

## Preparation of sorbents from selected polymers

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In this work, the results of studies on the preparation of sorbents from selected polymers were presented. The polymers were carbonized and subsequently physically activated by steam or carbon dioxide, or alternatively, chemically activated with potassium hydroxide. For the obtained materials, a specific area was evaluated by means of low-temperature nitrogen adsorption and benzene adsorption, iodine number was also determined. The obtained results indicated a possibility to procure hydrophobic sorbents of microporous structure. Sorbents having the best properties, i.e. the specific area of above 2000 m<sup>2</sup>/g were produced from poly(ethylene terephthalate) and phenol-formaldehyde resin.

**Keywords:** polymers, carbonization, physical activation, chemical activation, carbon sorbents.

### INTRODUCTION

The use of adequate raw material, which should demonstrate a low amount of volatile substances, high concentration of elemental carbon, specified porosity and mechanical endurance, is essential for the production of carbon sorbents<sup>1</sup>. The raw materials used for the production of carbon sorbents are: hard coal, lignite, peat as well as fruit husks and stones<sup>2-4</sup>. Literature data shows that the precursors for carbon sorbent production can also be synthetic polymers<sup>5</sup>, especially poly(ethylene terephthalate)<sup>6-11</sup>, e.g. Kartel et al.<sup>12,13</sup> obtained sorbents from poly(ethylene terephthalate) (PET) by chemical activation with ZnCl<sub>2</sub> or H<sub>2</sub>SO<sub>4</sub>. László et al.<sup>11</sup> obtained from this polymer carbon sorbent used to adsorb chlorophenols from waste-waters, using the process of physical activation with the mixture of steam and nitrogen. Yang et al.<sup>14,15</sup> obtained carbon sorbents from novolak resin mixed with hexamethylenetetramine and poly(vinylbutyral) or poly(oxyethylene)diol. On the other hand, the authors<sup>16</sup> of the used ion-exchange resins for the preparation of carbon sorbents by carbonization and activation with CO<sub>2</sub>.

This work presents the results of the studies aimed at the evaluation of the possibilities to use the selected polymers for the preparation of carbon sorbents. These studies will provide a basis for an application of polymers as the modifiers of bitumen and the preparation of carbon sorbents from these binders.

### EXPERIMENTAL

Polymers of different chemical structure of macromolecules were used in this work:

- poly(ethylene terephthalate) (PET) produced by Zakłady SK Eurochem in Włocławek, Poland,
- phenol-formaldehyde resin Nowolak 09A (PF), produced by Zakłady Chemiczne Organika-Sarżyna S.A., Poland,
- high-melting coumarone-indene resin (CIR), produced by "Węglpochodne Ltd.", Kędzierzyn-Koźle, Poland,
- cured polyester resin Estromal 103E (UP), produced by Zakłady Tworzyw Sztucznych "Erg", Pustków, Poland,

– polycarbonate (PC), production waste from automotive industry, granulated by Drewnex Recykling Plastics, Dąbrowa Górnicza, Poland,

– polyacrylonitrile (PAN), produced by "Polymir" S.A., Novopolotsk.

Carbonization was carried out in two stages:

– the first stage of initial carbonization was conducted by heating the sample to the temperature of 520°C with the temperature increase rate of 5°C/min, in nitrogen atmosphere (nitrogen flow rate 20 l/h) and holding the sample at this temperature for 1 hour,

– the second, main stage of carbonization was carried out by heating the sample to the temperature of 520°C with the heating rate of 15°C/min and then to 850°C (final temperature was maintained for 1 hour) with the rate of 5°C/min. The process was conducted in nitrogen atmosphere (nitrogen flow rate of 20 l/h).

The obtained carbonizates were activated by selective gasification with steam at 800°C or with carbon dioxide at 850°C. The activation was carried out till 50% mass loss was reached.

For the selected polymers also the process of carbonization and chemical activation with KOH was carried out. In this case the samples were initially carbonized at 520°C and subsequently chemically activated. The mixture of the pulverized KOH and the product of the initial carbonization (mass ratio of 4:1) was heated to the temperature of 800°C with the heating rate of 10°C/min, and then annealed at this temperature for 1 hour. The process was carried out in nitrogen atmosphere (nitrogen flow rate of 20 l/h). After the completion of this process the product was cooled, rinsed with distilled water, 5% HCl and then the hot distilled water till a neutral reaction was reached.

For the obtained sorbents the following parameters were determined:

– the adsorption value of iodine (LJ) according to PN-83C-97555.04 standard,

– the specific surface by means of the volumetric low-temperature nitrogen adsorption method S<sub>BET</sub> (N<sub>2</sub>),

– the adsorption and desorption of benzene vapours by means of the McBain-Bakr method. On the basis of the experimentally obtained adsorption and desorption of benzene vapour isotherms, the specific surface by the BET method – S<sub>BET</sub> (C<sub>6</sub>H<sub>6</sub>), micropore volume (V<sub>mic</sub>) and

mesopore volume ( $V_{mes}$ ) were calculated. All the calculations were carried out using the "IZOTERMY" software<sup>17</sup>,

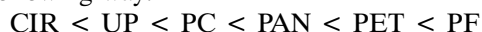
– the adsorption of hydrocarbons according to the methods described in W. Hermanowicz's work for industrial waste waters<sup>18</sup>. For the raw and purified waste waters the ether extract was estimated by the gravimetric method. The petrochemical waste water used in the study was received from the Zakład Wodno-Ściekowy in PKN ORLEN S.A. The content of hydrocarbon products in that waste water amounts to 54.1 mg/dm<sup>3</sup>.

## RESULTS AND DISCUSSION

The polymers designated for the study were carbonized and physically activated with steam and for the obtained samples iodine number, the specific surface and the porous structure were determined.  $S_{BET}$  ( $N_2$ ) specific surface by low-temperature nitrogen adsorption,  $S_{BET}$  ( $C_6H_6$ ) assuming the horizontal and vertical orientation of benzene molecules, micropore ( $V_{mic}$ ) and mesopore ( $V_{mes}$ ) volume were calculated. The results are presented in Table 1.

From among the carbon sorbents obtained during the physical activation with steam, the materials produced from phenol-formaldehyde resin and poly(ethylene terephthalate) had the highest specific surface  $S_{BET}$  ( $N_2$ ) and  $S_{BET}$  ( $C_6H_6$ ) (regardless of benzene molecules orientation) as well as the highest iodine number.  $S_{BET}$  ( $N_2$ ) for these sorbents was in the range of 1300 – 1500 m<sup>2</sup>/g.

The tested polymers, according to the increasing ability to develop the high specific surface, can be arranged in the following way:



All the samples after the activation had the hydrophobic properties, which was indicated by iodine numbers and the  $S_{BET}$  specific surface values determined by the adsorption of benzene vapour ( $S_{BET}$  ( $C_6H_6$ )), assuming the horizontal and vertical orientation of benzene molecules and low-temperature nitrogen adsorption ( $S_{BET}$  ( $N_2$ )). The specific surface values assuming the horizontal orientation of benzene molecules in the adsorption layer were lower than the values determined basing on the nitrogen adsorption method.

The micropore volume ( $V_{mic}$ ) and mesopore volume ( $V_{mes}$ ) indicated the microporous structure of the obtained

sorbents. The materials obtained from phenol-formaldehyde resin and poly(ethylene terephthalate) had the highest micropore volumes. Sorbent prepared from phenol-formaldehyde resin had also the highest volume of mesopores.

The results of the investigations on the properties of sorbents prepared from polymers in the process of carbonization and activation with steam indicated that the best precursors for their production were phenol-formaldehyde resin and poly(ethylene terephthalate). That is why for these polymers the studies on the physical activation with carbon dioxide and chemical activation with KOH, were carried out. The results of the properties of the obtained materials are presented in Table 1 and Figs. 1 and 2.

The type of the activating agent influenced the development of the specific surface of the sorbents. The best structural parameters, expressed by high the development of the specific surface determined by means of nitrogen adsorption, had sorbents prepared by the chemical activation with potassium hydroxide. The specific surfaces evaluated for the sorbents made from both tested polymers had values above 2000 m<sup>2</sup>/g. For the sorbents prepared by the activation with steam and carbon dioxide the values of the specific surface were in the range of 1300 – 1500 m<sup>2</sup>/g. The potassium hydroxide as alkali directly reacts with the carbon atoms of carbonizate thus catalyzing the dehydrogenation and oxidation processes. At the temperature of 800°C there is probably intensive emission of CO from the reaction mixture causing quick gasification of the carbonaceous material, developing the porous structure. The gaseous products of the physical activation with steam or carbon dioxide act as inhibitors between the activating agent and the carbonaceous material, and limit the development of the specific area<sup>19-21</sup>.

The hysteresis loops of benzene vapour adsorption and desorption isotherms (Figs. 1 and 2) obtained for the sorbents made from phenol-formaldehyde resin and poly(ethylene terephthalate) have a similar course, regardless of the activating agent. According to the IUPAC nomenclature they can be classified to the H4 type. They indicate the presence of narrow pores created between the planes, characteristic of the microporous sorbents. Materials of this type of structure can be used i.e. for the storage of gases.

**Table 1.** Properties of carbon sorbents obtained from selected polymers

Polymer	LJ [mg/g]	$S_{BET}$ ( $N_2$ ) [m <sup>2</sup> /g]	$S_{BET}$ ( $C_6H_6$ ) [m <sup>2</sup> /g]		$V_{mic}$ [cm <sup>3</sup> /g]	$V_{mes}$ [cm <sup>3</sup> /g]	Reduction of hydrocarbon content [%]
			Horizontal orientation	Vertical orientation			
Physical activation with steam							
PET	1544	1312	673	451	0.402	0.098	16.30
PF	1649	1463	701	493	0.395	0.380	29.53
CIR	609	425	182	101	0.125	0.093	–
UP	671	450	190	102	0.127	0.098	–
PC	756	679	271	192	0.183	0.092	–
PAN	934	821	401	352	0.297	0.110	–
Physical activation with carbon dioxide							
PET	1599	1415	552	387	0.420	0.085	10.91
PF	1617	1489	623	365	0.411	0.181	20.59
Chemical activation with KOH							
PET	2115	2058	844	527	0.431	0.163	60.05
PF	2158	2089	896	571	0.405	0.393	68.01

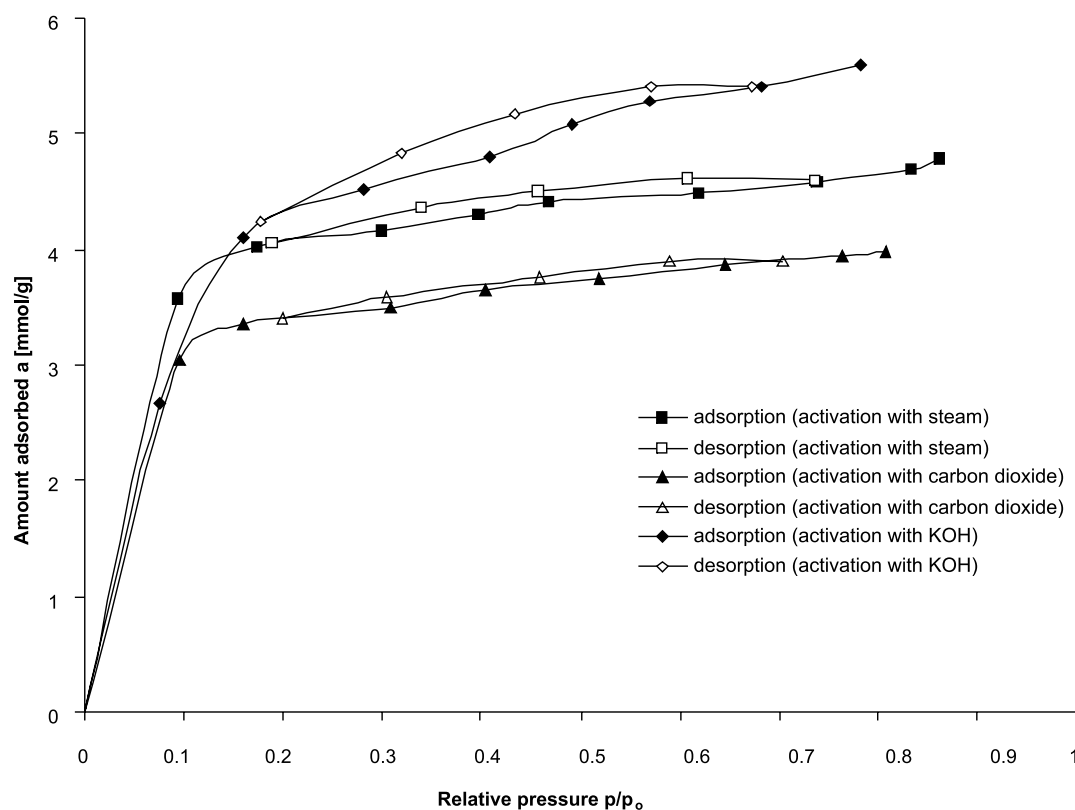


Figure 1. Isotherms of adsorption and desorption of benzene vapour for carbon sorbents prepared from poly(ethylene terephthalate)

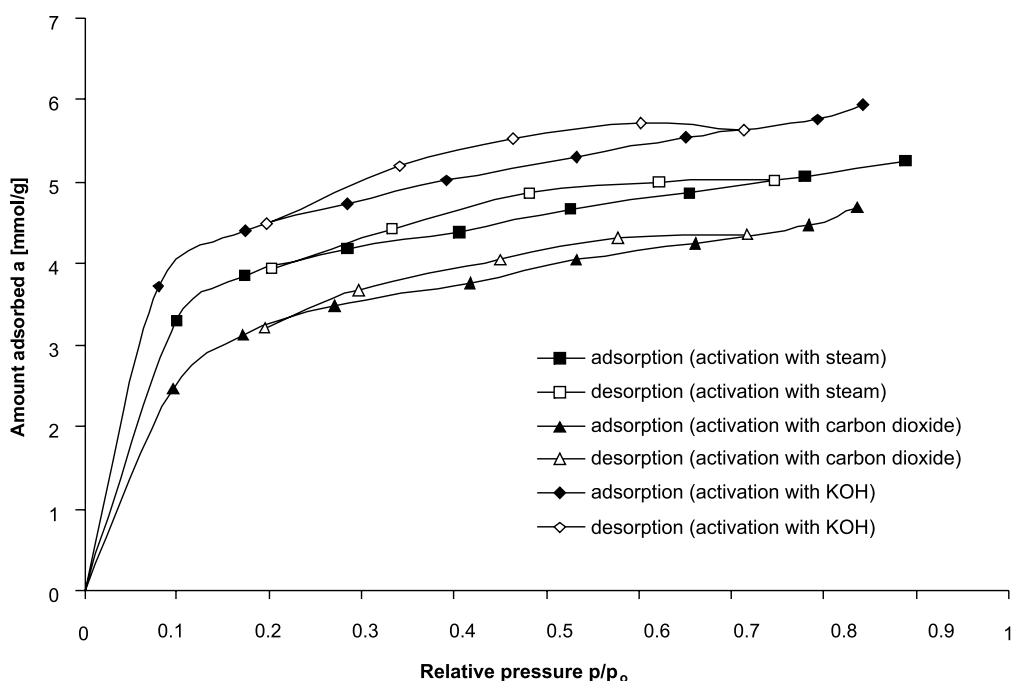


Figure 2. Isotherms of adsorption and desorption of benzene vapour for carbon sorbents prepared from phenol-formaldehyde resin

The values of iodine number and the comparison of the  $S_{\text{BET}}$  values determined on the basis of benzene vapour adsorption assuming the horizontal and vertical orientation of benzene molecules with the  $S_{\text{BET}}$  values calculated basing on the low-temperature nitrogen adsorption indicate that the obtained sorbents have hydrophobic properties. That is why for the carbon sorbents prepared from PET and PF the adsorption measurements of hydrocarbons from petrochemical waste waters were carried out. The results are presented in Table 1.

The obtained results pointed out that the best sorption properties of hydrocarbons were exhibited by the sorbents prepared by chemical activation with KOH. For these samples the higher than 60% reduction of hydrocarbon content in waste waters was achieved. The sorbents prepared by the physical activation with steam or carbon dioxide adsorbed up to 30% wt. of hydrocarbons.

## CONCLUSIONS

This work indicated the possibility to prepare the sorbents of the highly developed specific surface from polymers. The level of surface development depended on the type of polymer and the method of sorbent preparation. From among the tested polymers, phenol-formaldehyde resin and poly(ethylene terephthalate) proved to be the best precursors for the preparation of sorbents. Carbon sorbents of the specific surfaces higher than 2000 m<sup>2</sup>/g were obtained from these polymers by carbonization and chemical activation with potassium hydroxide. Activation of carbonizates with steam or carbon dioxide allowed the development of the specific surface to ca. 1300 – 1500 m<sup>2</sup>/g. All the sorbents prepared from polymers had microporous, hydrophobic structure. Because of the microporous structure the obtained materials can find applications i.e. for the storage of gases. The sorbents produced from phenol-formaldehyde resin and poly(ethylene terephthalate) produced in the process of chemical activation with KOH have the ability to adsorb hydrocarbons and can be used in the purification of industrial waste waters.

The obtained results indicate the possibility to apply some polymers for the modification of coal tar pitch and polymer-pitch binders to prepare carbon sorbents.

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