

**STUDY ON EFFECTS OF PVA(POLYVINYL ALCOHOL) ON SUPERCOOLING  
PHENOMENA OF WATER**

Hiroyuki KUMANO  
Shinshu University  
4-17-1 Wakasato, Nagano,  
380-8553, Japan

Tetsuo HIRATA  
Shinshu University  
Nagano, Japan

Tomoya KUDOH  
Shinshu University  
Nagano, Japan

\*Correspondence author: Fax: +81-26-269-5104 Email: [kumano@shinshu-u.ac.jp](mailto:kumano@shinshu-u.ac.jp)

**ABSTRACT**

In this paper, effects of polymer additive on supercooling of water were investigated experimentally. Polyvinyl alcohol (PVA) were used as the additives, and the samples were prepared by dissolving PVA in water. Since characteristics of PVA are decided by degree of polymerization and saponification of PVA, concentration, degree of polymerization and saponification of PVA were varied as the experimental parameters. Moreover, effects of purity of the water was also considered. The sample was cooled, and the temperature at the instant when ice appears was measured. Since freezing of supercooled water is statistical phenomenon, many experiments were carried out and average degrees of supercooling were obtained for each experimental condition. As the result, it was found that PVA affects nucleation of supercooling and the degree of supercooling increases by adding the PVA despite of low purity of the water. Especially, it is found that the average degree of supercooling increases with increase of degree of saponification of PVA. However, the average degree of supercooling are independent of the degree of polymerization of PVA in the range of this study.

**NOMENCLATURE**

$T_{ave}$  : average degree of supercooling at freezing, K  
 $\Delta T$  : degree of supercooling at freezing, K

**INTRODUCTION**

In recent years, ice thermal energy storage systems have been attracting attention for load leveling of electric power<sup>[1]</sup>. In particular, ice slurry with fluidity is used as secondary refrigerant in dynamic ice thermal energy storage systems. Therefore, because the ice slurry includes very fine ice particles, cold thermal energy can be transported directly and the ice slurry has a high heat exchange rate.

As a method of generation of ice slurry, the supercooling state of water or aqueous solution is used<sup>[2, 3]</sup>. In this method, after water or aqueous solution is cooled and a supercooling state is achieved, ice slurry is produced by releasing the supercooling state. Since the supercooling state is unstable, if it is released during the cooling process and the transportation, then a blockage of pipelines occurs. Therefore, in an actual system of ice slurry generation, the degree of supercooling of water or aqueous solution is set at about 2K to prevent unexpected release of the supercooling state. Thus, if a method for maintaining the supercooling state is established, stable operation of ice slurry generation can be achieved. Moreover, if the degree of supercooling can be increased, the ice generation rate can be increased.

The effect of additives on ice crystals has been investigated for polymer additives, such as PVA, added to water or aqueous solution<sup>[4-7]</sup>. It is speculated the recrystallization of ice crystals is

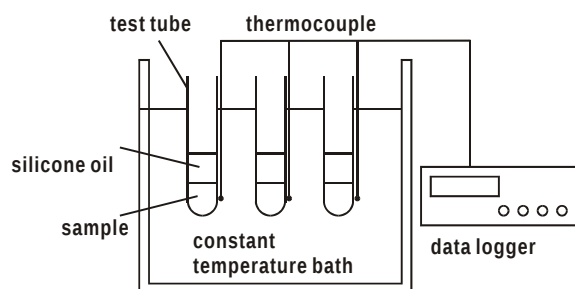


Figure 1

Schematic diagram of experimental apparatus

inhibited due to adsorption of PVA to the surface of the ice crystals. Thus, PVA is expected to affect ice nucleation, and this may maintain a supercooling state of water and aqueous solution. Therefore, in this study, the effect of PVA on the release of the supercooling state is investigated experimentally. Degrees of polymerization and saponification of PVA are varied as experimental parameters, and the effects of the degrees of polymerization and saponification on the supercooling phenomena of water are investigated to determine the characteristics of PVA for supercooling phenomena of water. Moreover, experiments are carried out using several kinds of water to reveal the effect of the purity of water.

## EXPERIMENTS

**Experimental apparatus:** Fig. 1 shows the experimental apparatus. The experimental apparatus consists of cooling and measurement systems. 1 ml of water with PVA was put into a polypropylene test tube and the sample was covered with 1 ml of silicone oil to avoid inclusion of dust or frost to the sample, since such inclusion releases the supercooling state. The sample was then placed in a constant temperature bath and cooled at a constant rate. The temperature at the instant when ice appeared was measured. The temperature was measured outside the test tube by thermocouples. In a preliminary experiment, the temperatures inside and outside the test tube were measured. These temperature variations are shown in Fig. 2. From the figure, it is found the release of the supercooling state occurs at about  $-10^{\circ}\text{C}$ , and the temperature increases owing to the latent heat of fusion. The temperatures inside and outside the test tube are in agreement before the release of the supercooling state. Therefore, the temperature was measured outside the test tube since a thermocouple

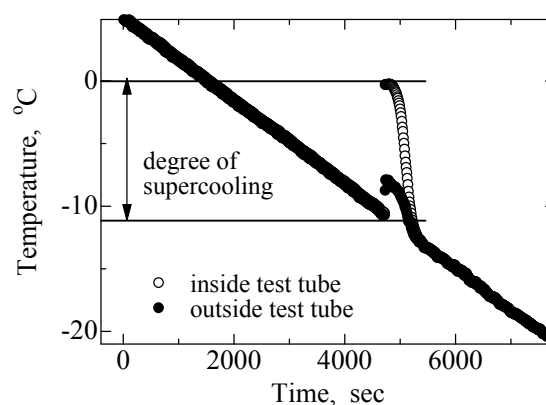


Figure 2

Temperature variation inside and outside the test tube at the moment of supercooling release

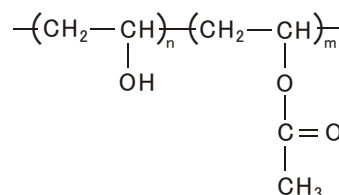


Figure 3

Chemical composition of PVA

inside the tube may release the supercooling state. The absolute value of temperature at the instant when ice appears in the sample is defined as the degree of supercooling at freezing. The cooling rate is constant and set at  $0.2\text{ K/min}$ .

In this experiment, the characteristics of PVA, concentration of PVA and purity of water were varied as experimental parameters. Since the freezing of supercooled water is a statistical phenomenon, many experiments were carried out. For each experimental condition, more than 40 experiments were performed, and the average degree of supercooling at freezing was obtained for each experimental condition.

**Characteristics of PVA:** PVA is a high polymer material having hydroxyl groups. Characteristics of PVA are decided by its molecular weight and the degree of saponification, which relates to the number ratio of hydroxyl groups. Fig. 3 shows the chemical composition of PVA.  $n + m$  expresses the degree of polymerization, which refers to the length of the PVA molecule, and  $100n / (n + m)$  expresses the degree of saponification. In this study, the degree of polymerization and degree of saponification were varied as experimental

Table 1  
Characteristics of PVAs

| degree of polymerization | degree of saponification | molecular weight | depression of freezing point, K |
|--------------------------|--------------------------|------------------|---------------------------------|
| 300                      | 88                       | 14700            | 0.004                           |
| 500                      | 72-99                    | 22200-27900      | 0.002-0.003                     |
| 1000                     | 88                       | 49000            | 0.001                           |
| 1500                     | 88                       | 73600            | 0.001                           |
| 2400                     | 88                       | 117700           | 0.0005                          |
| 3500                     | 88                       | 171600           | 0.0003                          |

parameters. Table 1 shows the characteristics of PVAs used in this study. The degree of polymerization was varied from 300 to 3500, and the degree of saponification varied from 72% to 99%. The effect of the concentration of PVA was also examined. Moreover, the freezing temperature depression due to PVA is given in Table 1 for PVA of 3 wt.% added to water. It was found the freezing temperature depression can be ignored because PVAs are high polymer materials.

In this experiment, tap water, pure water and ultra pure water were used as samples. The different purities of the samples were indicated by their resistivities, 1.2 K $\Omega$ ·cm, 0.1 M $\Omega$ ·cm and 18.3 M $\Omega$ ·cm, respectively. After PVA was added to a water sample, the sample was heated to 95 °C and stirred for about 1 hour to dissolve PVA into the water. Samples without PVA were examined to compare with the samples with PVA, with the same procedures carried out.

## RESULTS AND DISCUSSION

**Effect of concentration of solution:** The effects of PVA on the supercooling of water were investigated. First, the experiments were carried out using water without PVA to clarify the effect of adding the PVA. As the results, it was found the average degrees of supercooling were 14.7 K, 15.8 K and 19.2 K for the tap water, pure water and ultra pure water samples, respectively, and the average degrees of supercooling at freezing increase with the purity of the water.

The effect of the concentration of PVA was considered. PVA with a degree of polymerization of 500 and 88 to 99% saponification was used, and the concentration of PVA was varied from 1 wt.% to 5 wt.%. The samples were tap water and ultra pure water. Fig. 4 shows the relation between the

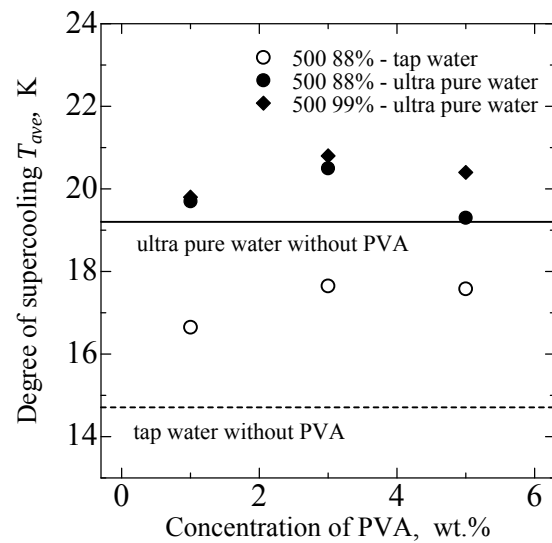


Figure 4  
Effect of concentration of PVA  
on the average degree of supercooling

average degree of supercooling at freezing and the concentration of PVA. Lines express the average degrees of supercooling of the water without PVA. When the concentration of PVA was 1 wt.%, it was found the effect of PVA is not significant. However, the average degree of supercooling increases in the case of 3 wt.%. Moreover, it was found the average degree of supercooling decreases slightly in the case of 5 wt.%, compared with 3 wt.%. From these results, it is considered that 3 wt.% PVA addition is effective in inhibiting the release of supercooling, and 3 wt.% was used as a standard concentration in the following experiments.

**Effect of the degree of polymerization:** The effect of the degree of polymerization of PVA on the release of supercooling was investigated. The degree of polymerization of PVA was varied from

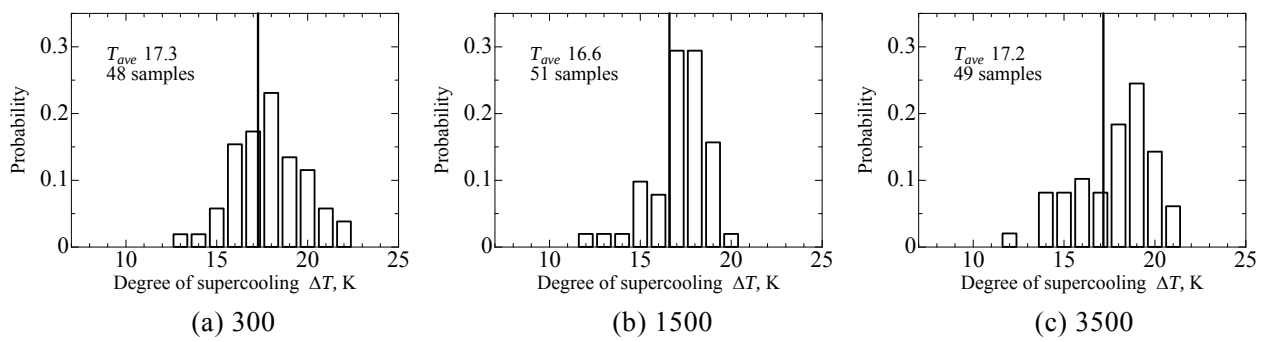


Figure 5

Probability distribution of the degree of supercooling for various degrees of polymerization of PVA (1 ml tap water, concentration 3 wt.%, degree of saponification 88%)

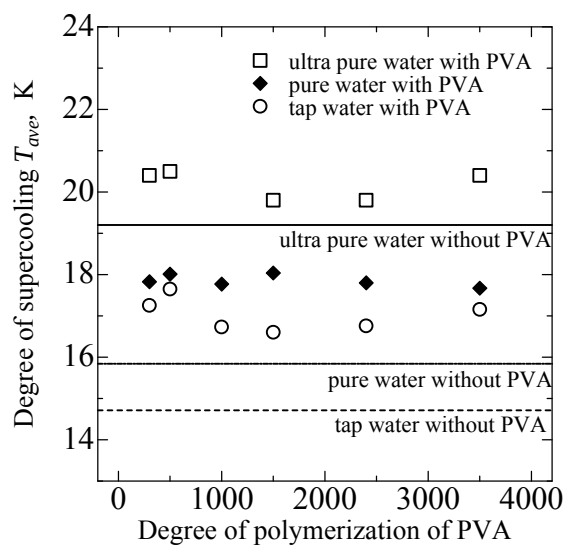


Figure 6

Effect of the degree of polymerization on the average degree of supercooling (1 ml water, concentration 3 wt.%, degree of saponification 88%)

300 to 3500. The degree of saponification of PVA was 88% and set as a constant through the experiments. As mentioned above, the concentration of the PVA was 3 wt.%. Therefore, the number of hydroxyl groups was constant without reference to the degree of polymerization, because the concentration of the PVA was constant.

The distributions of the degree of supercooling at freezing are shown in Fig. 5 as examples of the results, with degrees of polymerization of PVA of 300, 1500, 3500, and the samples being tap water. Solid lines express the average degree of supercooling at freezing in the figures. The degree of supercooling is distributed from 12 K to 22 K, and there is no difference in the

distributions of the degree of supercooling for each degree of polymerization.

Fig. 6 shows the relation between the average degree of supercooling at freezing and the degree of polymerization of PVA. Lines represent the average degree of supercooling of the sample without PVA for each water type. It was found the average degree of supercooling increases by about 2 K, compared with the results of the samples without PVA. Moreover, the average degree of supercooling is independent of the degree of polymerization. As mentioned above, since the concentration of PVA is 3 wt.% and the number of hydroxyl groups is constant, it seems the effect of PVA on the nucleation of ice is the same.

**Effect of the degree of saponification:** The effect of the degree of saponification of PVA on the supercooling of water was examined. The degree of polymerization of PVA was 500 and was set constant, and the degree of saponification was varied from 72 to 99%. The molecular weight of PVA varies depending on the degree of saponification. Therefore, the molar concentration was set constant to determine the effect of the degree of saponification. The molar concentration was set at  $1.26 \times 10^{-3}$  mol/kg, which corresponds to 3 wt.% of PVA with a degree of polymerization of 500 and 88% saponification.

Fig. 7 shows the relation between the average degree of supercooling at freezing and the degree of saponification of PVA. Lines express the average degree of supercooling of water without PVA. From the figure, the average degree of supercooling was similar to the results without PVA in the case of a low degree of saponification. However, it was found the average degree of supercooling increases

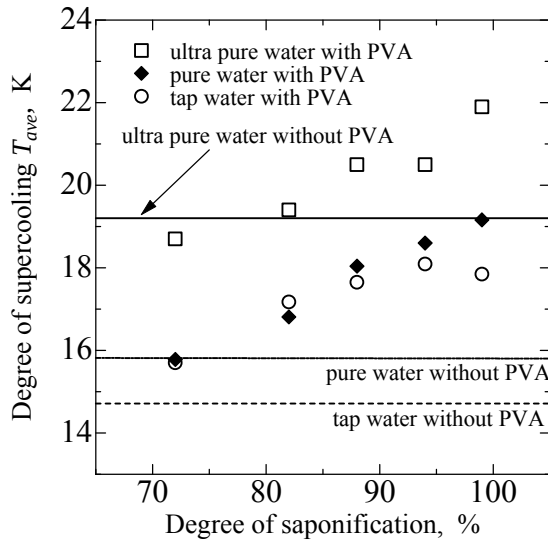


Figure 7

Effect of the degree of saponification on the average degree of supercooling (1 ml water, concentration  $1.26 \times 10^{-3}$  mol/kg, degree of polymerization 500)

with the degree of saponification in the case of a high degree of saponification. Since the molar concentration is constant, the number of hydroxyl groups increases with the degree of saponification. Therefore, it is speculated the release of supercooling is inhibited owing to the adsorption of PVA to the surface of the ice nuclei, and the effect of adsorption increases with the degree of saponification. That is to say, the hydroxyl groups of PVA adsorb onto the surface of minute ice nuclei called as embryo and the impurities in the water, and inhibit a growth of the ice nuclei. It seems that these effects of PVA inhibit the release of supercooling.

**Effect of the purity of water:** The effect of the purity of water on the release of supercooling was considered. Tap water, pure water and ultra pure water were used as solvents. The different purities were indicated by resistivities of the water samples. Fig. 8 shows the relation between increments in the average degree of supercooling and the resistivity of the water. The increments in the average degree of supercooling represent the difference between the average degree of supercooling at freezing for water without PVA and that with PVA. It was found there is a tendency for the average degree of supercooling to increase in the case of low purity. It seems the PVA acts on impurities in the water, and

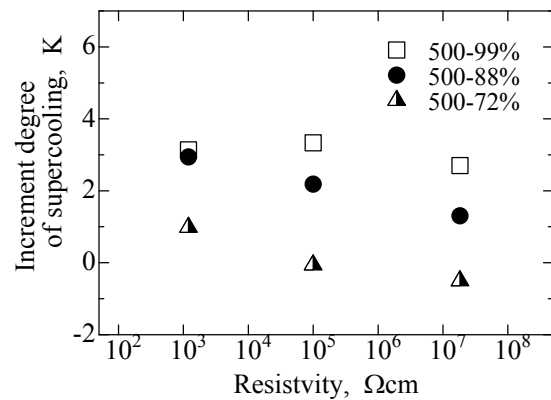


Figure 8

Effect of resistivity of water on the increment of the degree of supercooling (1ml water, concentration  $1.26 \times 10^{-3}$  mol/kg, degree of polymerization 500)

inhibition of the release of supercooling occurs in the case of low purity. Moreover, tap water is used in actual systems generating ice slurry, and hence it is found PVA can be used in real application.

## CONCLUSION

In this study, the effect of PVA on the supercooling of water was investigated experimentally. In particular, the concentration of PVA, degrees of polymerization and saponification of PVA and purity of water were varied as experimental parameters. As a result, it was found that the average degree of supercooling at freezing increased by about 2 K for each experimental condition, compared with the results of samples without PVA, and the average degree of supercooling was independent of the degree of polymerization. Moreover, the average degree of supercooling at freezing increased with the degree of saponification in the case of a high degree of saponification. Tap water, pure water and ultra pure water were used as solvents, and there was a tendency for the average degree of supercooling at freezing to increase in the case of low purity.

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