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STUDY OF INFRARED ABSORPTION SPECTRA IN THE PROCESS OF CURING A RESOL PHENOL-FORMALDEHYDE RESIN

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At present, extensive material has been accumulated on absorption spectra in the infrared region for various types of phenol-formaldehyde resins. Nevertheless, infrared spectroscopy methods have been used very little for studying the curing processes of phenolic resins. The few works available in this area have not introduced new data into the existing ideas about the structure of cured resins.

In the present work, we studied the IR absorption spectra of a resol phenol-formaldehyde resin during its curing in the temperature range from 20 to 200°, using a more accurate spectral method—in pressed KBr windows. A resol resin of industrial type was used, prepared by us according to the procedure described in more detail in work ([1]). After drying in vacuum, the resin was subjected to molecular distillation at 80° and at a vacuum of about 10^{-4} mm Hg. Samples of cured resin were prepared by pressing in a cylindrical heated mold as follows: the initial resin was loaded into the cold mold, a pressure of about 220 kg/cm^2 was applied, heating was switched on, and the temperature of the mold was raised at a rate of 1.5° per min to the specified value and then held at this value for 15 min. After this, the mold was rapidly cooled to room temperature and unloaded. The cylindrical samples obtained in this way, 10 mm in diameter and 4-5 mm high, were ground in a magnetic vibratory mill, mixed with KBr powder, and pressed under vacuum at a pressure of 10 t/cm^2 ([2]); the thickness of the windows was 1.45 mm, and the content of cured resin was 6 mg. The windows obtained in this way were used to record the absorption spectra of the cured resin. The spectra were recorded on a Hilger H-800 double-beam spectrometer with an NaCl prism in the region from 700 cm^{-1} to 4000 cm^{-1}.

The use of KBr windows for recording IR spectra made it possible to maintain accurately the thickness of the absorbing layer of the sample and thereby to obtain sufficiently reliable data for conclusions about the nature of changes in the resin spectrum during curing. In order to make sure that the adopted method of preparing samples for recording IR spectra (vibration grinding, the use of high pressures in pressing the windows, KBr medium) does not substantially change the spectra of cured resins, spectra were recorded from samples of resin cured in

Fig. 1. Infrared absorption spectra of resol resin cured at different temperatures.

Figure 1: Fig. 1. Infrared absorption spectra of resol resin cured at different temperatures.

a drying oven without pressure, followed by vibratory grinding with KBr, and also from samples of resin pressed in KBr and cured in windows. The spectra obtained showed that the adopted method of preparing samples does not affect the character of the curing process.

Using the procedure described above, we recorded the IR spectra of resol phenol-formaldehyde resin cured at temperatures of 70, 130, 170, and 200°, as well as the spectrum of the original uncured resin. The data obtained by us are shown in Fig. 1.

On the basis of the work of a number of authors (3), the bands observed in the spectrum of the resol resin can be interpreted with a certain degree of confidence as follows: the broad band at 3000-3600 cm^{-1}—stretching vibrations of OH bonds; a series of bands in the region 2800-3000 cm^{-1}—stretching vibrations of CH bonds; 1610, 1510, 1480 cm^{-1}—in-plane vibrations of the benzene ring; 1450 cm^{-1}—deformation vibrations of CH bonds; 1370 cm^{-1}—vibrations of OH of the phenyl ring; 1225 cm^{-1}—deformation vibrations of OH and stretching vibrations of C—O bonds; 1020 cm^{-1}—deformation vibrations of OH of methylol groups; bands in the region 750-900 cm^{-1}—out-of-plane deformation vibrations of aromatic CH bonds, characteristic of different types of substituted ring.

Fig. 1. Infrared absorption spectra of resol resin cured at different temperatures.
a—initial uncured resin, *b*—70°, *v*—130°, *g*—170°, *d*—200°.

As can be seen from the data presented in Fig. 1, with an increase in the heating temperature of the samples, substantial changes occur in the resin spectra. The bands characteristic of OH groups decrease, which is associated with the process of resin condensation—a decrease in the number of methylol groups. At the same time, a broad band at 1050 cm^{-1} appears, which may be assigned to the stretching vibration of a C—O ether bond. The appearance of this band agrees well with the existing view that methylol groups first pass into ether bridges. Subsequently, at 150° the 1050 cm^{-1} band decreases and disappears completely at 170°.

Of particular interest is the considerable decrease in the 1370 cm^{-1} band, characteristic of vibrations of OH groups of the phenyl ring. This decrease is already observed at relatively low temperatures (70° and above). Such a sharp decrease in the band may be explained by the entry of phenolic hydroxyl into the reaction. Another confirmation of the fact that phenolic hydroxyl enters into reaction is the appearance in the spectrum of cured resol resin (Fig. 1, *g*, *d*) of a band at 1015 cm^{-1}, characteristic of aromatic ethers. In addition to this band, a band

appears in the spectrum at 1645 cm^{-1}, characteristic of a C=C bond, which was observed earlier in the spectra of cured resins and was explained by the formation of quinoid structures (4). In this connection, attention is drawn to the fact that the absorption band of the double bond is already detected at 130° and then increases with increasing curing temperature. Comparison of the absorption spectra of cured resins, undistilled and subjected to molecular distillation, showed that the 1645 cm^{-1} band is more clearly expressed in the distilled resin.

The change in the number and position of bands in the region 700-900 cm^{-1}, characteristic of various substituted benzenes, is explained by the processes of resin condensation, during which the number of substituents in the ring changes. This is indicated by the disappearance of the 827 cm^{-1} band, characteristic of

of a trisubstituted benzene ring, and the appearance of two bands in the region 850-880 cm^{-1}, characteristic of tetrasubstituted benzenes. It is interesting that in the spectrum of the cured resins there also appears a band at 1379 cm^{-1}, which may be assigned to the formation of methyl groups. This band is clearly manifested at high curing temperatures (170-200°).

From the data we have obtained, it is difficult to draw any conclusions about the strengthening or weakening of hydrogen bonds during the curing of the resole resin. It can only be stated with certainty that the number of hydroxyl groups decreases; at the same time the band at 3200-3600 cm^{-1}, characteristic of stretching vibrations of O—H bonds, decreases and its contour changes —it becomes sharper. The study of infrared absorption spectra appears to us most fruitful when the spectroscopic data can be correlated with changes in other properties of the curing resins, above all their mechanical properties. The study of changes in the mechanical properties of a resole resin during curing (1) led to the conclusion that, in the mechanism of curing of resole resins, an important role is played by the formation of labile polymer chains, their thermal decomposition, and recombination of the active centers that arise, with the formation of stable spatial networks. The results of the present work make it possible to suppose that the labile polymer chains arising in the initial stages of curing of the resole resin sample studied by us are polyoxybenzyl ethers, formed through interaction of methylol groups with one another. This conclusion is in full agreement with the results of a number of studies carried out on model products (5). Thus, it seems very probable that the decomposition of ether bridges is the source of the formation of active centers, whose recombination leads to a number of secondary reactions ultimately causing the formation of stable spatial networks—resites.

With respect to the mechanism of decomposition of the ether bridge and the nature of the active centers formed in this process, there are several hypotheses. In particular, there is the view (6) that decomposition of the ether bridge leads to the formation of quinone methides—highly reactive compounds capable of further curing reactions. As we saw above, the appearance of the absorption band of a double bond, which is ascribed to quinone methides, was observed by us already at comparatively low temperatures. In addition, the products of

dimerization and trimerization of quinone methides are low-activity compounds incapable of forming polymer chains. Also unlikely are "rearrangement reactions" of the ether bridge, for example into a methylene bridge (7). In this case it is difficult to explain the experimentally observed effects of strong thermal destruction, leading to a sharp drop in the mechanical properties of resole resins at temperatures above 130°.

We believe that a radical mechanism for the decomposition of the ether bridge is highly probable. In this case, the entry of the phenolic hydroxyl into the curing reaction, as well as the appearance of the methyl group, can be explained by processes of recombination of the free radicals formed. A more detailed consideration of this hypothesis will be made in the following paper.

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