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Radiation-induced degradation of an epoxy thermoset supported by hydrogen peroxide

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HIGHLIGHTS

- Mechanism of the radiation induced degradation of epoxy resin was proposed.
- Epoxy thermoset swelled with H₂O₂ is radiation susceptible.
- Radiation treatment followed by H₂O₂ swelling can be applied for resin recycling.

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ABSTRACT

Epoxy resin was decomposed applying two complementary treatments, namely (1) soaking up with 30% aqueous solution of hydrogen peroxide and (2) exposure of the swelled material to ionizing radiation in air atmosphere over doses up to 1000 kGy. The phase transition characteristic determined by the DSC technique revealed that both factors, swelling with oxidizing agent and irradiation applied sequentially induce in the resin deep structural changes resulting in the rise of two new exothermic transitions assigned to hydrogen peroxide decomposition and resin oxidation. The flexural stress at break measurements confirmed significant influence of H₂O₂ on the mechanical properties of the irradiated material which, under applied conditions, is efficiently decayed via oxidative degradation. On the basis of results obtained by EPR spectroscopy chemical mechanism of the radiation induced degradation was proposed.

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1. Introduction

Epoxy resins are widely used in many branches of industry (Alessi et al., 2007; Benfarhi et al., 2004; Dispenza et al., 2002). Therefore, development of the effective technologies for their recycling is necessary, especially that thermosets can be recycled neither by remelting in the molding process nor by depolymerization to their original constituents. One of the methods under consideration is a radiation treatment (Burillo et al., 2002; Czikovszky, 1995; Davenas et al., 2002) that in some cases might facilitate degradation and further reprocessing some polymeric materials, e.g. butyl rubber. However, epoxy resins demonstrate unusual radiation resistance resulting not only from their chemical structure but also from relatively low oxygen diffusion coefficient that reduces oxidative degradation of the material. Longi eras et al. (2007) studied a distribution of the oxidation products across irradiated epoxy resin films. They found that upon irradiation with a dose of 5 MGy only 20 µm external layer experienced oxidation leading to the formation of carboxylic terminal groups and that below a few MGy decomposition of bulk epoxy resin

was negligible. Consequently, radiation technology cannot be directly implemented due to extremely high energy consumption and costs of the operation, and the process needs appropriate pretreatment.

Reported investigations were focused on the decomposition of diglycidyl ether of bisferol-A (DGEBA) hardened with triethylene tetramine (TETA). Upon swelling with hydrogen peroxide solution the resins were irradiated with electron beam in air atmosphere. The degradation extent was characterized by the comparison of the results obtained for neat epoxy resin and irradiated one, swelled previously with hydrogen peroxide aqueous solution. We expected that incorporation of the readily available and inexpensive liquids into epoxy resins enhanced the range of oxidative degradation initiated by ionizing radiation providing an attractive solution to the problem of the thermoset recycling.

2. Experimental

2.1. Materials

Epoxy monomer (diglycidyl ether of bisphenol-A, DGEBA) and hardener (triethylene tetraamine, TETA), both purchased from

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Aldrich Co, were compounded in a ratio of 10:1. The prepared mixture was poured into the aluminum molds in the form of bars and submitted to a two-step temperature program: the samples were kept at 25 °C for 16 h, and subsequently at 95 °C for 2 h. Dimensions of the tested samples were as follows: $4 \times 10 \times 120 \text{ mm}^3$. The process allowed to achieve fully cured and thermally stable epoxy resin. 30% $\text{H}_2\text{O}_{2\text{aq}}$ was obtained from POCh.

2.2. Swelling measurements

Swelling of the resin was examined by immersing the samples in double distilled water or 30% aqueous solutions of hydrogen peroxide in closed glass containers at ambient temperature for periods indicated in Fig. 1. Swelling was calculated by the following equation:

$$\text{Swelling (\%)} = [(w_s - w_o) / w_o] 100\%$$

where w_s and w_o represent the weights of swelled and initial (dry) samples, respectively.

2.3. Exposure to ionizing radiation

Irradiations were carried out in air atmosphere using an Elektronika 13/10 accelerator. The samples were irradiated with 10 MeV electron beam at ambient temperature. The specimens of epoxy resin, both non-swelled and swelled, were placed in a conveyor and transported under the accelerator window at a rate that allowed the samples to absorb ca. 25 kGy per pass.

2.4. Thermal characteristic

Thermal properties of the epoxy resin were investigated by a differential scanning calorimetry (DSC) method using TA Instruments MDSC 2920 apparatus. Phase transition temperatures were determined in nitrogen flow at a heating rate of 10 °C/min.

2.5. EPR spectroscopy

EPR (Electron Paramagnetic Resonance) spectroscopy was applied in order to monitor radicals generated by ionizing radiation, and to compare their relative concentrations in various systems. The EPR measurements were performed at ambient temperature with a Bruker ESP 300 spectrometer equipped with a rectangular X-band TE 102 microwave cavity at the following parameters: sweep width 30.0 mT, microwave power 0.1 mW, conversion time 81 ms and modulation amplitude 0.09 mT.

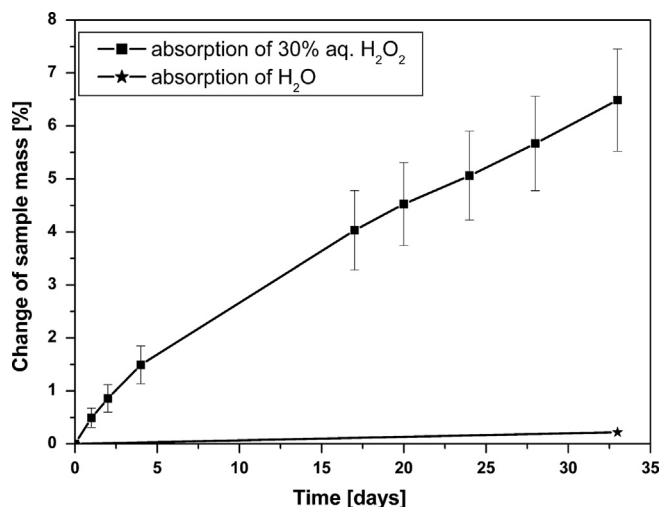


Fig. 1. Swelling of epoxy resin with H_2O and 30% $\text{H}_2\text{O}_{2\text{aq}}$.

2.6. Mechanical characteristic

The characterization was performed using an Instron 5565 machine according to PN-EN ISO 178:2006. The crosshead speed was set at 2 mm/min, whereas the span length at 50 mm. The reported data are the average of four independent measurements.

3. Results and discussion

3.1. Swelling

The relationships between swelling of the epoxy resin samples kept either in water or in 30% aqueous solution of H_2O_2 and the time of swelling are shown in Fig. 1. Water uptake did not exceed 1% and seemed to be insufficient from practical point of view. Swelling of the epoxy resin with $\text{H}_2\text{O}_{2\text{aq}}$ after 33 days achieves about 6% but diffusion of the molecules has to be relatively slow as the correlation shows that after that time saturation has not been reached yet. Relatively high sorption effect in $\text{H}_2\text{O}_{2\text{aq}}$ and negligible swelling in H_2O suggest that predominantly H_2O_2 molecules slowly diffuse from hydrogen peroxide solution into the polymeric matrix and water penetration is limited.

3.2. DSC measurement

As shown in Fig. 2A, bottom thermogram, for the epoxy resin obtained according to the procedure described in Section 2.1, only one glass transition temperature (T_g) at about 87 °C was found whereas the sample swelled with H_2O_2 solution shows two distinct exothermic peaks spread over a wide range of temperatures from 75 °C to 200 °C. Two transitions at 122 °C and 158 °C demonstrate enthalpies -212 J/g and -63 J/g , respectively. There is no endothermic peak around 100 °C attributed to a water boiling point, thus swelling of the epoxy resin with water originated from the hydrogen peroxide aqueous solution seems to be restricted, and predominantly H_2O_2 molecules penetrate three dimensional network of the thermoset.

More efficient mobility of H_2O_2 than H_2O in the epoxy resin results probably from lower polarity of hydrogen peroxide that facilitates diffusion of the molecules in a moderately hydrophilic polymeric matrix. Hydrogen peroxide molecules that migrate in the resin are far from liquid state, and undoubtedly they are not subjected to the interactions occurring in aqueous solutions. This factor determines the decay temperature of H_2O_2 which, according to the obtained data, is approaching 122 °C.

The multistage decomposition of H_2O_2 involves many competitive reactions. One of the product, i.e. strongly oxidizing hydroxyl radical, might play an important role in the thermal degradation of polymeric matrix initiating radical processes. Due to oxidation processes the second exothermic transition at 158 °C shown in the DSC diagram might be attributed to oxidative degradation of the epoxy resin.

The next sequence of thermograms shows phase transitions for the swelled epoxy resin before and after exposure to ionizing radiation, Fig. 2B. When absorbed doses are increasing, the relative intensities of both detected exothermic signals are changing in the opposite directions—the low temperature peak gradually decreases, and eventually for the samples irradiated with a dose of 750 kGy disappears, whereas simultaneously the high temperature exothermic signal gets broader and higher. The low temperature peak attributed to the H_2O_2 decay diminishes with increasing dose thus population of the molecules in the system decreases. All observed changes presumably result from consumption of hydrogen peroxide by the radicals initiated in epoxy resin during exposure to ionizing radiation.

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