

A Thermospectral Setup for Evaluating the Content of Unbound Components in Microscopic Samples of an Epoxy Polymer

N. S. Naumkin^a, N. P. Shestakov^{a,b}, A. A. Ivanenko^{a,b}, V. F. Kargin^c, and A. B. Shestakov^a

^a Siberian Federal University, Svobodnyi pr. 79, Krasnoyarsk, 660041 Russia

^b Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences,
ul. Akademgorodok 50/38, Krasnoyarsk, 660036 Russia

e-mail: nico@iph.krasn.ru

^c Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences,
ul. Karla Marksa 42, Krasnoyarsk, 660049 Russia

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Abstract—A setup and a technique for optical measurements intended for evaluating the content of unbound compounds in an epoxy polymer are described. The principle of operation of the setup is based on measurements of the spectra of absorption of infrared (IR) radiation by condensed products of evaporation of unbound components. The needed mass of a sample is about 0.01 g. The results of measurements of the IR radiation absorption as a function of the concentrations of the mixture components—ED-22 epoxy resin, isomethyltetrahydrophthalic anhydride (hardener), and a cure promoter (УП-606/2)—are presented. The relative content of chemically unbound components in the structure of a polymer matrix is evaluated as a function of the hardener concentration, thus allowing determination of the stoichiometric ratio of the initial components of an epoxy mixture. The obtained results are compared to those obtained by the extraction method.

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INTRODUCTION

Epoxy polymers are the strongest polymer materials that solidify as a result of a chemical reaction. When a polymer solidifies, a cross-linked structure must be formed, which ideally unites all molecules into a common material that does not melt at elevated temperatures and is not dissolved in ordinary solvents. The solidification mechanism of epoxy polymers has been investigated incompletely. The quality of the epoxy matrix depends on the solidification technique and the used fillers. In this case, the stoichiometric ratio of the components may differ depending on the types of fillers and the curing conditions. The existing methods for determining the optimal oligomer-to-hardener ratio [1, 2] require large expenditures of time, labor, and materials. This study was aimed at the development of an experimental setup and a spectral technique for proximate investigations of the relative content of unbound components in microscopic samples of an epoxy polymer.

THERMOSPECTRAL METHOD

In studies of the interfaces of molecular blocks of epoxy polymers, it was revealed [3] that, when these are heated above the vitrification temperature, excessive components of the initial mixture in the form of microscopic droplets appear on the polymer surface (see Figs. 1 and 2). The size of droplets and their num-

ber depend on the content of chemically unbound components in samples.

This phenomenon was used during the development of the setup for measuring the content of unbound polymer components. When the polymer is heated above the vitrification temperature, droplets appear on the surface and evaporate. Vapors condense on a cooled transparent substrate in the form of a thin

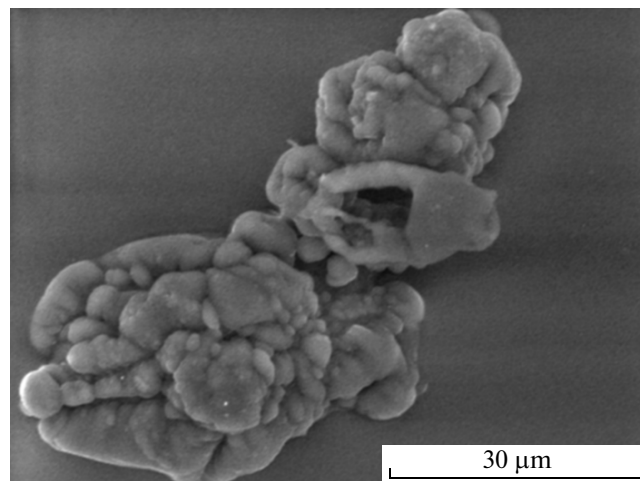


Fig. 1. Excess of the epoxy resin in the polymer. Photographs obtained with a TM-1000 electron microscope.

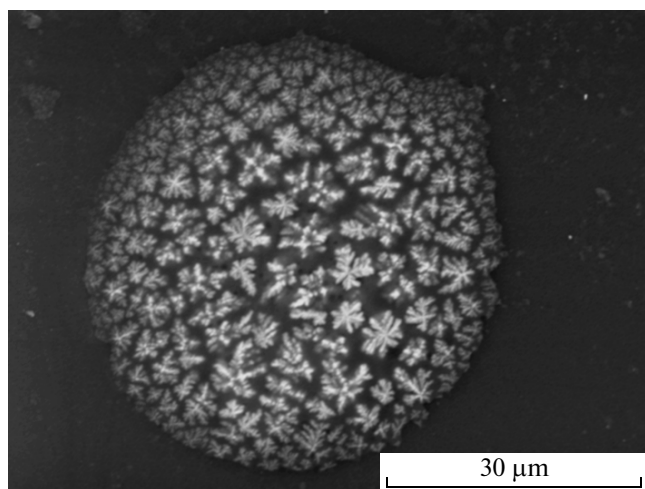


Fig. 2. Excess of the hardener in the polymer. Photographs obtained with a TM-1000 electron microscope.

film positioned above the sample. The light absorption by the film is analyzed by an IR spectrometer.

THERMOSPECTRAL SETUP

The setup (its diagram is shown in Fig. 3) includes a Vertex 70 IR Fourier spectrometer equipped with a Hyperon 2000 (by Bruker Optics), a heated stage (THMS 600 Temperature Controlled Stage), and a T96 temperature controller (Linkam Scientific Instruments Ltd.). Heated stage 5 is a microscope stage with the possibility of blowing nitrogen through the chamber and regulating the sample temperature with a controller.

A TB-19-1.0-1.3 CHR cylindrical microrefrigerator with a circular hole at the center is used to cool window 4. The cold surface of the microrefrigerator is in contact with the surface of the ZnSe window with a diameter of 20 mm and a thickness of 0.5 mm, which is transparent in the IR region. The hot surface of the microrefrigerator is cooled by a metallic radiator, which is blasted with dry air. A sample of an epoxy polymer in the form of a flat disk with a central hole is placed on the heater so that the hole in the sample coincides with the hole in the heater. The gap between the sample and the cold window is 7 mm.

Pure nitrogen is blown through the chamber with the heated stage, which is hermetically sealed and disconnected from the standard blowing-through device during the experiment. The spectrometer and temperature control is fully automated. The heating of a sample and measurements of IR spectra start simultaneously. When a sample is heated, the components that are not chemically bound to the epoxy polymer and that bleed through the surface evaporate and precipitate on cold upper window 4. As a result, a film that consists of a liquid condensate is formed on its surface.

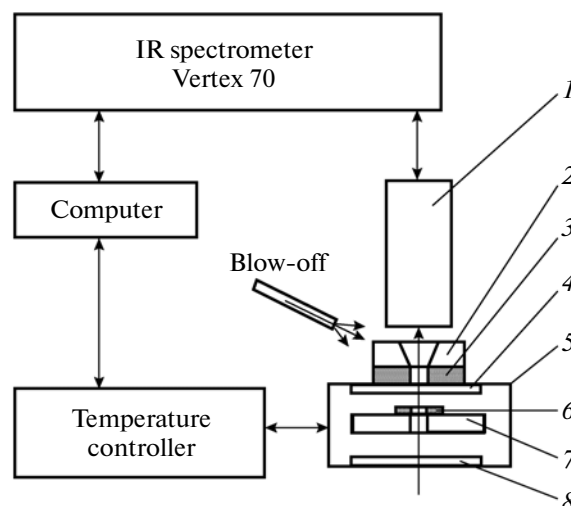


Fig. 3. Schematic of the setup for the thermospectral analysis: (1) Hyperion 2000 microscope, (2) radiator, (3) Peltier microrefrigerator, (4, 8) crystal ZnSe windows, (5) THMS 600 thermal stage, (6) polymer sample in the form of a 0.08-mm-thick disk 6 mm in diameter with a 1-mm-diameter hole, and (7) heater.

As the film thickness increases, the light absorption increases as well (Fig. 4).

The cessation of the increase in the absorption of IR lines, which are characteristic of the hardener (isomethyltetrahydrophthalic anhydride (TU 38.103149-85)) and ED-22 epoxy resin (GOST (State Standard) 10587-84), serves as the criterion for evaluating the time required for evaporation of the free component from the epoxy polymer (Fig. 5). The choice of the sample shape in the form of a 0.08-mm-thick flat disk was dictated by the following reasoning. Because the evaporation rate of chemically unbound components depends on the sample thickness (Fig. 6), a relatively small thickness was chosen in order to restrict the measurement time within a reasonable range. A Struers DK-2750 tool with a diamond disk was used to cut disks from a cylindrical billet. A sample in the form of a disk with a central hole makes it possible to produce homogeneous condensate films at the center of the upper window of the heated stage.

It follows from Fig. 6 that, for samples with thicknesses of 50–330 μm and a time of 2.5 h, for which a sample is held at $T = 200^\circ\text{C}$, the mass loss is virtually independent of the sample thickness. Therefore, a slight lack of parallelism of the disk surface has no effect on the mass loss. In our experiments, 0.08-mm-thick samples were used. Figure 7 shows the results of studies of the dependence of the absorption intensity of the spectral lines that are characteristic of ED-22 and the hardener in samples with different concentrations of components.

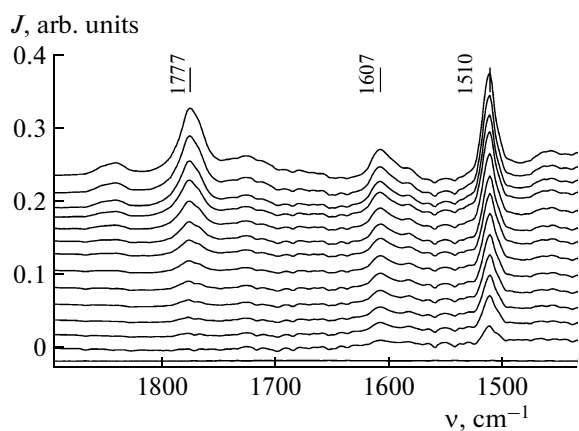


Fig. 4. Increase in the absorption of IR radiation by a condensate film during deposition. The temperature of the 0.08-mm-thick epoxy polymer sample is 200°C. Measurements were performed every 15 min, the total observation time was 210 min. J is the absorption intensity of IR radiation, and ν is the wave number.

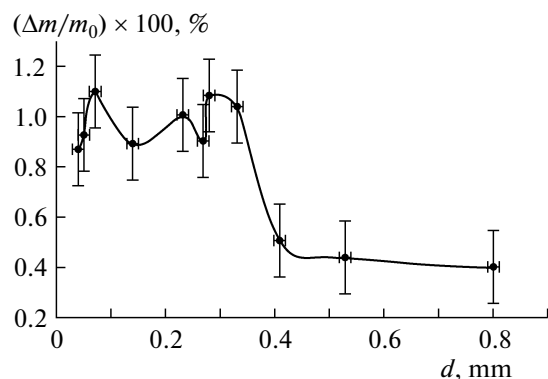


Fig. 6. Dependence of the relative mass loss $\Delta m/m_0$ on the sample thickness d measured at $T = 200^\circ\text{C}$ and a sample heating time of 2.5 h (m_0 is the initial sample mass).

The intersection of curves corresponds to the minimum content of free initial components in the polymer samples.

METHOD OF IR SPECTROSCOPY OF POLYMER EXTRACTS

It is known that chemically cross-linked polymers are not dissolved in ordinary solvents [4]. However, actual samples of an epoxy polymer always contain some amount of chemically unbound molecules that are washed out by the solvent. A number of samples with different ratios of the initial components were prepared. The samples were milled, and equal powder masses were placed into identical volumes of chemically pure acetone. After soaking in acetone, the extract was drawn from the solutions and inserted into a KBr powder, from which pellets of identical shapes

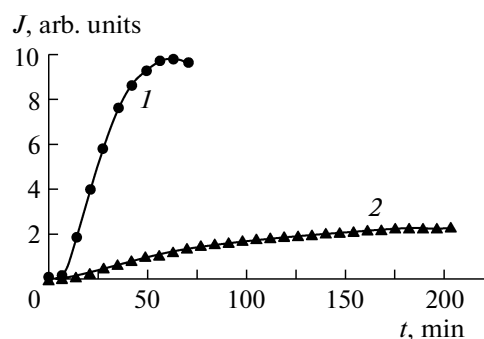


Fig. 5. Time dependence of the integral absorption intensity of IR radiation for free components of the epoxy polymer that precipitated on the upper window of the thermal stage: (1) for the hardener (1776- cm^{-1} spectral line) and (2) for ED-22 (1510- cm^{-1} spectral line). The heater temperature is 200°C.

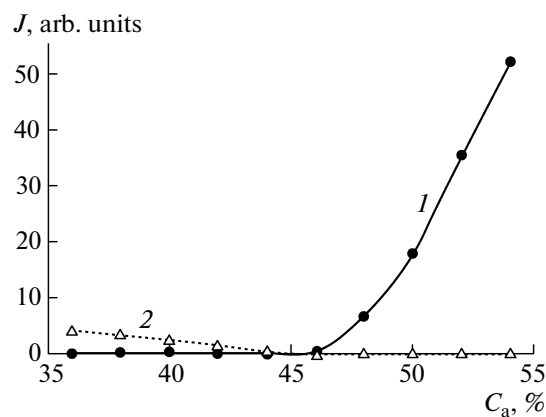


Fig. 7. Dependence of the integral absorption intensity of IR radiation for free components of the epoxy polymer on the anhydride concentration C_a in the polymer: (1) for the hardener (1776- cm^{-1} spectral line) and (2) for ED-22 (1510- cm^{-1} spectral line).

and masses were then manufactured. Figure 8 shows the absorption spectrum of the thus produced extracts of samples.

Lines of 1856, 1776, and 1708 cm^{-1} correspond to C—O vibrations in molecules of the the hardener; lines of 1608, 1582, and 1510 cm^{-1} correspond to those in ED-22 molecules. The presented spectral range is remarkable because its left part from 1650 to 2000 cm^{-1} contains IR-radiation lines of absorption by the hardener but no lines inherent in the ED-22 oligomer. In the right part (1450–1650 cm^{-1}) of the spectral range, the lines of ED-22 are observed, but the hardener lines are absent. A spectral line of 1735 cm^{-1} corresponds to C—O vibrations of the polymer matrix. The absorption intensity of this line increases at large deviations from the stoichiometric ratio of components. This is caused by the fact that at large deviations from the optimal proportion, the samples are milled into smaller parti-

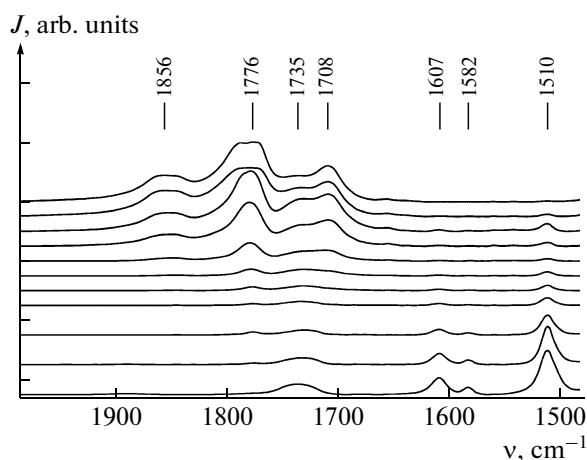


Fig. 8. Absorption spectra in extracts of samples with different ratios of the initial components. The concentration of the hardener in samples of the epoxy polymer increases in the upward direction: 36, 38, 40, 42, 43, 44, 45, 46, 48, 50, and 52%.

cles, a part of which do not precipitate. Therefore, the extract spectrum contains the 1735-cm^{-1} polymer line. $\Theta\text{D-22}$ is washed out of the polymer to a lower degree than the anhydride does, thus leading to a decrease in the intensities of the 1608- , 1582- , and 1510-cm^{-1} lines in the extract; on the other hand, these lines are present in the spectrum of the epoxy matrix, and their intensity correspondingly increases owing to the presence of submicron polymer particles in the extract.

The plot shown in Fig. 9 indicates the presence of chemically unbound anhydride and $\Theta\text{D-22}$ molecules in extracts of the epoxy polymer with different concentrations of the the hardener. The intersection of the characteristics corresponds to the optimal ratio of the initial components with the minimal content of the free components in $\Theta\text{D-22}$ and the hardener.

CONCLUSIONS

The thermospectral method distinguishes itself by the following advantages: measurements are automated, the measurement time of one sample is not long, 210 min, the sample mass is ~ 0.01 g, and chemical reagents are unnecessary. The results of measurements agree with the data obtained by the methods of extraction and mass-loss measurement [1, 2, 5].

The presented techniques can be used for evaluating the number of unbound molecules in an epoxy polymer and selecting the polymerization conditions and conditions for optimizing the ratio of the main components and fillers.

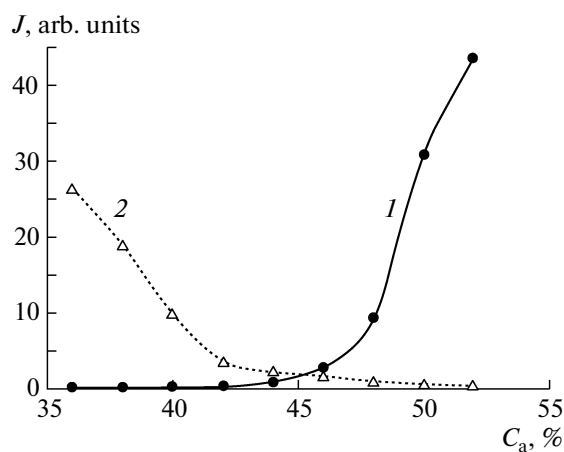


Fig. 9. Dependence of the integral absorption intensity of IR radiation for free components of the epoxy polymer on the anhydride concentration C_a in the polymer obtained by the extraction method: (1) for the hardener (1776-cm^{-1} spectral line) and (2) for ED-22 (1510-cm^{-1} spectral line).

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