Polymer Degradation and Stability 118 (2015) 111–119

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

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

ARTICLE INFO

Article history:
Received 8 January 2015
Received in revised form
19 March 2015
Accepted 24 April 2015
Available online 1 May 2015

Keywords:
Epoxy resin
Thermal aging
Chemical structure
Thermal-mechanical properties
Free volume

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).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.04.017
0141-3910/

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 $\mathrm{BaF_2}$ crystal and a XP2020Q PMT. Approximately 20 μg of Ci $\mathrm{Na^{22}Cl}$ was directly deposited onto each sample, and then, each sample was sandwiched between two identical pieces of the epoxy samples to be tested ($10 \times 10 \times 1.5\ \mathrm{mm}^3$). 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]:

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

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]:

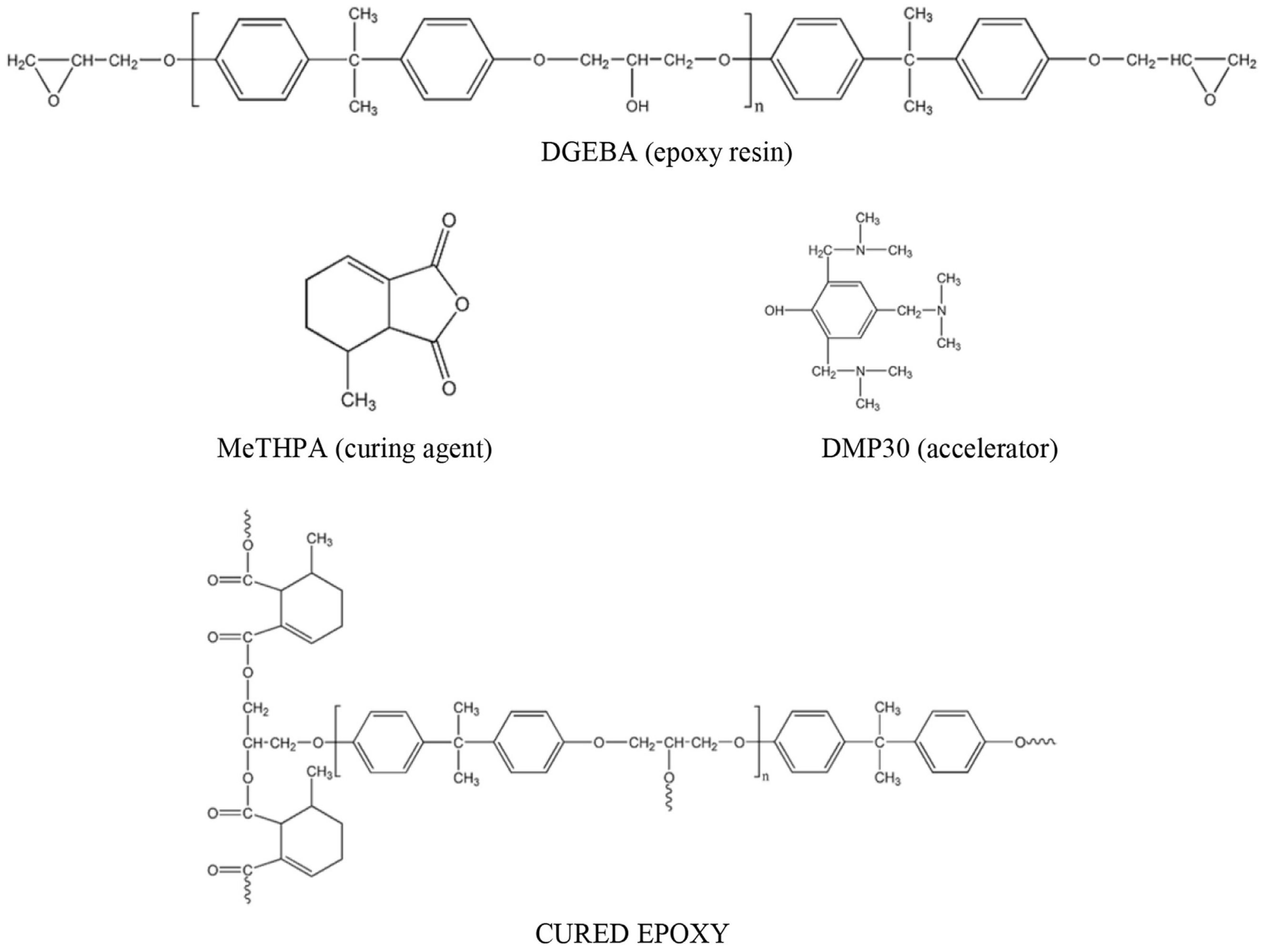


Fig. 1. Chemical structure of DGEBA, MeTHPA, DMP30 and cured epoxy.

$$F_v = 4\Big/3\pi R^3 I_3 \tag{2}$$

Note, in the present paper, the apparent free volume fraction (F_v) is not the absolute free volume fraction value and can be only used for comparison.

3. Results and discussion

3.1. Thermal aging on the chemical structures

In the present study, the thermal aging temperatures considered were in the range of 130 °C–160 °C, and the FTIR measurements were mainly performed for epoxy samples aged up to 150 °C to illustrate the variation of the chemical structures of the epoxy system. Fig. 2 shows the FTIR spectra of the epoxy resin from the core part of the samples. As shown, for the epoxy from the core part, there are no changes in the functional groups between the control and the 150 °C aged samples. This result indicates that no thermal degradation in the chemical structures occurred in the core parts of the epoxy. In the following, therefore, only the FTIR spectra of the epoxy from the sample surfaces were analyzed.

Fig. 3 shows the FTIR spectra of the epoxy resin on the surfaces of the control or the 150 °C aged samples, while the assignments of the characteristic absorption bands are given in Table 1. The absorption bands near 1739 cm^{-1} is the characteristic of stretching vibration of the C=O groups in the ester group. After 5 days of aging at 150 °C (Fig. 3b), the increase in the intensities of the 1739 cm^{-1} band was observed. As is known, the curing of DGEBA with MeTHPA accelerated by tertiary amine will produce ester

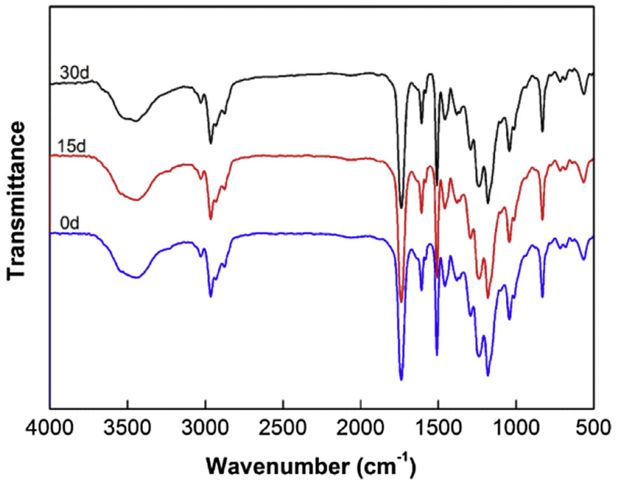
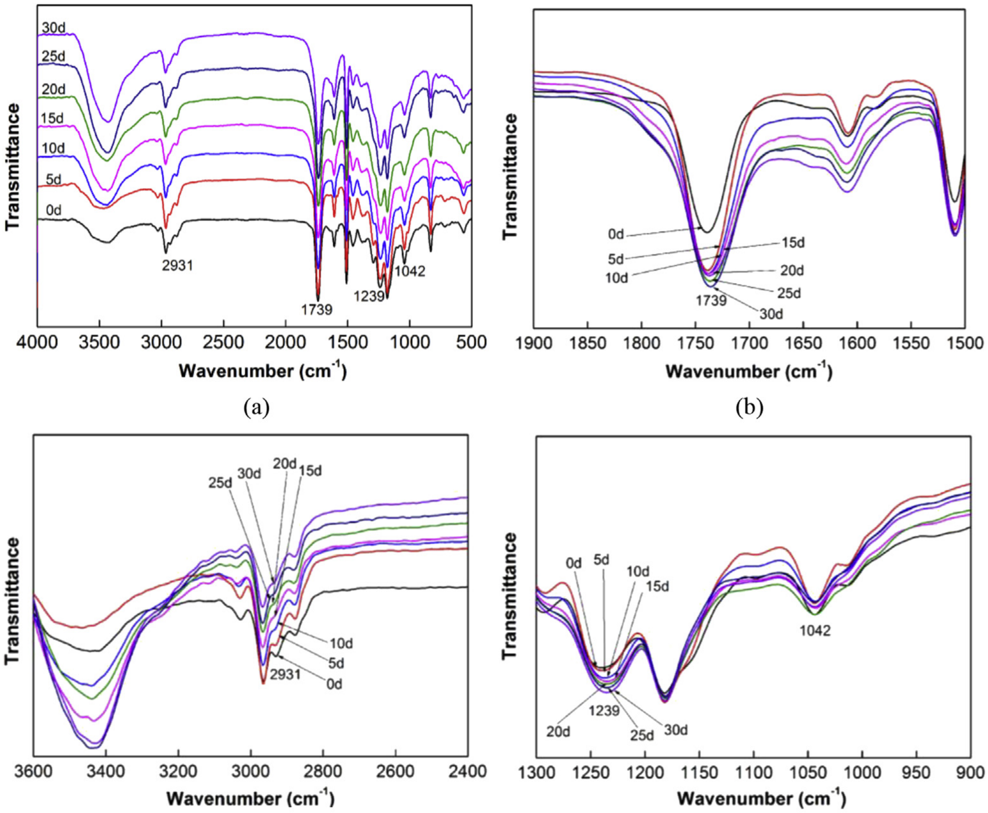


Fig. 2. FTIR spectra of the control and the 150 °C aged epoxy system (sample taken from the core part).



(a) (b) (c) (d)

Fig. 3. FTIR spectra of the control and the 150 °C aged epoxy samples (scratched from the sample surfaces): (a) entire range of wave numbers considered; (b) wave number range of 1900–1500 cm^{-1}; (c) wave number range of 3600–2400 cm^{-1}; (d) wave number range of 1300–900 cm^{-1}.

Table 1
Assignments of the characteristic absorption bands in the FTIR spectra.

Absorption bands (cm^{-1})	Assignment
2931	Stretching vibration of –C–H in methylidyne
1739	Stretching vibration of C=O in a non-conjugate ester
1239	Asymmetrical stretching vibration of C–O–φ
1042	Symmetrical stretching vibration of C–O–φ

groups (see Fig. 1). Thus, the increase of the intensities of 1739 cm^{-1} can be attributed to the post-curing of the epoxy resin during the early thermal aging stage [36]. Note that the glass transition temperature of the control epoxy is approximately 138 °C, as determined via DMA (see in the following). Thermal aging at 150 °C is effective for the post-curing process of the epoxy resin system.

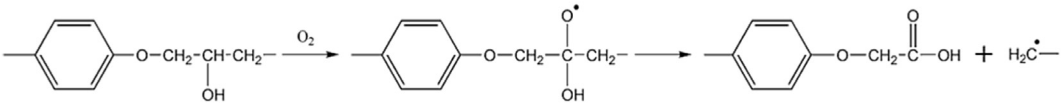
After 10 days of aging at 150 °C, the absorption band of the C=O group in ester at 1739 cm^{-1} moves toward lower wave numbers and enhances with increasing aging time (Fig. 3b). This result can be attributed to the formation of carbonyl groups from the hydroxyl groups due to oxidation [11–16]. The possible reaction schemes are summarized in Scheme 1 [13,14].

Meanwhile, the intensity of the bands near 2931 cm^{-1} (Fig. 3c), which is the characteristic stretching vibration of C–H in methylidyne groups, decreases with the thermal aging time. This result confirms that oxidation of the hydrogen placed on the tertiary carbon in the α position of the ester is associated with the limited chain scission, which can lead to the formation of various carbonyl groups, in particular, ketone and ester groups [17,18]. The possible reaction is shown in Scheme 2 [18].

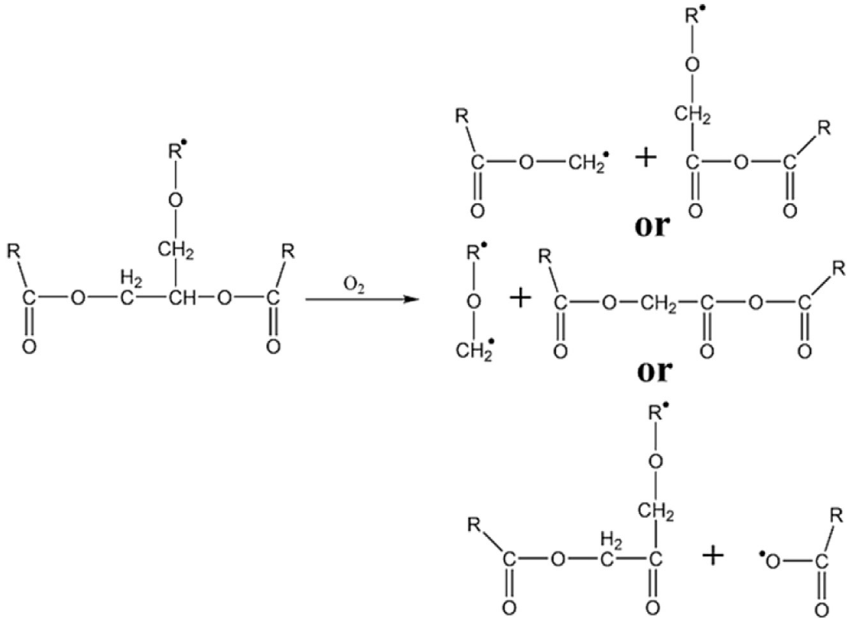
The absorption of the band near 1042 cm^{-1} (Fig. 3d), which corresponds to the symmetrical stretching vibration of C–O–φ (φ represents benzene ring) [18,37], decreases in intensity with thermal aging time. These results indicate that C–O–φ is destroyed during thermal aging. Furthermore, the absorption band near 1239 cm^{-1}, which corresponds to the asymmetric stretching vibration of C–O–φ, moves toward lower wave numbers and becomes broadened with thermal aging, which is assigned to the formation of φ–O–φ [13,27]. The possible reaction is shown in Scheme 3 [13].

Fig. 4 shows the mass change of the epoxy samples during thermal aging. From the figure, with the increase of the aging time and temperature, the mass increases. This result is due to incorporation of oxygen into the chemical structures through oxidation of active groups [20].

Through the above-described FTIR spectra analysis, it can be concluded that the changes of the chemical structure of epoxy on



Scheme 1. Possible reaction producing carbonyl groups.



Scheme 2. Possible reactions producing carbonyl groups.

the sample surface includes the following: the hydroxy groups and the hydrogen on the tertiary carbon in the α position of the ester tend to be oxidized to form various carbonyl groups and form the φ–O–φ groups due to molecular rearrangement. With increasing aging time, the reaction becomes more serious, as indicated by the variation of the FTIR peaks with aging time.

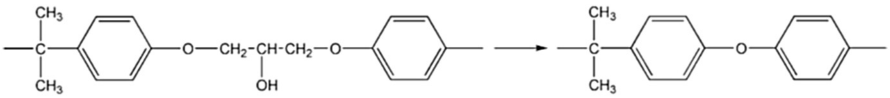
3.2. DMA results

Fig. 5 shows the *tan δ* curves of 150 °C aged epoxy samples for various aging times. Fig. 5a shows that, for the control epoxy sample, one main *tan δ* peak is found at 138 °C, which can be designated as the T_g of the epoxy system. In addition, a very weak shoulder peak is observed at higher temperature (~160 °C). With the increase of the aging time, the shoulder peak is found to become increasingly intense and eventually exceeds the intensity of the lower temperature peak (Fig. 5b–d). The emergence of the secondary peaks was attributed to the “skin-core” structures, which may be generated by different degrees of oxidation and degradation on the skin and core of the samples [13,14]. To verify this assumption, an epoxy sample aged at 150 °C for 30 days was polished to remove the skin and then was tested following the method used for the data shown in Fig. 5. The samples were polished to remove the surface layer of thicknesses of approximately 30 μm, 60 μm and 100 μm. Fig. 6 shows the obtained *tan δ* curves for these samples. As shown in the figure, as more of the sample surface is removed, the high temperature *tan δ* peak diminishes and finally vanishes. When 100 μm of the skin was removed, only one defined *tan δ* peak was observed. This result supports the above assumption that the oxidation or molecular rearrangement occurred on the surfaces of the epoxy resin under the present thermal aging conditions. The depth of the epoxy surface affected by the thermal aging is in the range of 60–100 μm for the epoxy aged at 150 °C for 30 days.

As revealed above, the thermal aging on the epoxy skin is related to the oxidation and re-arrangement of the epoxy molecular chain structures. Because the oxidation (shown in Schemes 1–2) leads to molecular chain scission, the *tan δ* peak temperatures should decrease due to the reduced amount of cross linkage [38]. Therefore, the results shown in Fig. 5 that the secondary *tan δ* peak related to exposure to higher temperatures increases with increasing aging time, which indicates that the re-arrangement of the molecules is dominant, resulting in the formation of much denser crosslinking structures. As expected, the re-arrangement of the molecules is complex, which involves Schemes 1–3. The formation of the free radicals during oxidation (see Schemes 1 and 2) may lead to new cross linkage.

In addition, the weak high temperature *tan δ* peak of the control samples (as shown in Fig. 5a) can be attributed to the thermal aging during the curing process (120 °C and 150 °C for 90 min). The low temperature *tan δ* peaks can be attributed to the core parts of the epoxy. The shift of the *tan δ* peaks to higher temperatures with increasing the aging time is assigned to the post curing of the bulk epoxy.

Fig. 7 presents the variation of the glass transition temperatures of the aged epoxy samples, T_{g1} and T_{g2}, determined from the low and high temperature *tan δ* peaks, respectively. As shown in the figure, after 5 days of thermal aging at temperatures higher than 130 °C, T_{g1} increased from 138 °C to ~144 °C. With the further increase of the aging time, almost no change occurred for T_{g1}. As mentioned above, the variation of T_{g1} is related to the post curing of the bulk samples, and the post-curing process is completed in 5



Scheme 3. Possible reaction producing φ–O–φ.

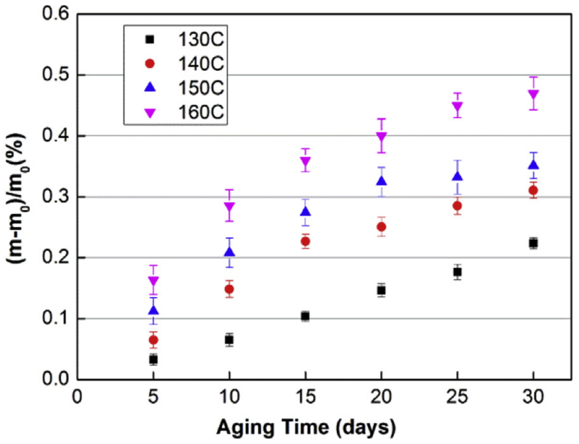


Fig. 4. Mass changes of the thermally aged epoxy samples as a function of aging time at various temperatures. m is the mass at the given aging time and m_0 is the original mass.

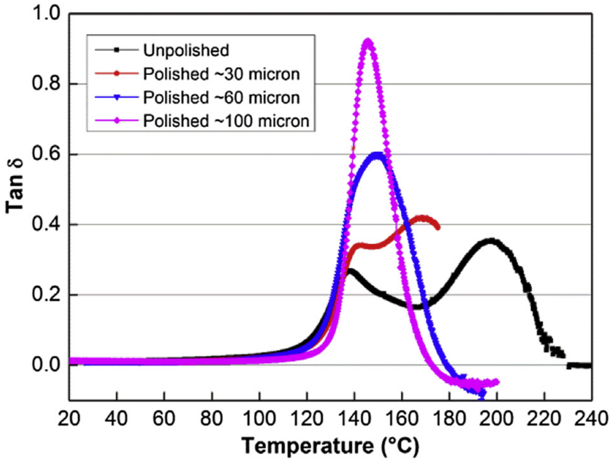


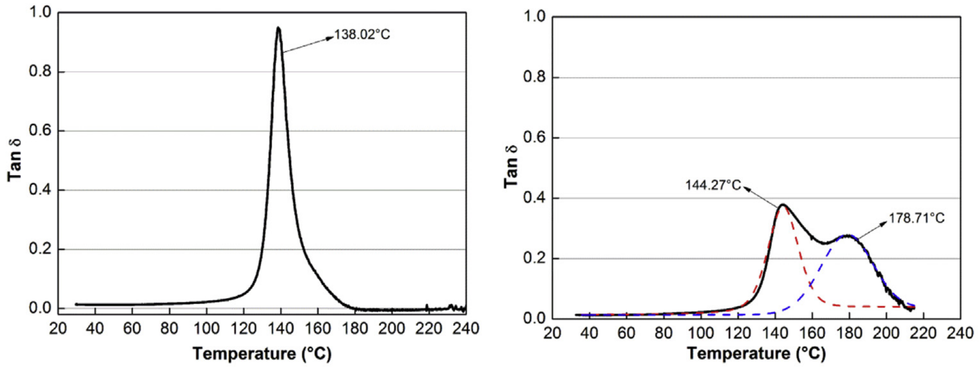
Fig. 6. *tan δ* curves of thermally aged epoxy samples (150 °C, 30 days). Note that the sample plates were polished to remove the surfaces of various depths.

days for temperatures higher than 130 °C. For 130 °C aged epoxy samples, after 15 days of aging, T_{g1} reaches the stable values. As is known, the T_g of the un-aged epoxy sample is 138 °C, the thermal aging at the temperature less than T_g corresponds to a much reduced post-curing effect and requires a longer time to reach full curing.

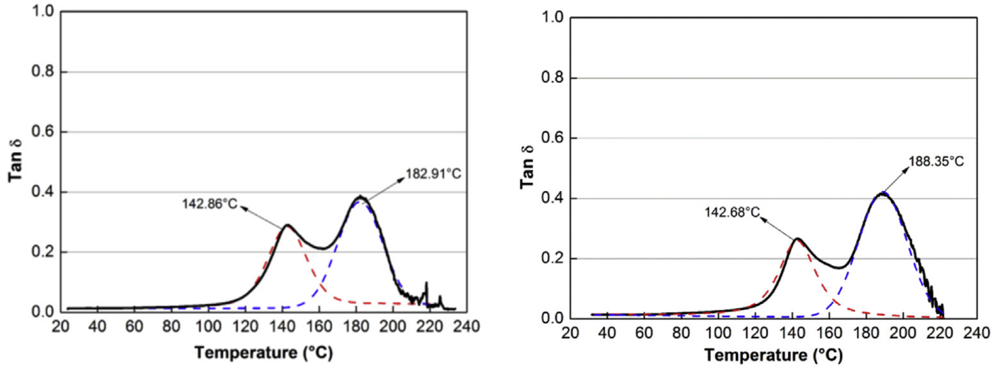
With the increase of the aging time, T_{g2} steadily increases (Fig. 7b) with the thermal aging temperature. For a determined epoxy system, T_g is related to the cross linkage, with a higher T_g corresponding to a denser cross linkage [38]. The increase of T_{g2} suggests that the cross linkage of the epoxy skin continues to be enhanced with thermal aging time. This result corresponds to the FTIR results shown in Fig. 3.

3.3. PALS results

Variation of the apparent free volume fraction (F_v) of the skin or the bulk epoxy samples was determined using the PALS method.

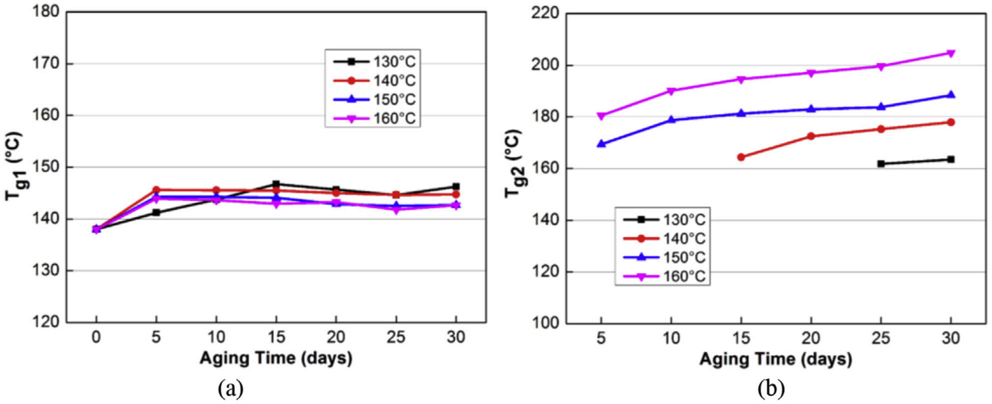


(a) 0d (b) 10d



(c) 20d (d) 30d

Fig. 5. *tan δ* curves of the 150 °C aged epoxy samples for various aging times.



(a) (b)

Fig. 7. Variation of T_{g1} (a) and T_{g2} (b) as a function of aging time.

Note that the thermally aged epoxy samples polished to remove approximately 200 μm were designated to be the "bulk" samples. Because the PALS method is primarily sensitive to a layer of the sample of thickness less than 100 μm, the unpolished samples were designated as "skin" samples.

Fig. 8 shows the apparent free volume values of the skin and bulk epoxy samples, both of which were aged at 130 °C–160 °C for 30 days. Clearly, for the skin samples, F_v reduced from 1.92% (control sample) to 1.51% (130 °C aged sample), 1.35% (140 °C aged one), 1.29% (150 °C aged one) and 1.08% (160 °C aged one). The higher the aging temperature, the lower is the value of F_v observed. The reduced F_v is attributed to the rearrangement of the molecular chains during the thermal aging process that causes the increase of T_{g2} (see Fig. 7). The increase of F_v of a polymer coating during UV aging was reported elsewhere [26], which was also attributed to the chain segmental rearrangement.

Regarding the bulk samples, compared to the skin samples, the value of F_v was much less affected by thermal aging. For the 130 °C, 140 °C and 150 °C aged bulk samples, F_v reaches values in the range of 1.88%–1.89%, slightly less than the value of 1.92% of the control samples. The relatively lower F_v can be attributed to the increased crosslinkage of the bulk samples due to the post-curing process (see above). Comparatively, the 160 °C aged bulk epoxy sample exhibits a value of F_v (= 1.70) less than those of the samples aged at lower temperatures, which also corresponds to the variation of T_{g1} (see Fig. 7). In addition to post curing, rearrangement of the molecular structure may also occur, which corresponds to denser crosslinkages, and thus the lower value of F_v.

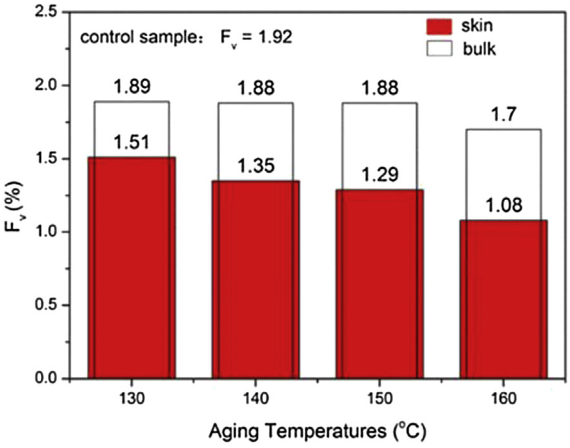


Fig. 8. Apparent free volume fraction (F_v) of epoxy samples thermally aged for 30 days.

Table 2 presents the average radius (R) of the free volume hole. As presented in the table, the value of R of the skin samples is less than that of the bulk samples, indicating that thermal aging reduces the radius of the free volume. Compared to the skin, the value of R of the bulk sample is much less affected by the thermal aging temperatures.

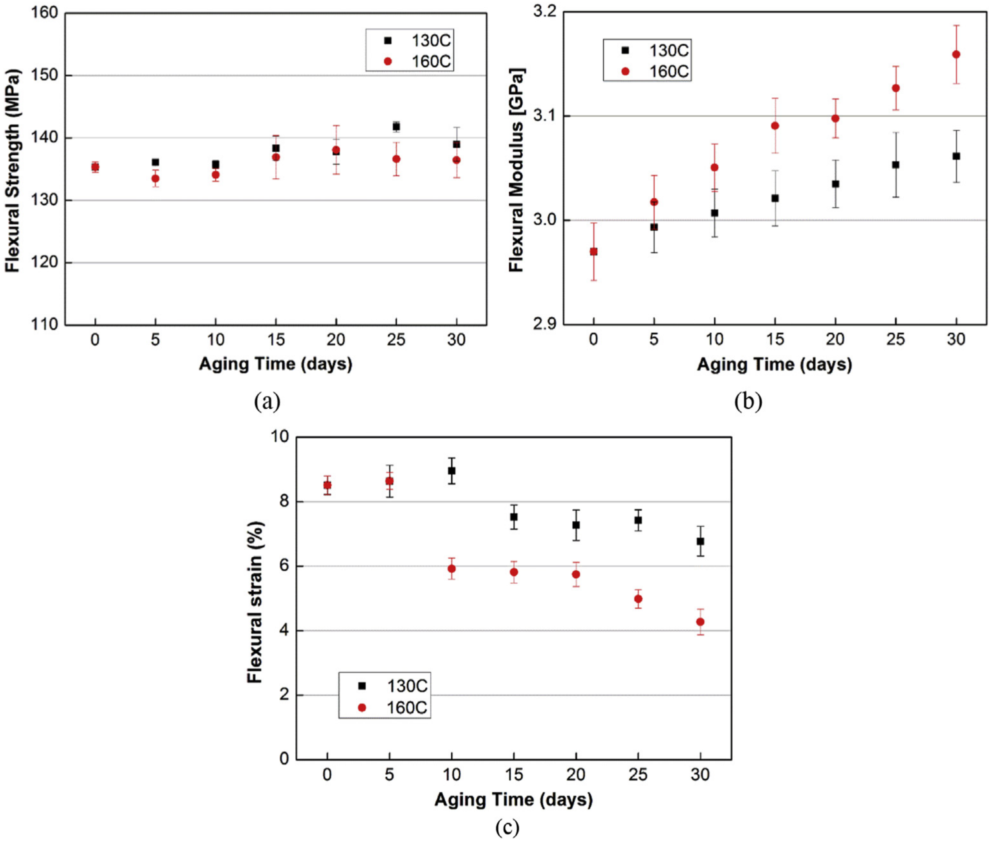
3.4. Flexural properties

The flexural strength, modulus and break strain of the thermally aged epoxy samples are presented in Fig. 9. As shown in Fig. 9a, the flexural strength was only slightly affected by the thermal aging temperatures from 130 °C to 160 °C. The comparison between the tensile strengths shown in Fig. 9a indicates that the 130 °C aged samples exhibit slightly higher flexural strength than the 160 °C aged samples. Unlike the flexural strength, the flexural modulus increases with the aging time, and higher aging temperatures correspond to higher modulus values (see Fig. 9b). The enhanced flexural modulus is attributed to the post curing of the bulk samples and the much denser crosslinkage due to the re-arrangement of the molecular chain structures during thermal aging. The higher the aging temperature, the lower the value of F_v of the skin epoxy and the higher the modulus.

Fig. 9c shows the variation of the break strain of the cured epoxy resin samples. As shown in the figure, the break strain is significantly reduced for both of the aging temperatures considered. After 30 days of thermal aging, the break strain decreases by 20% and 50.6% for the aging temperatures of 130 °C and 160 °C, respectively. Similar results were also reported for thermally aged polymers [10,19]. The reduction in the break strain of the epoxy samples is attributed to the post curing in the bulk samples and the reduced F_v of the skin, which leads to much reduced flexibility of the molecular chains.

Table 2
The average radii (R) of the free volume holes aged for 30 days.

Samples	R (nm)	
	Skin	Core
Control	0.268	
130 °C aged Sample	0.266	0.268
140 °C aged Sample	0.264	0.268
150 °C aged Sample	0.268	0.27
160 °C aged Sample	0.262	0.267



(a) (b)

(c)

Fig. 9. Flexural strength (a), modulus (b), and break strain (c) of the 130 °C and 160 °C aged sample as a function of aging time.

4. Conclusions

This paper presented the results of the study of the variation of the chemical structures and thermo-mechanical properties of an epoxy system subjected to the thermal aging at 130 °C–160 °C for 30 days. Based on the experimental results of FTIR, DMTA, and Positron annihilation lifetime spectroscopy as well as flexural property measurements, the following conclusions can be drawn:

1. Thermal aging at 130–160 °C leads to oxidation and molecular chain re-arrangement in the skin of the epoxy samples. The skin thickness affected by thermal aging (150 °C for 30 days) conditions is less than 100 μm.
2. The apparent free volume fractions of the skin and bulk epoxy samples were characterized by positron annihilation lifetime spectroscopy (PALS). A remarkable reduction of the apparent free volume fraction is found in the skin epoxy, while the bulk samples exhibit a very slight change due to thermal aging.
3. The flexural test results indicate that thermal aging obviously reduced the break strain, while the flexural strength was only slightly affected and the value of the modulus increased.

Acknowledgments

This work is financially supported by the NSFC with Grant No. 51178147 & 51478145, the National Key Basic Research Program of China (973 Program) with Grant No. 2012CB026200, and Key Fundamental Research Project of Shenzhen Science & Technology Research Fund (JC201005250051A).

References

[1] Zarrelli M, Skordos AA, Partridge IK. Investigation of cure induced shrinkage in unreinforced epoxy resin. Plast Rubber Compos 2002;31:377–84.

[2] Anderson BJ. Thermal stability of high temperature epoxy adhesives by thermogravimetric and adhesive strength measurements. Polym Degrad Stab 2011;96:1874–81.

[3] Wen X, Wang X, Cai Z, Pi P, Cheng J, Yang Z. Cure kinetics and chemorheological behavior of a wind epoxy resin system and its viscoelastic properties reinforced by glass fiber matt with process of vacuum assisted resin transfer molding. High Perform Polym 2011;23:477–84.

[4] Nardone F, Ludovico M, Basalo FJC, Prota A, Nanni A. Tensile behavior of epoxy based FRP composites under extreme service conditions. Compos Part B Eng 2012;43:1468–74.

[5] Kalavagunta S, Naganathan S, Mustapha KNB. Capacity assessment and design of CFRP-strengthened steel channel columns. Indian J Sci Technol 2013;6:4255–61.

[6] Böer P, Lisa H, Kang THK. Independent environmental effects on durability of fiber-reinforced polymer wraps in civil applications: a review. Constr Build Mater 2013;48:360–70.

[7] Agelaridou-Twohig A, Tamanini F, Ali H. Thermal analysis of reinforced concrete chimneys with fiberglass plastic liners in uncontrolled fires. Eng Struct 2014;75:87–98.

[8] Gillen KT, Assink R, Bernstein R, Celina M. Condition monitoring methods applied to degradation of chlorosulfonated polyethylene cable jacketing materials. Polym Degrad Stab 2006;91:1273–88.

[9] Larche JF, Bussiere PO, Therias S, Gardette JL. Photooxidation of polymers: relating material properties to chemical changes. Polym Degrad Stab 2012;97:25–34.

[10] Middleton J, Burks B, Wells T, Setters AM, Jasiuk I, Kumosa M. The effect of ozone and high temperature on polymer degradation in polymer core composite conductors. Polym Degrad Stab 2013;98:2282–90.

[11] Musto P, Ragosta G, Russo P, Mascia L. Thermal-oxidative degradation of epoxy and epoxy-bismaleimide networks: kinetics and mechanism. Macromol Chem Phys 2001;202:3445–58.

[12] Dao B, Hodgkin J, Krstina J, Mardel J, Tian W. Accelerated aging versus realistic aging in aerospace composite materials. II. Chemistry of thermal aging in a structural composite. J Appl Polym Sci 2006;102:3221–32.

[13] Pei Y, Wang k, Zhan M, Xub W, Ding X. Thermal-oxidative aging of DGEBA/EPN/LMPA epoxy system: chemical structure and thermal–mechanical properties. Polym Degrad Stab 2011;96:1179–86.

[14] Li K, Wang K, Zhan M, Xu W. The change of thermal–mechanical properties and chemical structure of ambient cured DGEBA/TEPA under accelerated thermo-oxidative aging. Polym Degrad Stab 2013;98:2340–6.

[15] Galant C, Fayolle B, Kuntz M, Verdu J. Thermal and radio-oxidation of epoxy coatings. Prog Org Coat 2010;69:322–9.

[16] Mailhot B, Morlat-Therias S, Ouahioune M, Gardette JL. Study of the degradation of an epoxy/amine resin, 1. Macromol Chem Phys 2005;206:575–84.

[17] Ollier-Dureault V, Gosse B. Photo-oxidation and electrical aging of anhydride-cured epoxy resins. IEEE Trans Diel Elect Insul 1998;5:935–43.

[18] Monney L, Belali R, Vebrel J, Dubois C, Chambaudet A. Photochemical degradation study of an epoxy material by IR-ATR spectroscopy. Polym Degrad Stab 1998;62:353–9.

[19] Fayolle B, Richaud E, Colin X, Verdu J. Review: degradation-induced embrittlement in semi-crystalline polymers having their amorphous phase in rubbery state. J Mater Sci 2008;43:6999–7012.

[20] Celina MC. Review of polymer oxidation and its relationship with materials performance and lifetime prediction. Polym Degrad Stab 2013;98:2419–29.

[21] Guermazi N, Elleuch K, Ayedi HF. The effect of time and aging temperature on structural and mechanical properties of pipeline coating. Mater Des 2009;30:2006–10.

[22] Celina MC, Dayile AR, Quintana A. A perspective on the inherent oxidation sensitivity of epoxy materials. Polymer 2013;54:3290–6.

[23] Odegard GM, Bandyopadhyay A. Physical aging of epoxy polymers and their composites. J Polym Sci Part B Polym Phys 2011;49:1695–716.

[24] Dong Y, Zhou Q. Relationship between ion transport and the failure behavior of epoxy resin coatings. Corros Sci 2014;78:22–8.

[25] Cao H, Yuan J, Zhang R, Huang C, He Y, Sandreczki TC, et al. Degradation of polymer coating systems studied by positron annihilation spectroscopy. 3. Wavelength dependence of UV irradiation effect. Macromolecules 1999;32:5925–33.

[26] Jean YC, Chen H, Zhang R, Li Y, Zhang J. Early stage of deterioration in polymeric coatings detected by positron annihilation spectroscopy. Prog Org Coat 2005;52:1–8.

[27] Liu F, Yin M, Xiong B, Zheng F, Mao W, Chen Z, et al. Evolution of microstructure of epoxy coating during UV degradation progress studied by slow positron annihilation spectroscopy and electrochemical impedance spectroscopy. Electrochim Acta 2014;133:283–93.

[28] Li L, Yu Y, Wu Q, Zhan G, Li S. Effect of chemical structure on the water sorption of amine-cured epoxy resins. Corros Sci 2009;51:3000–6.

[29] Zeng M, Lu C, Wang B, Qi C. Free volume hole size of cyanate ester resin/epoxy resin interpenetrating networks and its correlations with physical properties. Radiat Phys Chem 2010;79:966–75.

[30] Lu Z, Xian G, Li H. Effects of thermal aging on the water uptake behavior of pultruded BFRP plates. Polym Degrad Stab 2014;110:216–24.

[31] Montserrat S, Málek J, Colomer P. Thermal degradation kinetics of epoxy–anhydride resins: I.: influence of a silica filler. Thermochim Acta 1998;313:83–95.

[32] Levchik SV, Weil ED. Thermal decomposition, combustion and flame-retardancy of epoxy resins—a review of the recent literature. Polym Int 2004;53:1901–29.

[33] Huy le MH, Bellenger V, Verdu J, Paris M. Thermal oxidation of anhydride cured epoxies. I—mechanistic aspects. Polym Degrad Stab 1992;35:77–86.

[34] Huy le MH, Bellenger V, Verdu J, Paris M. Thermal oxidation of anhydride cured epoxies—III. Effect on mechanical properties. Polym Degrad Stab 1993;41:149–56.

[35] Hamielec A, Eldrup M, Mogensen O, Jansen P. Positron annihilation techniques (PAT) in polymer science and engineering. J Macromol Sci Rev Macromol Chem Phys 1973;9:305–37.

[36] Kamon T, Furukawa H. Curing mechanisms and mechanical properties of cured epoxy resins, in epoxy resins and composites IV. Adv Polym Sci 1986;80:173–202.

[37] Rivaton A, Moreau L, Gardette J-L. Photo-oxidation of phenoxy resins at long and short wavelengths—I. Identification of the photoproducts. Polym Degrad Stab 1997;58:321–32.

[38] Xian G, Karbhari VM. DMTA based investigation of hygrothermal ageing of an epoxy system used in rehabilitation. J Appl Polym Sci 2007;104:1084–94.