AN ANALYSIS OF CURING OF EPOXY RESIN BY STEADY-STATE FLUORESCENCE SPECTROSCOPY AND DETERMINATION OF A STORAGE TEMPERATURE

Michaela Mikulicova & Vojtech Kresalek

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Abstract

In this paper, steady-state fluorescence spectroscopy is used to analyse the curing of epoxy resin. The analysed mixture of epoxy resin EPOXY 1200 and hardener P11 is measured at seven different temperatures: at room temperature (23 °C), at the lower temperature (9 °C) and at the higher temperatures (30 °C, 40 °C, 50 °C, 70 °C and 80 °C). The results demonstrate that the process of curing of epoxy resin accelerates with increasing temperature. The measured data are further processed to determine a storage temperature. The appropriate storage temperature for the analysed mixture is stated as 4 °C or less.

Keywords: fluorescence spectroscopy; epoxy resin; curing; storage temperature

1. Introduction

Epoxy resins are versatile polymers with a wide range of applications in various fields [1], [2], [3], [4], [5]. Materials based on epoxies are very strong, flexible and have good electrical properties. Therefore, epoxies can be used as adhesives, paints, laminates, in automotive, aviation and shipping industry [2], [4], in electrotechnics [1], [2], [6], in dentistry [7], in optoelectronics [8]. An important property of the resin is a curing after application. Hardeners are used for curing. Hardeners are chemicals that react with epoxy groups to form a solid three-dimensional network [2]. To improve the quality of the epoxies, nanoparticles with different characteristics [9], [10], [11], [12] or dyes [8] can be added to the mixture.

The process of curing of epoxy resin is substantial for the quality of the resulting material [5], [13]. In order to achieve the required properties, the curing must take place under the optimum conditions given for the used material or mixture. The curing of resin can be investigated by various methods [1], [2], [3], [14]. The most commonly used methods include nuclear magnetic resonance, viscosity measurement, dielectric spectroscopy and Raman spectroscopy [4], [9], [13]. However, the present research is focused not only on the process of curing. To investigate epoxy properties which depend on composition, the spectroscopic methods NIR and MIR [14], [15] or UV-VIS and FTIR [16] are also used.

Another research is focused on material degradation or ageing. This research uses methods such as electroluminescence [1], [6], [11] and chemiluminescence [11], [17].

In this paper, steady-state fluorescence spectroscopy is used to analyse the curing of epoxy resin. Fluorescence spectroscopy is a simple, fast and sensitive method for analysing organic and inorganic substances. Moreover, it is non-invasive. Due to this, fluorescence spectroscopy is widely used in many scientific disciplines such as chemistry, biochemistry, environmental chemistry, forensic analysis and food industry.

The advantage of fluorescence spectroscopy for analysing the curing of epoxy resin is the simplicity of analysis with negligible influence on the process of curing or on the resin itself. In addition, measurement is contactless. The purpose of this paper is to demonstrate the usability of steady-state fluorescence spectroscopy to analyse the curing of epoxy resin and to determine the storage temperature of investigated resin using the measured data.

2. Instrumentation and Samples

The curing of epoxy resin was analysed by steady-state fluorescence spectroscopy. Emission spectra were obtained by an ISS PC1 spectrofluorometer which uses 300 W high-pressure xenon arc lamp as a source of excitation light and photomultiplier in photon counting mode as a detector. The measurement was performed using optical fibre pulled out of the instrument.

After a series of experiments, a suitable excitation wavelength was set to 260 nm. Epoxy resin EPOXY 1200 was mixed with hardener P11 in a ratio of 100:6.5. The thin layer of the resulting mixture was measured at room temperature (23 °C) for 24 hours. The sample was measured every 15 minutes. Subsequently, the measurements were repeated for samples cured at temperatures of 9 °C, 30 °C, 40 °C, 50 °C, 70 °C and 80 °C.

3. Results

The aim of the experiment was to prove the usability of steady-state fluorescence spectroscopy to analyse the curing of epoxy resin and to determine a storage temperature of the investigated resin. For this purpose, the mixture of epoxy resin EPOXY 1200 and hardener P11 was analysed.

Fig. 1. Emission spectra of epoxy resin measured at room temperature (23 °C) for 24 hours

Fig. 1 presents the emission spectra of resin measured at room temperature (23 °C) for 24 hours. As can be seen, after the initial fast decrease, the intensity of fluorescence decreased gradually. Then, in the last ten hours, a slightly decreasing trend was observed. This indicates that the process of curing decelerates with time.

It is worthwhile to note that resin was cured after 24 hours which was verified by the measurement after 48 hours. The emission spectra of resin measured at 9 °C, 30 °C, 40 °C, 50 °C, 70 °C and 80 °C were obtained in the same way.

Fig. 2. Velocities of curing for individual temperatures and their polynomial functions

To analyse the velocity of curing, the peak at 307 nm was chosen for further analysis. The intensity in time $t = 0$ h was marked as I_0 , the intensities measured during the process of curing were marked as I_t . Then, all intensities were converted into the new form (1). Time dependencies of these converted intensities are illustrated in Fig. 2. As can be seen, the process of curing of epoxy resin accelerates with increasing temperature. The velocities of this process are characterized by appropriate polynomial functions which correspond to the temperatures.

$$y = \ln \frac{I_0}{I_t} (-) \quad (1)$$

These polynomial functions were further processed to determine a storage temperature. Constants k_0 of all linear polynomials were connected to the relevant temperatures. As a result, the temperature dependency of k_0 was obtained. Then a polynomial trendline was fitted to the data. This trendline intersects temperature axis in the value 4 °C, as shown in Fig. 3. Obtained results mean that the crosslinking reaction of resin stops at the temperature of 4 °C. Due to this, the appropriate storage temperature for the analysed epoxy resin mixture is stated as 4 °C or less.

Fig. 3. Temperature dependency of k_0 and stated storage temperature (red dot)

4. Conclusion

Steady-state fluorescence spectroscopy was used to analyse the curing of epoxy resin EPOXY 1200 mixed with hardener P11. The given results indicate that the process of curing of epoxy resin decelerates with time. The dependence of curing velocity on temperature was also demonstrated. It was found that the process of curing accelerates with increasing temperature. Finally, the measured data were processed to determine a storage temperature. This temperature was stated as 4 °C or less because crosslinking reaction of resin stops at this temperature. Overall, curing of epoxy resins can be analysed by steady-state fluorescence spectroscopy. However, it should be borne in mind that this method provides no information about resin compounds which have no fluorescence properties. One of the challenges for future research is to test different kinds of resin and describe their behaviour with a mathematical model.

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6. References

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