

Thermal analysis of composite thermal insulation materials based on inorganic polymers

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Thermogravimetric, differential thermal and differential thermogravimetric analyses of liquid-glass compositions intended for the manufacture of thermal insulation materials, as well as the materials themselves, manufactured under the influence of microwave radiation and convective heating, were carried out. It is shown that the composite materials obtained under the influence of microwave radiation in the presence of zinc oxide and semi-aqueous gypsum modifiers for coagulation and crystallization processes are almost dehydrated. Small mass losses observed in the temperature range of 200-430°C indicate the presence of only bound water in the samples. Hydration water from microwave-heated samples begins to be removed at a higher temperature than from convective-heated samples. These temperatures are 655 and 600°C, respectively, which makes it possible to increase the operating temperature of microwave-heated materials to 650°C; in addition, at high temperatures (200-600°C), the strength of these materials increases.

Keywords: thermal insulation materials, liquid-glass compositions, modifiers of coagulation and crystallization processes, microwave radiation, convective heating, thermogravimetric, differential thermal and differential thermogravimetric analyses.

Термічний аналіз композиційних теплоізоляційних матеріалів на основі неорганічних полімерів. Т. Е. Рymar

Проведені термогравіметричний, диференційно-термічний і диференційно-термогравіметричний аналізи рідинноскляних композицій, призначених для виготовлення теплоізоляційних матеріалів, а також самих матеріалів, виготовлених під дією НВЧ випромінювання та при конвективному нагріві. Показано, що композиційні матеріали, які отримані під дією НВЧ випромінювання у присутності модифікаторів коагуляційно-кристалізаційних процесів оксиду цинку та напівводного гіпсу, майже зневоднені, оскільки невеликі втрати маси в них спостерігаються в інтервалі температур 200-430°C, що говорить про наявність в зразках тільки зв'язаної води. Гідратна вода з зразків, отриманих під дією НВЧ випромінювання починає видалятися за більш високої температури, ніж із зразків, отриманих при конвективному нагріві, 655 і 600 °С відповідно, що дозволяє підвищити температуру експлуатації матеріалів, отриманих під дією НВЧ випромінювання до 650°C, причому за високих температур (200-600 °С) відбувається підвищення міцності даних матеріалів.

1. Introduction

The use of thermal insulation products based on expanded liquid glass (LG) in comparison with currently used thermal insulation systems provides a significant economic effect due

to increased durability, non-flammability, and environmental friendliness of production and operation. According to a set of criteria – technical, environmental, and economic – thermal insulators based on granular liquid glass and

composite thermal insulation products based on it are effective, which makes it advisable to develop their production. Many scientists have studied the processes of obtaining liquid-glass thermal insulation materials (TIM) and modifying their properties [1-3], whose research has made it possible to improve the performance characteristics of these materials by introducing various fillers and chemical additives. In [4-7], processes of obtaining such materials by modifying them with aluminum-containing compounds to obtain so-called geopolymer foams were investigated. They allow for targeted regulation of structure formation processes in the liquid-glass matrix and the production of thermal insulation materials with improved properties.

The thermal insulation materials considered in this paper are manufactured under the influence of microwave radiation. The advantages of this technology are the homogeneous fine-pored structure of materials based on liquid glass and improved physical and mechanical properties at lower temperatures, as well as a reduction in the duration of their production due to the modification of the liquid glass matrix by microwave radiation [8-10].

In the production of thermal insulation materials based on liquid glass and compositions with it, mandatory stages are drying and thermal dehydration. The chemical mechanism of dehydration of liquid glasses is studied by IR spectroscopy. For example, the authors of [11] studied the IR spectra of thin films of Li, Na, and K silicates (modulus 3.5÷3.8) during their drying at 200-270 °C and found three stages of water separation: below 430 K (removal of water molecules tightly bound to polyions by hydrogen bonds), 430-480 K, and above 480 K (removal of silanol water during polycondensation and resynthesis of siloxane bonds, respectively). In this work, water-containing sodium-silicate glasses with a modulus of 2.7 were studied. At a content above 3% (which corresponds to heat treatment at 300°C), water is found mainly in the form of molecules linked by hydrogen bonds to one oxygen atom; and below 3%, water is found mainly in the form of molecules linked to two non-bridging oxygen atoms. In [12] it was shown that during the heat treatment of sodium hydrosilicates with a modulus of 3, the main part of free and adsorption water is removed in the temperature range of 130-150°C. When using liquid-glass materials with a modulus of 2.5÷3 with a complex of fillers and

additives, the temperature treatment interval is extended and amounts to 120÷350°C according to [13].

The aim of this work is to study the behavior of liquid-glass compositions intended for the manufacture of thermal insulation materials, as well as the materials at elevated temperatures during their manufacture under the influence of microwave radiation and convective heating.

2. Experimental

To achieve this goal, the following analyses were carried out: thermogravimetric (TG), differential thermal (DT) and differential thermogravimetric (DTG) analyses, which allow determining the level of softening and dehydration temperatures of LGC, water mass loss during heating and swelling of hydrogels, thermal stability of hydrogels and dehydrated swollen glasses. Thermogravimetric, differential thermal and differential thermogravimetric analyzes were performed in a dynamic mode at a heating rate of 7.5°C/min in an air atmosphere on a derivatograph Q-1500 D of the F. Paulik - J. Paulik - L. Erdey".

3. Results and Discussion

The liquid-glass composition used for the manufacture of composite thermal insulation materials contains: sodium liquid glass as the main component, hydrogen peroxide as a gas-forming component, oxyethylated alkylphenol (OP-10) as a foam stabilizer, and zinc oxide and semi-aqueous gypsum as modifiers of coagulation and crystallization processes. Non-swelling granules based on LG and zinc oxide are used as granular fillers.

Liquid glass for building purposes with a silicate modulus of 2.7÷3.3 and an average density of 1.36÷1.5 g/cm³ was chosen, in which the mass fraction of silicon dioxide is 24.8÷36.7%, since concentrated aqueous solutions sodium silicates with a modulus higher than 2 contain, in addition to oligomers, silica with a high degree of polymerization and a high degree of cohesion. The addition of ZnO helps to slow down the gelation of LGC, thus requiring more time to reach equilibrium, and provides optimal viscosity of the suspension for further porization. The hardening modifier for the liquid-glass composition CaSO₄·0.5H₂O provides the formation of new structures (CaSiO₃), which contribute to the formation of heterogeneous structure of thermal insulation materials with increased

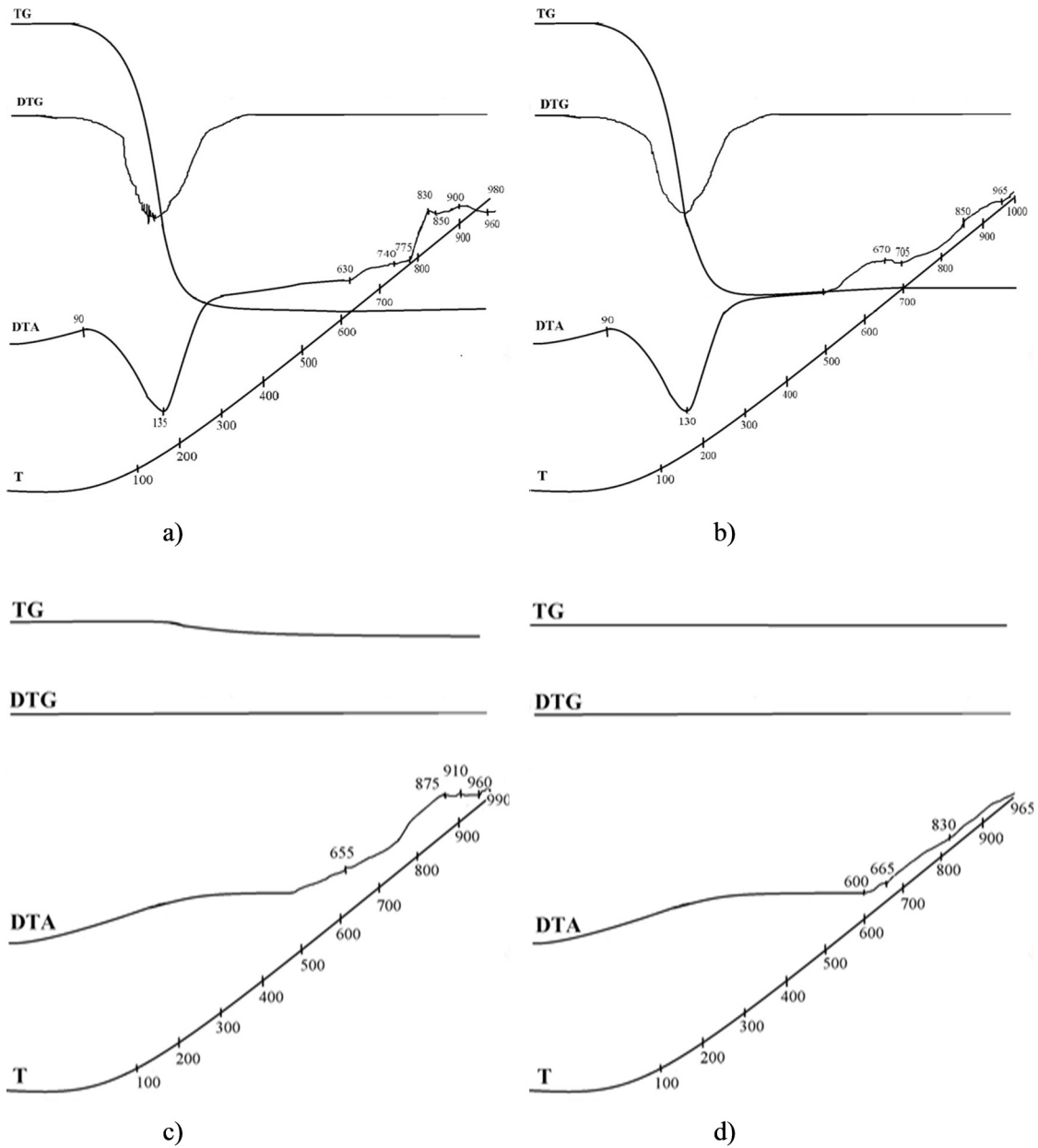


Fig. 1. The derivatograms of composite thermal insulation materials and starting substances: a) liquid glass, b) liquid glass with of modifiers ZnO + CaSO₄·0.5H₂O, c) composite thermal insulation materials obtained under the influence of microwave radiation (power 650 W, T=100-120 °C), d) composite thermal insulation materials obtained by convective heating (T= 500 °C)

strength and water resistance under the action of microwave radiation [9].

The thermal insulation materials were manufactured according to the technology described in [10]. The derivatograms of the samples are shown in Fig. 1.

According to [14], the following types of water are present in the composition of the LGC: free water (contained in cavities, voids and on the surface and quickly removed first); adsorption water (firmly retained by intermolecular

forces on the surface of pores in the form of a monolayer or several layers; its removal is associated with its transformation into steam inside the material); bound water (it is most difficult to remove only by evaporation at temperatures above 100-120°C; it has the highest binding energy with the material).

The process of pore formation of filled LGC was discussed in the work [15]. It consists of three main stages, the duration and nature of which depends on the type and amount of

moisture contained in the material. At the first stage, the material is heated to temperatures of 100–120 °C, when the initial solid material partially turns into a pseudopyroplastic state and begins to deform with volume. The second stage at temperatures of 130 - 150 °C is characterized by intensive release of free and adsorption water and intensive pore formation in the material. At the third stage, at a temperature above 150 °C, the bound water is removed, the residual structure is restructured, and the ongoing physical and chemical processes are completed. When forming the products with maximum structural homogeneity, the greatest contribution is made by crystallization water, which begins to be removed at temperatures above 150 °C. Removing excess adsorption water at the initial stages leads to the formation of large through pores and channels. Therefore, the initial liquid glass composition should contain a minimum amount of free and adsorption water. The amount of free water can be reduced by direct thermal drying and by converting liquid glass into xerogel by liquid granulation of soluble silicate in solutions of calcium, aluminum, magnesium chlorides or their mixtures (with subsequent drying) or by introduction of mineral fillers or chemical additives into liquid glass, causing the development of the gelation process and the conversion of the liquid initial mixture into a solid substance, which is granulated in screw granulators.

In the production of the TIM considered in this work, all three methods were used, namely: the introduction of modifying additives into the composition of LGC, which contribute to the slow gelation of LG; obtaining granules by coagulation of LG in a calcium chloride solution; preliminary drying of granules, before swelling, to a residual moisture content of ~50%, which ensured uniform porosity of the material and the formation of a homogeneous and predominantly closed-porous structure.

From the data in Fig. 1 (a, b) it is evident that for pure liquid glass, an intense mass loss occurs in the temperature range of 30 - 365 °C and amounts to 21.67 % (1.5 g sample, mass loss 325 mg). When the modifiers ZnO + CaSO₄ · 0.5H₂O are introduced into the composition, i.e., with an increase in the amount of the solid phase, the mass loss increases to 26.8 % (1.1 g weight, 295 mg mass loss); this confirms the conclusion that with an increase in the solid component in the LGC, its swelling ability increases, and the temperature range of intense

water release expands to 20-480 °C. In this range, free and adsorption water is released, and intensive swelling of the LGC (according to the thermogram) begins at a temperature of about 300 °C.

Such data are consistent with the literature. For example, the study of coagulated LGC [16] showed that at a temperature of 120°C, the loss of adsorbed water mass is 14.5 %, but water does not participate in swelling. The swelling process occurs at a temperature of 320 °C and above. In this temperature range, water is removed from the shells. This process is most intense (from 13.3 % water weight loss) at a temperature of 560 °C. The total weight loss of the sample was 28.7 % at a temperature of 970 °C.

The authors of [17] conducted a thermal analysis of dilute and undiluted LG solutions and found that the formation of sodium silicate occurs in three stages. Three endothermic effects were observed on the LG decomposition curve at temperatures of 80, 110, and 610 °C. At the first stage, the adsorption water that is part of the outer coordination sphere evaporates. At the second stage, intensive removal of crystallization water, which is part of the inner coordination sphere, occurred. At the third stage, at a higher temperature, hydrate water is released, thus, complete dehydration of sodium silicate occurs. When the LG is diluted, the adsorption water included in the outer and inner coordination spheres is removed without separation.

Similarly, it was shown in [3] that when liquid glass is heated, the mass loss is 52-55% due to the removal of free and adsorption water (temperature 115-120 °C), crystallization water (temperature 165-170 °C), and hydrated water (temperature 240-245 °C). In the temperature range of 600-650°C, dehydrated sodium silicate decomposes to form silica. Dehydration of liquid glass promotes low-temperature foaming of the mass and the formation of a highly porous structure. In addition, it has been shown that in the presence of sodium silicate hydrate additive, catalytic acceleration of mineral dissociation and formation of pyroplastic mass, as well as the emergence of new compounds is possible. The intensity of such thermal transformations is most likely for mixtures containing polymineral waste from ore enrichment.

In our studies (Fig. 1 a, b), no release of adsorption water was observed during heating. The release of hydrate water and complete dehydration of silicate is observed at temper-

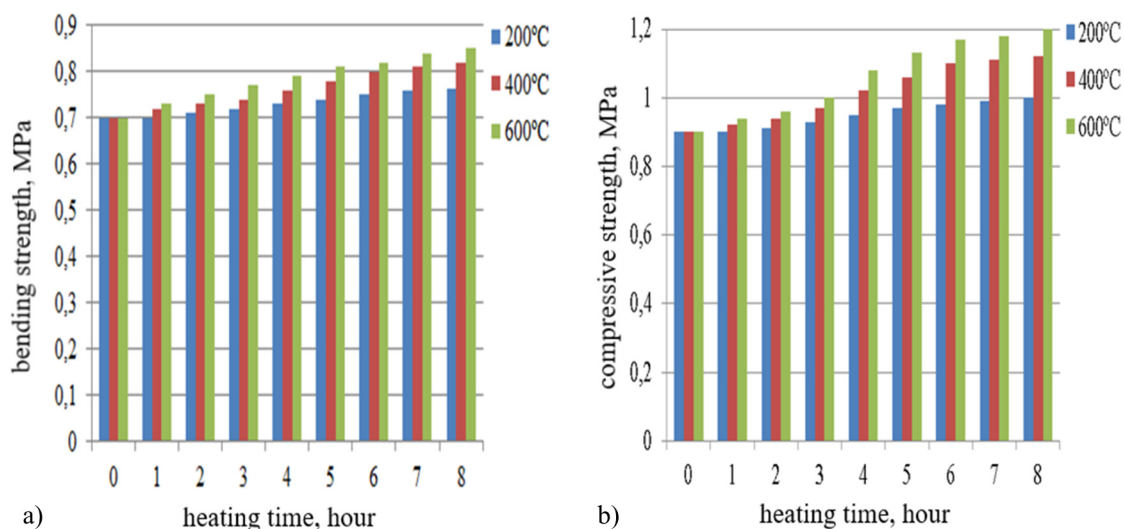


Fig.2. Strength of the composite TIM depending on temperature and heating time: a) bending, b) compressive

atures above 630°C in pure LG and 705°C in filled LG. Moreover, in the case of pure LG, a greater number of endothermic effects are observed, indicating the stage-based nature of the process, while in the case of filled LG, dehydration and crystallization of silicate proceeds faster. This is confirmed by the spectral studies of composite TIM samples obtained under microwave and convective heating [9]; it is shown that under microwave radiation, rapid coagulation and crystallization of liquid glass under the influence of semi-aqueous gypsum with the formation of CaSiO_3 (wollastonite) occurs. Also, a new crystalline phase of calcium silicate was identified under the influence of microwave radiation at temperatures of 110-120 °C, which is formed much less intensely under traditional convective heating, even at a temperature of 600°C. That is, under the influence of microwave radiation, complete rapid dehydration of LGC and the formation of wollastonite occur.

From the derivatograms of the TIM samples (Fig. 1 c, d), we can see that these materials are dehydrated. Thus, in the case of the material obtained by convective heating at a temperature of 500°C (process duration 1 hour), no mass loss is observed, but there is a slight increase in mass by 0.625 % (0.4 g sample, 2.5 mg mass gain) in the temperature range of 685-965°C; this is obviously due to the crystallization of the silicate. For the sample obtained under the influence of microwave radiation ($T \approx 120^\circ\text{C}$, duration 10 min), the mass loss is 1.42 % (weight 0.6 g, mass loss 8.52 mg), and the intensity of the loss is observed in the temperature range 200-430°C; this indi-

cates the presence of only bound water in the samples.

The endothermic effects on TIM derivatograms observed at high heating temperatures show that hydrated water from samples obtained under microwave radiation begins to be removed at a higher temperature (655°C) than from samples obtained by convective heating (600 °C). This allows the operating temperature to be increased to 650°C for materials obtained under the influence of microwave radiation. In addition, it should be noted that when using TIM at elevated temperatures (200-600°C), the strength increases by 15-20%, which is explained by the crystallization processes and the final structuring of LGC (Fig. 2).

During heat treatment of materials at elevated temperatures, thermal dehydration occurs, the internal stress and fragility of materials decreases. Thus, at temperatures of 200-400°C, silica-enriched crystalline structures appear in the LG matrix, and conditions are created for the development of further polymerization processes with the formation of crystals with a complex anionic composition up to quartz. A further increase in temperature to 400-600 °C leads to the consolidation of the liquid glass structure as a result of the crystallization of swelling products. With increasing temperature and duration of heat treatment, LG approaches the corresponding tempered glass in its structure (but does not completely equal it). But when the temperature rises above 800°C, decrystallization of the swollen structure of liquid glass occurs and a melt with needle-shaped and prismatic inclusions of so-

dium silicates is formed; and at 900-1000 °C, the crystalline phase completely disappears. Therefore, the operating temperature of these materials is limited to 600-650 °C.

Thus, the studies confirm the high efficiency of microwave radiation in the production of composite thermal insulation materials based on liquid glass.

4. Conclusions

The thermal studies have shown that composite thermal insulation based on LG, obtained under the influence of microwave radiation in the presence of coagulation and crystallization process modifiers – zinc oxide and semi-aqueous gypsum – are practically dehydrated. Small mass losses in the temperature range of 200-430 °C indicate the presence of only bound water in the samples. In the samples obtained under the influence of microwave radiation, hydrated water begins to be removed at a higher temperature (655°C), than for the samples obtained by convective heating (600°C); this makes it possible to increase the operating temperature of materials obtained under the influence of microwave radiation to 650°C; in addition, at high temperatures (200-600°C), the strength of these materials increases.

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