Investigations of the course of the synthesis of water-soluble acetone—formaldehyde resin*

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Dedicated to Ing. D. Berek, CSc., in honour of his 50th birthday

The composition of water-soluble acetone—formaldehyde resin prepared at acetone—formaldehyde mole ratio equal to 1 : 3 has been investigated. Using conventional analytical methods only few simple methyl derivatives of acetone were identified. By means of complementary investigations (IR spectroscopy, elemental analysis, chromatography) the general rules relating to the course of synthesis reaction were established. Moreover, the composition of the products formed in the presence of the excess of formaldehyde was determined.

Исследован состав растворяемых в воде ацетонно-формальдегидных смол полученных при молярном отношении ацетона и формальдегида равном 1 : 3. При помощи классических аналитических методов идентифицировано лишь несколько несложных производных ацетона. Используя дополнительные методы (спектроскопия ИК, элементарный анализ и хроматография) установились общие принципы касающиеся хода реакции синтеза. Кроме того определен состав продуктов формирующихся в присутствии избытка формальдегида.

Acetone—formaldehyde resins (A/F) are frequently used for stabilization of soils and cement mortars [1—3]. They are prepared by means of the reaction between acetone (A) and formaldehyde (F) in basic medium and depending on the reaction conditions, nature and amount of catalyst as well as on the mole ratio of the substrates (A : F) different products can be formed. Such diversity of the components complicates the investigations of the composition and the structure of individual products and influences the mechanism of their formation and hardening [3].

It is known from the literature [1—4] that the main components of water-soluble A/F resins are simple low-molecular ethers formed from hydroxymeth-

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ylacetones and numerous by-products, which deteriorate the quality of the final product.

On the basis of previous investigations [1—4] general rules were postulated relating to the course of this reaction in basic medium and defining the composition of the products formed in the excess of one of the reagents. Some difficulties appear however, when we want to determine the composition of the products, especially in the case when the mole ratio of reagents varies in the range from 1 : 2 to 1 : 4. Conventional analytical methods permit only to identify few simple methyl derivatives of acetone (4-hydroxybutanal, 3,5-bis(hydroxymethyl)tetrahydro-4-pyrone, and bis(hydroxymethyl)acetone [1—3]).

This paper presents the results of the investigations of the composition of the products formed during the synthesis of A/F resin [2]. High performance liquid chromatography method was used for this purpose. We have also compared the IR spectra of corresponding ACF-3 resins synthesized by Soviet investigators and equivalent to A/F resin as well as the results of elemental analysis of both these resins.

Experimental

Materials and reagents

Water-soluble A/F resins were synthesized according to *Giżyński*'s procedure [2]. Acetone : formaldehyde (A : F) mole ratio was equal to 1 : 3. The basic properties of the resin prepared are presented in Table 1.

Anal. grade methyl vinyl ketone, 4-hydroxybutanal, 3,5-bis(hydroxymethyl)tetrahydro-4-pyrone, and bis(hydroxymethyl)acetone purchased from Koch-Light Laboratories were used as standard substances. Other reagents obtained from POCh (Gliwice, Poland) were also of anal. grade.

Table 1

Main physical properties of water-soluble acetone—formaldehyde resin

Colour	Transparent, colourless
Density at 20 °C/(g cm $^{-3}$)	1.195
Viscosity at 20 °C/Pa s	84.1×10^{-3}
Content of dry substance/mass %	60.5
Solubility in water	Unlimited

Physicochemical and chromatographic measurements

Elemental analysis was made using Model 185 CHN analyzer (Hewlett—Packard, USA) and IR spectra were obtained using an SP-120 Pye—Unicam apparatus. The

Table 2

The results of elemental analysis for A/F and ACF-3 resins

Type of resin	w_i(calc.)/% w_i(found)/%	
	C	H
A/F	51.70	7.90
	49.47	7.83
ACF-3	51.70	7.90
	50.00	9.00

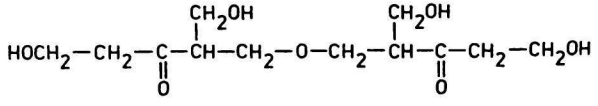
Note: Theoretical elemental composition was calculated for the substance characterized by formula *A*.

results of the elemental analysis and characteristic bands of IR spectra in the range of $\tilde{\nu} = 700$—$2000\ cm^{-1}$ compared to those obtained for ACF-3 resin [1—4] are listed in Table 2 and shown in Fig. 1. Chromatographic measurements were carried out using an LC-20 Pye—Unicam liquid chromatograph equipped with UV VIS and RI detectors (Varian). The samples were introduced onto the column by means of Model 7120 injection valve (Rheodyne Co., USA).

The analyses were carried out using 100 mm long stainless steel columns of 4 mm inner diameter (Chemical Reagents Factory — ZOCh Lublin, Poland) packed with Polsil ODS of particle diameter $d_p = 10\ \mu m$ [5]. The columns were packed by upward slurry technique [6] under the pressure of 45 MPa using a home-made packing apparatus.

Results and discussion

From the data listed in Table 2 and Fig. 1 it results that the A/F resin is practically equivalent to ACF-3 resin synthesized by Soviet authors [4]. Thus we can assume that the main component of such resin is the substance with the formula $C_{12}H_{22}O_7$ characterized by the following structure



(A)

It results from the chromatographic measurements that apart from the ethers mentioned above our A/F resin contains also other components.

Optimization of measurements conditions was made on the basis of appropriate choosing of composition of the binary mobile phase (methanol—water) and of its flow rate. The changes in mobile phase composition (10 % steps) permit to conclude that the suitable resolution ($R_{ij} \geq 1.5$) and time of analysis

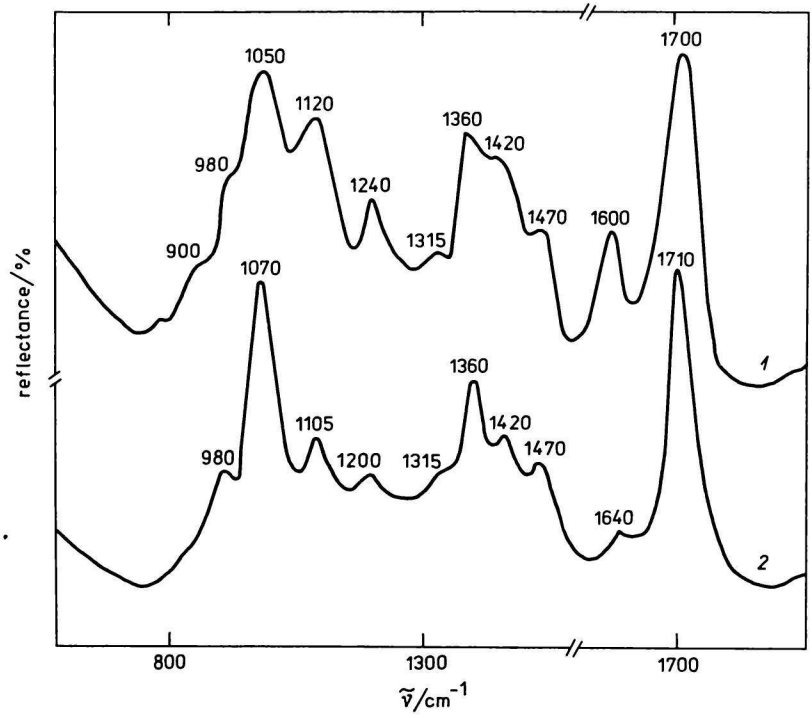


Fig. 1. Photogram of IR spectra of A/F (*1*) and ACF-3 (*2*) resins. Wavenumber range 700—2000 cm^{-1}.

Table 3

Contribution (%) of individual substances calculated by the use of phenanthrene as the internal standard (1×10^{-4} g/cm^3)

Number of peak	Substance identified	Individual components mass %
1	Water	7.89
2	Methanol	32.07
3	Formaldehyde	
4	Acetone	2.14
5	Methyl vinyl ketone	0.13
6	4-Hydroxybutanal	4.75
7	Bis(hydroxymethyl)acetone	3.15
8	Product of formula *A*	50.77
9	Tetrakis(hydroxymethyl)tetrahydro-4-pyrone	0.08

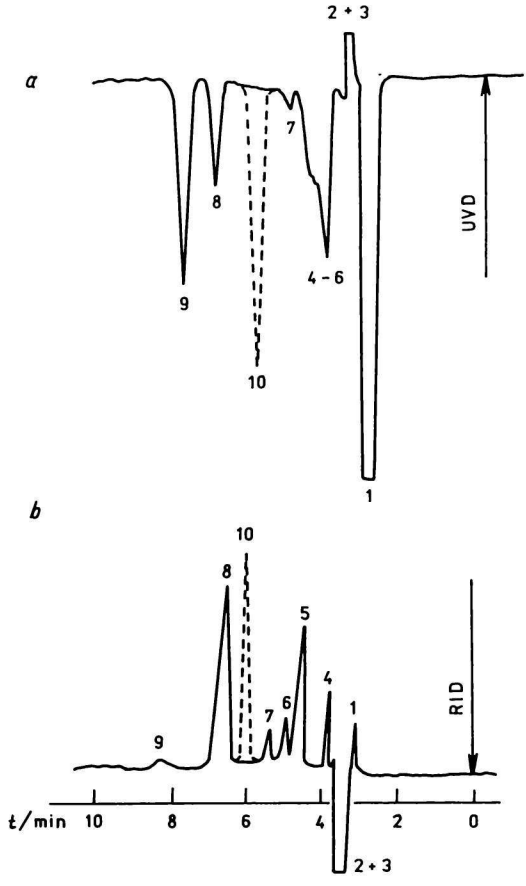


Fig. 2. Analysis of A/F resin by the HPLC method: *a*) using UV detector; *b*) using RI detector (for conditions of analysis see the text and Table 3).

can be obtained at the mobile phase composition MeOH—H_2O ($\varphi_r = 60:40$) and flow rate 0.9 $cm^3 min^{-1}$.

The application of the UV spectrophotometric detector was useless because most products analyzed did not contain appropriate chromophore groups (Fig. 2*a*). On the other hand, the RI detector enabled to obtain qualitative and quantitative analyses (Fig. 2*b*) of nine main components. Identification of these components was performed on the basis of comparison of retention times of individual standards. In this way we have identified the following substances: *1.* Water; *2.* methanol; *3.* formaldehyde; *4.* acetone; *5.* methyl vinyl ketone; *6.* 4-hydroxybutanal; *7.* bis(hydroxymethyl)acetone; *8.* main product described by formula *A*; *9.* tetrakis(hydroxymethyl)tetrahydro-4-pyrone.

The contribution of the above substances calculated by the use of phenan-

threne as the internal standard (1×10^{-4} g/cm^3) expressed in the form of percentages of individual components is listed in Table 3. It should be noted that the detection limit of the substances was 10^{-5} g/cm^3 and standard deviation of individual substances was lower than 5 %. The remainder has contained probably methanol (peak 1), water (peak 2) and other products of the synthesis, which can be concluded on the basis of number and height of the remaining peaks.

References

1. Kawasaki, A., Katagiri, T., and Gato, R., *Nippon Kagaku Zasshi 79*, 177 (1979).
2. Giżyński, W., *Polimery* (Warsaw) *25*, 24 (1980).
3. Walker, J. F., *Formaldehyde*. Reinhold Publishers, New York, 1964.
4. Arkhipov, M. I., Frolov, S. S., Borodkina, N. I., and Mirnova, V. M., *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 13*, 576 (1970).
5. Buszewski, B., Suprynowicz, Z., Lodkowski, R., and Nasuto, R., *Chem. Anal.* (Warsaw) *26*, 685 (1981).
6. Buszewski, B., Suprynowicz, Z., and Pastuszak, T., *Chem. Anal.* (Warsaw) *28*, 513 (1983).