

Study on the preparation of activated carbons from pitch-polymer compositions

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Introduction

Activated carbons are most often produced from natural feedstocks, such as hard coal, lignite, wood, stones and peels of the fruits [1–3]. Based on the literature data, a conclusion can be drawn that also synthetic polymers can be used for the preparation of activated carbons [4]. Marzec et al. [5] obtained from poly(ethylene terephthalate) mixed with polyacrylonitrile an activated carbons of BET surface area up to 521 m²/g. László et al. [6] obtained from poly(ethylene terephthalate) an activated carbon of BET surface area 1170 m²/g and total volume of pores 0.63 cm³/g, useful for adsorption of chlorophenols from waste waters. Yang et al. [7, 8], used novolak resin mixed with hexamethylenetetramine and poly(vinylbutyral) or poly(oxyethylene)diol for the preparation of activated carbons of BET surface area up to 1610 m²/g. In other paper, the authors [9] used ion-exchange resins for the preparation of activated carbons up to 500 m²/g by carbonization and activation with carbon dioxide. Coal-tar pitch, produced by continuous distillation of coal tar and modified with polymers, can also be a precursor of activated carbons. However, there is only a few published experimental works relating to the production of activated carbons from pitch-polymer compositions, e.g. compositions containing poly(ethylene terephthalate) [10], phenolic resins [11] and polyvinylpyridine [12].

At the Institute of Chemistry of Warsaw University of Technology in Plock, studies on the modification of coal-tar pitch with polymers have been carried out for many years. They are aimed at the improvement of utility properties of coal-originated bitumen and utilization of waste polymers [13–15]. Modification of coal-tar pitch with polymers influence also reduced the content of carcinogenic compounds in bituminous substances, such as benzo(a)pyrene [16]. Investigations were also undertaken on the use of pitch-polymer compositions for the production of porous materials [17–19].

In this work, the results of studies on the use of pitch-polymer compositions containing selected polymers for the production of activated carbons are presented.

Materials and methods

The raw materials used in this study were coal-tar pitch (CTP) and selected polymers: poly(ethylene terephthalate) (PET), phenol-formaldehyde resin (PF), unsaturated polyester resin (UP), polyacrylonitrile (PAN). Pitch-polymer compositions containing from 10 to 50 wt% polymer were prepared in the conditions allowing to obtain homogeneous and stable mixtures:

- pitch-PET compositions obtained in the temperature 260°C, during 0.5 h
- pitch-PF compositions obtained in the temperature 150°C, during 2.5 h
- pitch-UP compositions obtained in the temperature 105°C, during 0.5 h
- pitch-PAN compositions obtained in the temperature 360°C, during 5 h, in nitrogen atmosphere.

For coal-tar pitch and pitch-polymer compositions the following measurements were carried out:

- softening point by „Ring and Ball” method ($T_{(PK)}$) according to the PN-EN 1427:2009 standard

- coking value (LK) according to the PN-C-97093:1993 standard
- content of components insoluble in toluene (TI), according to the method elaborated at the Institute of Chemistry, Warsaw University of Technology in Plock [16]. Measurement was consisted on the extraction of the sample (in amount 1g) in toluene at the temperature 200°C (60 min) and next washing the sample by liquefied solvent (90 min)
- content of components insoluble in quinoline (QI) according to the PN-C 97058:1999 standard.

Coal-tar pitch and pitch-polymer compositions were carbonized. 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 heating rate of 5°C/min, in nitrogen atmosphere and annealing in this temperature for 1 h
- in the second stage of carbonization, the obtained sample in the first stage of carbonization, heating rate of 15°C/min to the temperature of 520°C and then to 850°C with the heating rate of 5°C/min. The sample was annealed at 850°C for 1 h, in nitrogen atmosphere.

Prepared carbonizates were activated with steam at 800°C, to 50% burn-off, having an aim in the development of pores. Selected samples were activated with carbon dioxide at 850°C, to 50% burn-off and chemically activated with potassium hydroxide at 800°C, during 1 h, using 1:4 (sample/KOH) reagent ratio.

For the obtained activated carbons the determination of BET surface area ($S_{BET}(N_2)$) on the basis of low-temperature adsorption of nitrogen, BET surface area ($S_{BET}(C_6H_6)$) with the assumption of horizontal and vertical orientation of benzene molecules, micropore (V_{mic}) and mesopore (V_{mes}) volume from benzene adsorption/desorption isotherms (gravimetric McBain-Bakr method) were carried out.

Results and discussion

Selected results of the studies on physicochemical properties of coal-tar pitch and pitch-polymer compositions are presented in Table I.

Table I

Selected properties of pitch-polymer compositions

Compositions, wt%	$T_{(PK)}$, °C	TI, wt%	QI, wt%	LK, wt%
CTP	107.0	34.21	7.14	53.03
90 CTP + 10 PET	127.0	45.80	13.31	53.62
75 CTP + 25 PET	166.0	43.10	29.43	50.10
50 CTP + 50 PET	236.0	68.50	62.79	38.00
90 CTP + 10 PF	128.0	55.18	10.14	54.16
75 CTP + 25 PF	141.0	63.04	4.48	53.67
50 CTP + 50 PF	*	88.54	4.21	54.07
90 CTP + 10 UP	80.0	51.13	5.43	49.60
75 CTP + 25 UP	76.0	66.35	4.34	49.35
50 CTP + 50 UP	*	67.21	5.52	33.98
90 CTP + 10 PAN	118.6	39.36	**	51.87
75 CTP + 25 PAN	130.5	46.57	**	63.45
50 CTP + 50 PAN	*	61.43	**	69.07

* infusible composition; ** impossible determination

Modification of coal-tar pitch with polymers significantly influenced change of its physicochemical properties. Addition of poly(ethylene terephthalate), phenol-formaldehyde resin or polyacrylonitrile to the coal-tar pitch caused increase of softening point of the pitch. For the composition containing 50 wt% of PET, softening point, compared to unmodified pitch, increased by 129°C. Unsaturated polyester resin caused plastification of coal-tar pitch and decrease of softening point to 76°C for the composition containing 25 wt% of UP. For composition containing 50 wt% of UP, the softening point was impossible to determine – the process of cross-linking macromolecules of resin took place during the preparation of composition.

All pitch-polymer compositions had higher content of components insoluble in toluene compared to unmodified pitch. With the increase of polymer concentration in compositions, the content of TI components increased. Particularly significant changes occurred for the composition containing 50 wt% of PF, for which the content of TI components was higher by 54.33 wt% than in coal-tar pitch. In most cases the increase of TI amount caused the increase of softening point. The exception was made by compositions containing unsaturated polyester resin, where with the increase of TI components amount softening point decreased.

The content of quinoline insoluble component depended on the amount and type of polymer in the composition. Introduction of PET to the coal-tar pitch caused significant increase of the amount of QI components. For the composition containing 50 wt% of PET the amount of QI components increased by 55.65 wt%, compared to unmodified pitch. Addition of phenol-formaldehyde resin or unsaturated polyester resin to the coal-tar pitch caused the decrease of the amount of quinoline insoluble component. The exception was composition containing 10 wt% of PF which had higher amount of QI components (by 3 wt%) compared to coal-tar pitch. For PAN containing compositions the amount of QI components was impossible to determine – during the analysis the philters were being blocked.

With the increase of PET or UP content the values of coking value decreased to 33.98 wt%. Compositions containing phenol-formaldehyde resin, regardless of the amount of polymeric modifier had similar values of coking value (53.67–54.16 wt%) to the coal-tar pitch. On the other hand, with the increase of PAN amount in compositions, coking value increased. The highest value of coking value among studied pitch-polymer compositions, had the composition containing 50 wt% of PAN, for which coking value compared to unmodified pitch was higher by 16.04 wt%.

Table 2 presents the results of evaluation of porous structure of activated carbons obtained from coal-tar pitch and pitch-polymer compositions in the process of activation with steam.

Table 2
Parameters of porous structure of obtained activated carbons in the process of activation with steam

Compositions, wt%	$S_{\text{BET}}(\text{N}_2)$, m^2/g	$S_{\text{BET}}(\text{C}_6\text{H}_6)$, m^2/g		V_{mic} , cm^3/g	V_{mes} , cm^3/g
		horizontal orientation	vertical orientation		
CTP	323	153	96	0.094	0.057
90 CTP + 10 PET	285	126	79	0.077	0.056
75 CTP + 25 PET	320	147	92	0.089	0.078
50 CTP + 50 PET	960	541	338	0.305	0.085
90 CTP + 10 PF	413	223	140	0.135	0.112
75 CTP + 25 PF	391	217	136	0.129	0.109
50 CTP + 50 PF	1014	581	363	0.230	0.371
90 CTP + 10 UP	291	133	83	0.083	0.066
75 CTP + 25 UP	257	127	78	0.088	0.072
50 CTP + 50 UP	305	138	88	0.090	0.075
90 CTP + 10 PAN	331	172	110	0.153	0.081
75 CTP + 25 PAN	480	321	200	0.189	0.089
50 CTP + 50 PAN	500	332	202	0.201	0.090

The parameters of porous structure of obtained activated carbons depended on the type and amount of polymeric modifier added to the coal-tar pitch. In most cases activated carbons obtained from pitch-polymer compositions had better developed BET surface area, measured on the basis of both low-temperature nitrogen adsorption ($S_{\text{BET}}(\text{N}_2)$) and benzene vapour adsorption ($S_{\text{BET}}(\text{C}_6\text{H}_6)$), compared to activated carbon obtained from coal-tar pitch. The exception were activated carbons obtained from compositions containing ≤ 25 wt% of PET and ≤ 50 wt% of UP. Significant increase of BET surface area, compared to the adsorbent obtained from coal-tar pitch was obtained for activated carbons obtained from compositions containing 50 wt% of PET or PF and ≥ 25 wt% of PAN (Tab. 2).

From the comparison of S_{BET} values obtained from low-temperature nitrogen adsorption and benzene vapour adsorption with the assumption of horizontal and vertical orientation of benzene molecules a conclusion can be drawn that obtained activated carbons have hydrophobic properties. BET surfaces area with the assumption of horizontal orientation of benzene molecules in adsorption layer were smaller than S_{BET} values obtained on the basis of low-temperature nitrogen adsorption. On the other hand, different orientation of adsorbed benzene molecules was a result of determination of hydrophobic-hydrophilic properties of carbon adsorbents by various functional groups existing on the surface of carbon materials.

Analyzing the changes of micropore (V_{mic}) and mesopore volume (V_{mes}) it was observed that the increase of the amount of polymer added to the coal-tar pitch, regardless of its type caused the increase of both micropore and mesopore volume. The highest values of V_{mic} and V_{mes} , compared to the adsorbent obtained from coal-tar pitch had activated carbons obtained from compositions containing 50 wt% of PET and PF or PAN, irrespective of the polymer type. It was demonstrated that micropore and mesopore volume increased with the increase of BET surface area measured on the basis of both low-temperature nitrogen adsorption and benzene vapour adsorption.

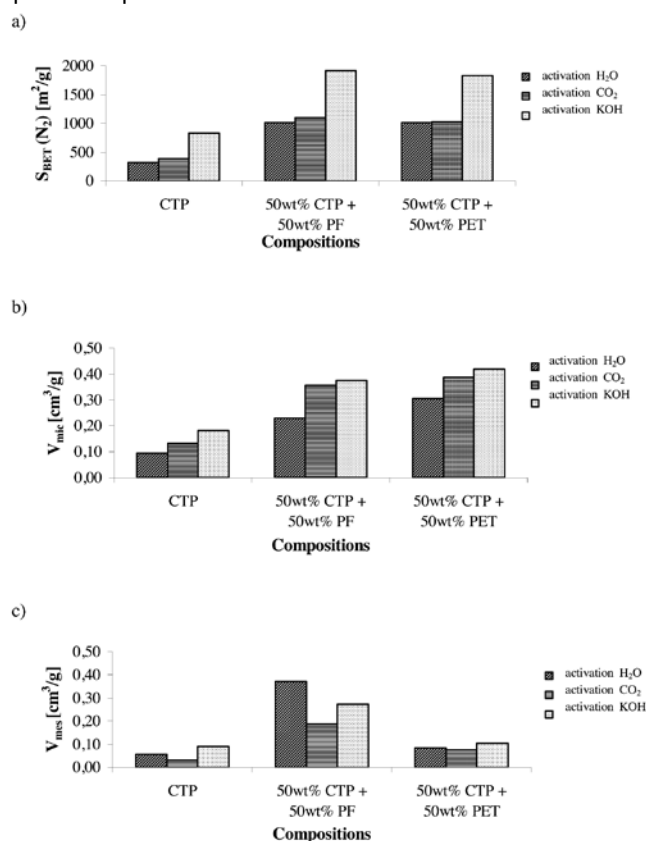


Fig. 1. Parameters of porous structure of obtained activated carbons in the process of activation with steam, carbon dioxide, potassium hydroxide; a) BET surface area ($S_{\text{BET}}(\text{N}_2)$), b) micropore volume, c) mesopore volume

Figure 1 presents the influence of the type of activating agent on porous structure of activated carbons obtained from compositions containing 50 wt% of PET or PF, which during activation with steam produced activated carbons of best developed BET surface area (Tab. 2).

Evaluating the efficiency of applied activating agents it was demonstrated that the highest development of BET surface area, as well as mesopore and micropore volume had activated carbons obtained during activation with potassium hydroxide. Activation with steam or carbon dioxide allowed to obtain adsorbents of similar development of BET surface area, varying in porous structure. Carbon adsorbents obtained during physical activation with steam had lowest micropore volume, while adsorbents obtained in the process of activation with carbon dioxide had lowest mesopore volume.

Conclusions

The results obtained in this work indicate that pitch-polymer compositions can be used for the production of activated carbons. It creates a possibility to find a new way to utilize polymers waste.

Modification of coal-tar pitch with polymers significantly influences the physicochemical properties and group composition of the bitumen. The best modifiers of the pitch, having in mind the production of activated carbons, because of their good miscibility with bitumen, high softening points, high amount of toluene insoluble components are poly(ethylene terephthalate) and phenol-formaldehyde resin, used in the amount of 50 wt%.

Activation with steam or carbon dioxide allows obtaining of activated carbons having BET surface area of up to ca. 1050 m²/g, while potassium hydroxide activated carbons have BET surface area developed to ca. 2000 m²/g. Activated carbons obtained from compositions containing 50 wt% of PET or PF, in the process of activation with potassium hydroxide because of well developed BET surface area and hydrophobic properties can be used for removal of aromatic hydrocarbons from petrochemical waste waters.

At the present, in cooperation with AGH-University of Science and Technology have been realizing of the scientific work financed from National Science Centre (N N209763640) about preparation of carbon adsorbents from waste polymers. Demonstration draft of the technological installation with economic balance of use the coal-tar pitch and waste polymers for preparation of activated carbons will showed in the next publications.

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