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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

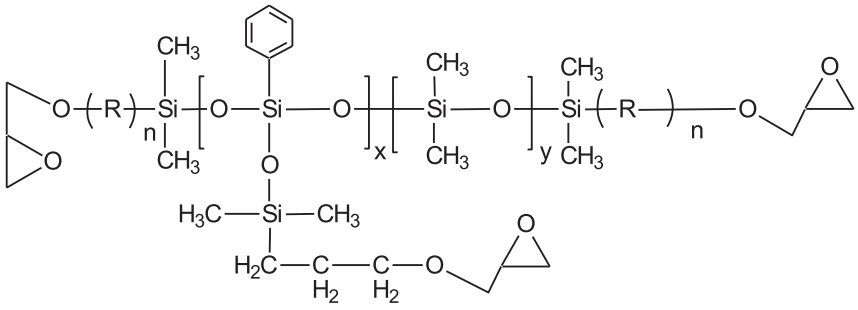
The dynamic mechanical properties of the cured samples were measured between −100 °C and 280 °C at a heating rate of 5 °C min^{-1} and a fixed frequency of 1 Hz, using a Q800 instrument (TA Instruments, Inc., New Castle, DE, USA).

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).