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SORPTION-ACTIVE CARBON-POLYMER NANOCOMPOSITES, BASED ON POLYETHYLENE

The keywords: sorbents, nano-carbon, high-temperature shift crushing, polyethylene, cellulose.

The method of obtaining of the molded composites on the basis of the mixtures of the powders of nano-dispersed polyethylene, cellulose and the ultra-dispersed carbonic materials is developed. These materials possess the assigned sorption properties and the physic-mechanical characteristics. They are suitable for the usage at the process of cleaning and separation of gas mixture.

Ключевые слова: сорбенты, нано-углерод, полиэтилен, целлюлоза.

Предложен метод получения нанокмпозитов на основе смесей полиэтилена, целлюлозы и ультрадисперсных углеродистых материалов. Материалы обладают требуемыми сорбционными свойствами сорбции и физическо-механическими особенностями. Данные материалы предназначены для процессов очистки и разделение газовых смесей.

Introduction

Currently, the creation of materials with high adsorption activity to a range of definite substances by controlling their surface structure has significant interest. Particularly, selective sorbents for separation processes, dividing or concentration of the components of different nature mixtures are developed on the basis of such composites.

The nature of the binder and the active components, and molding conditions are especially important at 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 at the process of such composites creating. First, the 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. Secondly, high degree of homogenization of the components facilitates their treatment process. Third, it is possible to create the composites with necessary magnetic, sorption, dielectric and other special properties combining volumetric content of components [1].

Powders of low density polyethylene (LDPE) prepared by high temperature shearing (HTS) used as one of prospective components of the developing functional composite materials [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 are conducted. As the basic sorbent material new - ultrafine nanocarbon (NC) obtained by the oxidative condensation of methane at a treatment time of 50 min (NC1) and 40 min (NC2) having a specific surface area of $200 \text{ m}^2 / \text{g}$ and a particle size of 30 - 50 nm is selected [4]. Highly dispersed 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 have great interest for the production of such material. It is known that a mixture of LDPE and CS powders have 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 a low softening point, allowing to conduct blanks molding at low temperatures. The 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's 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's why it has well-known sorption properties [5] towards polar liquids, gases and vapors.

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

Experimental

Fine 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 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 (БАУ-А mark) and the nanocarbon after it.

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

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

$$K = \frac{m_{\text{absorbed water}}}{m_{\text{sample}}} \times 100\%, \text{ wherein } m_{\text{absorbed water}} \text{ is}$$

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

The adsorption capacity (A) of the samples under static conditions for condensed water vapor, benzene, n-heptane determined by method of complete saturation of the sorbent by adsorbate vapor in standard conditions at 20 °C [6] and calculated by the formula: $A=m/(M \cdot d)$, wherein m - mass of the adsorbed benzene (acetone, n-heptane), g; M - mass of the dried sample, g; d - density of the adsorbate, g/cm³.

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

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

Results and Discussion

LDPE (obtained by the method of HTS) powder particles' size, dispersity and surface properties study

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 amorphous-crystalline polymers, which are typical heterogeneous systems, well exposed to high-temperature shear grinding process. For example, the process of HTS of LDPE almost always achieves a significant results [3]. Disperse composition is the most important feature of powders, obtained as result of high-temperature shear milling. Previously, on the basis of the conventional microscopic measurement, it was believed that sizes of LDPE powder particles obtained by HTS are within 6-30 micrometers. Electron microscopy gives the sizes of 60 to 150 nm. The active powder has a fairly high specific surface area (up to 2.2 m²/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 cm³/g, respectively. Therefore, the surface properties of LDPE powder more developed than the other polyethylene materials'.

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 - thermobaric pressing at a pressure of 127 kPa.

The mixture of LDPE/CS compacted into tablets at a temperature of 115-145 °C 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, that's why the lowest pressing temperature (120 °C) 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], this may lead to the destruction of the tablets. 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 tablets 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, which 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, 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 a 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 = 120 °C and a pressure of 127 kPa.

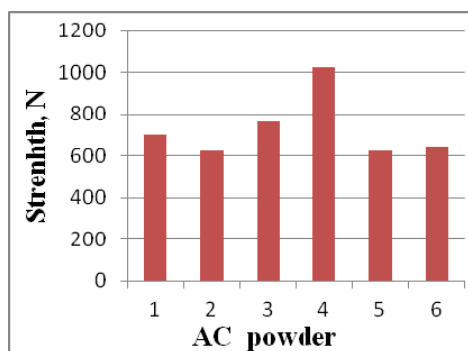


Fig. 1 - Comparison of strength of tablets, based on LDPE, CS (different species of wood) and AC powders. 1 – sorbent of LDPE/AC/CS = 20/50/30 wt. % based on the powders of jointly dispersed pellets of LDPE and softwood sawdust with subsequently addition of AC; 2 – sorbent of LDPE/AC/CS = 20/50/30 wt. % based on the powders of jointly dispersed pellets of LDPE and hardwood sawdust with subsequently addition of AC; 3 – 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; 4 – AC tablet; 5 – sorbent of LDPE/CS = 20/80 wt. %; 6 – sorbent of LDPE/AC = 20/80 wt. %

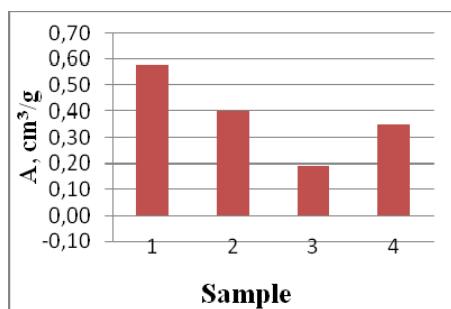


Fig. 2 - Static capacitance of sorbents, A (cm³/g) by benzene vapor (20°C): 1 – molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30wt. %; 2 - molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt. %; 3 - molded mechanical mixture of LDPE/AC/CS=20/50/30 wt. %; 4 – AC medical tablet (controlling)

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

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 appears 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 inferior 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.

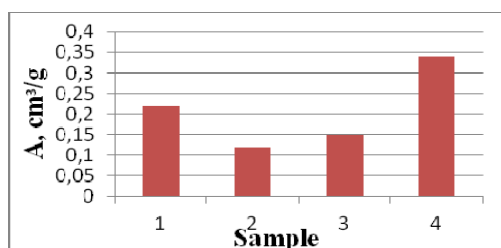


Fig. 3 - Static capacitance of sorbents, A (cm³/g) by n-heptane vapor (20 °C). – molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30wt. %; 2 - molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt. %; 3 - molded mechanical mixture of PE/AC/CS=20/50/30 wt. %; 4 – AC medical tablet (controlling)

Molded composite based on a mechanical mixture of PENP/AC/NC1/CS = 20/25/25/30 wt. % has a sorption capacity by acetone vapor comparable with the capacity of activated carbon (0.36 cm³/g) (Fig. 4).

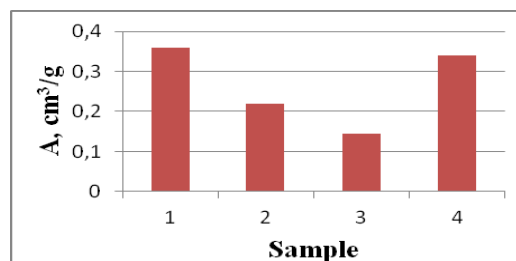


Fig. 4 - Static capacitance of sorbents, A (cm³/g) acetone vapor (20°C): 1 – molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30wt. %; 2 - molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt. %; 3 - molded mechanical mixture of LDPE/AC/CS=20/50/30 wt. %; 4 – AC medical tablet (controlling)

Sorbents' samples containing NC2 have a 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) shows that the minimal residual benzene content after its desorption from the pores at $t = 70$ °C for 120 minutes 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.

Table 1 - Sorbents' characteristics: total pore volume V_{tot} ; static capacitance (A) by benzene vapors at the sorption time of 2 days; residual wt. fraction of the absorbed benzene after drying at $t=70$ °C 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/ - / -	1,6	0,3523	32,0

Thus, the usage of nanosized LDPE as a binder gives a possibility to get the molded composite materials with acceptable absorption properties. 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. These facts allow to suggest that the proposed composites are expedient to use for separation and purification of gaseous and steam mixtures of different nature.

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.

Conclusions

1. It is revealed by electron microscopy that the dispersed LDPE particle sizes are 60-150 nm. It allows to obtain functional composite materials with a regular distribution of components and with the necessary physico-chemical properties, depending on their volume content, on its base.

2. Optimal conditions for molding of sorbents on the basis of three- and four-component mixtures of powdered LDPE, cellulose and ultrafine carbon materials were determined: temperature 120 °C and pressure of 127 kPa, content of the binder (LDPE) = 20 wt. %.

3. Established that molded mechanical mixture of LDPE/AC/NC1/CS (20/25/25/30wt. %) has a static capacity (by condensed vapors of benzene and acetone) = 0.6 cm³/g and 0.36 cm³/g respectively, what exceeds the capacity of activated carbon. The static capacitance of the compositions by the n-heptane vapors is 0.21 cm³/g, therefore, the proposed composites are useful for separation and purification of gaseous and steam mixtures of different nature.

Literature

1. E.F. Akbasheva, M.V. Bazunova. Tableted sorbents based on cellulose powder mixtures, polyethylene and ultra-dispersed carbon. *Materials Open School Conference of the CIS "Ultrafine and Nanostructured Materials" (11-15 october 2010)*, Ufa: Bashkir State University, p.106. (2010)
2. N.S. Enikolopyan, M.L.Fridman, A.Yu.Karmilov. Elastic-deformation grinding of thermo-plastic polymers. *Reports AS USSR*, 296, №1, pp. 134-138. (1987)
3. R.M. Akhmetkhanov, K.S. Minsker, G.E. Zaikov. On the mechanism of fine dispersion of polymer products at elastic deformation effects. *Plasticheskie Massy*, №8, pp.6-9. (2006).
4. V.B. Aleskovskiy, K.B. Galitseisky. Russian patent "Method of Ultrafine Carbon" № 2287543 from 20.11.2006.
5. LN Raspopov, LN Russiyan, YI Zlobinsky. Waterproof composites comprising wood and polyethylene dispersion. *Russian Polymer Science Journal*. 2007. 50, №3. pp. 547-552.
6. N.V. Keltsev. *Fundamentals of adsorption technology*. Moscow: Chemistry, 1984, 595 p.
7. E.R. Valinurova, A.D. Kadyrov, F.H. Kudasheva. Adsorption properties of carbon rayon// *Vestn. Bashkirs. Univer.*, V. 13, № 4. pp. 907-910 (2008).

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