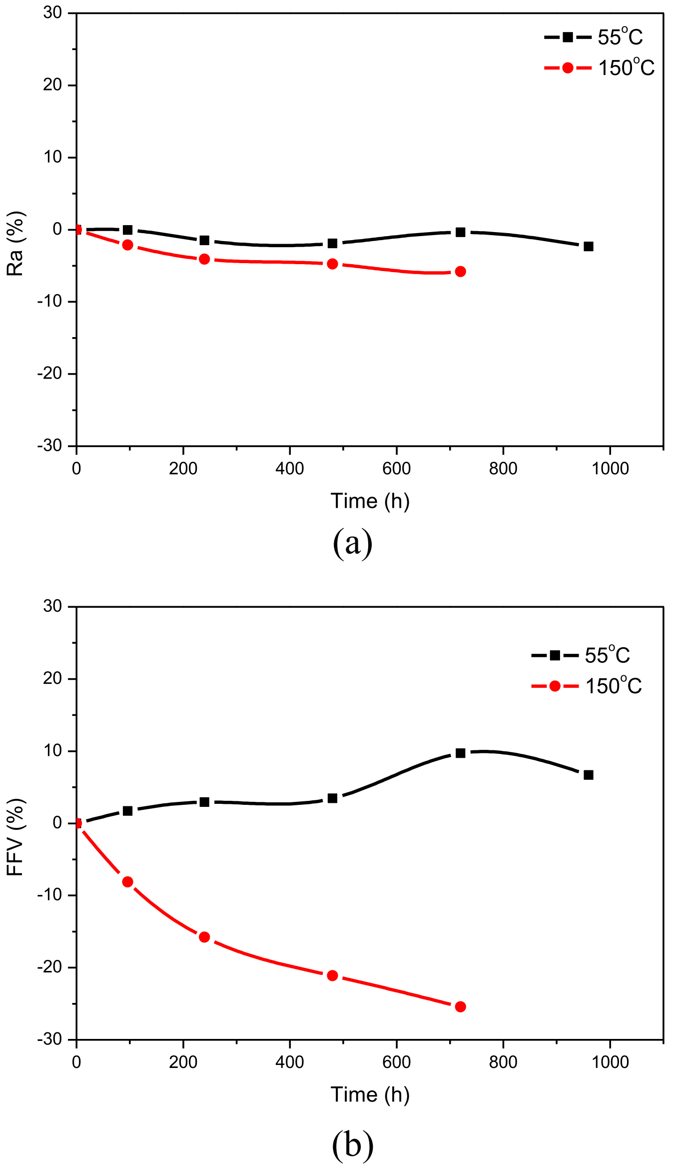


Fig. 5. Changes in the (a) free volume radius and (b) the fractional free volume after thermal aging at different temperatures.

The double additive exponential model is given by

$$\varphi(t) = A\exp\left(-t/\zeta_1\right) + B\ \exp\left(-t/\zeta_2\right) + C. \tag{2}$$

The KWW exponential model is given by

$$\varphi(t) = A\exp\left(-t/\zeta\right)^{\beta} \quad 0 < \beta \leqq 1. \tag{3}$$

In Eqs. (1)–(3), ζ_1, ζ_2, and ζ are the relaxation time constants and A, B, C, and β are positive constants. Usually, $\beta = 1$ corresponds to a single relaxation time or exponential behaviour. Smaller values of β represent a greater deviation from the exponential behaviour.

The equilibrium relaxation function $\varphi(t)$ of the free volume can be calculated using

$$\varphi(t) = \left(I_3(t) - I_{3f}(\text{eq.})\right) \Big/ \left(I_{3i}(t=0) - I_{3f}(\text{eq.})\right), \tag{4}$$

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

Table 4
Summary of the relaxation parameters fitted using the double additive and the KWW exponential models.

Temperature	Double additive exponential model			KWW exponential model		
	ζ_1 (h)	ζ_2 (h)	R^2	ζ_0 (h)	β	R^2
150 °C	584.5	584.5	0.80	68.3	0.50	0.98
55 °C	37.4	753.6	1	23.0	0.72	0.82

(4), and Eq. (3) can be rewritten as

$$\mathrm{Ln}(-\mathrm{Ln}\varphi(t)) = \beta\ \mathrm{Ln}\ t - \beta\ \mathrm{Ln}\ \zeta_0. \qquad (5)$$

Therefore, a least-square fitting program was used to calculate the relaxation constant for both ζ_0 and β. A summary of the parameters fitted to the KWW exponential model and the double fitting model are shown in Table 4.

For aging at 150 °C, both the double additive exponential model and the KWW exponential model can yield a single relaxation time. The relaxation time of DGEBA–PMSE-0.4 calculated by the KWW exponential model is 68.3 h, which is rather short compared to the results of our PALS experiments. On the other hand, the double additive exponential model yielded 584.5 h for the relaxation time of DGEBA–PMSE-0.4; this compares rather better with our PALS results. It is clear that the double additive exponential model provides a better description of the DGEBA–PMSE-0.4 relaxation behaviours during the aging process. In addition, the presence of a single relaxation time at 150 °C indicates that entire IPNs were involved in the thermal relaxation process. For thermal aging at 55 °C, the double additive exponential model provides an insight into the structural relaxation behaviours of IPN, indicating two individual relaxation times of 37.4 h (ζ_1) and 753.6 h (ζ_2). The shorter relaxation time ζ_1 of the IPN hybrid can be attributed to the PMSE network relaxation as the PMSE network is in the rubbery state but needs time to be released from the IPNs entanglement. The longer relaxation time ζ_2 can be attributed to the DGEBA network relaxation because of the glassy state of the DGEBA network.

4. Conclusions

We have investigated the cured network conformation and the structural relaxation behaviours of DGEBA–PMSE hybrids at different aging temperatures. The cured PMSE network possesses dimethyl- and phenyl-substituted siloxane chains that can be inserted into the cured DGEBA network to form interpenetrating polymer networks.

The PALS studies on DGEBA–PMSE-0.4 structural relaxation at aging temperatures of 150 °C and 55 °C clearly reveal that the thermal aging effects on the thermally stable DGEBA–PMSE hybrids were actually physical aging processes that caused conformational rearrangement to form compacted networks. The aging-induced relaxation of the DGEBA–PMSE hybrid shows complicated relaxation behaviours because of the existence of interpenetrating polymer networks. For such IPNs, the double additive exponential model can effectively predict IPNs relaxation times that are highly dependent on the difference between the thermal aging temperatures and the glass transition temperatures of the cured DGEBA and PMSE networks.

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