



Applied Problems of Selecting Synthetic Polymer Waste as Raw Material For Production of Active Carbon

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ABSTRACT

The widespread use of polymers in engineering and for household needs is accompanied by the formation of large amounts of waste, which leads to the necessity of solving the problem of their utilization and recycling. This paper shows the results of studies on thermal processing of synthetic large-tonnage polymeric wastes with receipt of active carbons (AC). AC of synthetic polymeric materials are characterized by high purity, low ash content, regular structure, and the possibility of direct forming of porous structure. Sorption properties of AC depend on physical and chemical properties of polymeric wastes. The aims of the present work are to study the processes of thermal degradation of polymeric materials with different chemical structures and physical and chemical properties to obtain carbon sorbents and to develop requirements for chemical composition of waste synthetic polymers as a raw material for the production of AC. Samples of polymer materials, widely used in business activities and having different chemical structure and physical and chemical properties, such as technical polypropylene, polycarbonate based on bis-phenol A, granulated polystyrene, bound rubber on the base of styrene and butadiene copolymer, textile laminate (cotton fabric reinforced with phenol resin and pressed), filled polymer impregnated and cured with epoxy resin, were selected for this study. The influence of the structure of polymer structural unit and its physical and chemical properties on AC porous structure formation has been defined, and requirements to chemical composition of polymer wastes as raw material for AC production have been proved. These requirements include: polymer aromatic structure, location of benzene rings in polymer backbone, presence of heteroatoms (oxygen, nitrogen), high aromaticity index and oxygen mass content in the polymer composition.

INTRODUCTION

In recent decades, the production of polymer materials has been increasing by an average 5-6% annually and by 2013 it has reached more than 250 million tons/year, due to unique properties of these materials, such as strength, corrosion resistance, lightness, multipurpose usefulness and low cost. The widespread use of polymers in electrical engineering industry, consumer goods and food industry, machines, ship- and rocket manufacturing, construction industry, and use of polymers as packing materials are accompanied by the formation of large-tonnage waste volumes, which lead to the necessity of solving their utilization and reworking problem. More than 3.3 million tons of waste synthetic polymers are generated in Russia annually, of which only 10-15% is recycled. Household wastes, dumped tires, used packaging and machine parts are practically non-recoverable and are most often disposed together with municipal solid waste (MSW) at MSW landfills that is accompanied by long-term negative impacts on the environment, therewith resources and energy potential of

such polymer waste is irretrievably lost (Lyubeshkina 1990).

The step by step implementation of sanitation and cleaning services for cities with a selective collection of municipal solid waste, construction of waste sorting plants and the use of different sorting equipment allow to perform the selection of individual types of polymeric wastes and to process them separately (La Robe 2007).

It is the vital task to create methods for a target-specific processing of polymeric wastes, allowing to use their energy and resource potential and to get targeted products that can compete with known market analogues. Analysis of scientific-technical data, experience of polymers recycling in highly developed European countries showed that the most common ways of their utilization were recycling and thermal destruction, based on methods of burning and low-temperature pyrolysis, and obtaining of carbonic sorption materials (Schwartz et al. 2005).

One of the main problems related to the polymeric waste recycling is their compositional inhomogeneity and limited sphere of producing granulates application.

Goods made of recycled polymers become often non-competitive in comparison with their analogues produced from primary raw materials, which is linked with the high costs of recycling and with the decrease of their performance properties.

Thermal methods of polymeric waste recovery allow not only to use the energy potential to the fullest extent possible, but also to produce the marketable goods (liquid fuel, fuel briquettes, carbon sorbents).

Currently, along with polymeric waste burning, the methods of the low-temperature pyrolysis (400-600°C) are investigated and implemented in the industrial practice; such methods are based on polymers destruction processes in inert ambient atmosphere and are accompanied with carbonization and pyrolysis gases generation (Sazanov & Gribanov 2013).

Lack of oxygen facilitates the intense course of wastes heating, melting and thermal destruction. Generated pyrolysis gases have the ability of condensing with the formation of a liquid fraction (boiling point of 300-400°C), which can be used as a boiler fuel or can be reworked into high-quality motor fuels. High calorific values of the liquid fraction (40-42 MJ/kg) and of an uncondensed gas (30-35 MJ/kg) allow to perform the auto thermal process, using pyrolysis gases for keeping the necessary temperature in the pyrolysis furnace. Carbonized material represents valuable raw material, which can be then processed into sorption materials, the carbon sorbents (CS).

The increasing demands of the quality of wastewater treatment and gas emissions lead to the necessity of using the sorption methods that achieve the regulated requirements. Manufacturing of carbonic sorbents in process of synthetic polymer wastes reworking will allow to solve a problem of their utilization, as well as to widen considerably the variety of sorption materials for technological and ecological purposes.

The relevance of such trend is evidenced by the increasing number of publications in foreign scientific journals in past years: the methods of AC (active carbons) manufacturing from the wastes of polyethylene terephthalate (PET) (Parra et al. 2004), polyacrylonitrile (PAN), spent ion-exchange resins (copolymer of styrene and divinylbenzene), PVC, polyurethane (Laszlo & Bota 2000), rubber tire by activation of carbonized materials with steam (Lian et al. 2011) or carbon dioxide (Klushin 2006), thermal processing of polymers at the utilization of cars with receiving AC.

The interest of researchers to the problem is explained by the opportunity of preparation of carbon sorbents with high purity, low ash content, regularity of structure, the

possibility of the directed formation of porous structure from synthetic polymer materials. Sorption and operational properties formed AC depend on a chemical structure and physical and chemical properties of precursors.

OBJECTIVES OF THE PAPER

- Investigation of the thermal destruction of polymeric materials which vary in chemical structure and physical and chemical properties, with obtaining of active carbons (AC).
- Motivation and development of requirements to the chemical composition of organic polymer wastes as raw material for carbon sorbents production.

MATERIALS AND METHODS

To achieve this goal, the samples of polymer materials were selected, widely used in business activities and having different chemical structure and physical and chemical properties: technical polypropylene PP, polycarbonate based on bisphenolA - PC (with monolithic and honeycomb structure), granulated polystyrene-PS, bound rubber on the base of styrene and butadiene copolymer, which is the most widely used in tire industry, textile laminate (cotton fabric reinforced with phenol resin and pressed under a pressure of more than 1100 kg/sm²)-PPT (phenylphenyleneterephthalate), organic polymer - the filled polymer, made in the form of bundles of synthetic aramid fibres, impregnated and cured with epoxy resin. Properties of the investigated samples are presented in Table 1 (Kantselona 198, Madorskiy 1967).

Other samples contain the aromatic rings in the structural unit, here benzene rings in the tire rubber are located in branches of the main chain, and in the polycarbonate and epoxy resin in the main chain. PPT represents three-dimensional high-impact polymer with a dense network, its cross-linkage degree is determined by the ratio of phenol and formaldehyde during its synthesis. The chemical structure of the organoplastic (poly-para-phenyleneterephthalamide) polymer matrix consists of benzene rings, connected to each other by strong chemical bonds via a-NH-CO-group. Polymers also contain heteroatoms-oxygen, sulphur, nitrogen, connecting the benzene rings.

The process of the samples destruction were investigated by thermal analysis methods: differential-thermal analysis (DTA) and thermogravimetry (TG, DTG). The experiments were conducted with derivatographic device Q1500D in carbon dioxide with heating rate 5 and 10°C/min. For the analysis of the thermal destruction products the laboratory device was developed allowing to heat samples in the laboratory muffle furnace without oxygen access, then to

condense the releasing organic substances and concentrate the outgoing gases. Analysis of non-condensable gases was conducted by chromatographic method. Carbonized substance properties were assessed regarding main features: carbonized substance output, mechanical strength, total porosity, determined by the water absorption capacity, ash value and volatile-matter content.

In order to obtain carbon sorbent samples, the method of carbonized substances activation with a steam at 850-900°C to the 45-50% burning degree was used. The process was performed in the laboratory rotary furnace with an external electric heating. The mass ratio of carbonized substance : steam was 1: 3-4.

Analysis of porous structure and physical and chemical properties of the carbon sorbent sample, characteristic energy of adsorption and the size of slit half-width for the slit-shaped micropore was conducted using standard techniques accepted in the adsorption technique. The parameters of the CS porous structure were determined on the base of the analysis of nitrogen adsorption isotherms (temperature of 77 K (-196°C), obtained with the use of the “Sorbometr - 1800” device (Carlo Erba company) and calculated on the base of the Dubinin-Radushkevich equation from the theory of micropores volume filling.

An important characteristic of CS, which determines the sorbent application sphere, is the micropore size. In accordance with current concepts about the micropore slit-shaped form (Dubinin et al. 1975, 1985), the flat slit half-width X (nm) was calculated according to the formula:

$$X_o = \frac{K_o}{E_o} \dots(1)$$

Where, E_o - characteristic energy of adsorption, kJ/mole; K_o - constant, depending on the radius of micropores gyration during small-angle X-ray scattering. For industrial active carbons (AC) in satisfactory approximation, $K_o = 12,0$ kJ-nm/mole.

To determine the technical and sorption characteristics of the obtained sorbent samples, the standard methods of analysis were used: adsorption activity on iodine and methylene blue dye, determination of bulk density, ash mass content and wear resistance.

RESULTS AND CONSIDERATIONS

The derivatographic investigations of selected samples in carbon dioxide at temperature intervals of 20-800°C and heating rates of 5° and 10°/min were held to determine regularities of processes of polymeric material thermal destruction. Fig. 1 shows derivatograms for PP and PC samples.

It was stated that all samples were affected by degradation at temperature intervals of 20-800°C with formation of carbonized substance. Depending on the polymer nature, the powder and cracked products are obtained in pyrolysis and carbonization process. Carbonized products on the base of thermoset and crystalline polymers (PP, laminated textile and organo plastics) keep the form of original particles; in the process of PC, PS and tire rubber degradation, the highly dispersed carbonized products were formed. Heating velocity does not influence the carbonized product output.

It was noted that reducing of the heating rate during organo plastics (OP) degradation led to some lowering of temperature of material degradation maximum and accord-

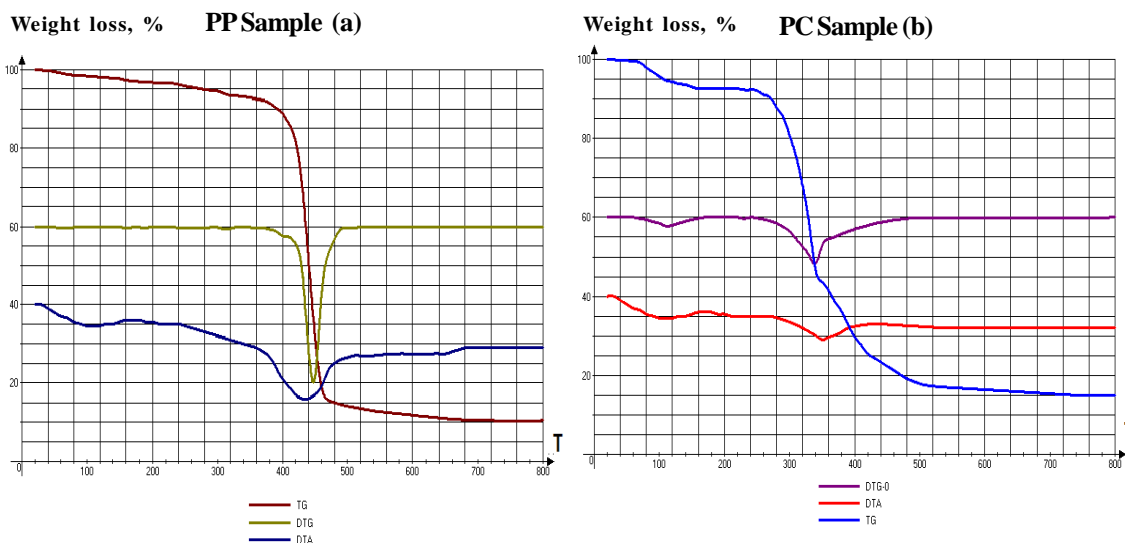
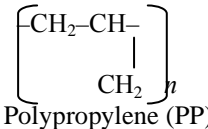
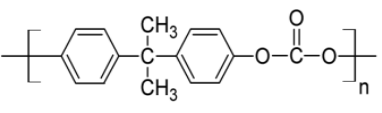
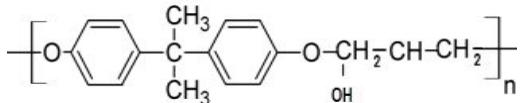
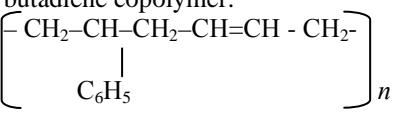


Fig. 1: Derivatograms of PP and PC samples: a-PP, b-PC.

Table 1: Main physical and chemical properties of polymers.

Polymer	Softening T°C	Degradation T°C	Properties
 Polypropylene (PP)	176	220-250	isotactic crystalline polymer
Polycarbonate (PC) 	220-230	330	Linear polyesters of carbon acid and dihydric phenol. Melting T is close to degradation T. Tear resistance ≥ 60 MПа
Polystyrene (PS) $[-CH_2-C(C_6H_5)H-]_n$	87-92	240-260	Thermoplastic atactic amorphous polymer with linear structure.
Textile laminate. Bonding material – phenolic-formaldehyde resin $[-C_6H_3(OH)-CH_2-]_n$	200-250	331-350	Bonding material-phenolic formaldehyde resolesin. Tear resistance for plates of 1-2 mm thick - 39,0 MПа or 400 (kilogram-force /sm ²)
Organoplastics. Bonding material - epoxide  Filling material – aramide fibres - aromatic polyamide. (polyparafenilenthertalamide = aramide)	85-100	250-450	Epoxyresins (ER) - oligomeric products of polycondensation of epichlorhydrin with polyatomic phenol.
Tيرubber (TR) on the base of styrene and butadiene copolymer. 	130-170	More than 200	Noncrystallized copolymer with irregular structure, with statistical distribution of monomer units, filling material - technical carbon

ingly to decreasing of volatile content from 50% (10°C/min) to 46% (5°C/min) at 800°C.

An analysis of the PS (polystyrene) sample derivatogram demonstrated that the main mass loss (96%) was observed in temperature intervals of 300-450°C with endothermic peak at 350°C. At temperature 800°C the total mass loss is 97.2%. Correspondingly, the fixed residue outcome is nonsignificant (2.8 mass %), and in this case its usage for CS preparation is unpractical. During the thermal

degradation of PS in carbon dioxide media the polymer degradation takes place with benzene, ethyl benzene and styrene evolution and practically no carbonization follow this process.

The experimental batches of carbonized substances were obtained for investigation of carbonized substances and of their activation processes on laboratory pattern equipment at temperature 500°C, speed of temperature rise 8-10°C/min and the hold up for 30 minutes at the final tem-

Table 2: Main characteristics of thermal degradation process of samples.

Characteristic	Polymer materials				
	PP	PC	PPT (phenylphenylene ether phthalate)	Tire rubber	OP (organoplastic)
Product outcome, %					
Pyrolysis/condensing gases (liquid fraction)	64.1	67.0	28.0	36.0	28.7
Pyrolysis noncondensing gases	25.0	14.5	11.0	30.0	12.3
Solid residue	10.9	18.5	61.0	34.0	59.0
Carbonized substances characteristics					
Carbonized substance form	Keeps the form of initial particles	Fine substance	Keeps the form of initial particles	Fine substance	Keeps the form of initial particles
Carbonized substance ash content, %	3.2	2.1	0.5	11.0	2.8
Pores total volume, sm^3/g	0.25	0.45	0.40	0.15	0.36
Strength, %	60	-	85	-	80
Volatiles content, %	25	18	8.0	32	10.1

Table 3: Characteristics of porous structure parameters of AC samples produced from polymer wastes.

Characteristics	Polymer materials					AC CAC
	CS-PP	CS-PC	CS-PPT	CS-tire rubber	CS-OP	
Pore total volume, $V\Sigma$, sm^3/g	0.42	0.61	0.75	0.52	0.82	0.8-0.9
Micropores volume, V_{mi} , sm^3/g	0.20	0.37	0.32	0.12	0.29	0.35-0.41
Mesopores volume, V_{me} , sm^3/g	0.10	0.04	0.07	0.18	0.12	0.10-0.12
Macropores volume, V_{ma} , sm^3/g	0.19	0.20	0.26	0.12	0.41	0.35-0.40
Limiting volume of sorption space, W_0 , sm^3/g	0.18	0.39	0.35	0.12	0.30	0.45-0.56
Characteristic energy of adsorption, E_a , kJ/mole	21.4	24.8	21.1	14.6	19.7	24-26
Size of the micropore slit half-width, X , nm	0.56	0.52	0.57	0.9	0.61	0.45-0.55
Area of micropores surface, S , m^2/g	321.0	711.5	614	146	475	730-770-
Area of surface, S_{BET} , m^2/g				398.5		
Sorption space volume, W_s , sm^3/g	0.35	0.42	0.39		0.43	0.45-0.5

perature. The investigation results are presented in Table 2.

It was found that the greatest output of the carbonized substance was observed in result of the degradation of the textile laminate and organoplastic (61 and 59%, respectively).

During pyrolysis of PP and PC 10.9 and 18.5 % of the carbonized substance formed respectively, while the shares of liquid fraction (hydrocarbons with boiling temperature upto 350°C), were 78% and 67%.

High yield of the heat-absorptive fractions during pyrolysis of polymeric materials allow to carry out the process in autothermal mode and to use pyrolysis gases for heating pyrolysis and activation furnaces, as well as liquid fuel.

The samples of the carbonized substances received during the degradation of cross-linked thermosetting polymers: OP (organoplastics) and PPT (phenyl phenylene ether phthalate) have the most mechanical abrasion resistance.

In the process of activation of carbonized substance samples, the cracked CS (CS-PPT, CS-OP, CS-PP) and

powder CS (CS-PC, CS-tire rubber) were obtained. Characteristics of the porous structure of the AC samples are presented in Table 3.

The characteristics of the porous structure of AC brand CAC (activated carbon from coconut shell) are also presented in the Table 3 for comparison purposes. Samples of CS obtained in the process of PC and PPT (phenyl phenylene ether phthalate) treatment can be attributed as microporous adsorbents. Micropores volume values for these samples are comparable with industrial microporous AC of CAC brand. The micropore sizes of the emerging CS are also different.

It is known that the micropore AC is itself divided into the proper micropores of radius 0.5-0.7 nm and super micropores with radius 0.7-1.6 nm.

Micropore samples of the CS-tire rubber are super micropore. Other samples are characterized with the narrow distribution of pore size, predominately with the existence of micropores proper. In the porous structure of AC-PP and AC-tire rubber predominate the meso- and macropores. Ratio

Table 4: Sorption properties of obtained AC samples.

Sample name	Adsorptive activity - iodine mg/g	Brightening activity mg/g	Bulk density g/sm ³
CS - PP (MAC*)	530	200	0.28
CS - PC (PAC**)	910	180	0.32
CS - PPT (phenyl phenylenetherephthalate) (MAC)	800	250	0.42
CS - tire resin (PAC)	400	320	0.38
CS - ER (epoxy resin) (MAC)	820 (in powder)	240	0.39
CAC (MAC)	1000	260	0.37
BC-A (PAC)	Non relevant	225	0.23-0.25

MAC* - milled active coal, PAC**- powder active coal.

Table 5: Influence of aromaticity degree and oxygen content in the structural unit of synthetic polymers to the formation of CS porous structure.

Polymer	Aromaticity degree* %	Oxygen atoms content** %	Carbonized substance outcome, %	Porous structure of carbon sorbents			X, nm
				V _{mis} m ³ /g	V _{mes} m ³ /g	V _{mi} /(V _{me} +V _{ma})	
PS (polystyrene)	74	0	Less than 3	-	-	-	
PC	59,0	18,75	18,5	0,37	0,04	1,54	0,52
Phenol-formaldehyde resin	80,0	16,9	61,0	0,32	0,07	0,71	0,57
Organoplastic:Epoxy resin + Aramide fiber	63,8	13,4	59,0	0,29	0,12	0,58	0,9
Copolymer of styrene and butadiene	48,7	0	34,0	0,12	0,18	0,4	0,61

*, **Aromaticity degree and oxygen content in composition of investigated synthetic polymers are calculated as mass share of C₆H₅- and O in the polymer structural unit

of $V_{mi}/(V_{me} + V_{ma})$ for AC-PP, AC-tire rubber and AC-PC is 0.67, 0.4 and 1.54 correspondingly.

The adsorption properties of obtained sorbent samples were determined by the values of sorption activity of the samples in relation to iodine, the size of the molecules of which corresponds to the size of AC micropores and in relation to methylene blue dye, the size of the molecules of which are large enough ($S = 1.97 \text{ nm}^2$) and their adsorption is possible in large micropores and mesopores. The research results compared with the known AC-CAC (shredded coconut activated carbon) and BC-A (brightening active coal, powder) are presented in Table 4.

Analysis of the obtained results showed that the samples of CS-PC, CS-PPT (phenyl phenylene therephthalate) and CS-ER (epoxy resin) possessed the most adsorptive activeness; the samples of mesoporous CS-tire rubber had the most adsorptive capacity in relation to methylene blue.

The performed research showed that the porous structure and adsorptive properties of CS samples, obtained from different types of polymer wastes in similar conditions, differed considerably, which can be explained by the influence of chemical structure and bonding strength in polymer structural unit to process their degradation and carbonization.

It is known that AC represent a variation of microcrystal carbon where the polycrystalline matter consists of planes formed by condensed aromatic rings, but orientation of certain planes, typical for graphite, is violated and some layers are shifted disorderly relative to one another. AC contains also upto 2/3 amorphous carbon and heteroatom oxygen, nitrogen. Heterogeneous mass, which consists of graphite and amorphous carbon crystallites, determines the unique porous structure of AC. In accordance with current concepts regarding AC porous structure, two micropore variants are presented: slit-like micropores in carbon crystallites (their radius is 0.6-0.7 nm) and inter-crystallite micropores with radius 0.6-1.6 nm (Dubinin et al. 1975). Complex of micropores of such two types form the microporosity areas with 10-60 nm length. Slits bulk volume between the microporosity areas is the mesopores volume for the sorbent mass unit.

During polymer pyrolysis, accompanied with carbonization, formation of carbon-carbon bonds and the structure graphitization due to the polymer chains cross-linking, should have placed. Analysis of Tables 3 and 4 results demonstrated that AC samples generated in a process of polymers thermal degradation and having oxygen atoms in their structural unit (phenol-formaldehyde resins, epoxy resins PC) possessed the largest micropore volume.

Participating in dehydration and partial decarboxylation an oxygen hastens the cross bonds formation, thus influencing the polymer cross-linking and graphitization during its thermal processing.

Analysis of the obtained results showed that the presence of benzene rings in branches from the main chain (tire rubbers) led to the formation of AC mesoporous structure; i.e., could be believed that, in the process of tire rubber destructive pyrolysis and carbonized substance activation, small graphite crystallites are formed and bigger inter-crystallite pores played the main role in adsorptive processes. Increasing of methylene blue adsorptive capacity for AC samples, generated from tire rubber, can be explained by correlation of given coal pores (2-3 nm) to dimensions of methylene blue molecules.

Thermal destruction of isotactic PP is accompanied with considerable emission of pyrolysis gases (89%) in result of dehydrogenation and depolymerization processes; carbonization is accompanied with structural chains and PP submolecular structures cross-linking processes with formation of graphite-like structures. Due to the low outcome of the carbonized substance during the PP pyrolysis (10%), alternative methods are advisable to process PP wastes, for example, catalytic pyrolysis with obtaining of liquid fuels.

Conducted analysis of research results in obtaining CS from different kinds of polymer wastes, allowed to find that the main factors which influenced CS porous structure formation were the polymer aromaticity degree, location of benzene rings in the structural unit, oxygen presence in the precursor composition (Table 5).

As it is seen from the given data, increase of the aromaticity degree and oxygen atoms content, leads to the formation of carbon sorbents microporous structure and to the increase of micropores volume.

CONCLUSION

Performed research on the thermal processing of synthetic

polymer materials with different composition resulting in CS formation, allowed to discover the correlation between the polymer structural unit composition, its physical and chemical properties and porous structure of the obtained CS; also the mentioned results allowed to justify requirements for chemical composition of polymer waste as to the raw material for CS production. Such requirements are:

- Aromatic structure of the polymer.
- Location of the benzene rings in the main chain of the polymer.
- High mass content of the oxygen in the polymer composition.
- High degree of the precursor aromaticity.
- Low ash value of the precursor.

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