

Chromatographic monitoring of the residual concentrations of volatile hydrocarbon components in a cured epoxy adhesive

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Chromatography was applied to determine the specific rate of release of residual volatile hydrocarbon components from the surface of a hardened epoxy adhesive.



Epoxy adhesives are widely used in instrument engineering, in particular, for the manufacture of microelectronic and vacuum devices, because of their manufacturability, good adhesion to various materials, small shrinkage upon curing and chemical resistance. Stringent requirements are imposed on the release of residual volatile compounds from adhesive joints for keeping a vacuum within such devices for a long lifetime. However, the outgassing processes of cured epoxy adhesives are poorly understood. According to published data, the gaseous products released from epoxy resins primarily include inorganic components such as H₂O, N₂ and SO₂.¹ The weight loss of epoxy polymers in a vacuum varies from a few percents at 100 °C to 80% at 300 °C.² Previously, Basarab *et al.*³ used mass spectrometry to analyze volatile compounds released from commercial adhesives. According to these data, prolonged vacuum degassing makes it possible to create a vacuum device with internal adhesive joints in which a residual pressure does not exceed 10⁻⁴ Pa within 10 years. However, the outgassing conditions of cured adhesives can be specified only based on a kinetic model of gas evolution from the adhesives, and labor-intensive experiments should be performed for the development of this model. The release of hydrocarbons is the most important factor for the majority of vacuum devices (these compounds are not absorbed by well-known gas absorbers, and they mainly form a residual gas atmosphere⁴); therefore, it is reasonable to restrict the outgassing study to these compounds with the use of gas-chromatographic analysis.

Note that the structure of cured epoxy adhesives depends on temperature: at a temperature over the glass-transition range, the structural mobility and mechanical characteristics of the adhesive (viscosity, modulus of elasticity, internal friction, *etc.*)⁵ changed abruptly. There are no published data on changes in the specific rate of outgassing for adhesives on passing through the glass-transition range, but it is reasonable to assume that such changes occur. This circumstance should be taken into account both in the measurements of the specific rates of the release of volatile components and in the construction of a kinetic model for the outgassing of adhesive joints.

The aim of this work was to determine the specific rate of the release of residual hydrocarbons from a cured epoxy adhesive using gas chromatography and to study the temperature dependence of outgassing on going through the glass-transition range.

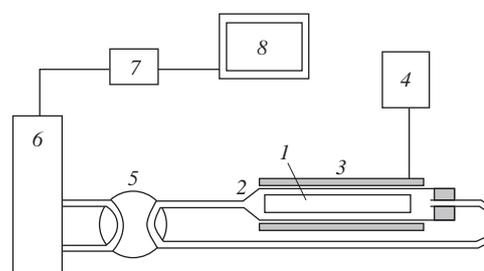


Figure 1 Schematic diagram of the experimental setup: (1) adhesive sample; (2) Pyrex reactor; (3) electric furnace; (4) TRM-10 temperature regulator; (5) four-way valve; (6) Chrom-5 chromatograph; (7) ADC; and (8) computer.

Figure 1 schematically shows the experimental setup used for the determination of the specific rate of outgassing. A thin layer of an epoxy adhesive (~0.05 g) based on commercial ED-20 epoxy resin (Russia) was applied to the internal surface of a glass tube 4.3 mm in diameter and 71 mm in length. The adhesive surface area was ~960 mm². After curing in accordance with technical specifications, the adhesive sample was degassed in a vacuum ($P = 5$ Pa) at 150 °C for 48 h. The specified glass-transition range of this adhesive is 100–130 °C. Adhesive sample 1 was placed in Pyrex flow reactor 2, which was arranged in cylindrical electric furnace 3. The reactor temperature was maintained to within 1 °C using TRM-10 temperature regulator 4. The reactor with the sample was connected to four-way valve 5, which made it possible to inject a gas sample from the reactor loop into the carrier-gas line of chromatograph 6 and to analyze it. A Chrom-5 chromatograph with a flame-ionization detector and a column 1.3 m in length packed with Porapak N was used for the determination of the residual hydrocarbon content of the adhesive sample. The column temperature was 110 °C. Chemically pure nitrogen was used as a carrier gas; the carrier-gas flow rate was 40 ml min⁻¹.

After heating the adhesive sample at a specified temperature for 30 min, gas from the reactor loop was injected into the chromatographic column. The gas-sample injection time was 25 s, which is sufficient for the complete removal of the extracted volatile compounds from the reactor. This gas sample was separated in the column, and the components arrived at the detector, whose

signals were converted by ADC 7 and transferred to computer 8. The gas chromatograph was calibrated against hydrocarbons with the use of acetylene as an internal standard (0.1 ml at a pressure of ~ 750 Torr and a temperature of 23°C). The maximum sensitivity of the instrument to hydrocarbons was 10^{-10} mol (error, 10%). The volatile compounds were identified based on chromatographic retention times. The residual outgassing was quantitatively characterized by the specific rate of gas release, which was calculated from the equation $\nu = N/St$, where N is the amount of substance (mol) released for the time t (s) from the adhesive surface area S (m^2).

It is evident that this rate depends on both temperature and the individual properties of the adhesive. Moreover, we experimentally found that the rate of outgassing depends on the adhesive surface area rather than on the weight (film thickness) of the adhesive. Thus, the specific rate of outgassing changed by only a few percents as the adhesive film thickness was increased by a factor of 4 (at the same adhesive surface area).

To determine the effect of temperature on the release of hydrocarbons from the cured adhesive, we calculated the effective activation energy of this process. Figure 2 shows the temperature

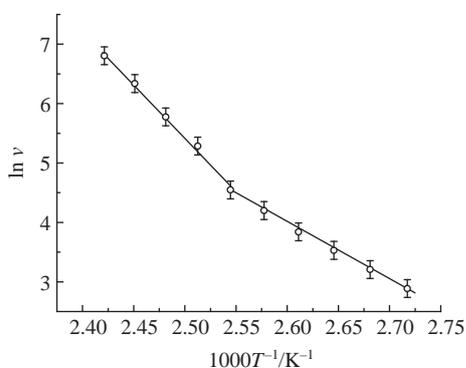


Figure 2 Arrhenius plot of the release of butene from the cured adhesive.

dependence of the release of residual butene from the cured adhesive in the Arrhenius coordinates. This plot clearly exhibits two temperature ranges corresponding to different effective activation energies. A drastic change in the activation energy occurred at $\sim 120^\circ\text{C}$: $E = 77.8 \pm 0.4$ and 140.6 ± 1.5 kJ mol^{-1} in the low-temperature and high-temperature zones, respectively. These two temperature zones are indicative of a change in the mechanism of outgassing on passing through the glass-transition range. A drastic change in the diffusion coefficient of hydrocarbons in the adhesive caused by the softening of its structure can be considered the most probable reason for this behavior. This sharp change in the kinetic parameters of the outgassing process should be taken into account in the calculation of the temperature dependences of the specific rates of outgassing for epoxy adhesives.

Thus, the rapid chromatographic analysis described above makes it possible to detect volatile hydrocarbon compounds released from cured epoxy adhesives and to determine the specific rates of this process to 10^{-10} $\text{mol m}^{-2} \text{s}^{-1}$ in a practically important temperature range.

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