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Abstract

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ON THE QUESTION OF THE RADICAL MECHANISM OF CURING OF RESOL RESINS

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The curing process of thermosetting resins is based on a chemical reaction proceeding between the active functional groups of the molecules ([1]). The formation of a three-dimensional structure through chemical bonds arising in the course of curing explains, in general terms, the change in the physical and chemical properties of the resin.

In recent years, quite a lot of data have been obtained indicating a definite role of free-radical processes in the mechanism of curing of phenol-formaldehyde resins ([2]). In the present work new data are presented that confirm this point of view. It could be expected that the free radicals formed during curing of a resol resin are capable of initiating polymerization of unsaturated compounds. To verify this assumption, we studied the polymerization rate of triethylene glycol dimethacrylate (TGM-3) in the presence of resol resin. The triethylene glycol dimethacrylate was purified from stabilizer by passage through a chromatographic column filled with alumina. The resol resin was purified by molecular distillation ([3]).

Fig. 1. IR spectra of TGM-3 and TGM-3 with 10% resol resin, initial and heated at 160° for 9 min.

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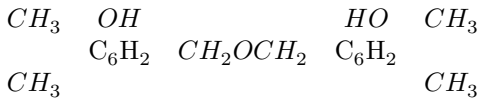
IR spectra were recorded for two samples: pure TGM-3 and TGM-3 with 10% (by weight) resol resin. The spectra were recorded under strictly identical conditions at room temperature and at 160°. The IR spectra were taken on a Hilger H-800 spectrograph with a NaCl prism, between NaCl windows in a heated cell. The spectra obtained by us are shown in Fig. 1. In the IR spectra the region from 1500 to 1700 cm^{-1} is presented; the 1640 cm^{-1} band is characteristic of C=C double bonds ([4]). The different rate of decrease in the intensity of this band in the samples indicates different rates of polymerization. Calculation of the optical density of the 1640 cm^{-1} band shows that D_{1640} for the initial TGM-3 sample is 0.8993; after heating at 160° for 9 min, $D_{1640} = 0.3296$, i.e., the concentration of double bonds decreases by a factor of 2.6. The TGM-3 sample with resol resin has, in the initial state, $D_{1640} = 0.5441$; upon heating at 160° for 9 min, $D_{1640} = 0.0780$—the concentration of double bonds decreases by a factor of 6.9. The initiation of thermal polymerization of the unsaturated

compound can be explained by the appearance of free radicals formed during thermal cleavage of dimethylene ether bridges ([5]).

In previous works ([6]), the presence of free radicals during curing of phenol-formaldehyde resin was detected by the ESR method in the form of a singlet line of resonance absorption. This made it possible to express purely qualitative considerations concerning the presence of free radicals in the cured resin and their concentration. In order to obtain completely definite proof of the cleavage of the dimethylene ether bridge in resol resin into free radicals and to determine the structure of the formed···

···of the free radicals formed, we studied, by the EPR method, the thermal decomposition of a model product of the following structure:



bis-2-hydroxy-3,5-dimethylbenzyl ether, which was synthesized by the method of Hultzsch ([7]). The model product was mixed with ground silica gel, previously dried in a drying oven to constant weight. The mixture contained 0.1 g of the model product and 0.2 g of silica gel. The mixture was placed in an ampoule; the ampoule was evacuated under vacuum. After heating the ampoule at a temperature of 160–170°, it was placed in the resonator of the EPR spectrograph, where the EPR spectrum shown in Fig. 2 was recorded. It is seen from Fig. 2 that the spectrum consists of five components of hyperfine structure; the splitting between the components is 11–13 oersteds; the g-factor is close to the g-factor of DPPH; the concentration of radicals per 1 g of substance was $1.2 \cdot 10^{16}$ units. The EPR spectrum obtained may be interpreted as the spectrum of a low-activity benzyl radical, which is stabilized on the surface of silica gel. The presence of five components indicates interaction of the unpaired electron with four protons.

Fig. 2. EPR spectrum of the model product bis-2-hydroxy-3,5-dimethylbenzyl ether

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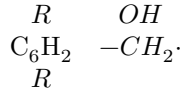
The results of the present experimental data make it possible, with high probability, to assert that the decomposition of dimethylene ether bonds during the curing of resol phenol-formaldehyde resins proceeds by a radical mechanism and is accompanied by the formation of radicals



and, probably,

$$\begin{matrix} R & OH \\ \mathrm{C_6H_2} & -CH_2O\cdot \\ R & \end{matrix}$$

Secondary reactions involving these free radicals lead to the formation of stable spatial networks characteristic of resins in the resite stage. It is very probable that the radical

$$\begin{matrix} R & OH \\ \mathrm{C_6H_2} & -CH_2O\cdot \\ R & \end{matrix}$$

decomposes with elimination of formaldehyde, analogously to what has been found in several other cases ([8]); in this process the radical

$$\begin{matrix} R & OH \\ \mathrm{C_6H_2} & -\cdot \\ R & \end{matrix}$$

should be formed. Identification of the last two types of radicals, as well as the nature of the secondary reactions involving these radicals, requires further study.

Thus, the results obtained in the present work make it possible to regard as proven the important role of free-radical processes in the mechanism of curing of resol phenol-formaldehyde resins.

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Note: Figure translations are in progress. See original paper for figures.