# Effect of plasticizer on the molecular dynamics of amorphous amylopectin

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Amylopectin (AP) is a branched polymer of glucose known as a major component of starch. AP of starchy food products is commonly amorphous, and the physical properties change drastically by glass transition. The glass transition temperature ($T_g$) of anhydrous AP is extrapolated to 520 K according to the water content dependence of $T_g$ determined by differential scanning calorimetry. The $T_g$ of hydrophilic amorphous material decreases with an increase in the plasticizer content. On the other hand, it was noted that the mechanical property of glassy AP-based food sample became harder by the addition of plasticizer (i.e., anti-plasticizing effect) in our previous studies. From the result, it was suggested that the glassy AP has partially mobile region microscopically because of the gap spaces caused by the branching structure. When the gap spaces are filled by the addition of plasticizer, the microscopic mobility will decrease, and thus the mechanical property becomes harder. The purpose of this study was to understand the microscopic molecular mobility of AP with and without $D_2O$ and deuterated glucose (D-glucose), and anti-plasticizing effect was discussed in the viewpoint of molecular dynamics.

AP and AP-D-glucose mixture (0.2 g-glucose/g-AP) were gelatinized, and then freeze-dried. The freeze-dried powders were subsequently vacuum-drying for the preparation of anhydrous samples. For the preparation of wet samples, the anhydrous samples were equilibrated with saturated NaCl-$D_2O$ solution (water activity 0.75). For comparison, anhydrous amorphous H-glucose was prepared by the quenching of molten glucose. Incoherent elastic neutron scan was carried out using AGNES (C3-1-1). The energy resolution was 120 μeV, and covered $Q$ range was 0.20–2.7 $Å^{-1}$ ($\lambda$ = 4.22 Å, standard resolution mode). The sample was cooled to 100 K and heated to 360 K in a step manner. The mean squire displacement (MSD) was obtained from the $Q$-dependence of elastic intensity as the function of temperature.

The MSD of anhydrous and wet AP samples began to increase from 200 K. The wet AP showed slightly lower MSD than the anhydrous AP. The temperature-dependence of MSD for anhydrous AP, AP/D-glucose, and H-glucose samples is shown in Fig. 1. The MSD values of AP and H-glucose were almost equivalent below 270 K, but AP tended to be higher MSD than H-glucose above 270 K. At 298 K (typical room temperature), anhydrous AP was more mobile than glucose. Similar results were observed in a previous study [1]. AP/D-glucose showed unclear MSD behavior, but similar to glucose rather than AP. These results support the "anti-plasticizing effect" of water and glucose; the microscopic mobility of AP is reduced by the addition of plasticizer. To obtain clear MSD behavior for AP/D-glucose, further investigation using high resolution mode will be effective.

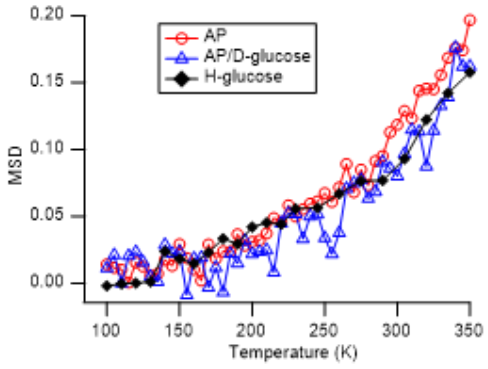


Fig.1. Temperature-dependence of MSD for anhydrous amorphous AP, AP/D-glucose, and H-glucose samples.

Reference

[1] Di Bari, M., et al. *Chem. Phys.* 292.2-3 (2003): 333-339.