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Ice strengthening resulted from joint addition of polyvinyl alcohol and superfine silica nanoparticles

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The results of ice hardening by doping with polyvinyl alcohol at concentrations ranging from $3 \cdot 10^{-3}$ to 1.5 wt.% and ultradisperse ($\sim$ 10 nm) silica nanoparticles at concentrations of $3 \cdot 10^{-1}$ wt.%, introduced separately and jointly into distilled water prior to crystallization, are presented. The concentration dependences of peak stresses, inelastic deformation and fracture work were established by the uniaxial compression method. The combined effect of the two types of impurity had a stronger effect than the effect of each of them separately.

Keywords: ice, mechanical properties, ice composites, nanoparticles.

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A number of countries (Russia, China, USA, etc.) have adopted state programs for the exploration of the Arctic, the Moon and Mars. In this regard, interest in ice as a promising building material that does not have to be transported from the mainland of land and disposed of at the end of the life of the structure is continuously increasing [1]. Ice has other advantages: in northern latitudes, it is universally available in the cold season, its sources (water, cold) are renewable, it is environmentally safe, non-flammable, has low density and is not difficult for any kind of processing.

However, ice as a building material has a number of significant disadvantages: low strength and fracture toughness, tendency to creep and sublimation [2,3]. In this regard, approaches and methods of ice [4] hardening have been searched for several decades. In recent years, they have intensified due to the development of plans to build habitable stations on the Moon and Mars, including ice [5,6]. The presence of water ice in the circumpolar regions of the Moon and Mars and the much lower temperature than in the Arctic, which makes ice stronger, favors its use as a building material.

To improve the mechanical properties of ice, various additives are usually added to the water before freezing: from polymer solutions [7,8] and nanoparticle (NPs) [9–11] to microfibers of different composition [12,13] and macrocomponents [14]. In the vast majority of cases, a single type of additive with a characteristic size in the molecular to macroscopic range was introduced. Such additives, taken individually, act on various elements of ice structure at different scales (from water molecules to the ice matrix as a whole). This provides ice hardening by a factor of 2–4 (in rare record cases up to 5–6 times), which makes it possible to build quite large structures from ice composites (IC). In particular, a prototype aircraft carrier and domed buildings tens of meters [15–17] in size were constructed from sawdust-reinforced IC — pykerete.

However, it has not been possible to achieve radical (at least by an order of magnitude) ice hardening by introducing macro- and microscale additives. They act as reinforcing components in the IC without changing the microstructure of the weak matrix — the ice itself. Meanwhile, the theoretical strength of defect-free ice is about $10^{-1}E_d \approx 1$ GPa [18] (here $E_d \approx 10$ GPa — dynamic Young's modulus), which exceeds the experimental values by two - three orders of magnitude. Thus, there is a large and as yet untapped reserve for further strengthening of ice by modifying its microstructure. Simultaneous introduction of two or more multiscale additives of different chemical compositions and sizes into the IC precursor can yield difficult-to-predict combined effects.

The aim of the present work is to modify the ice structure by introducing polyvinyl alcohol (PVA) and ultrafine silicon dioxide particles (SiO_2) in small concentrations (< 2 wt.%) into distilled water separately and jointly, as well as to establish the concentration dependences of the maximum achievable stress, irreversible deformation and fracture work of the obtained ICs under uniaxial compression.

IC samples were fabricated using SiO_2 NPs (Aldrich, USA) with the manufacturer's reported size of 10–20 nm and PVA (Aldrich, USA) with a molar mass of $(8.5-12.4) \cdot 10^4$ g/mol. First, a PVA solution with a polymer mass fraction of $c = 1.5$ wt.% was prepared by dissolving PVA granules in distilled water at 90°C for 1 h under continuous mechanical stirring with a vertical propeller-type stirrer until the PVA granules were completely dissolved and a clear solution was formed. PVA solutions with $c = 3 \cdot 10^{-3}-1.5$ wt.% were prepared from the prepared solution by serial dilution with distilled water. Another set

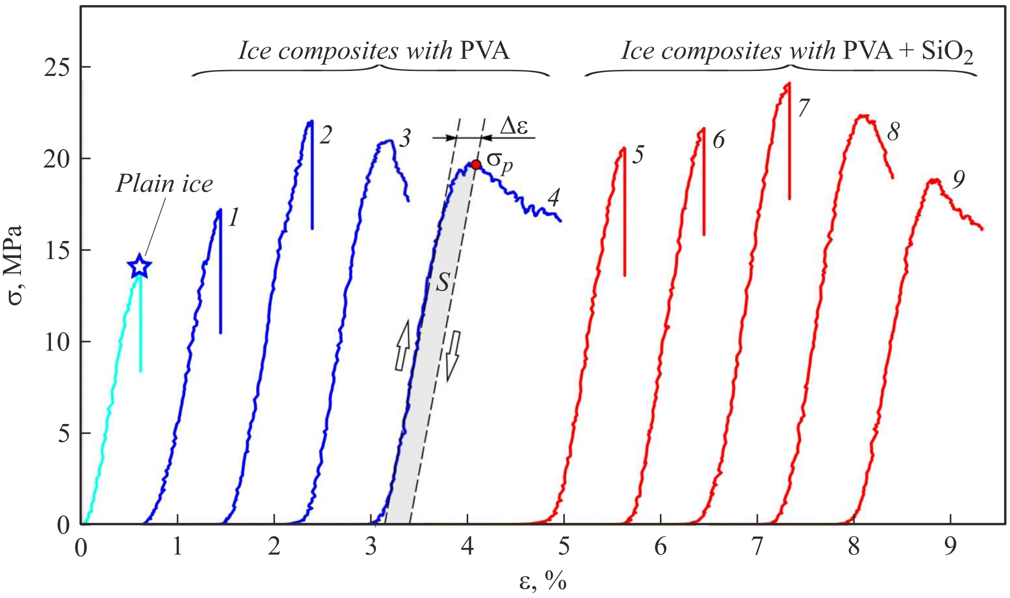

Figure 1. Typical $\sigma-\varepsilon$ loading diagrams for pure ice (curve with asterisk), IC with PVA only (curves *1–4* with PVA concentrations equal to 10^{-2}, 10^{-1}, $5\cdot10^{-1}$, respectively) and IC with PVA+SiO$_2$ (curves *5 – 9* with PVA concentrations equal to 0, 10^{-2}, 10^{-1}, $5\cdot10^{-1}$, 1.5 wt.%, respectively). S — area proportional to the specific work A, done before reaching the peak stress σ_p.

of PVA solutions with the same range of PVA concentrations but containing $3\cdot10^{-1}$ wt.% NP SiO$_2$ was then obtained in a similar manner. For this purpose, the corresponding NP SiO$_2$ suspensions were dispersed in PVA solutions using a Vibra-Cell VCX 750 probe ultrasonic homogenizer (Sonics & Materials, USA). The ultrasonic frequency was 20 kHz and its power did not exceed 100 W, which prevented the suspension from heating up. The prepared suspensions were stable for a week or more. To obtain pure ice and IC samples, the solutions were poured into $10\times10\times20$ mm isolated cells cut in a PTFE cuvette. A 48-cell cuvette was thermally insulated on top and placed inside the freezer on a solid metal plate. The samples were frozen at -15°C for 48 h.

The mechanical strength of the fabricated specimens was investigated by uniaxial compression with constant strain rate $\dot{\varepsilon}=4\cdot10^{-3}\,\mathrm{s}^{-1}$ on a servo-hydraulic testing machine MTS 870 Landmark (MTS, USA) equipped with a climatic chamber inside which the temperature -15°C was maintained by blowing it with liquid nitrogen vapors. A total of 190 samples were prepared and tested.

Fig. 1 shows two series of IC loading diagrams in the coordinates engineering stress σ- relative strain ε for PVA-hardened and co-doped by PVA and SiO$_2$ ICs. It can be seen from this figure that modification of ice by PVA leads first to an increase in peak stresses σ_p, which the specimen withstands, and then to IC softening at a PVA concentration $c>3\cdot10^{-1}$ wt.%. This change in the effect of PVA on σ_p with increasing c is accompanied by an evolution in the appearance of the diagrams of $\sigma-\varepsilon$. For large c, the stresses do not jump to zero after reaching σ_p, as for small c, but decrease smoothly over many per cent of strain. This indicates the transition from brittle fracture to ductile fracture. Addition of $3\cdot10^{-1}$ wt.% SiO$_2$ to the PVA solution leads to additional growth of σ_p. Fig. 2, *a* shows the concentration dependences of σ_p for both types of IC. The regularities of hardening of IC by SiO$_2$ NPs alone at different concentrations in the freezing suspension are described in [10,11]. Fig. 2, *b* illustrates the dependence of the PVA and SiO$_2$ contributions to the overall hardening. It follows that at small c, these contributions are approximately equal, and at $c>10^{-1}$ wt.% the decrease in the SiO$_2$ fraction is accompanied by an increase in the PVA fraction. After the transition to the ductile fracture mode ($c>1$ wt.%), their contributions to ice hardening become equal again.

Not only σ_p, but also the magnitude of the irreversible strain $\Delta\varepsilon$ before reaching σ_p changes with growth of PVA concentration Fig. 3, *a* demonstrates the dependence of $\Delta\varepsilon$ on c. In combination with the data on the increase with increasing c of the specific work of irreversible deformation A before reaching σ_p (Fig. 3, *b*), these results also indicate a change in the fracture mode with increasing c. Near the PVA content of $c=10^{-1}$ wt.%, a brittle-ductile transition occurs in both investigated IC types.

To summarize briefly, we note the following. Modification of ice by simultaneous addition of two components belonging to different hierarchical levels: molecular level and nanoparticle level (in our case PVA and NP SiO$_2$, respectively) leads to an enhanced strengthening effect compared to the action of each of them separately. Presumably, both polymer macromolecules and nanoparticles influence the process of nucleation and inhibit the growth of ice grains both due to the formation of strong hydrogen bonds between water and PVA molecules and due to the

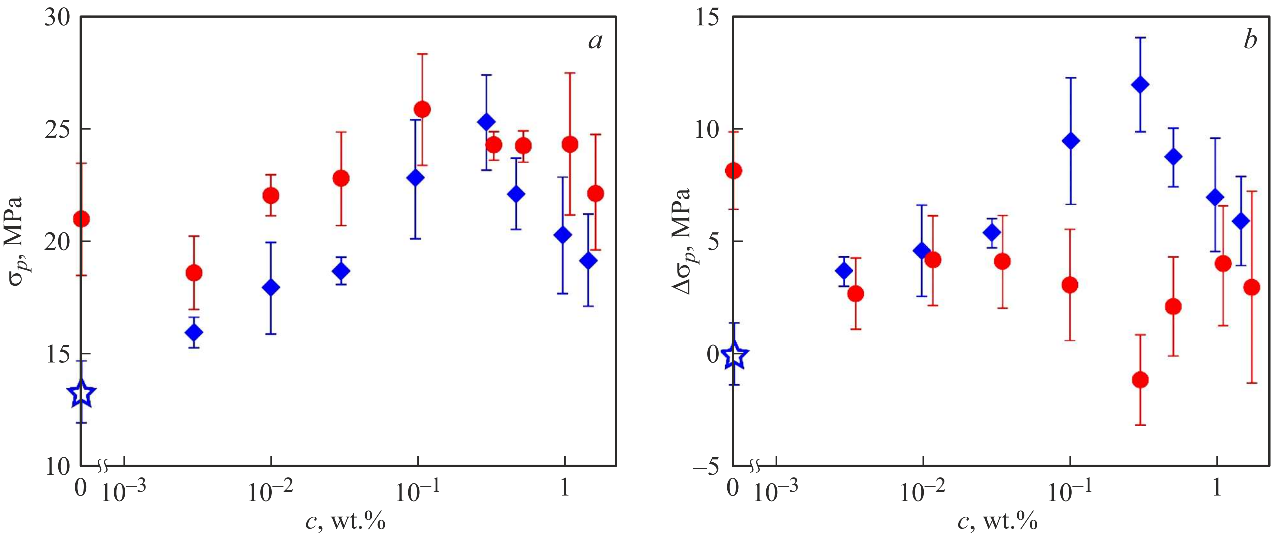

Figure 2. Dependences of peak stresses σ_p (a) sustained by IC under uniaxial compression and dependence of contributions to their hardening $\Delta\sigma_p$ (b) on the mass fraction of PVA additive. Mechanical characteristics of pure ice are shown with an asterisk, IC with PVA only — rhombuses, and IC with PVA + SiO$_2$ — circles. For IC with PVA $\Delta\sigma_p = \sigma_p(\text{PVA}) - \sigma_p(plain\,ice)$. For IC PVA+SiO$_2$ $\Delta\sigma_p = \sigma_p(\text{PVA} + \text{SiO}_2) - \sigma_p(\text{PVA})$.

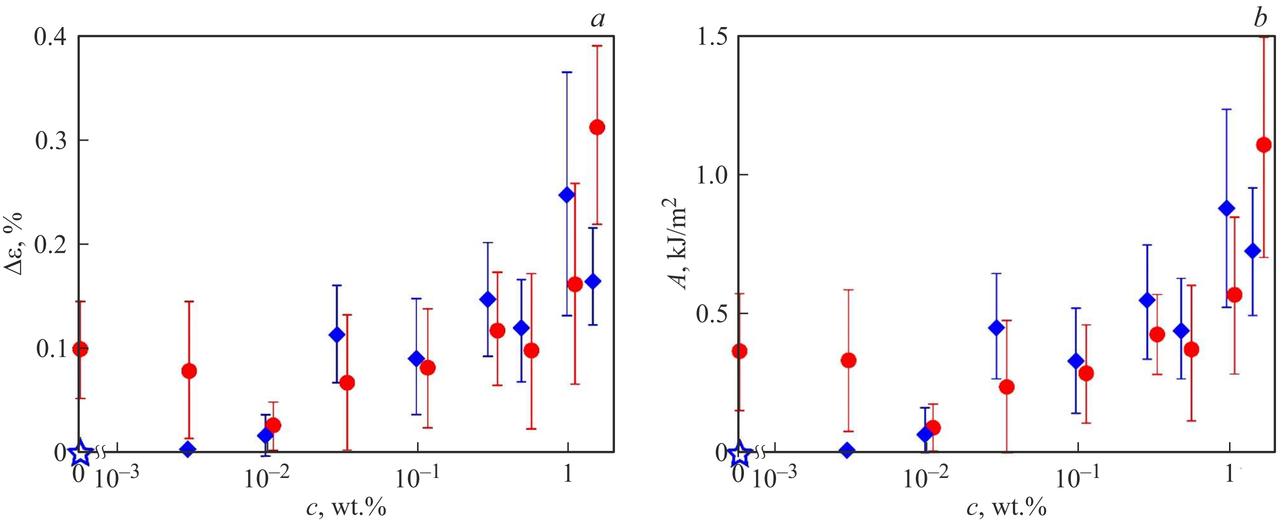

Figure 3. Dependences of inelastic relative strain $\Delta\varepsilon$ (a) and specific work A (b) up to reach σ_p on PVA concentration for two types of ICs: with PVA only (rhombuses) and ICs with PVA+SiO$_2$ (circles). The parameters of pure ice are shown with an asterisk.

introduction of additional crystallization centers in the form of SiO$_2$NPs and the presence of the latter in the joints of ice grains, which prevents the movement of their boundaries. Finally, a decrease in the grain size of polycrystalline ice leads to an increase in its strength (Hall-Petch and Griffiths relation).

In the pair we investigated — PVA and ultradisperse SiO$_2$NPs — increasing the concentration of one of the additives leads to a weakening of the effect of the other. Apparently, this is due to their interaction in suspension. Optimizing the composition of such pairs or a larger number of components can realize the potential of multi-component ice doping to a greater extent.

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Conflict of interest

The authors declare that they have no conflict of interest.

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