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BRIEF COMMUNICATIONS

Effect of the Modification of Aluminosilicate Ash Microsphere Surfaces on Physical-Mechanical Properties of Polyurethane Foam

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Abstract—The rigid polyurethane foam materials based on ODF-M complex oligoester filled by hollow silica-alumina microspheres with various surface nature were studied. Physical-mechanical properties of the obtained materials were studied.

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At present aluminosilicate ash microspheres (AM) taken from the ash-ablation formed upon coal combustion at heat power plants gain ever-growing use as filling agents of various polymers.

The effect of aluminosilicate ash microspheres on physical-mechanical properties of filled polyurethane foam (PUF) obtained on the basis of a polyether was studied earlier [1]. It was shown that the inclusion of AM results in increasing viscosity of the filled composition and in changing its strength properties. Therewith the thermal conductivity coefficient of the filled material remains unchanged.

To prepare polyurethane foams, polyols based on both polyethers and complex oligoesters are used. Thus it is known that the nature of a polyester exerts a crucial effect on the strength properties of PUF compositions [2]. The main physical-mechanical characteristics: strength, thermal conduction, and water adsorption of PUF compositions based on complex oligoesters are lower than those of the compositions based on polyethers. In this connection development engineers of products are facing an important problem to create materials based on complex oligoesters and possessing a high level of operational properties due to the inclusion of active filling agents.

EXPERIMENTAL

The aim of this work was to study an opportunity of using AM as a filling agent for rigid PUF material based on complex oligoesters ODF-M (technical specifications 2226-003-58646534-2006). Hollow unfractionated AM (technical specifications 14.2-25595170-001-2003) with particle size from 60 up to 300 μm and bulk weight of 0.40–0.68 g cm^3 were used in the work.

It is known that microspheres are modified by various finishing agents to provide a strong adhesion between a filling agent and a polymeric matrix [3].

Copolymers of derivatives of (meth)acrylic acid (sodium salt, amide, and methyl ether) of various molecular weight, and also silane derivatives such as γ-aminopropylethoxysilane (AGM-9) were used in the present work as modificators of AM surfaces [4]. The kinematic viscosity of 1% solutions of copolymers was determined according to GOST 18249. The kinematic viscosity of the low-molecular (LM) copolymer is 20 cP and that of the high-molecular (HM) copolymer, 200 cP. Ash microspheres were treated on a rotor evaporator at the degree of depositing a finishing agent of about 1% of the AM weight.

Table 1. Kinetic foaming parameters of the PUF system

Filling agent content, wt %	Time, s		
	Start	Gel formation	Foam rise
0	70	200	240
5	70	200	240
10	72	205	240
15	74	210	245
20	80	215	250
25	85	220	250
30	90	225	260

Table 2. Parameters of water adsorption by the PUF material filled by AM with various surface nature

Filling agent content, wt %	Water adsorption, %			
	Untreated AMs	Treated AMs		
		LM	HM	AGM-9
0	22.0	–	–	–
5	30.1	25.1	23.6	22.5
10	31.2	28.8	25.1	24.7
15	33.4	33.4	27.4	28.6
20	36.6	36.3	29.5	31.6
25	43.0	38.0	30.3	34.2
30	46.0	38.9	32.9	35.1

Composition PUF materials were obtained by the free foaming method. The filling agent, ash microspheres, were included into component A at room temperature. As component B 4,4-diphenylmethanediizocyanate (MDI) of BASF production was used.

The kinetic parameters of foaming (times of start, gel formation, and foam rise) were controlled by a stop watch. It is seen from Table 1 that before filling agent inclusion (up to 20 wt %) the kinetic parameters of foaming changed only slightly, and when 30 wt % of AM was added the start time has increased by 28 and the gel formation time by 15%. The foam rise time remained practically unchanged.

Thermal conduction λ (W m^{-1} K^{-1}) was determined by measuring density of a stationary heat flux at a monotonous mode of heating on an ITP-MG4 device according to the service manual [4].

The coefficient of thermal conductivity of samples with various AM contents has not changed, as the thermal conduction of the material is caused by the content of closed pores.

Mechanical characteristics were determined on a Zwick tension testing machine. The rate of squeezing was 50 mm min^{-1}, the measurements were carried out up to the 20% strain. Samples did not fall to pieces and collapse upon the trials. The strain arising at a sampled deformation was recorded automatically.

Moisture absorption was determined by the gravimetrical method: weighted samples (50 × 50 × 50 mm) placed on a lattice of a desiccator filled up to a certain level by water was exposed for 24 h. Then the samples were weighed and the moisture absorption B (%) was calculated by the formula

$$B = \frac{m(\tau) - m(0)}{m(0)} \times 100,$$

where $m(0)$ is the average weight of samples before trials (g), $m(\tau)$ is the average weight of samples after 24 h (g).

Water adsorption was determined analogously, but at complete plunging of samples in water for 24 h (Table 2).

It is seen that the water adsorption of the PUF material is doubled on loading 30 wt % of the initial AM as a filling agent, and it increases by time and half at the same content of the initial AM modified by a BM copolymer. The water adsorption reduction is caused by the fact that the polymer on the AM surface is solvated and swells, thus reducing water intrusion inside the sample. It is caused not only by the ability of the AM surface to be moistened by water, but also by the physicochemical properties of the complex oligoester, one of the PUF components of the system [5].

The moisture absorption plotted against contents of AM with various surface nature is presented in Fig. 1. It is seen that the moisture absorption of the compositions changes antibately to the concentration of the filling agent. Due to adsorption of water vapor by a copolymer, diffusion of a liquid in a sample volume stops in a surface layer.

Table 3. Physical-mechanical parameters of filled PUF material

Filling agent content, wt %	Bending strength, MPa			
	Untreated AMs	Treated AMs		
		LM	HM	AGM-9
0	12.10	–	–	–
5	6.27	11.10	10.15	11.82
10	8.12	9.85	9.20	11.45
15	8.76	9.15	9.20	10.95
20	8.80	8.46	9.55	10.46
25	8.90	8.23	10.85	10.15
30	9.05	8.10	12.65	9.85

When 30 wt % of the initial AM is added the moisture absorption of the PUF material is halved, and when AM modified by finishing agent AGM-9 is used it decreases by the factor 7.

The bursting bending stresses are presented in Table 3. It is seen that when 5 wt % of untreated AM is used as a filling agent the bending strength is halved, however the further increase in its content results in the 30% decrease of the material strength as compared to unfilled PUF.

The modification of the AM surface also reduces bending strength, but not so sharp, as on using untreated AM.

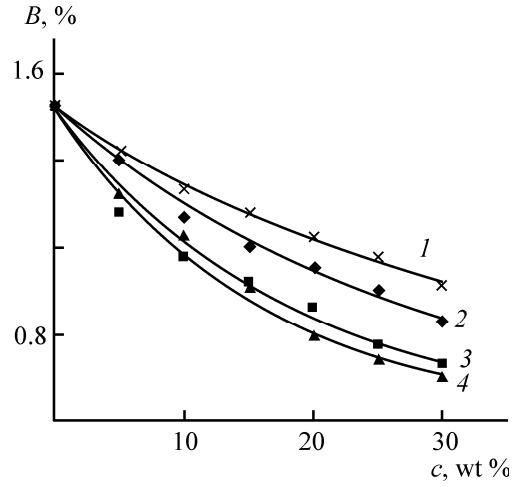

Fig. 1. Dependence of moisture absorption B (%) of PUF material on the content c (wt %) of AM with various surface nature. (*1*) untreated AM; modificator: (*2*) BM copolymer, (*3*) LM copolymer, and (*4*) AGM-9; the same for Fig. 2.

The dependences of the bursting compressive strength for PUF compositions with various filler contents are presented in Fig. 2.

It is seen that the inclusion of 15 wt % of untreated AM as a filling agent increases the strength of the material by 40% (curve *1*), whereas the further increase in the AM content reduces the strength, which probably is caused by a destruction of the PUF polymeric matrix. When modified AM are used the strength increases and the compressive stress does not decrease as in the case of using the initial AM. The treatment allows the filler content in a polymetric compound to be increased without reduction of strength parameters.

CONCLUSIONS

(1) The inclusion of aluminosilicate ash microspheres with various surface natures in polyurethane foam based on a complex oligoester results in the enhancement of physical-mechanical and operating characteristics of the polyurethane foam material.

(2) At the 30 wt % content of aluminosilicate ash microspheres modified by AGM-9 finishing agent, the moisture absorption of the material decreases by the factor of three compared to polyurethane foam containing the same quantity of initial ash microspheres.

(3) The modification of the surface of ash microspheres allows the filler level to be increased up to 30 wt % of the polyurethane foam composition

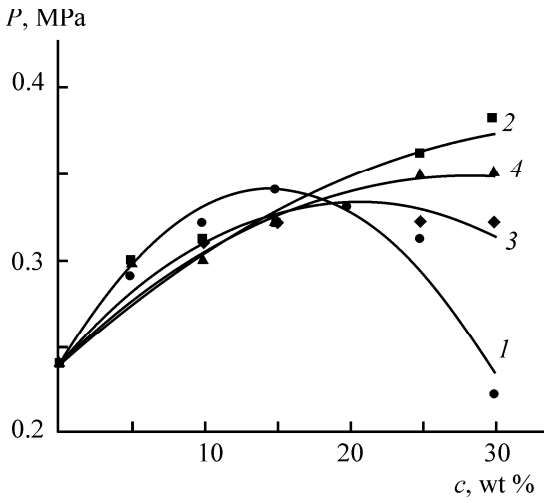

Fig. 2. Dependence of compressive strength P (MPa) at 10% deformation of the PUF material filled by AM with various surface nature; c is filler content (wt %).

without deterioration of its physical-mechanical properties.

(4) It was shown that the modification of the surface of ash microspheres by copolymers of derivatives of (meth)acrylic acid and γ-aminopropylethoxysilane allows bending strength of polyurethane foam compositions to be increased as compared to the material filled with untreated ash microspheres.

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