Study of shrinkage of heat storage materials for building envelope structures

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Abstract. The article presents the results of thermophysical properties developed by the authors of heat storage materials for building envelope structures. Based on the results obtained, the materials obtained by mixing individual n-alkanes are distinguished by stable thermo-physical characteristics. Results of shrinkage of the developed heat storage materials depending on the temperature during crystallization and expansion during melting. Several shrinkage peaks and two heat release peaks were determined during crystallization and phase transition, which explains that the shrinkage coefficient curves and heat release graphs do not coincide. This is due to the complexity of the chemical composition of commodity paraffin, which contains other groups of hydrocarbons along with n-alkanes. The dependence of shrinkage of heat storage materials on temperature is obtained and their shrinkage coefficients from temperature are analyzed. Developed heat storage materials with a melting point of 25°C provide energy savings by increasing the heat capacity of building envelope structures and can be used in the design of energy-efficient buildings.

One of the promising methods of heat energy storage is the use of phase transition materials. To ensure the long-term functioning of the accumulated energy, comprehensive knowledge of the nature of melting and freezing of substances that accumulate heat of melting, their reproducibility as a result of repeated melting and freezing of these substances is necessary. Great attention is paid to the operation of the heat storage material in heat accumulators by the shrinkage property.

Commodity paraffins in the crystallized state are a solid mass and its volume increases when they fill the heat accumulators of various heat storage devices with subsequent melting of paraffin. [1-2]. Different expansion of the heat storage material may cause an increase in pressure in the hermetic heat accumulator. It is known that the pressure increases in the heat accumulator with heat storage materials based on commodity paraffins can reach from 10 up to 50 MPa [3-4]. But it should also be noted that an increase in pressure in a heat storage device or apparatus causes an increase in the melting temperature of heat storage materials by several degrees [5,6]. In this regard, when choosing a heat storage material for heat accumulators and evaluating the pressure that develops during filling in the solid state and subsequent melting of the material, it is necessary to evaluate the shrinkage and expansion of the heat storage material during operation.
According to the research methodology, changes in the volume and shrinkage of individual n-alkanes and developed heat storage materials HSM-25-1 and HSM-25-2 were determined and analyzed at the first stage. The shrinkage of individual n-alkanes and paraffin mixtures was determined in a glass dilatometer using the method described in the report [7].

Graphs of the dependence of changes in the volume of individual n-alkanes and HSM-25-1, HSM-25-2 on temperature are presented in accordance with figure 1.

Even individual n-alkanes C\textsubscript{16}H\textsubscript{34} and C\textsubscript{18}H\textsubscript{38} first crystallize into crystals of the hexagonal symmetry group, and then turn into crystals of the stable rhombic symmetry group during the phase transition in the crystalline state. Their total shrinkage was 14.1% and 15.2% of the volume.

![Figure 1. Graphs of the dependence of changes in the volume of n-alkanes and HSM-25 from the temperature.](image1)

Crystallization of odd individual n-alkanes C\textsubscript{17}H\textsubscript{36} and C\textsubscript{19}H\textsubscript{40} occurs in two stages. At the first stage, crystals of an unstable high-temperature hexagonal symmetry group are formed. In the second stage, when cooled, they undergo a phase transition in the crystal state, forming crystals of a stable low-temperature rhombic symmetry group. The total shrinkage during crystallization and phase transition was 13.8... 14.4% of the volume. It should be noted that in this case, during the phase transition for odd n-alkanes, the shrinkage was 21.2-22.4% of the total shrinkage.

![Figure 2. Graphs of the dependence of the shrinkage coefficient of individual n-alkanes and HSM-25-1/HSM-25-2 from the temperature.](image2)
At the next stage of the study, in order to get a clearer figure of the phenomena occurring during shrinkage, the results were depicted on the curve of the shrinkage dependence on the temperature \( \Delta V/\Delta t \).

The dependences of the HSM-25-1 and HSM-25-2 shrinkage coefficient obtained by mixing different ratios of n-alkanes in comparison with the shrinkage of individual n-alkanes taken as components are shown in figure 2.

According to works [8, 9] when heat storage materials are crystallized from mixtures of even n-alkanes \( \text{C}_{16}\text{H}_{38} \) and \( \text{C}_{20}\text{H}_{42} \) at a melting temperature of 35\( ^{\circ} \)C, the shrinkage takes on a complex character with the observation of four shrinkage peaks. According to the studies and graphs of figure 3, the first peak corresponds to the crystallization of the individual n-alkane \( \text{C}_{20}\text{H}_{42} \), which crystallizes into a hexagonal symmetry group, then the eutectic of the n-alkanes \( \text{C}_{16}\text{H}_{36} \) and \( \text{C}_{18}\text{H}_{38} \) are crystallized at a temperature of 28.5\( ^{\circ} \)C, followed by the crystallization of the individual n-alkane \( \text{C}_{18}\text{H}_{38} \) at a temperature of 23.5\( ^{\circ} \)C.

![Figure 3. Dependence of the shrinkage coefficient of n-alkanes \( \text{C}_{18}\text{H}_{38} \) and \( \text{C}_{20}\text{H}_{42} \) and HSM-35 obtained during their mixing from the temperature [10].](image)

The last stage of crystallization occurs during the phase transition to the rhombic symmetry group with a small shrinkage at a temperature of 18-20\( ^{\circ} \)C.

When crystallizing a mixture of two odd n-alkanes \( \text{C}_{19}\text{H}_{40} \) and \( \text{C}_{21}\text{H}_{44} \) having two peaks of shrinkage and obtained by mixing them HSM-35, four peaks of shrinkage are present according to figure 4. This is due to the fact that the crystallization of individual odd n-alkanes takes place in two stages. At the first stage, crystals of the unstable hexagonal symmetry group \( \text{C}_{19}\text{H}_{40} \) and \( \text{C}_{21}\text{H}_{44} \) are formed, which then undergo a phase transition during cooling, forming crystals of the stable rhombic symmetry group. The total amount of shrinkage during crystallization and phase transition of individual n-alkanes consists of 13.8-14.4\% of the volume.

It should be noted that for a mixture of odd n-alkanes, the boundaries of the shrinkage processes are expanded and somewhat reduced in comparison with the original n-alkanes. The dependence of the shrinkage coefficient of the heat storage material HSM-25-1 obtained by mixing n-alkanes mainly \( \text{C}_{17}\text{H}_{36} \) and \( \text{C}_{18}\text{H}_{38} \) from the temperature, according to figure 2, is similar to the dependence of the shrinkage during crystallization of a mixture of odd (\( \text{C}_{17}\text{H}_{36} \)) and even (\( \text{C}_{20}\text{H}_{42} \)) n-alkanes having two shrinkage peaks, and the material HSM-25-1 obtained by mixing these individual n-alkanes has four shrinkage peaks. The total shrinkage during crystallization and phase transition was 9.56\% of the volume.

In comparison with the graphs in figure 4, the shrinkage dependences on the temperature of HSM-25-2 obtained by mixing two odd n-alkanes \( \text{C}_{17}\text{H}_{36} \) and \( \text{C}_{19}\text{H}_{40} \) in accordance with figure 2 also have
two shrinkage peaks of individual n-alkanes and four shrinkage peaks of HSM-25-2. The total shrinkage of this mixture was 10.01% of volume for HSM-25-2.

**Figure 4.** Dependence of the shrinkage coefficient of n-alkanes C_{19}H_{40} and C_{21}H_{44} and HSM -35 obtained during their mixing from the temperature [10].

It should be noted here that for a mixture of odd n-alkanes, the boundaries of the shrinkage processes are expanded in comparison with the original individual n-alkanes.

Paraffins and n-alkanes in the liquid state become low- viscosity transparent liquids with a relative density in the range of 750-800 kg/m³. Due to shrinkage, paraffins and n-alkanes in the crystalline state become solid substances with a density of 860-900 kg/m³ [11-13].

Figure 5 shows the shrinkage curves of HSM-25-3 obtained by mixing commodity liquid and solid paraffins.

**Figure 5.** Graph of the dependence of the shrinkage coefficient of HSM-25-3 obtained by mixing commercial liquid and solid paraffin from the temperature.

The graph in figure 5 shows that there are four main shrinkage peaks in HSM-25-3 compared to the graphs of the shrinkage dependence on the temperature of individual n – alkanes in accordance with figure 2. This is explained by the fact that at 25°C, a number of hydrocarbons crystallize at the same time upon cooling of this heat storage material. It should be noted that the total value of the thermal effect of HSM-25-3 is significantly lower than that of a mixture of individual n-alkanes with the same melting point.

This is due to the complexity of the chemical composition of commodity paraffin, which contains hydrocarbons of other groups along with n-alkanes, it is believed that these hydrocarbons have a much lower melting point compared to individual n-alkanes. In addition, some of these hydrocarbons may not crystallize during cooling, forming a solid crystalline mass. For these HSM-25-3, the shrinkage
during crystallization consisted of 9.02% of the volume, during the phase transition to the crystalline state – 0.77% of the volume, and the total shrinkage was 9.79% of the volume.

From this we can conclude that the width of the fractional composition of the heat storage material significantly affects the shrinkage of HSM-25-3: it does not change for the phase transition, and it slightly decreases during melting.

Comparison of data on shrinkage of developed heat storage materials obtained by mixing n-alkanes HSM-25-1 and HSM25-2 and mixing liquid and solid paraffins HSM-25-3 shows that HSM-25-1 and HSM-25-2 have higher shrinkage values than HSM-25-3.

From this it can be concluded that the width of the fractional composition of the heat storage material does not affect the shrinkage during the phase transition and has little effect on their shrinkage during melting.

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