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Effect of neutron irradiation on neat epoxy resin stability in shielding applications

DOI 10.1515/secm-2016-0312
Received November 29, 2016; accepted February 25, 2017; previously published online April 27, 2017

Abstract: Epoxy resin is a thermoset polymer and is one of the main candidates for radiation shielding application. In this investigation, carbon, hydrogen, and nitrogen analysis showed that the presence of the light element of nitrogen in cured epoxy could lead to more effective neutron shielding ability compared with physical curing. The effect of neutron irradiation of amine-cured epoxy was studied by infrared spectroscopy. Neat epoxy samples were irradiated at the core of the Tehran Research Reactor in the same neutron flux in the order of $10^{13}$ (neutron/cm$^2$×s) at several radiation times (up to 12 h). The results indicated that neutron irradiation caused moderate changes in peak absorption locations of epoxy spectra. This result indicates that, in this neutron flux and irradiation time, the molecular structure of epoxy remains stable.

Keywords: epoxy; molecular stability; neutron radiation; shielding.

1 Introduction

Polymers are beneficial because they are lightweight and could easily be laminated in comparison to metal matrix composites. Polymers are low Z materials that are known as one of the best candidates for use in the aerospace [1, 2] or nuclear industries such as in particle accelerators, nuclear reactors, and especially in spent fuel casks [3, 4]. Among these, polyethylene mixed with boron oxide is widely used as a neutron shielding material but it has poor mechanical strength, poor thermal stability, and poor durability for neutron and gamma radiation, so it cannot be in service for a long time [5].

Epoxy resin, also known as epoxide, is a thermoset polymer and is one of the main candidates for radiation application. The main features of epoxide are its ease of processing, low shrinkage and therefore good dimensional stability, excellent adhesion to many reinforcements, high heat resistance, resistance to environmental degradation, high mechanical strength, and being chemical-proof [6, 7]. Figure 1 illustrates the molecular structure of epoxy resin, where $n$ is polymerization degree.

There are some valuable experimental studies on radiation shielding of this polymer. For example, the effects of carbon filler type on the electromagnetic radiation shielding properties of nanocarbon-epoxy composites were investigated by Vovchenko et al. [8]. In another work, Zhong et al. [9] investigated the cosmic radiation shielding of ultrahigh molecular weight polyethylene fiber/nanoepoxy composites for spacecraft safety missions. Gamma and neutron shielding properties of ferrochromium slag loading-hardened epoxy resin samples were studied by Korkut et al. [10] using Co-60 and radioisotope neutron sources ($^{241}$Am-Be), respectively. In another investigation, the properties of boron-containing ores/epoxy composites for slow neutron shielding were spotted and a macroscopic cross-section of the shield was reported [11]. Aygün et al. [12] opened up a new horizon in this regard by inserting molybdenum powder in the epoxy matrix to increase the neutron shielding capacity of the pure epoxy. In a recent investigation, Adeli et al. [13] studied neutron irradiation tests on B4C/epoxy composite in the thermal column of the Tehran Research Reactor (TRR) and evaluated the parameters.

Using the composite materials in extreme radiation environments may damage the molecular structure of the polymer. Ionization radiation such as neutron or gamma radiation could produce free radicals that may cause chain scission or cross-linking. Extensive investigations were carried out several decades ago [14–20], although it was limited in some scopes. Therefore, the purpose of this study was to determine the neutron radiation resistance of epoxy polymer for neutron shielding applications.
2 Experimental approach

2.1 Materials

In this study, diglycidylether of bisphenol A-based epoxy resin (ML-526, Mokarrar Engineering Materials Co., Iran) was used as a thermosetting polymeric matrix and a polyamine curing agent (HA-11, Mokarrar Engineering Materials Co., Iran) was used as a hardener.

2.2 Sample preparation

To prepare a neat epoxy sample, certain amounts of ML-526 epoxy resin and HA-11 hardener, with ratio of epoxy to hardener of 1:0.25 were weighed. To avoid porosity formation, the use of low viscosity materials is recommended. Amine hardener was added and mixed with the epoxy resin by hand-mixing with a glass rod to avoid possible porosity and to reduce the channeling effect in neutron shielding. The samples were allowed to set overnight and were postcured at ambient temperature.

To introduce the sample to the reactor, a scalpel was used to cut it into small pieces. The powder was then transferred to a quartz capsule, and then sealed in an aluminum can in ambient conditions. Figure 2 shows primary radiation equipment to introduce the samples to the reactor core. Three neat epoxy samples with the same H/E ratio equal to 25% were prepared and irradiated in the reactor core.

2.3 Carbon, hydrogen, and nitrogen analysis

A total of $5 \pm 0.1$ mg per rigid cured neat epoxy was delivered for carbon, hydrogen, and nitrogen elemental analysis (Vario EL, Germany). The hardener to epoxy ratios for the sample was 25 weight fraction percentage (wt%).

2.4 Fourier transform infrared analysis

Mid-infrared (mIR) spectroscopy (in the region 4000 cm$^{-1}$ to 400 cm$^{-1}$) has been widely used for the characterization of organic compounds such as polymers. In this study, the qualitative analysis of epoxy spectra was obtained using this technique. The chemical stability of the treated sample was monitored using a Bruker-Vector 22 (USA), infrared spectrometer, fitted with Fourier transform infrared (FTIR) analysis.

2.5 Neutron irradiation condition

In this study, the TRR is considered as a neutron source. TRR is a pool-type research reactor and is designed to operate at a maximum power of 5 MW. It has a rectangular-shaped core with low enriched uranium. This reactor is cooled by light water, and water also acts as a moderator and biological shield.

There are few empty channels as irradiation boxes for irradiating samples. The samples were located in one of the irradiation boxes of the core at a height of 15.5 cm. Table 1 summarizes the neutron fluxes, which were reported in the sample position at a power of 4 MW.

Neat cured samples were irradiated in several irradiation times at the flux in order of $10^{13}$ (neutron/cm$^2 \times$ s). Table 2 shows the irradiation conditions. These irradiation conditions were used to quantify the changes in the chemical structure and physical properties of the epoxy resin due to neutron irradiation.

Table 1: Neutron fluxes in sample position at reactor power of 4 MW.

<table>
<thead>
<tr>
<th>Neutron fluxes (neutron/cm$^2 \times$ s)</th>
<th>Thermal</th>
<th>Epithermal</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$4.417 \times 10^{13}$</td>
<td>$1.296 \times 10^{13}$</td>
<td>$1.954 \times 10^{13}$</td>
</tr>
</tbody>
</table>
times were chosen just as primary stages for the investigation of the neutron stability of epoxy resin.

3 Results and discussion

3.1 Elemental analysis of neat epoxy

In this study, we glanced at the elemental structure of manufactured samples to obtain more information about the nature and behavior of cured neat epoxy that was exposed to neutron irradiation. Figure 3 shows the results of carbon, hydrogen, and nitrogen analysis of the neat epoxy with a hardener to epoxy ratio (H/E) equal to 25%. The presence of nitrogen concentration in the composition of the cured epoxy resin is due to a polyamine-based curing agent (−NH₂). From a neutron shielding point of view, adding and increasing the elements that have higher neutron absorption cross-sections could provide a more effective thermal neutron shield. Table 3 shows the obvious differences between the thermal neutron absorption cross-section of light elements that are present in the cured epoxy. These data clearly show that the light element of nitrogen has higher neutron absorption cross-sections in comparison with hydrogen, carbon, and oxygen. Therefore, as far as we are concerned in polyamine-based chemical curing, we can have a more effective neutron shield rather than the physical curing, which uses electron beam for curing the resin.

3.2 FTIR analysis of irradiated neat epoxy

Figure 4 shows the FTIR spectrum of the cured neat epoxy before any irradiation in the mIR region. In this figure, the broad band at 3500 cm⁻¹ is assigned to O-H stretching of hydroxyl groups [21], revealing the presence of high molecular weights of bisphenol A or newly formed O-H groups due to opening of the epoxy ring during amine-based curing [22]. The peaks lying between 2927 and 2865 cm⁻¹ can be assigned to the methylene group [23]. The fingerprint absorption broad band at approximately 3050 or 1132 cm⁻¹, and at 915 cm⁻¹ of the oxirane ring [21, 24], completely disappeared due to the curing process. The other reference peaks such as 830 cm⁻¹ [24, 25], 1183 cm⁻¹ [26], 1509 cm⁻¹ [25, 27], and 1609 cm⁻¹ [28, 29] represent

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Irradiation time</th>
<th>Power needed for irradiation (MW h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>10 min</td>
<td>0.66</td>
</tr>
<tr>
<td>C</td>
<td>2 h</td>
<td>8</td>
</tr>
<tr>
<td>D</td>
<td>12 h</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 2: Irradiation condition for neat epoxy in the reactor core.

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Mass number (g mol⁻¹)</th>
<th>σₘₘ (barn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1.01</td>
<td>0.33</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>12.01</td>
<td>0.0035</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>14.01</td>
<td>1.9</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>16.00</td>
<td>0.00019</td>
</tr>
</tbody>
</table>

Table 3: Neutron absorption cross-sections for thermal neutrons of various elements.
the stable aromatic rings, which are clearly obvious in the spectrum. Moreover, the qualitative use of N-H bands for amine-based hardener in mIR is limited due to its position in the spectra because the N-H stretching is very close to the strong O-H absorption band [29]. In addition, due to the nature of cured epoxy resin with a polyamine hardener, the sharp peak in the middle of the spectrum, approximately at 2300 cm\(^{-1}\), does not refer to triple bonds such as nonpolar C≡C bond, and might be due to the entry of CO\(_2\) into the system [17].

The effect of neutron irradiation of amine-cured epoxy was studied by FTIR spectroscopy. Three samples were irradiated in TRR reactor core in the same neutron flux \((3\times10^{13} \text{ neutron/cm}^2\times\text{s})\) at several irradiation times as indicated in Table 2. The samples were irradiated at 10 min, 2 h, and 12 h. FTIR spectra of the irradiated samples are illustrated in Figures 5–7, respectively. The color of the tiny nonirradiated cured epoxy changes to brown especially after 12 h of irradiation. In these figures, the spectra of the irradiated samples are compared with nonirradiated neat epoxy. To implement this, a qualitative analysis of epoxy spectra in the mIR range was done. As clearly obvious in these figures, transmittance peaks are different according to their intensity. The difference between peak intensities is due to the sample concentration on each potassium bromide pellet.

From Figure 4, it is clear that the FTIR spectrum of nontreated neat epoxy also shows two sharp peaks at 3848 and 3736 cm\(^{-1}\). These bands correspond to the stretching mode of the OH group, which is contributed by water contents [30, 31]. Heat produced in the irradiated sample causes the moisture of neat cured epoxy to vanish. As can be seen from the irradiated epoxy spectra, the peak intensity of these two bands, 3848 and 3736 cm\(^{-1}\), gradually disappears and, after 12 h of neutron irradiation, is completely removed from the FTIR spectrum, as seen in Figure 7. Confidently, samples with higher irradiation times are affected not only by the neutron but also by the temperature increasing. Although in this study, we could not have any access to measuring the temperature gradient, it was confirmed that the irradiated neat cured epoxy exhibited a matching IR spectrum to that of the nontreated one in the absorption peak intensities and locations. Furthermore, the peaks of the spectrum for the irradiated cured resin are wider than the one for the nonirradiated cured resin, which might mean that the degree of

![Figure 5](image5.png)  
**Figure 5:** The IR spectrum of the epoxy resin before (A) and after 10 min of neutron irradiation (B) in the TRR reactor core.

![Figure 6](image6.png)  
**Figure 6:** The IR spectrum of the epoxy resin before (A) and after 2 h of neutron irradiation (C) in the TRR reactor core.

![Figure 7](image7.png)  
**Figure 7:** The IR spectrum of the epoxy resin before (A) and after 12 h of neutron irradiation (D) in the TRR reactor core.
curing for the more irradiated resins is higher. This result indicates that in this neutron irradiation situation, the molecular structure of the epoxy remains stable.

4 Conclusions

Recently, epoxy resin has become widespread because of its perfect properties as a structural material in the nuclear safety and radiation application areas and due to its good thermodynamic and mechanical properties. To the best of our knowledge in polyamine-based chemical curing, we can have a more effective neutron shield rather than the physical curing, which uses an electron beam for curing the resin because of the higher thermal neutron absorption cross-section of nitrogen in comparison with hydrogen, carbon, and oxygen. In this study, the effect of neutron irradiation of the amine-cured epoxy, before and after irradiation, was also analyzed by FTIR spectroscopy. Three samples were irradiated at the core of the TRR in the same neutron flux in order of $10^{13}$ (neutron/cm$^2$×s) at several radiation times. The data show that the irradiated neat cured epoxy exhibited a matching IR spectrum to the same neutron flux in order of $10^{13}$ (neutron/cm$^2$×s) at several radiation times. The data show that the irradiated neat cured epoxy exhibited a matching IR spectrum to that of the nontreated one in the absorption peak intensities and locations. This result indicates that the molecular structure of the epoxy remains stable in this situation. Surely, more time intervals should be considered in the neutron stability of epoxy resin. Furthermore, preparing the samples in a standard dumbbell shape and investigation of bulk properties of irradiated samples such as mechanical properties or changes in density could give more comprehensive views to the researcher.

Acknowledgments: The authors would like to thank the supervisor of TRR and all of its technicians, as well as the technicians at the Jaber-ebn-Hayan laboratory for supporting this investigation. In addition, we would like to thank Mr. Honarju E. for his grammatical editing of the manuscript.

References