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SPECIAL TECHNOLOGICAL SOLUTIONS

Synthesis of Hydrophobic Aerogel Heat Insulation Materials Based on Polyvinyl Alcohol/Carbon Black Composite

O. A. Kokhanovskaya* and V. A. Likholobov

Institute of Hydrocarbons Processing, Siberian Branch, Russian Academy of Sciences,
ul. Neftezavodskaya 54, Omsk, 644040 Russia
**e-mail: kokolga@yandex.ru*

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Abstract—Modification of the composition of polyvinyl alcohol/carbon black aerogel composite materials was performed to make them hydrophobic. The physicochemical properties of the matrices obtained, including their thermal conductivity and resistance to aggressive media and water, were studied. Materials with the moisture capacity decreased by up to 96%, exhibiting resistance to aggressive organic media and high heat insulation properties, were obtained.

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Aerogel carbon composite materials (ACMs) are a new class of low-density carbon materials containing simultaneously a matrix polymer (in many cases, polyvinyl alcohol, PVAl [1–5]) and a solid carbon filler (carbon nanotubes [1], graphene oxide [2], carbon black [6], etc.). A study of the physicochemical properties of such systems demonstrated good prospects for their use as heat insulators [6, 7] instead of traditional materials such as foamed polystyrene, mineral wool, foamed polyurethane, foamed plastic, etc. Aerogel matrices are free of many drawbacks of traditional heat insulators. Namely, they are capable of operating at considerably higher temperatures, resistant to the majority of aggressive media, nontoxic, and resistant to degradation under the action of other external factors.

As we demonstrated previously [7], ACM that we prepared from PVAl and carbon black shows promise as a heat insulator. However, high hydrophilicity of this material does not allow its use under the conditions of high humidity.

This study was aimed at modification of the previously developed ACM to eliminate this drawback and make the aerogel matrices hydrophobic, so as to make them suitable for use as heat insulators in humid media.

EXPERIMENTAL

As investigation objects we chose polyvinyl alcohol/carbon black aerogel composite materials. Polyvinyl alcohol of Sandiol 1399M grade (MM = 75 000) was used as a matrix polymer. Highly dispersed carbon black of P 399-E grade, prepared in an experimental reactor of the Institute of Hydrocarbon Processing Problems, Siberian Branch, Russian Academy of Sciences in accordance with TU (Technical Specification) 38 41582–86, with the specific surface area of 716 (NSA) or 500 $m^2 g^{-1}$ (STSA), bulk density of 0.22 $g cm^{-3}$, and pH 7.22 served as hydrophobized carbon filler. To obtain the hydrophilized carbon filler, P 399-E carbon black was oxidized according to [8] in a hydrogen peroxide/ozone medium until pH of the aqueous suspension decreased to 4.22. 136–157M methylhydrosiloxane polymer served as a hydrophobic modifier.

PVAl/carbon black ACM samples were prepared by the cryogenic procedure under the conditions of gas saturation [7, 8] in several steps: introducing the carbon component in the form of an aqueous suspension into polyvinyl alcohol hydrogel, foaming the matrix using a glass frit, freezing the matrix, keeping it in the frozen state, thawing, and drying under normal pressure at a temperature no higher than 60°C.

The hydrophobic modifier was introduced either by adding aqueous emulsion in the step of preparing the composite polyvinyl alcohol hydrogel or by impregnating with it the ready ACM.

The bulk density ρ (g cm^{-3}) was calculated as the ratio of the sample weight to its volume.

The relative hydrophilicity Z (%) of ACM was calculated using the formula

$$Z = \frac{M_1}{M_{\mathrm{ACM}}} \times 100\%,$$

where M_1 is the moisture capacity of the modified sample, and M_{ACM} is that of the initial ACM (hydrophilic).

The moisture capacity was determined gravimetrically as the weight difference between the sample saturated with water for 1 h and the dried sample.

The chemical resistance of ACM to aggressive media was evaluated by the ACM weight change (%) after 24-h contact with aggressive liquid. The materials whose weight loss did not exceed 2% were considered as stable (S); those with the weight change in the interval 2–15%, as relatively stable (R); and those with the weight change exceeding 15%, as unstable (U) [9].

The mean thermal conductivity coefficient λ (W m^{-1} K^{-1}) of ACM was determined with an ITEM-1 device as the mean result of no less than three replicate determinations.

RESULTS AND DISCUSSION

We tested three main methods for decreasing the hydrophilicity of aerogel-type materials: (1) introduction of hydrophobic carbon filler in the course of ACM synthesis, (2) introduction of hydrophobic emulsion in the course of ACM synthesis, and (3) treatment of ready ACM with a hydrophobic liquid.

In the first method, we introduced hydrophobized P 399-E carbon black in the course of ACM synthesis in the step of preparation of its precursor (composite hydrogel) in the form of a 0.1–2 wt % suspension. The time for preparing a stable suspension of hydrophobized P 399-E carbon black increased by a factor of 2 relative to the time for preparing a suspension of hydrophilized P 399-E carbon black of similar concentration.

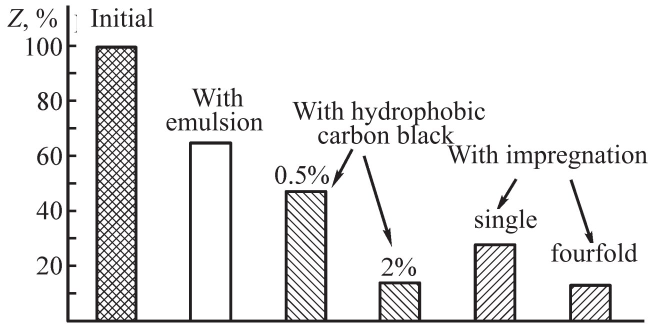

Fig. 1. Relative hydrophilicity Z of ACM samples.

In the second method, we introduced a hydrophobic 25% emulsion of methylhydrosiloxane polymer in water in the course of ACM synthesis in the step of preparation of its precursor (composite hydrogel). The emulsion concentration was 2 mg per square meter of the surface area of carbon black filling the composite hydrogel. Higher concentrations of the emulsion in ACM are undesirable, because they prevent the subsequent foaming of this ACM precursor.

In the third method, we impregnated ACM by immersing its sample into a hydrophobic liquid (methylhydrosiloxane polymer), keeping in it at 22 ± 2°C for 30 min, and drying to constant weight. One to four impregnations of the ACM samples were performed.

The moisture capacity of the modified materials appreciably decreased relative to the unmodified ACM. The results of calculating the relative hydrophilicity of ACM are shown in Fig. 1.

The most pronounced increase in the hydrophobicity of the aerogel materials (Fig. 1) was reached after multiple impregnation of the ready ACM with methylhydrosiloxane polymer or after introduction of hydrophobized carbon black in the step of the ACM synthesis. In both cases, the moisture capacity of the materials does not exceed 14% of that of the initial ACM. However, the density of ACM hydrophobized by impregnation is no less than 0.37 g cm^{-3}, and the density of ACM with the hydrophobized filler does not exceed 0.3 g cm^{-3}.

Combination of two methods, namely, introduction of 2% hydrophobized P 399-E carbon black into the structure and subsequent impregnation of the ready material with methylhydrosiloxane polymer, ensured the maximum possible hydrophobicity of ACM (the moisture capacity decreased by 96% relative to that of ACM filled with hydrophilized carbon black, Fig. 2), but the density

Table 1. Chemical resistance of heat insulators to aggressive media[a]

Aggressive medium	Foamed polyurethane [9]	Mineral wool [9]	ACM
Benzene, toluene, xylene, gasoline, kerosene	S	S	S
Methylene chloride, carbon tetrachloride	R	S	S
Alcohol, acetone, styrene, ethyl acetate	R	S	S
Concentrated hydrochloric acid	R	U	U
Concentrated nitric acid	U	U	U
Concentrated sulfuric acid	U	U	R
Dilute acids and alcohols	S	S	S
Water	S	U	R

[a] (R) Relatively stable, (S) stable, and (U) unstable.

Table 2. Properties of different heat insulators

Material	Thermal conductivity coefficient λ, W m^{-1} K^{-1}	Bulk density, g cm^{-3}
ACM PVAl/0.1% hydrophilized P 399-E carbon black	0.040	0.23
ACM PVAl/2% hydrophobized P 399-E carbon black	0.050	0.30
ACM PVAl/2% hydrophobized P 399-E carbon black + single impregnation with methylhydrosiloxane polymer	0.083	0.40
ACM PVAl/0.1% hydrophilized P 399-E carbon black + four impregnations with methylhydrosiloxane polymer	0.076	0.37
Foamed polyurethane	0.020–0.041	0.03–0.15
Mineral wool	0.038–0.120	0.05–0.15

of such material was no less than 0.4 g cm^{-3}. Further increase in the number of impregnations and carbon black concentration does not make the material significantly more hydrophobic.

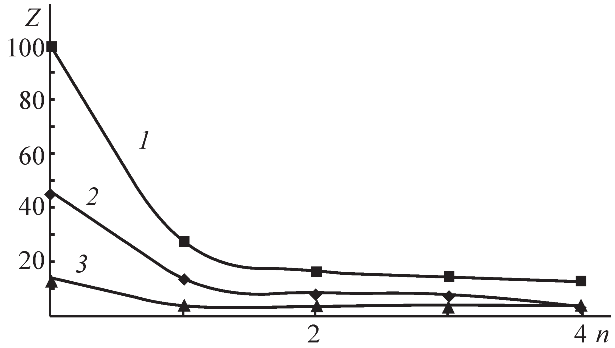

Fig. 2. Relative hydrophilicity Z of ACM samples as a function of the number n of impregnations with methylhydrosiloxane polymer. Concentration of hydrophobic carbon black, %: (*1*) 0.1, (*2*) 0.5, and (*3*) 2.0.

Data on the chemical resistance of ACM and other heat insulators in aggressive media are given in Table 1.

The ACM samples are stable in benzene, toluene, ethanol, carbon tetrachloride, toluene, and acetone. They dissolve in concentrated nitric can hydrochloric acids and swell in sulfuric acid. On the whole, the ACM samples are comparable in the resistance to aggressive media with foamed polyurethane and mineral wool.

The thermal conductivity coefficients of the modified ACM samples were below 0.1 W m^{-1} K^{-1} (Table 2), which confirms high heat insulation properties of the systems.

CONCLUSION

A series of low-density samples of aerogel materials with increased hydrophobicity and low thermal conductivity coefficients, resistant to aggressive media, were synthesized. The samples of the modified composite materials can be recommended for tests in ready items as heat-insulating materials contacting with aggressive media and/or water.

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