

The structural properties of melamine-formaldehyde and phenolic-formaldehyde resins

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Four types of phenolic-formaldehyde and melamine-formaldehyde porous sorbents were synthesized by using the fumed silica and aluminum oxide as inorganic templates. The changes in composition of reacting mixture and in conditions of post-synthesis treatment allowed differentiating the porosity and surface area of these materials. The analysis of pore structure was based on the comparison of nitrogen adsorption isotherms on a given porous sorbent and a standard nonporous polymer. The synthesis allowed obtaining the materials of narrow pore size distributions with pore sizes over the range: 3.3 – 10.5 nm, and specific surface areas up to 325 m²/g.

1. INTRODUCTION

The porous organic polymers have attracted considerable attention in recent years because of their important industrial applications. They are widely used as column packings in gas and liquid chromatography and in other processes relevant to polymer-solvent mixtures. In all above-mentioned processes the pore structure of polymer material plays an important role.

The cross-linked porous polymers are structurally composed of small microgel particles agglomerated together to form the clusters. The porosity arises from the void spaces between and within the clusters and spaces produced after removal of inorganic matrix.

In conventional suspension polymerization first the stable dispersion of fine monomer droplets is obtained by a strong mechanical agitation in a second liquid phase containing a suspending agent and an initiator. During

polymerization the small polymer beads are produced. Most common styrene-divinylbenzene copolymer bead is produced by suspension copolymerization in the presence of an inert diluent [1-3]. The size and pore distribution in polymer structure are determined by type and amount of diluent employed. Another method to produce the porous polymers consists in the bulk polymerization in pores of inorganic matrix. As an inorganic matrix usually porous silica gel or alumina are used [4,5]. After completing the polymerization the inorganic matrix is removed by dissolution in alkaline solution.

Textural characterization of polymeric sorbents is difficult to obtain in comparison to rigid inorganic adsorbents. Several methods can be used to investigate the characteristics of pores, including adsorption of inert gases, mercury intrusion porosimetry, small angle scattering of X-rays or neutrons, thermogravimetric porosimetry, and more recently NMR spectroscopy and positronium annihilation spectroscopy [6-14]. In the wet state, when the solute size is known, size exclusion chromatography can be used to characterize the pore structure of column packing material [15]. The pore dimensions differ usually when are evaluated in the swollen state in comparison to the dry state as in adsorption experiment.

In low-temperature adsorption of nitrogen at 77 K polymers demonstrate some tendency to crush and deform, however, due to their glassy state in this temperature and weak interaction with nitrogen molecules the swelling effect may be neglected. The porosity parameters derived from low-temperature adsorption data are usually different than those obtained by other methods [16]. Thermal desorption of liquids indicates that the pore radii of melamine-formaldehyde resins wetted with water are higher than radii estimated from nitrogen isotherm. Moisture adsorption and swelling process in epoxy resins is of significant technical importance [17,18]. Textural parameters depend strongly on the particle dimensions and chemical character of wetting liquid [19,20]. The rate of swelling depends mainly on the interactions of adsorbate with polymer network and the interaction of the molecules with themselves. Thus, the same porous polymers may exhibit various structural characteristics being in contact with various gas or liquid media, especially when cross-linking process is not completed. Internuclear chain elasticity of porous polymer influences pore properties and swelling ability.

Taking into account the problems arising from swelling process it seems that for comparative investigations of geometrical structure of various polymeric sorbents the nitrogen method is of great importance.

In the present paper the results of investigations of the porosity of four types of cross-linked porous phenolic-formaldehyde and melamine-formaldehyde polymers are presented. As a template forming the pore structure of resulting polymers the fumed silica and alumina particles were used. In order to

investigate the porous structure the measurements of low-temperature adsorption/desorption isotherms of nitrogen molecules were performed. The BET specific surface area and the total pore volume were evaluated by using the standard methods. The mesopore and micropore volumes and external surface area were calculated by applying the α_s -method. As standards the nonporous phenolic-formaldehyde and melamine-formaldehyde polymers were used. The pore size distributions were obtained from desorption branches of nitrogen isotherms using the Barrett-Joyner-Halenda (BJH) method.

2. EXPERIMENTAL

Resin Synthesis. The synthesis of hyper-cross-linked phenolic-formaldehyde resin was performed by contacting a reacting mixture of bisphenol, paraformaldehyde with the inorganic template in the form of aluminum oxide at controlled pH [17]. This mixture was aged during 3 days and heated. Next the template alumina particles were removed from the cross-linked copolymer by dissolution in alkaline solution (NaOH) having a pH at about 12, without destruction of the polymerizate. The obtained phenolic-formaldehyde resin was marked as PHA-1. A part of this polymer was further washed with a base under a high pressure; this sample was marked as PHA-1M. Prior to experiment the final products were washed with hot water and acetone. Chemical character of the phenolic-formaldehyde resin surface is determined mainly by the presence of polar hydroxyl groups and hydrophobic benzene rings. In Figure 1 the structure of phenolic-formaldehyde polymer is presented.

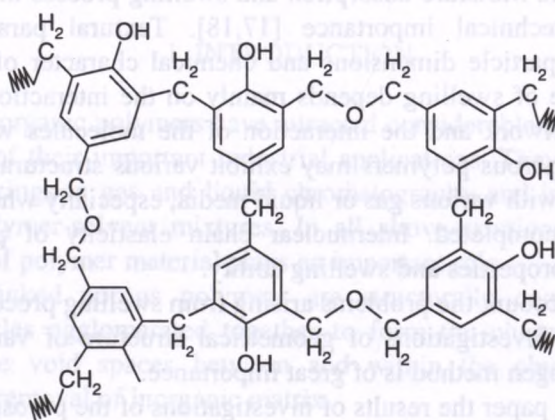


Fig. 1. The structure of phenolic-formaldehyde resin

The synthesis of hyper-cross-linked melamine – formaldehyde resins was conducted by contacting a reacting mixture of melamine and paraformaldehyde with the fumed silica as inorganic template at controlled pH [21]. The further procedure was the same as in the case of synthesis of phenolic-formaldehyde polymers. Changing the composition of reacting mixture, two samples of melamine-formaldehyde resins ME-10 and ME-11 were obtained. Chemical character of the melamine-formaldehyde resin surface is determined mainly by the presence of polar amine groups, hydrophobic hydrocarbon segments and nitrogen atoms in triazine rings. The structure of melamine-formaldehyde resin is given in Figure 2.

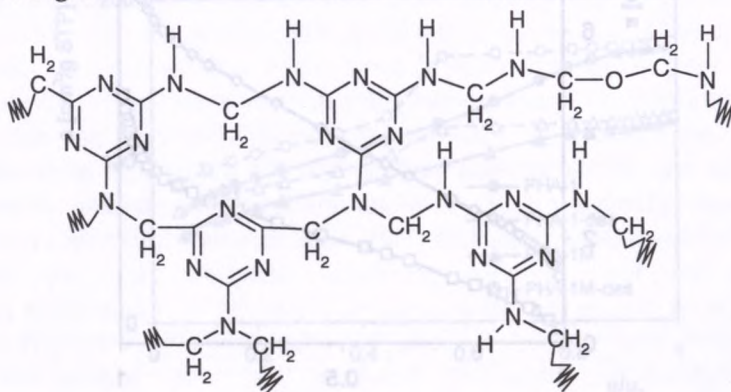


Fig. 2. The structure of melamine-formaldehyde resin

Gas Adsorption Experiments. Nitrogen adsorption/desorption isotherms at 77 K were determined volumetrically using ASAP 2405N analyzer (Micromeritics Corp., USA). Before the experiment the adsorbents were degassed (10^{-4} mmHg) at 493 K.

3. RESULTS AND DISCUSSION

The low-temperature nitrogen adsorption/desorption data were used to evaluate the BET specific surface area, S_{BET} , and the total pore volume, V_t , by applying the standard methods (S_{BET} from the linear BET plots and V_t from the adsorption at the relative pressure $p/p_s=0.975$) [6]. The external (macropore) surface area, S_{ext} , and the sum of mesopore and micropore volume, $V_{\text{meso+micro}}$, were obtained from the α_s -plot method [6,22]. This method is based on the comparison of nitrogen isotherm on a studied solid with the standard isotherm on a reference nonporous adsorbent. This standard reduced isotherm α_s is defined as the ratio of adsorption value corresponding to a given relative

pressure p/p_s , and the adsorption value at the point $p/p_s=0.4$ (p_s is the saturation pressure, $p/p_s=0.4$ is a starting point of isotherm hysteresis loop for nitrogen adsorption) As the reference adsorbents the specially synthesized nonporous phenolic-formaldehyde PH-0 and melamine-formaldehyde resin ME-0 was used [23] (Figure 3). The mesopore structure was characterized by the distribution function of mesopore volume calculated by applying the Barrett-Joyner-Halenda (BJH) method [24].

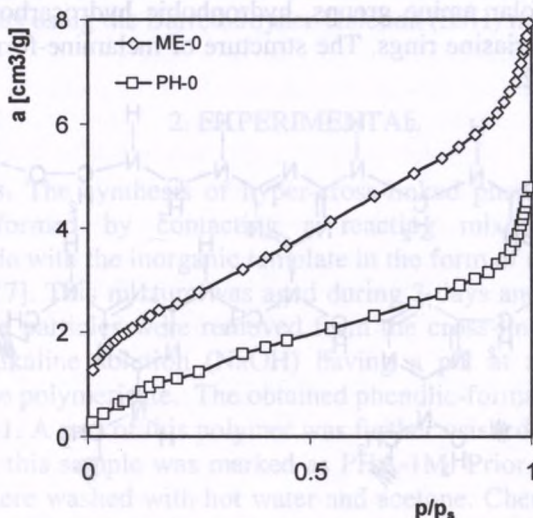


Fig. 3. The nitrogen adsorption isotherms on the nonporous melamine-formaldehyde ME-0 and phenolic-formaldehyde PH-0 resins

First, the standard parameters characterizing the porous structure: the BET specific surface area, S_{BET} and the total pore volume, V_t were evaluated for the phenolic-formaldehyde (PHA-1, PHA-1M) and melamine-formaldehyde resins (ME-10, ME-11). These values are summarized in Table 1.

Tab. 1. The values of parameters characterizing porous structure of polymeric sorbents, calculated from nitrogen adsorption/desorption isotherms

Resin	S_{BET} [m ² /g]	V_t [cm ³ /g]	$V_{\text{meso+micro}}$ [cm ³ /g]	S_{ext} [m ² /g]	D [nm]	$V_{\text{meso+micro}}/V_t$
PHA-1	325	0.26	0.24	19	3.5	0.89
PHA-1M	260	0.19	0.16	22	3.3	0.85
ME-10	68	0.15	0.10	38	6.5	0.67
ME-11	69	0.22	0.17	45	10.5	0.75

In Figure 4 the adsorption/desorption isotherms of nitrogen on the resins PHA-1 and PHA-1M are presented. Generally, for both studied polymers one can observe a monotonic increase of adsorption over the whole pressure range; the isotherms have a similar shape. The existence of hysteresis loop corresponding to capillary condensation phenomenon evidences that the synthesized resins have the mesoporous structure. In the case of resin PHA-1 higher adsorption values are observed over the whole pressure range. It corresponds well with higher values of specific surface area, S_{BET} , and total pore volume, V_t , for this polymer.

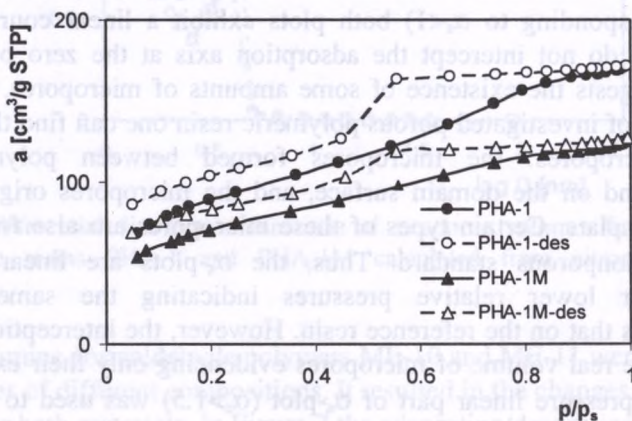


Fig. 4. The nitrogen adsorption/desorption isotherms for the phenolic-formaldehyde resins PHA-1 and PHA-1M

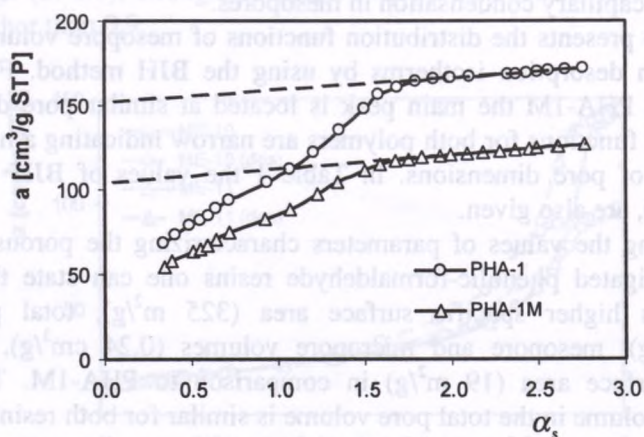


Fig. 5. The α_s plots for nitrogen adsorption isotherms for the phenolic-formaldehyde resins PHA-1 and PHA-1M

In Figure 5 the α_s -plots are drawn for the studied phenolic-formaldehyde polymers; whereas, the values of parameters (the external surface area, S_{ext} , and the mesopore and micropore volume, $V_{\text{meso+micro}}$) calculated by using the higher-pressure parts of these plots are compared in Table 1. In the case of both resins very similar course of the α_s -plots is observed in a wide range of pressures, suggesting the same type of porosity for both polymers. However, for PHA-1 the α_s -plot corresponds to higher adsorption values. Three main parts can be distinguished on the plots under study: two linear in low- and high-pressure regions and one nonlinear for medium pressures. For low-pressure region (corresponding to $\alpha_s < 1$) both plots exhibit a linear course but these straight lines do not intercept the adsorption axis at the zero point. Such a behavior suggests the existence of some amounts of micropores. Considering the structure of investigated porous polymeric resin one can find three types of possible micropores: the micropores formed between polymer domain boundaries and on the domain surface, and the micropores originating from inorganic template. Certain types of these micropores are also formed on the surface of nonporous standard. Thus, the α_s -plots are linear for porous polymers for lower relative pressures indicating the same adsorption mechanism as that on the reference resin. However, the interception point may not reveal the real volume of micropores evidencing only their existence. The second high-pressure linear part of α_s -plot ($\alpha_s > 1.5$) was used to estimate the sum of micropore and mesopore volume (from the intercept of this straight line with adsorption axis) and the external surface area (from the slope of straight line). The nonlinear behavior observed for average pressure range ($1 < \alpha_s < 1.5$) reflects the capillary condensation in mesopores.

Figure 6 presents the distribution functions of mesopore volume calculated for nitrogen desorption isotherms by using the BJH method. For the resins PHA-1 and PHA-1M the main peak is located at similar pore diameter. The distribution functions for both polymers are narrow indicating a high degree of uniformity of pore dimensions. In Table 1 the values of BJH average pore diameter, D , are also given.

Analyzing the values of parameters characterizing the porous structure of both investigated phenolic-formaldehyde resins one can state that the resin PHA-1 has higher specific surface area ($325 \text{ m}^2/\text{g}$), total pore volume ($0.26 \text{ cm}^3/\text{g}$), mesopore and micropore volumes ($0.24 \text{ cm}^3/\text{g}$), and smaller external surface area ($19 \text{ m}^2/\text{g}$) in comparison to PHA-1M. The share of mesopore volume in the total pore volume is similar for both resins indicating a small content of larger pores. Thus, the difference between the structure characteristics of resins PHA-1 and PHA-1M may be attributed mainly to higher content of mesopores and resulting development of specific surface area in the case of the resin PHA-1. The applied process of washing the polymer

under high pressure (PHA-1M) diminished the specific surface area and mesopore amount as a result of further polymerization in the treated material.

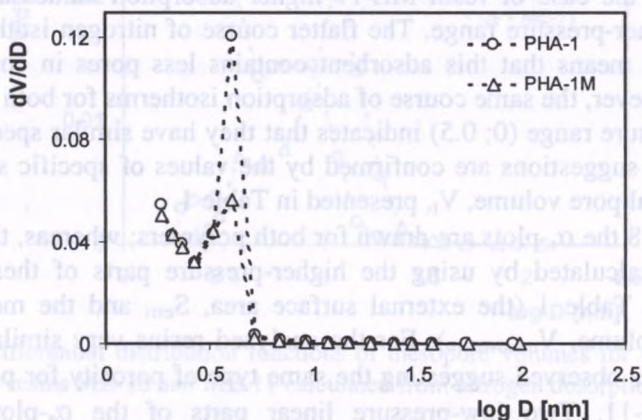


Fig. 6. The differential distribution functions of mesopore volumes for the phenolic-formaldehyde resins PHA-1 and PHA-1M calculated from nitrogen desorption isotherms

Two melamine-formaldehyde polymers ME-10 and ME-11 were synthesized from mixtures of different compositions. It resulted in the changes of adsorptive properties for both materials. In Figure 7 the adsorption/desorption isotherms of nitrogen on the resins ME-10 and ME-11 are presented. Both isotherms have a similar shape; one can observe a monotonic increase of adsorption over the pressure range (0; 0.8), stronger increase for $p/p_s > 0.8$, and its stabilization for pressures higher than 0.9.

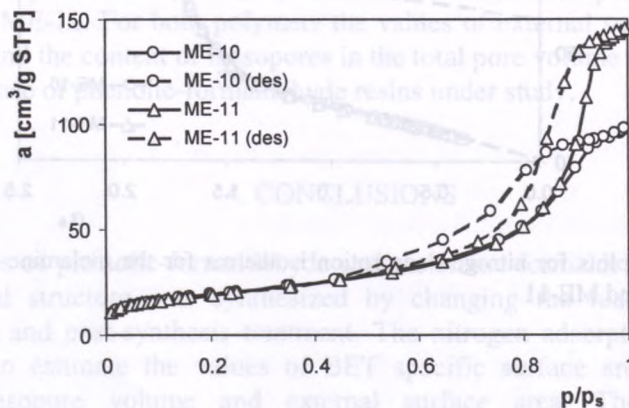


Fig. 7. The nitrogen adsorption/desorption isotherms for the melamine-formaldehyde resins ME-10 and ME-11

The existence of hysteresis loop corresponding to capillary condensation phenomenon evidences that the synthesized resins have the mesoporous structure. In the case of resin ME-11 higher adsorption values are observed over the higher-pressure range. The flatter course of nitrogen isotherm for the resin ME-10 means that this adsorbent contains less pores in comparison to ME-11. However, the same course of adsorption isotherms for both polymers in the low-pressure range (0; 0.5) indicates that they have similar specific surface areas. These suggestions are confirmed by the values of specific surface area, S_{BET} , and total pore volume, V_t , presented in Table 1.

In Figure 8 the α_s -plots are drawn for both polymers; whereas, the values of parameters calculated by using the higher-pressure parts of these plots are compared in Table 1 (the external surface area, S_{ext} , and the mesopore and micropore volume, $V_{\text{meso+micro}}$). For the analyzed resins very similar course of the α_s -plots is observed suggesting the same type of porosity for polymer ME-10 and ME-11. Two low-pressure linear parts of the α_s -plots for both melamine-formaldehyde resins are more distinct in comparison to these plots corresponding to phenolic-formaldehyde polymers studied. In low-pressure region (corresponding to $\alpha_s < 1$) the α_s -plots for ME-10 and ME-11 do not intercept the adsorption axis at the zero point, however, their behaviour suggests the existence of smaller amounts of micropores than for the phenolic-formaldehyde resins.

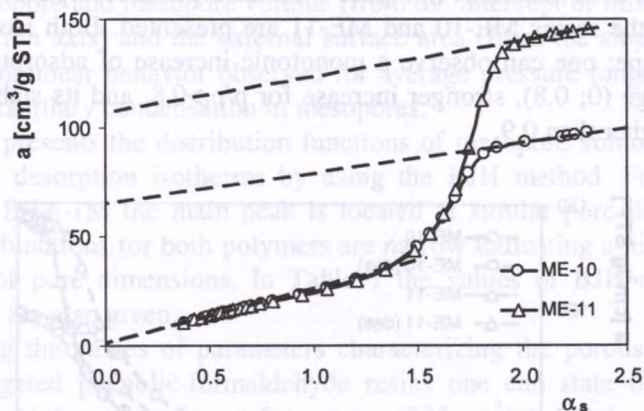


Fig. 8. The α_s plots for nitrogen adsorption isotherms for the melamine-formaldehyde resins ME-10 and ME-11

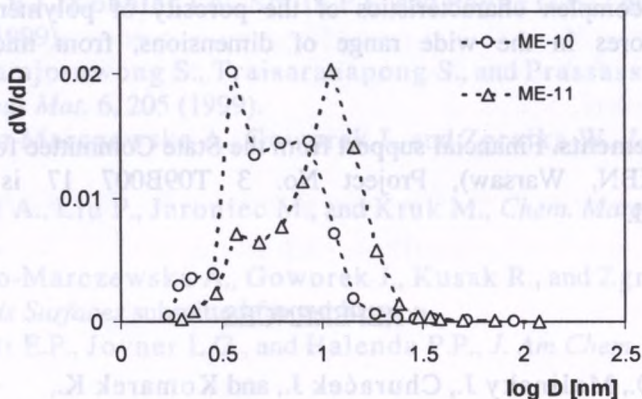


Fig. 9. The differential distribution functions of mesopore volumes for the melamine-formaldehyde resins ME-10 and ME-11 calculated from nitrogen desorption isotherms

Figure 9 presents the distribution functions of mesopore volume calculated from nitrogen desorption isotherms by using the BJH method for two melamine-formaldehyde resins. Both distributions are bimodal indicating existence of two types of pores in the structure of melamine-formaldehyde resins analyzed. The main peaks are located at different pore diameter. In Table 1 the values of BJH average pore diameter, D , are also given.

Analyzing the values of presented parameters one can state that both resins have similar specific surface area ($68, 69 \text{ m}^2/\text{g}$), however, the resin ME-10 is characterized by smaller total ($0.15 \text{ cm}^3/\text{g}$), and mesopore and micropore volumes ($0.1 \text{ cm}^3/\text{g}$), and mesopore diameter (6.5 nm) in comparison to ME-11. Thus, the difference between the structure characteristics of polymers ME-10 and ME-11 may be attributed mainly to content of larger mesopores in the case of the resin ME-11. For both polymers the values of external surface area are rather high and the content of mesopores in the total pore volume is much lower than in the case of phenolic-formaldehyde resins under study.

4. CONCLUSIONS

The series of phenolic-formaldehyde and melamine-formaldehyde resins of differentiated structure was synthesized by changing the reacting mixture composition and post-synthesis treatment. The nitrogen adsorption isotherms were used to estimate the values of BET specific surface area, total pore volume, mesopore volume and external surface area. The parameters characterizing the porous structure were compared in order to find the resemblances and differences among the studied sorbents. The adsorption data

demonstrate complex characteristics of the porosity of polymeric sorbents containing pores in the wide range of dimensions, from micropores to mesopores.

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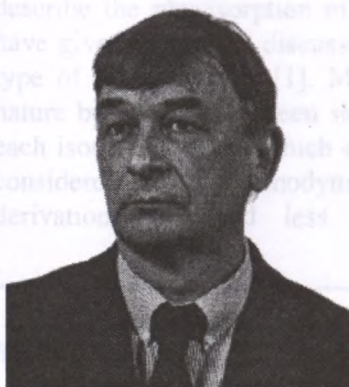
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