

Leszek CZEPIRSKI¹, Jakub SZCZUROWSKI¹, Mieczysław BAŁYS¹
Wiesława CIESIŃSKA², Grzegorz MAKOMASKI², Janusz ZIELIŃSKI²

¹ AGH-University of Science and Technology, Faculty of Energy and Fuels
al. Mickiewicza 30, 30-059 Kraków

² Warsaw University of Technology, Institute of Chemistry in Plock
ul. Łukasiewicza 17, 09-400 Plock

Pore structure of activated carbons from waste polymers

Activated carbons are widely used in gas purification and separation, solvent recovery, wastewater treatment, etc. It is recognized that the pore structure is the most important property of activated carbons for their application in adsorption processes. Many investigations have been performed to explore novel raw materials (such as waste polymers) and to optimize the preparation conditions to obtain activated carbons with the desired porous properties.

In this paper the preparation and characterization of activated carbons from poly(ethylene terephthalate), poly(methylene methacrylate), phenol/formaldehyde resin and coal-tar pitch was studied. The influence of the mass ratio pitch/polymer, carbonization conditions, as well as the activation agent used (steam, carbon dioxide, potassium hydroxide) on the characteristics of the samples were considered. The textural characteristics were studied by adsorption of gases and vapors. These allow to establish the influence of the experimental treatment parameters in the porous network of the samples. Moreover, the analysis of the adsorption data has been carried out by BET and Dubinin-Radushkevich (DR) equations as well as by the Monte Carlo (MC), Density Functional Theory (DFT) and Barrer-Joyner-Halenda's methods. The results of these analysis were very consistent and permitted to determine the porous structure of the samples and also to identify the individual adsorption mechanism.

Keywords: porous structure, activated carbon, waste polymers

Introduction

Activated carbons are widely used in gas purification and separation, solvent recovery, gas storage, wastewater treatment, etc. [1, 2]. They are most often produced from natural feedstocks, such as hard coal, lignite, biomass (wood, peat, stones, fruit peels). Many investigations have been performed to explore novel raw materials (such as waste polymers) and to optimize the preparation conditions to obtain activated carbons with the desired porous properties [3-5]. Waste polymers are promising activated carbon precursors for two reasons. First, they contain a high percentage of carbon and second, they are readily available in a relatively pure state from waste recovery. It is recognized that the pore structure is the most

important property of activated carbons for their application in adsorption processes.

In this study the evaluation of the possibilities to use coal-tar pitch modified with waste polymers for the preparation of activated carbons was carried out. The influence of the mass ratio pitch/polymer, carbonization conditions, as well as the activation agent used (steam, carbon dioxide, potassium hydroxide) on the characteristics of the samples were considered. The textural characteristics were studied by adsorption of nitrogen and carbon dioxide. These allow to establish the influence of the experimental treatment parameters in the porous network of the samples. The results of these analysis were very consistent and permit to determine the porous structure of the samples and also to identify the individual adsorption mechanism.

1. Experimental

1.1. Raw materials

The raw materials used in this study were coal-tar pitch (CTP) and selected municipal waste polymers of different chemical structure of macromolecules: PET - poly(ethylene terephthalate), PF - phenol/formaldehyde resin, and PMMA - poly(methylene methacrylate).

1.2. Preparation of activated carbons

Compositions with different pitch/polymer ratios were prepared in the conditions allowing to obtain homogeneous and stable mixtures. Depending on the polymer type, the components were homogenized in the temperatures from 423 to 523 K, during 0.5÷2.5 h. The details on thermal and rheological properties of pitch - polymer mixtures have been reported in [6].

Composites were next carbonized in two stages:

- primary carbonization by heating the sample to 793 K with the heating rate of 5 K/min, in nitrogen atmosphere and annealing it in this temperature for 1 h,
- secondary carbonization by heating the sample to 793 K with the heating rate of 15 K/min, and then to 1123 K with the heating rate of 10 K/min. The sample was annealed at 1123 K for 1 h.

The obtained carbonizates were next activated by selective gasification with steam at 1073 K or with carbon dioxide at 1123 K to 50% burn-off.

For the selected samples also chemical activation with KOH was carried out. In this case the mixture of the pulverized KOH and the product of the primary carbonization (mass ratio of 4:1) was heated in nitrogen atmosphere to the temperature of 1073 K with the heating rate of 10 K/min, and then annealed at this temperature for 1 h. After the completion of this process the product was cooled, rinsed with distilled water, 5% HCl and then hot distilled water till a neutral reaction was reached.

1.3. Characterization of activated carbons

The textural properties of the activated carbons were determined using physical adsorption of gases (N_2 at 77 K and CO_2 at 273 K) using a Quantachrome Autosorb 1C analyzer. All calculations were carried out using the software supplied by Autosorb-1C. The parameters obtained are: BET surface area; total pore volume (pore < 20 nm); micropore volume determined by applying the Dubinin-Radushkevich (DR) equation. BET method was applied only in the range of relative pressures between 0.01 and 0.1, for which linearity could be observed. It was also found that the N_2 adsorption in the relative pressure range $0.00001 \div 0.01$ can be described by a unique D-R linear region. The mesopore volume and the pore size distribution of the mesopore region were determined using BJH desorption branch and the pore size distribution of the micropore region determined from the density functional theory (DFT) assuming a slit pore model, as well as Monte Carlo method [7-10].

2. Results and discussion

Nitrogen adsorption isotherms at liquid nitrogen temperature for activated carbons from composites of 50% of coal-tar pitch and 50% of poly(ethylene terephthalate) activated with different agents are shown in Figure 1. The rise in the adsorption isotherm at a low relative pressure is attributed to adsorption in the micropores, and the larger this rise is, the more the micropores have developed. Moreover, the small increase in the adsorbed amount at larger relative pressures ($p/p_0 > 0.1$) is attributable to adsorption in mesopores.

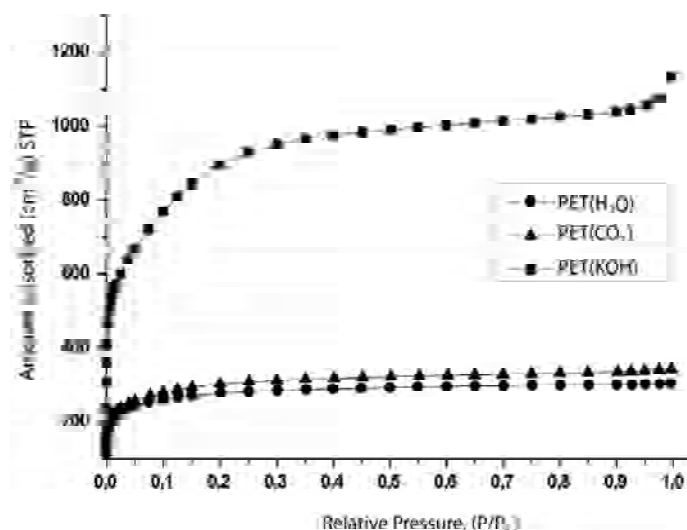


Fig. 1. Nitrogen adsorption (77 K) isotherms of activated carbons from PET

Rys. 1. Izotermy adsorpcji azotu (77 K) dla węgla aktywnych z PET

Table 1 shows the influence of activating agent used on porous texture of above presented samples. Figure 2 represents the pore size distribution in micro-/mesopore region calculated from DFT theory.

Table 1. Porous texture of activated carbons from PET

Tabela 1. Tekstura porowata węgla aktywnych z PET

Activating agent	H ₂ O	CO ₂	KOH
<i>N₂ ad-/desorption isotherm, 77 K</i>			
BET surface area, m ² /g	1042	1122	2815
Total pore volume, cm ³ /g	0.468	0.523	1.447
Volume of micropores, cm ³ /g	0.385	0.403	0.961
Surface area of micropores, m ² /g	1080	1145	2704
Volume of mesopores, cm ³ /g	0.040	0.053	0.397
Surface area of mesopores, m ² /g	32	32	228
Average radius of mesopores, nm	1.52	1.71	2.15
DFT volume of pores: 0.35÷40 nm, cm ³ /g	0.431	0.485	1.410
DFT surface area of pores: 0.35÷40 nm, m ² /g	1001	1054	2329
<i>CO₂ adsorption isotherm, 273 K</i>			
DFT volume of pores: 0.35÷1.5 nm, cm ³ /g	0.230	0.229	0.465
DFT surface area of pores: 0.35÷1.5 nm, m ² /g	709	710	1276
Monte Carlo pore volume, cm ³ /g	0.230	0.229	0.465
Monte Carlo surface area, m ² /g	709	710	1276

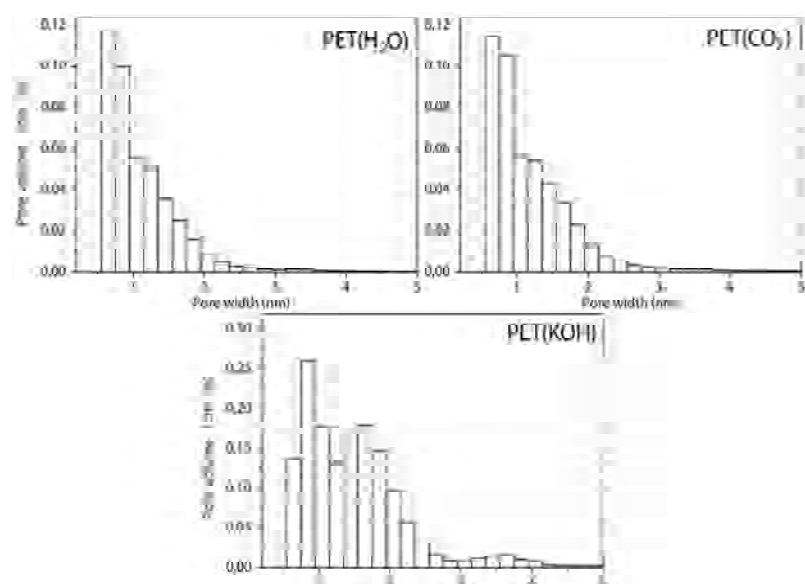


Fig. 2. Effect of activated agent on pore size distribution of activated carbons from PET

Rys. 2. Wpływ czynnika aktywującego na rozkład porów węgla aktywnych z PET

Based on these results, it is believed that the activating agent mainly contributes to the development of pores in the micropore and mesopore range.

Table 2 illustrates the influence of precursor polymer on porous texture of activated carbons for composites of 50% of coal-tar pitch and 50% of polymer activated with KOH.

Table 2. Porous texture of samples activated with KOH

Tabela 2. Tekstura porowata próbek aktywowanych KOH

Precursor polymer	PMMA	PET	PF
<i>N₂ ad-/desorption isotherm, 77 K</i>			
BET surface area, m ² /g	3134	3265	3345
Total pore volume, cm ³ /g	1.539	1.639	1.751
Volume of micropores, cm ³ /g	1.024	1.060	1.062
Surface area of micropores, m ² /g	2875	2983	2989
Volume of mesopores, cm ³ /g	0.162	0.328	0.258
Surface area of mesopores, m ² /g	102	167	214
Average radius of mesopores, nm	1.70	2.16	1.53
DFT volume of pores: 0.35÷40 nm, cm ³ /g	1.430	1.557	1.633
DFT surface area of pores: 0.35÷40 nm, m ² /g	2488	2591	2598
<i>CO₂ adsorption isotherm, 273K</i>			
DFT volume of pores: 0.35÷1.5 nm, cm ³ /g	0.453	0.503	0.506
DFT surface area of pores: 0.35÷1.5 nm, m ² /g	1201	1287	1296
Monte Carlo pore volume, cm ³ /g	0.486	0.518	0.541
Monte Carlo surface area, m ² /g	1212	1265	1304

Table 3 shows the influence of polymer content in composites on porous texture of activated carbons from coal-tar pitch and poly(methylene methacrylate) composites activated with KOH.

The results reported in this work show that composites of coal tar pitch and waste polymers are appropriate raw materials for the synthesis of nanoporous carbons with negligible ash content and a well-developed porosity. In spite of the high carbon content of the precursors, the porous structure developed during the preparation is strongly influenced by the original matrix structure of the polymers, as well as it greatly depends on the carbonization and activation conditions. All the activated carbons prepared were essentially microporous or presented some small mesopores.

A good combination of activating agent, ratio of activating agent/precursor and carbonisation/activation temperature allows the production of activated carbons with specific chemical and structural characteristics, which are properties very important for identifying an application.

Table 3. Porous texture of activated carbons from PMMA

Tabela 3. Tekstura porowata węgla aktywnych z PMMA

Polymer content, wt, %	10	50
<i>N₂ ad-/desorption isotherm, 77 K</i>		
BET surface area, m ² /g	2917	3134
Total pore volume, cm ³ /g	1.439	1.535
Volume of micropores, cm ³ /g	0.949	1.017
Surface area of micropores, m ² /g	2670	2862
Volume of mesopores, cm ³ /g	0.127	0.162
Surface area of mesopores, m ² /g	80	102
Average radius of mesopores, nm	1.70	1.70
DFT volume of pores: 0.35÷40 nm, cm ³ /g	1.334	1.430
DFT surface area of pores: 0.35÷40 nm, m ² /g	2312	2488
<i>CO₂ adsorption isotherm, 273 K</i>		
DFT volume of pores: 0.35÷1.5 nm, cm ³ /g	0.493	0.453
DFT surface area of pores: 0.35÷1.5 nm, m ² /g	1287	1201
Monte Carlo pore volume, cm ³ /g	0.526	0.486
Monte Carlo surface area, m ² /g	1292	1212

Because contribution of micropores and mesopores in the total porosity is considerable, the obtained porous carbons are potentially capable to adsorb molecules of various sizes, therefore, this feature can be considered as an important advantage in specific applications. The adsorption properties of obtained carbons make them superior in numerous emergent applications such as methane or hydrogen storage, storage of electrical energy in supercapacitors, CO₂ capture, adsorption of specific contaminants in liquid phase, etc.

Conclusions

The results of this work provided us with a good method for preparation of activated carbons with controlled pore structure and gave us a further understanding of the formation mechanism of carbon materials. These results may also allow to devise processes for a proper utilization of polymeric wastes, which is a very important issue both for economy and ecology. For its wide commercial application, its conversion to activated carbon offers a way of recycling.

Acknowledgment

Acknowledgments are made to the National Science Centre (NCN) - project No. N N209763640.

References

- [1] Marsh H., Rodriguez-Reinoso F., Activated Carbon, Elsevier Science & Technology Books 2006.
- [2] Activated Carbon Surfaces in Environmental Remediation, ed. T.J. Bandosz, Elsevier Ltd. 2006.
- [3] Fei Lian, Baoshan Xing, Lingyan Zhu, Comparative study on composition, structure, and adsorption behavior of activated carbons derived from different synthetic waste polymers, Journal of Colloid and Interface Science 2011, 360, 725-730.
- [4] Ciesińska W., Makomaski G., Zieliński J., Brzozowska T., Preparation of sorbents from selected polymers, Polish Journal of Chemical Technology 2011, 13(1), 51-54.
- [5] Bratek W., Świątkowski A., Pakuła M., Biniak S., Bystrzejewski M., Szmigielski R., Characteristics of activated carbon prepared from waste PET by carbon dioxide activation, Journal of Analytical and Applied Pyrolysis 2013, 100, 192-198.
- [6] Makomaski G., Zieliński J., Ciesińska W., Thermal properties of pitch-polymer compositions and derived activated carbons, Journal of Thermal Analysis and Calorimetry 2012, 109, 767-772.
- [7] NIST 2006, Porosity and Specific Surface Area Measurements for Solid Materials.
- [8] ISO 9277: 2010, Determination of the specific surface area of solids by gas adsorption - BET method.
- [9] ISO 15901-2: 2006, Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption - Part 2: Analysis of mesopores and macropores by gas adsorption.
- [10] ISO 15901-3: 2007, Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption - Part 3: Analysis of micropores by gas adsorption.

Struktura porowata węgla aktywnych z odpadowych tworzyw sztucznych

Zwiększająca się ilość odpadowych tworzyw sztucznych stwarza wiele istotnych problemów technicznych, ekologicznych i ekonomicznych. Konieczność rozwiązywania powyższych problemów narzucają także obowiązujące przepisy prawne. Interesującym z poznawczego i utylitarne punktu widzenia kierunkiem zagospodarowania niektórych odpadów polimerowych jest wytwarzanie z nich adsorbentów węglowych. Wysokie ceny i zmniejszająca się dostępność tradycyjnych źródeł surowcowych do produkcji adsorbentów węglowych powodują zainteresowanie możliwościami produkcji adsorbentów węglowych z surowców tańszych lub odpadowych (drewno, żywice jonowymiennne, zużyte opony samochodowe, tworzywa sztuczne). Produkcja adsorbentów węglowych w powiązaniu z udoskonalaniem metod karbonizacji, aktywacji i modyfikacji może stanowić alternatywną drogę utylizacji tego typu odpadów.

W pracy podjęto próbę wykorzystania odpadowego poli(tereftalanu etylenu), poli(metakrylanu metylu) i żywicy fenolowo-formaldehydowej oraz paku węglowego do otrzymywania adsorbentów węglowych.

Serię kompozycji pakowo-polimerowych o różnym stosunku masowym pak/polimer poddawano karbonizacji w różnych warunkach (szybkość ogrzewania, końcowa temperatura karbonizacji, czas utrzymywania próbki w końcowej temperaturze karbonizacji), a następnie aktywacji przy użyciu różnych czynników aktywujących (para wodna, ditlenek węgla, alkalia). Teksturę porowatą uzyskanych próbek scharakteryzowano na podstawie pomiarów izoterm adsorpcji i desorpcji par azotu (77 K) oraz izoterm adsorpcji ditlenku węgla (273 K), wyznaczając wielkość powierzchni właściwej BET, parametry struktury mikroporowatej (objętość i rozkład objętości mikroporów metodą Monte Carlo i Density Functional Theory), rozkład objętości i powierzchni mezoporów wg Barrera-Joynera-Halendy. Wykazano, że rodzaj surowca, warunki karbonizacji i aktywacji oraz rodzaj czynnika aktywującego umożliwiają otrzymanie adsorbentu węglowego o pożądanym z punktu widzenia potencjalnych zastosowań rozkładzie porów.

Słowa kluczowe: struktura porowata, węgiel aktywny, odpady z tworzyw sztucznych