Starch Crystallinity Determination and Resistant Starch Quantification in Rice after Hydrothermal Treatments Using Terahertz Spectroscopy

（テラヘルツ分光法を用いたコメの水熱処理におけるデンプンの結晶化度およびレジスタント スターチの定量化）

GUO HAN

Abstract

Rice is a staple food worldwide and the main energy source for over half of the world's population, providing minerals, vitamins, and compounds. However, excessive consumption of rice can lead to chronic diseases like diabetes and obesity due to a high glycemic index (GI), which poses risks to human health and decreases life quality. Recently, hydrothermal treatments are gaining considerable interest since they can lower the GI of rice by reducing starch digestibility. Conventional methods for evaluating starch digestibility use *in vitro* hydrolysis; a time-consuming, laborious, and destructive process. On the other hand, terahertz (THz) spectroscopy is sensitive to the crystalline structure of starch, highly correlated with starch digestibility, and thus has the potential for rapid and nondestructive measurement of starch digestibility for rice. These were investigated.

In Chapter 1, introduces the background to the research, especially that related to starch digestibility evaluation and the advantages of THz spectroscopy summarized. At the end, the objectives and an outline of this research are detailed.

Chapter 2 introduces the experimental procedures used in this research, including the Fourier transform-terahertz (FT-THz) spectroscopy, X-ray diffraction (XRD), and the Rietveld refinement method. Additionally, the details of sample preparation and measurement parameters are explained.

Since the crystallinity of starch is highly correlated with digestibility, Chapter 3 describes the use of FT-THz spectroscopy to document crystallinity changes in rice starch after a hydrothermal treatment, heat-moisture treatment (HMT). The crystallinity measurements derived from XRD spectra were correlated with THz spectra. As a result of the double helical crystal structure and the crystalline structure of amylose-lipid complex (ALC) in rice starch, crystallinity categorized as either A-type and Vh-type. The intensity of a second derivative spectra peak at 9.0 THz were found to be highly correlated with both A-type and Vh-type crystallinity (R^2>0.97). Additionally, three other peaks at 10.5, 12.2, and 13.1 THz were also sensitive to Vh-type crystalline structure (R^2>0.97). These results indicate that after HMT, the

crystallinity of ALC (Vh-type) and A-type starch can be quantitatively determined using THz peaks.

To determine if there is any matrix interference from fatty acids that could be present, the THz peaks of lauric acid (LA) and palmitic acid (PA) were measured after the complexation of gelatinized rice starch. The crystallinities of these amylose-fatty acid complexes and trapped PA crystals were determined from XRD spectra. The crystallinity of amylose-fatty acid complex (Vh type of ALC) was correlated with the intensity of second derivative spectra at 12.0 THz. Moreover, this peak did not overlap with the spectra of trapped PA peaks. This confirms that the intensity of the peak at 12.0 THz can be used to accurately and robustly determine the crystallinity of ALC (Vh-type) in gelatinized rice starch-fatty acid mixtures without inference from the presence of LA and trapped PA in the sample matrix (R^2=0.98).

Four THz peaks at 9.0, 10.5, 12.2, and 13.1 THz were identified as being sensitivity to the crystalline structure of rice starch in Chapter 3 and Chapter 4, and the potential to use these absorbance peaks to predict rice starch digestibility was investigated in Chapter 5. Models based on these starch four absorbance peaks was built to predict resistant starch (RS) content, an index of starch digestibility, in hydrothermally treated rice. The rice samples examined included those that had undergone annealing, heat-moisture treatment, and parboiling, as these are commonly used methods to alter starch digestibility. These models were confirmed to be correlated with the RS content (R^2>0.96), and thus can used to accurately predict the RS content of hydrothermally treated rice.

Finally, in Chapter 6 the conclusions and future plans for the research are explored.