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Thermal aging of an anhydride-cured epoxy resin

Yongming Yang [a, b], Guijun Xian [a, b, *], Hui Li [a, b], Lili Sui [c]

[a] Key Lab of Structural Dynamic Behavior and Control, Harbin Institute of Technology, Ministry of Education, Heilongjiang, Harbin 150090, China
[b] School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, China
[c] Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen, China

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ABSTRACT

Fiber reinforced polymer (FRP) composites with anhydride cured epoxy resin matrices are widely used in civil engineering (e.g., pultruded FRP plates and bars), and their thermal aging behavior is a concern when they are subjected to elevated temperatures (e.g., FRP chimney). In the present article, thermal aging of an epoxy resin matrix at 130 °C–160 °C for 30 days was performed, and the effects on the flexural properties, molecular structures, free volume fraction, and mechanical properties were investigated. FTIR spectroscopy indicated that oxidation and molecular rearrangement occurred in the skin of the epoxy samples during thermal aging. Dynamic mechanical thermal analysis (DMTA) further illustrates the dominant effect of the molecular rearrangement in the sample skin with a thickness less than 100 μm, leading to a new high temperature *tan δ* peak. The free volume fraction of the skin and the bulk epoxy sample was characterized by positron annihilation lifetime spectroscopy (PALS). The results indicate that a noticeable reduction of the apparent free volume fraction occurred in the sample skin, while the bulk sample was only slightly affected. The flexural results indicate that thermal aging obviously reduced the break strain, while the flexural strength was only slightly affected and the modulus increased.

1. Introduction

Due to their high mechanical properties, low shrinkage during cure, and ease of processing, epoxy resins have been widely used as resin matrices for fiber reinforced polymer (FRP) composite materials [1–4]. One of the rapidly increasing applications of FRPs is the rehabilitation and retrofitting of aged concrete or steel structures [5,6]. Among these applications, the service temperatures may be high and lead the epoxy matrix to be thermally aged, for example, the FRP chimneys or FRP retrofitted concrete chimneys that have been widely applied in recent years [7]. Compared to fibers, the epoxy resin matrix is more susceptible to elevated temperatures. Anhydride cured epoxy resin, one of the widely used resin matrices for fiber reinforced polymer (FRP) composites, is investigated on its thermal aging performances herein.

For an epoxy resin, the evolution of the chemical structures due to elevated temperatures can be categorized in the following stages sequently: post-curing, oxidation of active groups, and chain scission. Generally, the post-curing reaction is occurred during the initial stage of thermal aging [8–10]. For an anhydride-cured epoxy, the reactive groups to be oxidized include the secondary alcohol and the hydrogen placed on the tertiary carbon at the α position of the ester. The secondary alcohol in the epoxy resin can be oxidized to carbonyl groups [11–16]. Oxidation of the hydrogen connected to the tertiary carbon at the α position of the ester is associated with the limited chain scission, which can lead to the formation of various carbonyl groups, particularly of ketone and ester groups [17,18]. Chain scission involves the migration of the liberated segment under the decomposition of the molecular chain by thermo-oxidation [10,19]. In addition, thermo-oxidation of an epoxy resin is frequently associated with a mass increase due to the incorporation of oxygen to the molecules [20]. A possible correlation was found between the structural degradation and the mechanical degradation for an aged epoxy resin. The degradation process is enormously influenced by several factors, such as the aging temperatures and the aging time [21]. For a cured epoxy resin, generally, thermal aging results in an increased modulus and brittleness [22].

Free volume is the intermolecular space necessary for atoms, molecular segments, and the entire chain of the polymer to undergo thermal motion [23,24]. The detection of molecular-level micro-structural changes of the free volumes will provide an

* Corresponding author. 202 Haihe Road, Nangang District, Harbin 150090, China. Tel./fax: +86 451 8628 3120.
E-mail address: gjxian@hit.edu.cn (G. Xian).

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understanding of the origins, mechanisms, and progression of the thermo-oxidation degradation process [25–27], which may eventually lead to macroscopic structural changes and the loss of durability. The positron annihilation technique can be used to directly measure the free volume of a polymer sample [24,28]; the method was used to detect the variation of the free volume of a polymer material due to aging. As reported, ultraviolet aging of a polymer coating led to the decrease of the free volume content and thus the degradation of the mechanical durability [26]. The dependence of the other macro-mechanical properties and physical properties of the polymer materials on the free volume content were also reported [28,29].

The epoxy resin with a Diglycidylether of bisphenol-A (DGEBA) and MeTHPA (methyl tetrahydrophthalic anhydride) is one of the most common resin systems for pultruded FRPs. Such FRPs are widely used in construction, and in some cases, the FRPs must operate at elevated temperatures, e.g., chimney structures built or strengthened by FRPs. The evolution of the molecular structures and the mechanical properties of the FRPs due to the elevated temperatures, especially under long-term exposure, have rarely been studied. As expected, the resistance of the FRPs to long-term elevated temperature exposure may be mainly dependent on the degradation of the resin matrix as well as the bonding between fiber and the resin rather than the fibers [30]. In view of this background, thermal aging of an anhydride cured epoxy resin is studied as the first step in our series of investigations on the long-term performance of FRPs at elevated temperatures. It is worth noting that thermal aging of the epoxy-anhydride resin systems has been studied in terms of thermal degradation kinetics [31,32], mechanistic aspects [33], and thermo-mechanical properties [34]. The present work was conducted specially to correlate the variation of the chemical structures, free volume content and the thermo-mechanical properties of a DGEBA/MeTHPA resin system, which was thermally aged for a relatively long term.

2. Experimental

2.1. Sample preparation

The diglycidyl ether of bisphenol-A (DGEBA) used in this study was a commercial epoxy with a brand name of Fenghuang (Xing-Chen Chemicals Co., Ltd., Wuxi, China). The weight per epoxide of the epoxy resin is 185–192. The curing agent used was methyl tetrahydrophthalic anhydride (MeTHPA Qing-yang Chemistry Co., Ltd., Jiaxing, China). The accelerator was a tertiary amine tris (dimethylaminomethyl) phenol (Shan-Feng Chemical Industry Co., Ltd., Changzhou, China).

The resin system, composed of DGEBA, MeTHPA, and an accelerator in the ratio of 100:80:2 by weight, was mixed for 10 min by hand. After degassing under vacuum for 5 min, the mixture was cast into an aluminum mold with a cavity of 250 mm × 400 mm × 4 mm and was cured at 120 °C for 90 min, followed by a post-cure at 150 °C for 90 min in an oven. Fig. 1 shows the chemical structures of the raw materials.

Cured epoxy samples were cut with a water-cooled diamond saw to the dimensions required by the following tests.

2.2. Thermal aging test

An oven (TAISITE 101-1, Tianjin City, China) was used to perform the thermal aging of the cut samples. Four temperatures (130, 140, 150, and 160 °C) and six aging durations (5, 10, 15, 20, 25, and 30 days) were applied to the epoxy samples. The sample dimensions were determined by the following testing (such as, mechanical test, DMA test, etc.).

2.3. Gravimetric measurements

During thermal aging, the masses of the cured epoxy samples (70 mm × 10 mm × 3 mm) were recorded using an electronic scale with a precision of 0.1 mg. Ten specimens were measured for each aging temperature.

2.4. Flexural property measurement

A three-point bending test was performed for each sample according to ASTM D 790-07. The sample dimensions were 70 mm × 10 mm × 3.5 mm. The tests were performed in displacement control with a loading rate of 1.49 mm/min. For each condition, 5 tests were repeated and reported.

2.5. Fourier transform infrared (FTIR) spectroscopy

The chemical structures of the epoxy resin were analyzed using FTIR Spectroscopy (Nicolet company model OMNIC NICOLET6700) over a wave number range of 4000 to 500 cm^{-1}. The pellets were made from a mixture of KBr powder and the epoxy powders, which were scratched out from the surface or interior of the samples using a knife.

2.6. Dynamic mechanical analysis (DMA)

DMA of the epoxy samples was performed in single cantilever mode using a TA Instruments DMA Q800 (TA Instruments, USA) apparatus. The samples (38 mm × 10 mm × 1.5 mm) were tested under a constant deformation amplitude of 30 μm at a frequency of 1 Hz and under a temperature ramp of 5 °C/min over the temperature range of 20 °C–240 °C.

2.7. Positron annihilation lifetime spectroscopy (PALS)

Detailed information related to PALS can be found in the literature [26,28,29]. The following only explains how to determine the free volume size and content using PALS for the present study.

PALS measurements were conducted using a multichannel analyzer data buffer (Ortec Adcam mode) with a time resolution of 0.27 ns full width at half-maximum. The probe consists of a BaF_2 crystal and a XP2020Q PMT. Approximately 20 μg of Ci $Na^{22}Cl$ was directly deposited onto each sample, and then, each sample was sandwiched between two identical pieces of the epoxy samples to be tested (10 × 10 × 1.5 mm^3). Each spectrum was collected over a period of ~2 h and consisted of ~10^6 integrated counts.

The positron spectra were measured at room temperature, with three positron lifetimes resolved for the spectra. The longest-lived component, with a lifetime of τ_3 and an intensity of I_3, results from the pick-off annihilation of ortho-positronium (o-Ps) in the free volume holes. The lifetime τ_3 is assumed to be proportional to the free volume hole size, and the intensity I_3 is connected with the free volume hole number. Assuming that the free volume holes are spheres, the dependence of τ_3 on the average radii R of holes is as follows [35]:

$$\tau_3 = 1/2[1 - R/R_0 + 1/2\pi\sin(2\pi R/R_0)]^{-1} \quad (1)$$

where R_0 is the radii of the finite spherical potential, $R = R_0 - \triangle R$ is the radii of free volume, and $\triangle R = 0.1656$ nm is an empirical parameter that is obtained by fitting to the measured lifetime of cavities with a known size. The apparent free volume fraction (F_v) is given below [29]: