Changes in molecular dynamics of starch on scale of dozens of nanometers during retrogradation

Y. Hirata[A], H. Nakagawa[A]

[A]*JAEA*

Starch undergoes gelatinization (amorphization) upon heating with water, and the gelatinized starch gradually recrystallizes over time through a process known as retrogradation. Starch retrogradation causes undesirable textural changes (becoming harder and less sticky) of starchy foods (rice, noodles, bread, etc.). Therefore, elucidating the mechanisms underlying starch retrogradation is an important challenge in food processing. Retrogradation is commonly evaluated by XRD and DSC, which assess the crystallinity derived from the double-helix structure of starch chains. However, the crystallinity of retrograded starch is low, and most of it is amorphous, therefore the crystallinity determined by conventional methods does not completely assess the quality deterioration caused by retrogradation. Since macroscopic texture is closely related to molecular dynamics, characterizing molecular dynamics is essential for a better understanding of starch retrogradation.

We have revealed that starch retrogradation suppresses the angstrom-scale molecular dynamics of hydrogen in the starch of cooked rice using incoherent quasi-elastic neutron scattering (iQENS) [1]. However, to determine whether changes in angstrom-scale molecular dynamics are directly associated with macroscopic food quality deterioration, it is necessary to investigate molecular dynamics over a wider range of spatial scales. In this study, we investigated the molecular dynamics of starch in cooked rice at the nanoscale using neutron spin echo spectrometer (iNSE).

Native rice (75 g) was washed with D_2O. The washed rice was soaked in D_2O (108 g) and immediately cooked with a rice cooker. After cooking, the rice was cooled, stored at 283 K for 0–4 days, and then lyophilized. Lyophilized rice powder (400 mg) of 0-day stored cooked rice (D+0) and 4-day stored cooked rice (D+4) were mixed with D_2O (1.6 mL) and the mixed samples were placed in 2-mm path-length sample cells with demountable quartz windows and sealed. The native rice was washed twice with D_2O and then filled into the sample cells. iNSE (C2-3-1) experiment conducted at neutron wavelengths (λ) of 7.3 Å in the q-range of 0.061–0.085 $Å^{-1}$ (2θ= 5°). The measurements were carried out at 298 K. The intermediate scattering function, I(q,t), was obtained by normalizing the spin-echo polarization of the sample to that of a graphite standard measured under identical instrumental conditions.

Fig. 1 shows the I(q,t) plot of the native rice, D+0 and D+4. It was confirmed that while the native rice and D+4 showed almost no relaxation, D+0 exhibited slight relaxation. Although the relaxation function should in principle be written as f(t) = 1 - A + A exp(-t/tau), the limited time window makes it difficult to determine A and tau independently. Therefore, we estimated an effective relaxation time by fitting the data with a single exponential function, f(t) = exp(-t/tau). The obtained values were 102.6 ± 24.4 ns for Native, 48.9 ± 7.0 ns for D+0, and 91.4 ± 22.5 ns for D+4. Since this analysis corresponds to assuming A = 1, the true relaxation time would be shorter if the actual relaxation amplitude is A < 1.

[1] Y. Hirata *et al.*, *Food Hydrocolloids*, 141, 108728 (2023).

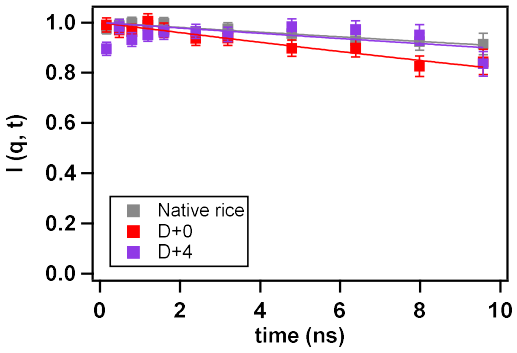

Fig. 1. I(q,t) plots of native rice, D+0 and D+4.