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Freezing of sessile droplets on glass surfaces coated with antifreeze polypeptides by a silane coupling agent

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To develop icephobic surfaces is an urgent issue because ice-covering surfaces cause serious troubles, such as (1) poor visibility through the windshields of aircraft, trains and automobiles; (2) poor visibility of traffic lights in snowy winter, (3) the breaking of power transmission lines; (4) a deterioration of the aerodynamic performance of aircraft wings. To date, many studies proposed icephobic surfaces. However, as far as the present authors know, there has not yet been proposed for the icephobic transparent surfaces, necessary for reducing the first two troubles. Concerning the ice growth on a transparent glass, the antifreeze protein type I bound on the glass surface was studied by Esser-Kahn et al. However, the denaturation of the antifreeze protein was not discussed. The present authors have looked for alternatives for icephobic surface coating because of the protein denaturation. Kun and Mastai synthesized three polypeptides inspired from antifreeze protein. Using an osmometer, they measured freezing point depression for a solution of one of these polypeptides. The amino-acid residues of this polypeptide were identical with the first twelve amino-acid residues of winter flounder antifreeze protein. We have expected that denaturation of the polypeptide does not occur in this case because the short helical structure of the polypeptide, which includes many hydrophobic residues, is maintained with strong hydrophobic interaction and hydrogen bonds. We showed the increase in the supercooling at the ice/solution interface and decrease in the ice growth rate for the polypeptide solution in the unidirectional freezing. However, we have not yet tried the adhesion of the polypeptide on a solid surface.
Based on these results, we have conducted experiments on the freezing of sessile pure-water droplets on cooling glass surfaces. The polypeptides were adhered on the glass surfaces with coupling agents and linkers. We measured supercooling temperature inside the droplets using a fine thermocouple. Also, we measured the surface adhesion strength of frozen droplets. In addition, we observed the surfaces using an atomic force microscope. The cooling rate of the surfaces was -2.0 ℃/min. It was found that the supercooling temperature in the case coated with the silane coupling agent was lower than that in the case of untreated surface. This is because the droplet contact area became small due to the hydrophobicity of the silane coupling agent. The supercooling temperature in the case with the polypeptides was the lowest. Also, the adhesion strength of frozen droplets in the case with the polypeptides was found to be lower than that in the other cases. In addition, it was observed with the atomic force microscope that many aggregates of the polypeptides in various size were adhered on the surfaces randomly. It can be surmised that the hydrophobic residues of the polypeptides are exposed in the aggregates, and that the hydrophobic hydration of water molecules occurs by the hydrophobic residues on the aggregates. This can be the reason for the decreases in the supercooling temperature and adhesion strength.

Significance statement

We conducted experiments on the freezing of water droplets on cooling glass surfaces. The polypeptides were adhered on the surfaces with coupling agents. The hydrophobic residues of the polypeptides in their aggregates can be the reason for decreases in the supercooling temperature and adhesion strength.

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