Vol. 9, No. 3, 2015 Chemistry

Sergei Kolesov[1], Marina Bazunova[1], Elena Kulish[1], Denis Valiev[1] and Gennady Zaikov[2]

A NEW APPROACH TO THE CREATION OF CARBON-POLYMER NANOCOMPOSITES WITH POLYETHYLENE AS A BINDER

[1]Bashkir State University
32, Zaks Validi str., 450076 Ufa, Bashkorstan; kolesovservic@mail.ru
[2]Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,
4, Kosygina str., 119991 Moscow, Russia; chembio@sky.chph.ras.ru

Received: March 18, 2014 / Revised: April o4, 2014 / Accepted: November 20, 2014

Abstract. Approach of obtaining molded composites on the basis of the mixtures of powders of nano-dispersed polyethylene, cellulose and ultra-dispersed carbonic materials has been developed. These materials possess the assigned sorption properties and the physic-mechanical characteristics. They are suitable for the usage in the process of cleaning and separation of gas mixtures.

Keywords: sorbent, nano-carbon, high-temperature shift crushing, polyethylene, cellulose.

1. Introduction

In solving the problems of environmental protection, medicine, cleaning and drying of hydrocarbon gases effective sorbents, including polymer nanocomposites derived from readily available raw materials, are indispensable.

The nature of binder and active components as well as molding conditions are especially important in the process of sorption-active composites creating. These factors ultimately exert influence on the development of the porous structure of the sorbent particles and its performance. In this regard, it is promising to use powders of various functional materials having nanoscale particle sizes in the process of such composites creating. Firstly, high degree of homogenization of the components facilitates their treatment process. Secondly, high dispersibility of the particles allows them to provide a regular distribution in the matrix, whereby it is possible to achieve improved physical and mechanical properties. Thirdly, it is possible to create the composites with necessary sorption, magnetic, dielectric, and other special properties combining volumetric content of components [1].

Powders of low density polyethylene (LDPE) prepared by high temperature shearing (HTS) are used as one of promising components for functional composite materials development [2, 3].

Development of the preparation process and study of physicochemical and mechanical properties of sorbents based on powder mixtures of LDPE, cellulose (CS) and carbon materials has been conducted. As the basic sorbent material new ultrafine nanocarbon (NC) obtained by the oxidative condensation of methane at the treatment time of 50 min (NC1) and 40 min (NC2) having a specific surface area of 200 m^2/g and a particle size of 30–50 nm has been selected [4]. Ultrafine form of NC may give rise to technological difficulties, for example, during regeneration of NC after using in gaseous environments, as well as during effective separation of the filtrate from the carbon dust particles. This imposes restrictions on the using of NC as an independent sorbent. In this connection, it should be included in a material that has a high porosity. LDPE and CS powders are of great interest for the production of such material. It is known that the mixture of LDPE and CS powders has certain absorption properties, particularly they were tested as sorbents for purification of water surface from petroleum and other hydrocarbons [5].

Thus, the choice of developing sorbents components is explained by the following reasons:

1. LDPE has low softening point, allowing to conduct blanks molding at low temperatures. The very small size of the LDPE particles (60 to 150 nm) ensures regular distribution of the binder in the matrix. It is also important that the presence of binder in the composition is necessary for maintaining of the material shape, size, and mechanical strength.

2. Usage of cellulose in the composite material is determined by features of its chemical structure and

properties. CS has developed capillary-porous structure. That is why it has well-known sorption properties [5] towards polar liquids, gases and vapors.

3. Ultrafine carbon components (nanocarbon and activated carbon (AC)) are used as functionalizing addends due to their high specific surface area.

2. Experimental

Ultrafine powders of LDPE, CS and a mixture of LDPE/CS are obtained by high temperature shearing under simultaneous impact of high pressure and shear deformation in an extrusion type apparatus with a screw diameter of 32 mm [3].

Initial press-powders are obtained by two ways. The first method is based on the mechanical mixing of ready LDPE, CS and carbon materials powders. The second method is based on preliminary high-shear joint grinding of LDPE pellets and sawdust in a specific ratio and mixing the resulting powder with the powdered activated carbon (BAU-A mark) and the nanocarbon after it.

Composites molding was conducted by thermobaric compression at the pressure of 127 kPa.

Measuring of the tablets strength was carried out on the automatic catalysts strength measurer PK-1.

The adsorption capacity A of the samples under static conditions for condensed water vapor, benzene, and *n*-heptane were determined by the method of complete saturation of the sorbent by adsorbate vapor under standard conditions at 293 K [6] and calculated by the formula:

$$A = m/(M \cdot d)$$

where m – mass of the adsorbed benzene (acetone, *n*-heptane), g; M – mass of the dried sample, g; d – density of the adsorbate, g/cm^3.

Water absorption coefficient of polymeric carbon sorbents is defined by the formula:

$$K = \frac{m_{ab.water}}{m_{sample}} \cdot 100\%$$

where $m_{ab.water}$ is mass of the water, retained by the sorbent sample, m_{sample} is mass of the sample.

Experimental error does not exceed 5 % in all weight methods at P = 0.95 and the number of repeated experiments n = 3.

3. Results and Discussion

Powder components are used as raw materials for functional composite molding (including the binder LDPE), because molding of melt polymer mixtures with the active components has significant disadvantages. For example, the melt at high degrees of filling loses its fluidity, at low degrees of filling flow rate is maintained, but it is impossible to achieve the required material functionalization.

It is known that semi-crystalline polymers, which are typical heterogeneous systems, are well exposed to high-temperature shear grinding process. For example, the process of HTS of LDPE almost always achieves significant results [3]. Disperse composition is the most important feature of powders obtained as the result of high-temperature shear milling. Electron microscopy gives the sizes of LDPE powder particles within 60–150 nm. The active powder has a fairly high specific surface area (up to 2.2 m^2/g).

The results of measurement of the water absorption coefficient and of the static capacitance of LDPE powder by *n*-heptane vapor are equal to 12 % and 0.26 cm^3/g, respectively. Therefore, the surface properties of LDPE powder are more developed than those of the other polyethylene materials.

3.1. Selection of Molding Conditions of Sorbents Based on Mixtures of LDPE, CS and Ultrafine Carbon Materials Powders

Initial press-powders obtained by two ways. The first method is based on the mechanical mixing of ready LDPE, CS and carbon materials powders. The second method is based on a preliminary high-shear joint grinding of LDPE pellets and sawdust in a specific ratio and mixing the resulting powder with the powdered activated carbon and the nanocarbon after it. The method of molding was thermobaric pressing at the pressure of 127 kPa.

The mixture of LDPE/CS compacted into cylindrical pellets at the temperature of 388–418 K was used as a model mixture for selection of composites molding conditions. Pressing temperature should be such that the LDPE softens but not melts, and at the same time forms a matrix to prevent loss of specific surface area in the ready molded sorbent due to fusion of pores with the binder. The composites molded at a higher temperature have a lower coefficient of water absorption than the tablets produced at a lower temperature; therefore the lowest pressing temperature (393 K) is selected. At a higher content of LDPE the water absorption coefficient markedly decreases with temperature.

Cellulose has a high degree of swelling in water (450 %) [5], which may lead to the destruction of the pellets. Its contents in samples of composites, as it has been observed by the sorption of water, should not exceed 30 wt %. There is a slight change of geometric dimensions of the pellets in aqueous medium at an optimal value of the water absorption coefficient when the LDPE content is 20 wt %.

Samples of LDPE/CS with AC, whose sorption properties are well studied, are tested for selecting of optimal content of ultrafine carbon. The samples containing more than 50 wt % of AC have less water absorption coefficient values. Therefore, the total content of ultrafine carbon materials in all samples must be equal to 50 wt %.

Static capacitance measurement of samples obtained from mechanical mixtures of powders of PE, CS and AC was conducted on vapors of n-heptane and benzene to determine the effect of the polymer matrix on the sorption properties of functionalizing additives. With a decrease of the content of AC in the samples with fixed (20 wt %) amount of the binder, reduction of vapor sorption occurs. It indicates that the AC does not lose its adsorption activity in the composition of investigated sorbents.

Strength of samples of sorbents (Fig. 1) is in the range of 620–750 N. The value of strength is achieved in the following molding conditions: T = 393 K and the pressure of 127 kPa.

Thus, optimal weight composition of the matrix of LDPE/CS composition is 20/30 wt % with 50 wt % containing of carbon materials.

3.2. Sorption Properties of Carbon-Polymer Composites by Condensed Vapors of Volatile Liquids

For a number of samples of sorbents static capacitance values by benzene vapor is identified (Fig. 2). They indicate that the molded mechanical mixture of 20/25/25/30 wt % LDPE/AC/NC1/CS has a maximum adsorption capacity that greatly exceeds the capacity of activated carbon. High sorption capacity values by benzene vapor appear to be determined by weak specific interaction of π-electron system of the aromatic ring with carbocyclic carbon skeleton of the nanocarbon [7].

For a number of samples of sorbents static capacitance values by benzene vapor is identified (Fig. 2). They indicate that the molded mechanical mixture of 20/25/25/30 wt % LDPE/AC/NC1/CS has a maximum adsorption capacity that greatly exceeds the capacity of activated carbon. High sorption capacity values by benzene vapor appear to be determined by weak specific interaction of π-electron system of the aromatic ring with carbocyclic carbon skeleton of the nanocarbon [7].

Static capacitance of obtained sorbents by heptane vapors significantly inferiors to capacity of activated carbon (Fig. 3), probably it is determined by the low polarizability of the molecules of low-molecular alkanes. Consequently, the investigated composites selectively absorb benzene and can be used for separation and purification of mixtures of hydrocarbons.

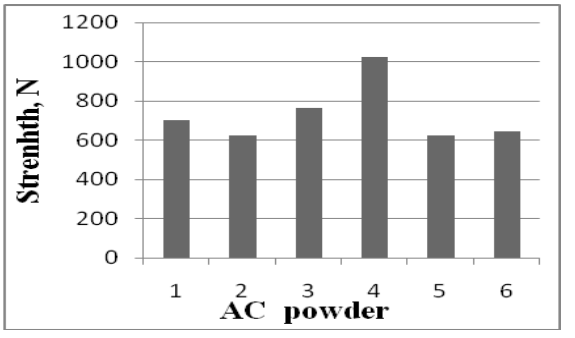

Fig. 1. Comparison of strength of pellets, based on LDPE, CS (different species of wood) and AC powders: sorbent of LDPE/AC/CS = 20/50/30 wt % based on the powders of jointly dispersed pellets of LDPE and softwood sawdust with subsequently addition of AC (1); sorbent of LDPE/AC/CS = 20/50/30 wt % based on the powders of jointly dispersed pellets of LDPE and hardwood sawdust with subsequent addition of AC (2); sorbent of LDPE/AC/CS = 20/50/30 wt % based on the mechanical mixtures of the individual powders of LDPE, CS from softwood and AC; AC tablet (4); sorbent of LDPE/CS = 20/80 wt % (5) and sorbent of LDPE/AC = 20/80 wt % (6)

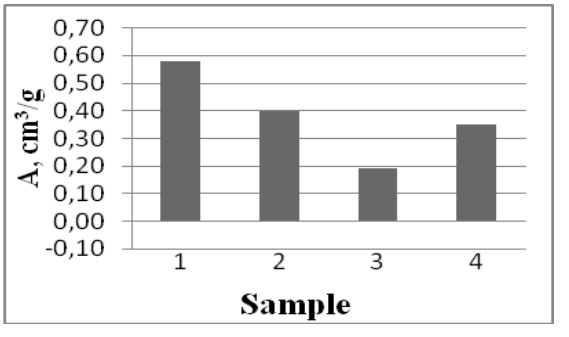

Fig. 2. Static capacitance of sorbents A, cm^3/g by benzene vapor (293 K): molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30 wt % (1); molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt % (2); molded mechanical mixture of LDPE/AC/CS=20/50/30 wt % (3) and AC medical tablet (controlling) (4)

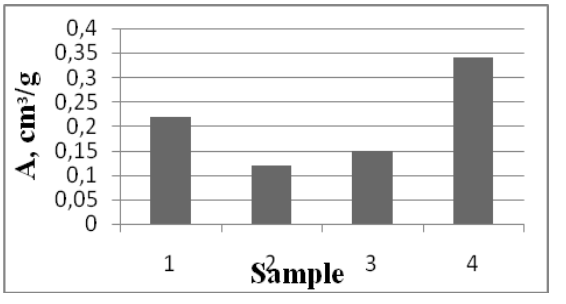

Fig. 3. Static capacitance of sorbents A (cm^3/g) by n-heptane vapor (293 K): molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30 wt % (1); molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt % (2); molded mechanical mixture of PE/AC/CS=20/50/30 wt % (3) and AC medical tablet (controlling) (4)

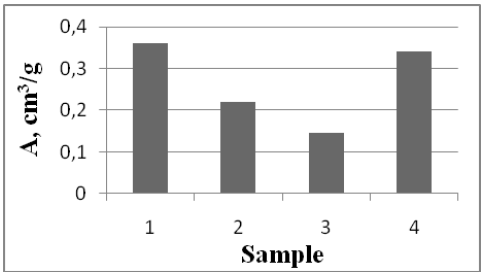

Fig. 4. Static capacitance of sorbents A (cm^3/g) by acetone vapor (293 K): molded mechanical mixture of LDPE/AC/NC1/CS = 20/25/25/30wt % (1); molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt %; molded mechanical mixture of LDPE/AC/CS=20/50/30 wt % (3) and AC medical tablet (controlling) (4)

Table 1

Sorbents characteristics: total pore volume $V_{tot.}$; static capacitance A by benzene vapors at the sorption time of 2 days; residual weight of the absorbed benzene after drying at T = 343 K for 120 min

LDPE/AC/NC/CS sorbent composition, wt %	$V_{tot.}$, cm^3/g	A, cm^3/g	Residual benzene content as a result of desorption, %
20/25/25/30	1.54	0.5914	2.9
20/50/ - /30	1.21	0.1921	10.3
- /100/ - / -	1.60	0.3523	32.0

Molded composite based on a mechanical mixture of LDPE/AC/NC1/CS = 20/25/25/30 wt % has a sorption capacity by acetone vapor comparable with the capacity of activated carbon (0.36 cm^3/g) (Fig. 4)

Sorbents samples containing NC2 have low values of static capacity by benzene, heptanes and acetone vapor. It can be probably associated with partial occlusion of carbon material pores by remnants of resinous substances – by-products of oxidative condensation of methane, and insufficiently formed porous structure.The residual benzene content measuring data (Table 1) show that the minimal residual benzene content after its desorption from the pores at T = 343 K for 120 min observes in case of sorbent LDPE/AC/NC1/CS composition = 20/25/25/30 wt %. It allows to conclude that developed sorbents have better ability to regenerate under these conditions in comparison with activated carbon.

4. Conclusions

Thus, the usage of nanosized LDPE as a binder gives the possibility to obtain the molded composite materials with acceptable absorption properties. Optimal conditions for molding of sorbents on the basis of mixtures of powdered LDPE, cellulose and ultrafine carbon materials were determined as follows: the temperature of 393 K and the pressure of 127 kPa, content of the binder (polyethylene) was 20 wt %.

By varying the ratio of the components of the compositions on the basis of ternary and quaternary mixtures of powdered LDPE, cellulose and ultrafine carbon materials it is possible to achieve the selectivity of sorption properties by vapors of certain volatile liquids. It was established that molded mechanical mixture of LDPE/AC/NC1/CS 20/25/25/30 wt % has a static capacity by condensed vapors of benzene and acetone 0.6 cm^3/g and 0.36 cm^3/g, respectively, which exceeds the capacity of activated carbon. The static capacitance of the compositions by the *n*-heptane vapors is 0.21 cm^3/g; therefore, the proposed composites are useful for separation and purification of gaseous and steam mixtures of different nature.

The developed production method of molded sorption-active composites based on ternary and quaternary mixtures of powdered LDPE, cellulose and ultrafine carbon materials can be easily designed by equipment and can be used for industrial production without significant changes.

References

[1] Akbasheva E. and Bazunova M. : Materialy Otkrytoi Shkoly-Conferencii Stran SNG "Ultramelkozernistye i Nanostructurirovannye Materialy". Bashkorstan, Ufa 2010, 106.
[2] Enikolopyan N., Fridman M. and Karmilov A.: Dokl. Acad. Nauk SSSR, 1987, **296**, 134.
[3] Akhmetkhanov R., Minsker K. and Zaikov G.: Plast. Massy, 2006, **8**, 6.
[4] Aleskovskiy V. and Galitseisky K.. Rus. Pat. 2287543, Publ. Nov. 20, 2006.
[5] Raspopov L., Russiyan L. and Zlobinsky Y.: Rus. Polym. Sci. J., 2007, **50**, 547.
[6] Keltsev N.: Osnovy Adsorbcionnoi Tehniki. Khimiya, Moskwa 1984.
[7] Valinurova E., Kadyrov A. and Kudasheva F.: Vestn. Bashkirs. Univ., 2008, **13**, 907.

НОВИЙ ПІДХІД ДО СТВОРЕННЯ ВУГЛЕЦЬ-ПОЛІМЕРНИХ НАНОКОМПОЗИТІВ ІЗ ПОЛІЕТИЛЕНОМ ЯК ЗВ'ЯЗУЮЧИМ

Анотація. *Розроблено підхід до отримання формованих композитів на основі суміші порошків нанодисперсного поліетилену, целюлози та ультрадисперсних вуглецевих матеріалів. Встановлено, що матеріали володіють заданими сорбційними властивостями та фізико-механічними характеристиками. Показана можливість їх застосування в процесах очищення та розділення газових сумішей.*

Ключові слова: *сорбент, нановуглець, високотемпературне подрібнення зсуву, поліетилен, целюлоза.*