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Molecular Weight Distribution of Modified Amino-Formaldehyde Resins

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Abstract—The molecular weight distribution of modified amino-formaldehyde resins synthesized at various melamine- and carbamide-to-formaldehyde molar ratios and catalyst modifier and diethylene glycol amounts was studied. Chromatograms of the obtained amino-formaldehyde resins are presented.

Keywords: amino-formaldehyde resins, modification, molecular weight distribution, liquid chromatograph

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Amino-formaldehyde resins play a huge role in the contemporary world. They are actively used in civil engineering, aviation, textile, and other industries; this stimulates the development of methods for the research and analysis of various polymer materials.

Almost all synthetic polymers are polydisperse; therefore, their molecular weight is an average statistical value and is determined by the molecular weight distribution (MWD) type and the averaging technique. The specific feature of transport methods is that primary information is obtained as the time distribution curves of macromolecule concentration. Since these curves are direct transformations of MWD functions, the transport methods are very suitable for determining molecular weights and polydispersity coefficients of polymers.

Unlike other transport methods, chromatography combines a continuous sample fractionation with the fraction analysis. This is a heterophase process, in which fractionation is based on a difference in the interfacial distributions of substances moving together with a solvent (mobile phase) through a highly dispersed medium of the stationary phase. Chromatographic methods are usually classified according to the chosen type of mobile and stationary phases: gas chromatography covers methods, in which gas serves as the mobile phase and liquid serves as the liquid phase. In accordance with the separation mechanism, there are ion-exchange, adsorption, precipitation, partition, and exclusion chromatography techniques [5].

In adsorption (chromatographic) fractionation, a polymer is deposited on an inert material with a high specific surface (packing) and placed in a column. An elution mixture consisting of two liquids, solvent and nonsolvent, is passed through the column with packing and the adsorbed polymer. The first fraction having the minimum adsorption capacity, usually this is the fraction with the least molecular weight, eluates from the column. Sequential separation of elution portions allows isolation of up to 20–30 of polymer fractions [4].

The analysis of MWD was performed on a Waters liquid chromatograph (Fig. 1) equipped with a Waters 2414 differential refractometric detector and a PDA 996 diode array spectrophotometric detector and a PLgel 5 μm MIXED-C column. Analysis was carried out under the following conditions: eluent *N*-methylpyrrolidone + LiCl (1.0 g of LiCl/0.5 L of NMP), the elution rate 1 mL/min, T_{col} = 70°C, and T_{ref} =

Fig. 1. Waters 2414 chromatograph.

50°C. The calibration dependence was obtained using standard polystyrene samples with molecular weights ranging from 580 to 3.7×10^6 Da. The resulting chromatograms were processed using the Empower program.

Polymer samples were dissolved in NMP + LiCl, and the polymer solution was filtered through an Anatop25 0.2 μm PTFE filter (Whatman).

Amino-formaldehyde resins modified at the synthesis stage were used as polymer samples.

In the synthesis of amino-formaldehyde resins, alkalis, in particular NaOH, is used to neutralize formalin. The Cannizzaro redox reaction is known to occur under these conditions; it involves reduction of a formaldehyde molecule with the simultaneous oxidation of another one:

$$2CH_2O + H_2O \rightarrow CH_3OH + HCOOH.$$

As a result of the Cannizzaro reaction, pH of the reaction mixture (determined by adding sodium hydroxide) decreases gradually; this process is especially rapid in the presence of compounds acting as catalysts [1, 2]. Amino-formaldehyde resins were synthesized in the presence of a catalyst modifier preventing the Cannizzaro reaction. A salt of polyfunctional organic acids was used as a catalyst modifier.

Four samples of amino-formaldehyde resins (Table 1) were synthesized using various amounts of the LN catalyst modifier, melamine (M)- and carbamide (C)-to-formaldehyde (F) molar ratios, and amounts of diethylene glycol (DEG). The base case was the unmodified melamine resin.

The properties of the resulting amino-formaldehyde resins were studied and compared with those of the base case (the base case was the unmodified melamine resin containing 35 wt % melamine). The results are listed in Table 2.

Table 1. Synthesized amino-formaldehyde resins

Amino-formaldehyde resin	LN, %	(M + C) : F	DEG, %
Sample 1	1	1 : 1.8	1
Sample 2	1	1 : 1.8	8
Sample 3	0.1	1 : 1.8	8
Sample 4	1	1 : 2.2	1

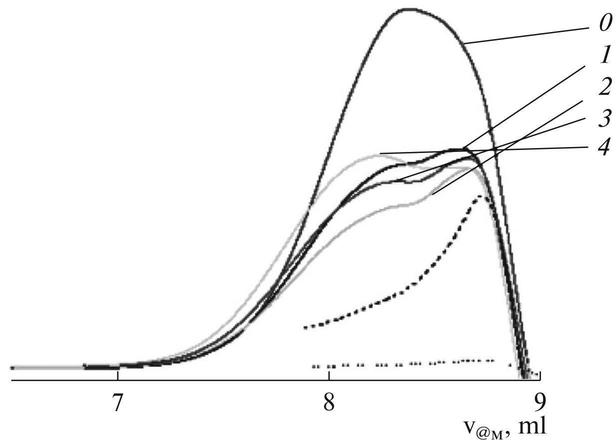

Fig. 2. Chromatograms of amino-formaldehyde resins: (*0*) base case; (*1*) sample 1; (*2*) sample 2; (*3*) sample 3; and (*4*) sample 4.

An analysis of the data presented in Table 2 makes it possible to infer that the resulting modified resins are characterized by a smaller content of free formaldehyde and a longer shelf life with the content of expensive melamine being lower.

Figure 2 shows the chromatograms of the amino-formaldehyde resins; black dashed lines denote the real chromatogram of *N*-methylpyrroldone + LiCl (the lowest curve), and the upper black dotted line denotes the same chromatogram magnified by 20 times.

An analysis of the graphs shown ted in Fig. 2 indicates that the weight-average molecular weight (M_w) increases in the following sequence: base sample → sample 1 → sample 4, while polydispersity for samples 1–4 remains almost unchanged.

Table 3 presents the molecular weight characteristics of the amino-formaldehyde resins; here, M_n is the number-average molecular weight, M_w is the weight-average molecular weight, M_p is the molecular weight in the higher molecular peak, and *PD* is the M_w/M_n ratio, which is referred as the polydispersity index.

Based on the data presented in Table 3 it can be stated that the modified amino-formaldehyde resins have higher molecular weights compared with the resin currently used in the industry. Thus, the modification of amino-formaldehyde resins with the salts of

Table 2. Properties of amino-formaldehyde resins

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Base case
Dry residue content at 105°C, %	59 ± 1	58 ± 1	59 ± 1	58 ± 1	58 ± 1
Hydrogen index, pH units	9.5	9.7	9.5	9.5	9.0
Conditional viscosity according to VZ-4 at 20°C, s	13.7	15.0	15.1	13.6	16.5
Resin miscibility with water, mL/mL	1 : 2.0	1 : 2.0	1 : 2.0	1 : 2.0	1 : 2.0
Content of free formaldehyde, %	0.25	0.35	0.28	0.35	0.5
Resin viability at 5–23°C, days	21	25	22	24	6–8

Table 3. Molecular weight characteristics of amino-formaldehyde resins

Sample	M_n	M_w	M_p	PD
Basic substance	790	1540	920	2.0
Sample 1	810	1770	1020	2.2
Sample 2	770	1860	1110	2.4
Sample 3	820	1960	1160	2.4
Sample 4	920	2180	1300	2.4

polyfunctional organic acids makes it possible to eliminate one of the disadvantages of modern impregnating resins.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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