



Porous structure and thermal properties of carbon adsorbents from pitch–polymer compositions

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Abstract

The study results of porous structure and thermal properties of carbon adsorbents (AC) obtained from pitch–polymer compositions were presented. The compositions were carbonized and activated with steam, potassium hydroxide, and magnesium and potassium carbonates. For the obtained AC, the thermal analysis and the determination of adsorption value of iodine and porous structure by adsorption/desorption of nitrogen at 77 K were carried out. The possibility of obtained activated carbons from pitch–polymer compositions was demonstrated. The use of untypical feedstock, as an effect of combination of bituminous substance with polymeric waste and improvement of the methods of production, creates the potential possibility to produce carbon adsorbents of interesting properties and porous structure.

Keywords Pitch–polymer compositions · Carbon adsorbents · DSC · Porous structure

Introduction

Carbon adsorbents, because of good mechanical durability, well-developed specific surface area and good sorption properties, from both gaseous and liquid phases, have found a widespread use in many branches of industry [1].

Activated carbons have been obtained from hard coal, lignite, wood, peat, fruit stones, coffee industry waste materials, waste tires, peel and shells [2–10]. Literature data show that some natural polymers, such as cellulose, as well as synthetic polymers and their waste, can be used for the production of activated carbons [11]. Laszlo and Szucs [12] obtained from poly(ethylene terephthalate) an carbon adsorbents of specific surface area $1170 \text{ m}^2 \text{ g}^{-1}$ and total volume of pores $0.63 \text{ cm}^3 \text{ g}^{-1}$, useful for adsorption of chlorophenols from waste waters. Similarly, from waste poly(ethylene terephthalate), through activation with ZnCl_2 or H_2SO_3 , Kartel et al. [13, 14] have obtained carbon adsorbents of specific surface area up to $1030 \text{ m}^2 \text{ g}^{-1}$. In yet other papers [15, 16], it has been reported that novolac

resin mixed with hexamethylenetetramine and poly(vinylbutyral) or poly(oxyethylene)diol can be applied in the preparation of activated carbons having specific surface area up to $1610 \text{ m}^2 \text{ g}^{-1}$.

The use of polymer waste for the preparation of carbon adsorbents by thermal–chemical processes is interesting from a cognitive and utilitarian viewpoint. However, the obtainment of good activated carbons depends on high coking value of the feedstock, its adequate physical state and repeatability of properties. Most polymer wastes do not meet these requirements. That is why it is purposeful to mix polymer wastes with bituminous substances (e.g., coal-tar pitch). Coal-tar pitch causes the increase in the amount of residue after carbonization or activation process, while polymer causes the increase in the surface area of carbon adsorbents. Obtaining carbon adsorbent from bitumen–polymer materials with the use of polymer waste can be an alternative direction to their recycling and the possibility to obtain good quality carbon adsorbents constituting a valuable complement to the current market offer.

At the Institute of Chemistry, Warsaw University of Technology in Plock, have been being carried out studies on bitumen–polymeric materials for several years. They are aimed at the improvement of utility properties of coal-originated bitumen and utilization of waste polymers [17–20]. It was demonstrated that pitch–polymer

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compositions can be used for the preparation of carbon adsorbents [21–23] and mineral–carbon adsorbents [24, 25].

This paper presents the results of studies of porous structure and thermal properties of carbon adsorbents obtained from pitch–polymer compositions in the activation with steam, potassium hydroxide, magnesium and potassium carbonates. A novelty in the conducted research was the preparation of activated carbons from pitch–polymer compositions in the process of activation with magnesium carbonate and potassium carbonate.

Experimental procedures

The raw materials used in this study were pitch–polymer compositions containing (1:1 by mass) coal-tar pitch (CTP) and wastes poly(ethylene terephthalate) (PET), phenol-formaldehyde resin (PF) or poly(methylene methacrylate) (PMMA). Pitch–polymer compositions were prepared in the conditions allowing to obtain homogeneous and stable mixtures: pitch–PET composition (CTP–PET) obtained at 260 °C, during 0.5 h, pitch–PF composition (CTP–PF) obtained at 150 °C, during 2.5 h, and pitch–PMMA composition (CTP–PMMA) obtained at 270 °C, during 1 h [26].

Pitch–polymer compositions were carbonized and activated with steam, potassium hydroxide and magnesium carbonate or potassium carbonate (Fig. 1).

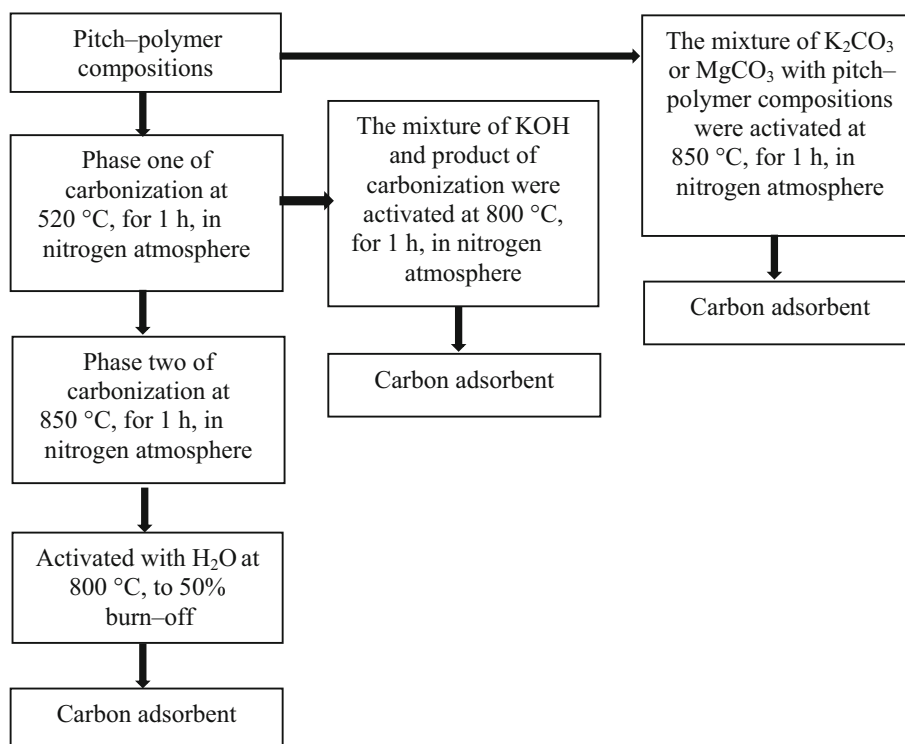
Carbonization was carried out in two stages:

- phase one of initial carbonization, performed by heating the sample to the temperature of 520 °C at the heating rate of 5 K min⁻¹, in nitrogen atmosphere and annealing it in this temperature for 1 h,
- phase two, executed in a horizontal furnace by heating the sample to the temperature of 520 °C with the heating rate of 15 K min⁻¹, and then to 850 °C with the heating rate of 10 K min⁻¹. The sample was annealed at 850 °C for 1 h.

The products of carbonization were activated with steam at 800 °C, to 50% burn-off.

Additionally, for prepared pitch–polymer compositions also the process of carbonization and chemical activation with KOH was carried out. In this case, samples were initially carbonized at 520 °C and subsequently chemically activated. The mixture of pulverized KOH and the product of initial carbonization (mass ratio of 3:1) was heated to the temperature of 800 °C with the heating rate of 10 K min⁻¹ and then annealed in this temperature for 1 h. The process was carried out in nitrogen atmosphere. Furthermore, pitch–polymer compositions were activated with carbonates (K₂CO₃ or MgCO₃). The mixtures consisting of pitch–polymer compositions and K₂CO₃ or MgCO₃ (mass ratio 3:7) were heated in air to 270 °C, cooled and again heated to 270 °C. Next, the mixtures were activated in nitrogen flow at 850 °C for 1 h. The heating rate was 10 K min⁻¹. Product of activation with KOH, K₂CO₃ or MgCO₃ was

Fig. 1 Diagram of preparation of carbon adsorbents from pitch–polymer compositions



rinsed with distilled water, 10% HCl till a neutral reaction. Obtained carbon adsorbents were dried at 105 °C for 12 h in air.

For obtained carbon adsorbents, the following parameters were determined: thermal properties by the thermal analysis. Scanning differential calorimetry curves were recorded by means of scanning differential calorimeter Netzsch Maia F3 on heating up to 250 °C with a rate of 10 K min⁻¹ in nitrogen atmosphere (samples mass about 6 mg). Thermogravimetric curves (TG and DTG) were recorded by means of Derivatograph-C (produced by MON Budapest) on heating up to 750 °C with a rate of 10 K min⁻¹ in nitrogen atmosphere (sample mass 19.5 mg). The sorption properties of obtained carbon adsorbents were characterized by adsorption value of iodine (*IN*) according to PN-C-97555.03:1982. Pore parameters in the obtained carbon adsorbents were evaluated from the adsorption/desorption isotherms of nitrogen gas at 77 K. Specific surface are (*S*_{BET}) was determined by the Brunauer-Emmett-Teller method. The micropore volume (*V*_{mic}) was determined by Dubinin-Radushkevich method, and mesopore volume (*V*_{mes}) was determined by Barrett-Joyner-Halenda method.

Results and discussion

Table 1 contains sorption properties and parameters of porous structure of obtained carbon adsorbents.

The type of composition and activation agent influenced the sorption capacity of carbon adsorbents (Table 1). While assessing the efficiency of applied activating agents on sorption properties of carbon adsorbents obtained from

pitch-polymer compositions, it was found that activated carbons obtained in the process of activation with KOH had significantly higher values of adsorption of iodine (above 2100 mg g⁻¹) than carbon adsorbents prepared in the process of activation with steam, potassium carbonate or magnesium carbonate. In addition, the obtained carbon adsorbents in the potassium hydroxide activation process have similar *IN* values.

Among carbon adsorbents obtained by steam activation, the highest *IN* value (1050 mg g⁻¹) was characterized by activated carbon AC CTP-PF(H₂O), while the smallest *IN* value (700 mg g⁻¹) was characterized by activated carbon AC CTP-PMMA(H₂O). In the case of carbon adsorbents obtained by the potassium carbonate activation process, the highest *IN* value (990 mg g⁻¹) was observed for activated carbon AC CTP-PF(K₂CO₃), while the smallest *IN* value (780 mg g⁻¹) was observed for carbon adsorbent AC CTP-PET(K₂CO₃). Among the carbon adsorbents obtained by the magnesium carbonate activation process, the highest *IN* value (750 mg g⁻¹) was observed for activated carbon AC CTP-PET(MgCO₃), while the smallest *IN* value (430 mg g⁻¹) was observed for carbon adsorbent AC CTP-PMMA(MgCO₃).

Molecule of iodine is quite small; it is a good indicator for the adsorption capacity an activated carbon. It is a measure of the micropore content of the activated carbon. The results of adsorption value of iodine (Table 1) showed that carbon adsorbents obtained in the process of activation with KOH had significantly the higher micropore content than carbon adsorbents prepared in the process of activation with steam, potassium carbonate or magnesium carbonate. In addition, a correlation was observed between the adsorption value of iodine and porous structure of carbon

Table 1 Sorption properties and parameters of porous structure of obtained carbon adsorbents from pitch-polymer compositions

Carbon adsorbents	<i>IN</i> /mg g ⁻¹	<i>S</i> _{BET} /m ² g ⁻¹	<i>V</i> _{mic} /cm ³ g ⁻¹	<i>V</i> _{mes} /cm ³ g ⁻¹
Activation with steam				
AC CTP-PET(H ₂ O)	1020	1042	0.381	0.040
AC CTP-PF(H ₂ O)	1050	1120	0.393	0.056
AC CTP-PMMA(H ₂ O)	700	401	0.152	0.036
Activation with potassium hydroxide				
AC CTP-PET(KOH)	2110	3265	1.060	0.328
AC CTP-PF(KOH)	2160	3345	1.062	0.258
AC CTP-PMMA(KOH)	2190	3134	1.017	0.162
Activation with potassium carbonate				
AC CTP-PET(K ₂ CO ₃)	780	1049	0.401	0.486
AC CTP-PF(K ₂ CO ₃)	990	715	0.276	0.066
AC CTP-PMMA(K ₂ CO ₃)	960	1142	0.438	0.074
Activation with magnesium carbonate				
AC CTP-PET(MgCO ₃)	750	577	0.208	0.496
AC CTP-PF(MgCO ₃)	430	316	0.083	0.117
AC CTP-PMMA(MgCO ₃)	610	289	0.104	0.142

adsorbents. Activated carbons having the highest of IN values were characterized by the highest S_{BET} and total pore volume.

The type of composition and the type of activating agent had been effect on the porous texture of the carbon adsorbents from pitch-polymer compositions. It has been shown that in the case of carbon adsorbents obtained by steam activation, the highest S_{BET} , V_{mic} and V_{mes} were characterized by activated carbon AC CTP-PF(H_2O), while the smallest S_{BET} , V_{mic} and V_{mes} were characterized by carbon adsorbent AC CTP-PMMA(H_2O).

Among the carbon adsorbents obtained by the KOH activation process, the highest S_{BET} and V_{mic} were observed for the activated carbon AC CTP-PF(KOH) obtained from composition containing 50 mass% of waste PF. The highest volume of mesopores was observed for the adsorbent AC CTP-PET(KOH). The smallest S_{BET} , V_{mic} and V_{mes} were observed for carbon adsorbents AC CTP-PMMA(KOH).

In the case of carbon adsorbents obtained by the K_2CO_3 activation process, the highest S_{BET} and V_{mic} were observed for activated carbon AC CTP-PMMA(K_2CO_3), while the highest volume of mesopores was observed for activated carbon AC CTP-PET(K_2CO_3). The smallest S_{BET} , V_{mic} and V_{mes} were observed for carbon adsorbents AC CTP-PF(K_2CO_3).

Among the carbon adsorbents obtained by the MgCO_3 activation process, the highest IN S_{BET} , V_{mic} and V_{mes} were observed for the carbon adsorbents AC CTP-PET(MgCO_3). The smallest S_{BET} was observed for the carbon adsorbent AC CTP-PMMA(MgCO_3), while the smallest volume of micropores and mesopores was observed for carbon adsorbent AC CTP-PF(MgCO_3).

It was found that the carbon adsorbent obtained by the activation with steam, KOH and K_2CO_3 (only for the activated carbons AC CTP-PF(K_2CO_3) and AC CTP-PMMA(K_2CO_3)) had the microporous structure. Activate carbons obtained by the activation with K_2CO_3 (for the activated carbon AC CTP-PET(K_2CO_3)) and MgCO_3 had the mesoporous structure. This is due to processes occurring between polymer macromolecules and group components of coal-tar pitch during carbonization and/or activation. Volatile products evolved in the process of high-temperature heat treatment of the compositions and secondary reactions, e.g., with activating agents, favorably affect the development of the porous structure of carbon adsorbents. In addition, selected polymer wastes contain oxygen in the structure of the chain that can promote dehydrogenation during carbonization and/or activation of the compositions. Probably, it positively affects the porous structure of carbon adsorbents.

Figure 2 presents the isotherms of adsorption and desorption of nitrogen gas at 77 K for studied carbon

adsorbents. Adsorption/desorption isotherms of studied carbon adsorbents obtained by the activation with steam, KOH and K_2CO_3 (only for the activated carbons AC CTP-PF(K_2CO_3) and AC CTP-PMMA(K_2CO_3)) belong to the I type, according to the IUPAC classification, i.e., they are typical for microporous materials. Activated carbons obtained by the activation with K_2CO_3 (for the activated carbon AC CTP-PET(K_2CO_3)) and MgCO_3 belong to the IV type, typical for mesoporous materials. For the carbon adsorbents obtained by the activation with KOH, adsorption capacity was higher than for the activated carbons obtained by the activation with steam, K_2CO_3 and MgCO_3 .

In Fig. 3, DSC curves of carbon adsorbents obtained from pitch-polymer compositions by the activation with steam, potassium hydroxide, magnesium carbonate or potassium carbonate are shown. Analyzing the courses of DSC curves of carbon adsorbents, only endothermic transition occurring in the range of temperatures from 32.7 to 61.7 °C (enthalpy values from -2.856 to -32.840 J g $^{-1}$) was observed. This transition is probably related to desorption of physically adsorbed water, probably occurred during storage. Furthermore, the hygroscopicity in carbon adsorbents can be related to the presence of oxygenated surface groups responsible for hydrogen bonds between the water and the oxygen molecules.

Based on DSC curves course for obtained activated carbons, the effect of the porous structure of carbon adsorbents on the values of desorption of water temperature was found. The highest values of desorption of water temperature were observed for carbon adsorbents AC CTP-PET(K_2CO_3) and AC CTP-PET(MgCO_3). These carbon adsorbents had the mesoporous structure. The smallest desorption of water temperature (from 32.7 to 42.3 °C) was observed for activation with steam.

Therefore, thermogravimetric (TG) measurements were taken for carbon adsorbents AC CTP-PET(K_2CO_3) (Fig. 4). Based on the course of TG and DTG curves of carbon adsorbent, two steps were observed. The first steps up to 115 °C show mass loss for the carbon adsorbent about 2% due to the desorption of physically adsorbed water on the porous material. The endothermic transition on the DSC curve (max. peak 61.5 °C) occurred in the same range as the transitions occurring on the TG and DTG (max. peak 59.6 °C). The decomposition product of the second mass loss steps can be assigned to the surface groups formed during the activation process, as well as to the carbon skeleton decomposition. Probably, in the second step groups such as carboxylic acids, carboxylic anhydrides and lactones, which are less thermally stable, decompose with the evolution of carbon dioxide between 300 and 400 °C.

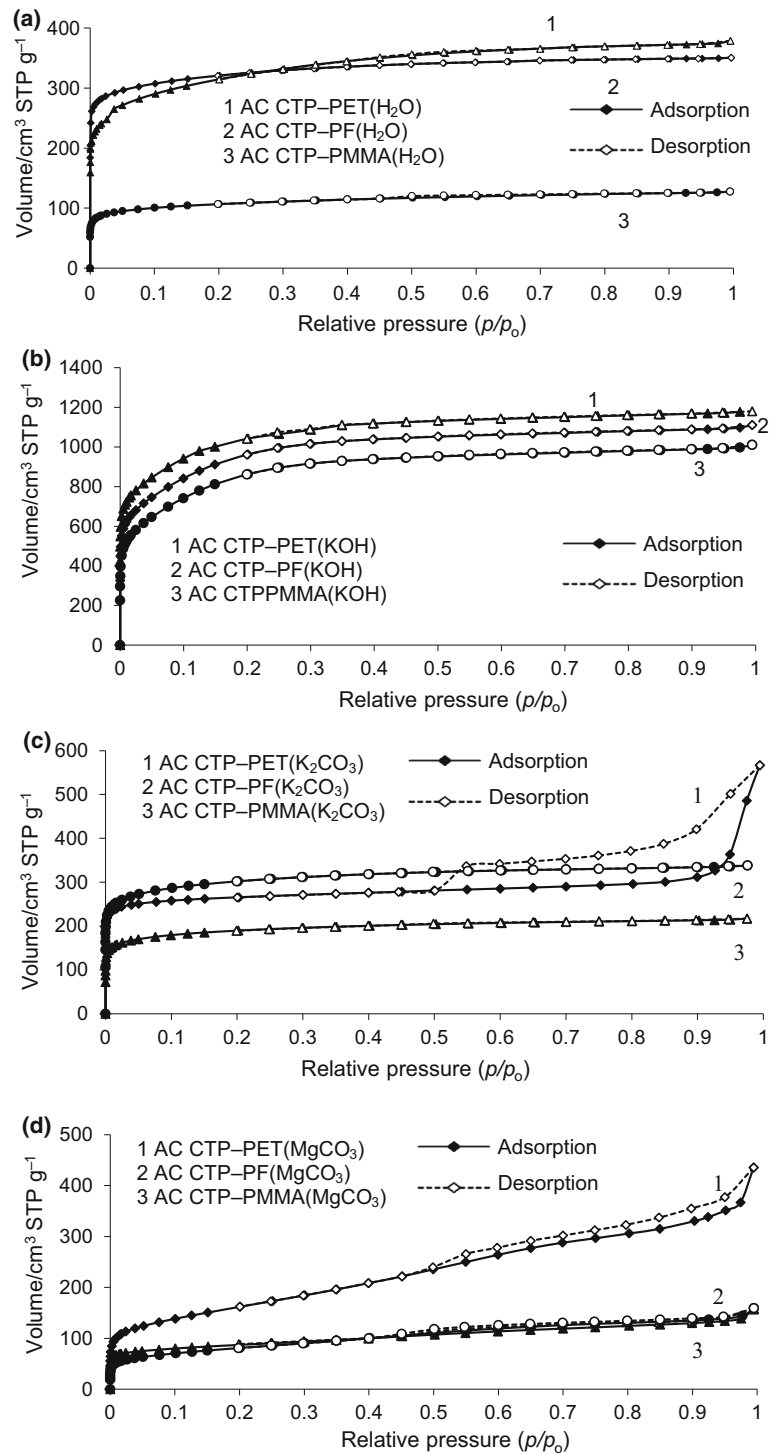


Fig. 2 Isotherms of adsorption/desorption of nitrogen vapor for obtained carbon adsorbents by activation with: **a** steam, **b** KOH, **c** K₂CO₃, **d** MgCO₃

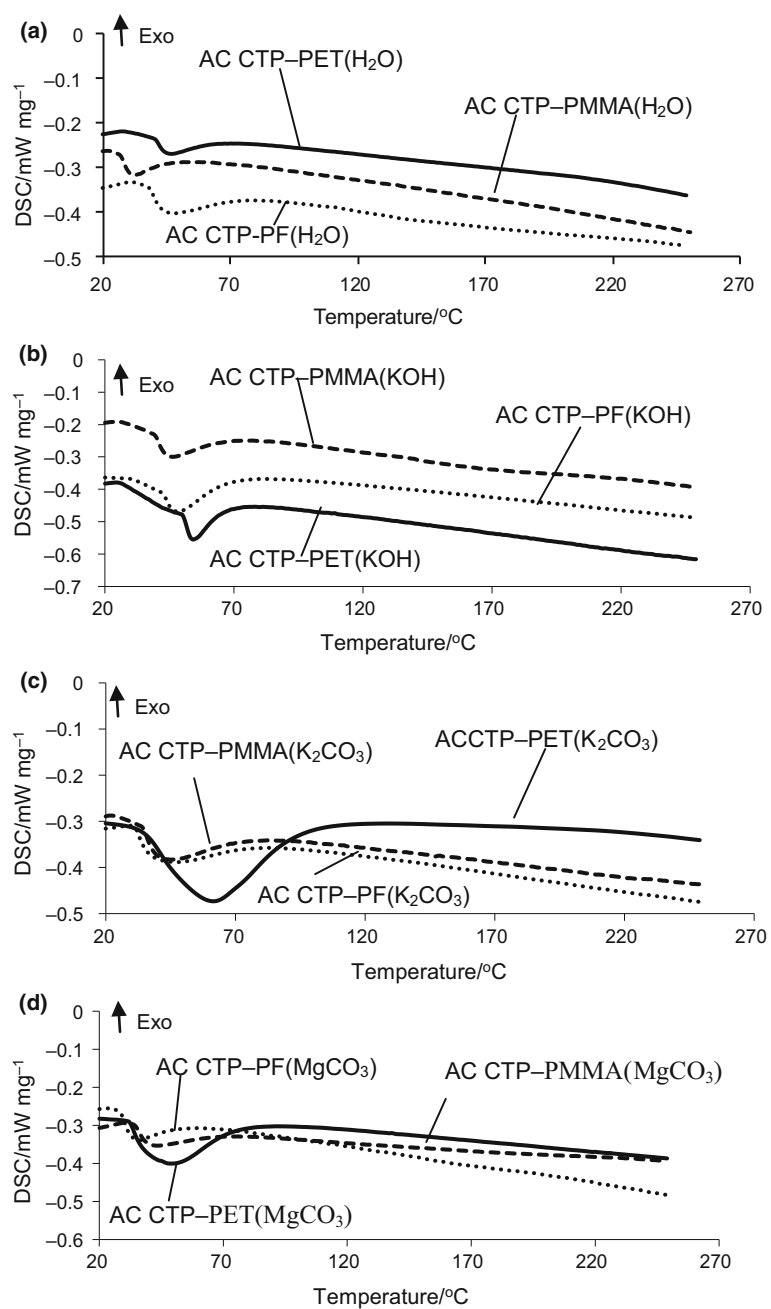


Fig. 3 DSC curves of carbon adsorbents by activation with: **a** steam, **b** KOH, **c** K_2CO_3 , **d** $MgCO_3$

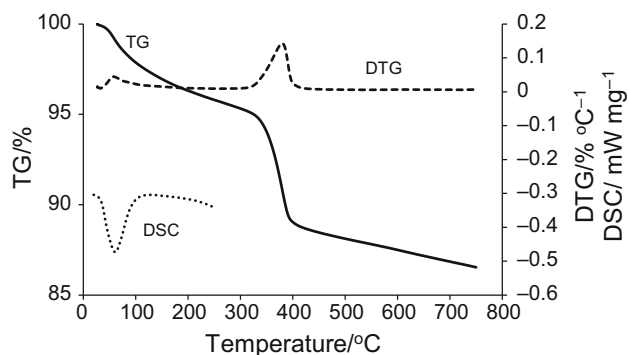


Fig. 4 TG, DTG and DSC curves of carbon adsorbent AC CTP-PET(K_2CO_3)

Conclusions

The use of untypical feedstock, as an effect of combination of bituminous substance with polymeric waste and improvement of the methods of production, creates the potential possibility to produce carbon adsorbents of interesting properties and porous structure.

The presence of the molecule of a polymer into coal-tar pitch beneficially influences the process of carbonization and/or activation and in effect the thermal properties, sorption capacity and porous structure of activated carbons. The sorption capacity and porous structure of activated carbons can also develop depending on the activating agents. It was found that activated carbons obtained in the process of activation with potassium hydroxide had significantly higher values of adsorption of iodine, specific surface area and micropore volume than those of carbon adsorbents prepared in the process of activation with steam, potassium carbonate or magnesium carbonate. Moreover, carbon adsorbent obtained by the activation with steam, KOH and K_2CO_3 (only for the activated carbons AC CTP-PF(K_2CO_3) and AC CTP-PMMA(K_2CO_3)) had the microporous structure. Activated carbons obtained by the activation with K_2CO_3 (for the activated carbon AC CTP-PET(K_2CO_3)) and $MgCO_3$ had the mesoporous structure.

The use of differential scanning calorimetry in the studies of activated carbons made possible the determination of water desorption temperature. The type of activating agents influenced the thermal properties of carbon adsorbents obtained from pitch-polymer compositions. It was found that mesoporous adsorbents obtained from pitch-PET compositions by the activation with K_2CO_3 or $MgCO_3$ had higher capacity for the physical adsorption of water from air.

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