

FTIR analysis of thermal and plasma treatments on riceberry brown rice

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Abstract. Riceberry brown rice (RB) is known as source for valuable nutrients. Recently our group has used plasma treatment on RB to effectively shorten their cooking time and soften their texture. During the plasma treatment, rice was also subject to elevated temperature. This sometimes has led to confusion whether the thermal effect dominate. In this study, we have carried on these issues by using Fourier Transform Infrared spectroscopy (FTIR) to follow changes in vibrational characteristics of RB after being plasma treated. The plasma treatment was performed using a low-pressure inductively coupling argon plasma system. This is done in comparison to conventional thermal treatment at 45°, 60°, and 75°C for 120 minutes. The O-H stretching group was found to increase in the plasma treated samples; while decreasing in all the other thermal treated samples. The decrement has varied monotonically with temperature. There is also significantly increasing of C-O-C skeletal mode of α -glycosidic linkage, C-O-H bonding, and C-O-C asymmetric stretching glycosidic bonds in the plasma treated samples; while the decrement was observed in the thermal treated samples. This is understood as a consequence of cross-linking effect; leading to increase in glycosidic bonds along with H₂O abstraction during the plasma treatment. It can be concluded that the plasma treatment has caused more inclusive effects which cannot be accounted for by the action of the thermal treatment alone.

1. Introduction

Rice (*Oryza sativa* L.) is the important staple food source for the world's population. A whole rice grain consists of four parts; husk, bran, germ, and endosperm, respectively. For normal rice-milling process, the whole rice grain was first having their husk removed or de-husking (available as brown rice - BR) and then further milling left the de-husked rice having the bran layer removed or milling (available as white rice - WR). Germ and bran parts are in fact rich in protein, vitamins, lipids, fiber, and minerals [1]. Nowadays, consumers are getting more concerns about their health; hence BR with their bran and germ intact, considering as significantly high nutrition are gain popularity [2]. However, BR still has quite a few undesirable points, namely, longer cooking time, poorer texture, and more prone to rancidity causing it to have shorter shelf life in comparison to WR [1–3].

Plasma is partially ionized gas that consists of electrons, ions, free radicals, and atoms. Recently, plasma has been applied to improve brown rice quality [1–2, 3–5]. This makes the brown rice become more readily to absorb water; hence helps reducing the cooking time. The texture of the cooked brown rice also becomes more soft and easier to chew [4]. Rice, especially the endosperm part, contains a lot of starch. Likewise, some researchers [6–8] have also applied plasma for treating starch. Several changes of the functional groups in starch were observed. Normally, during the plasma treatment (PT), the temperature inside a plasma reactor normally increases up by a few degrees. This sometimes has led to confusion whether the changing in the properties or the functional groups in brown rice treated by plasma is the result of plasma or mere thermal.

Therefore, in this work, we have carried on this question further to focus on comparing an effect of plasma treatment using a low-pressure inductively coupling argon plasma system (LP-ICP) versus thermal treatment (TT) using an oven. Then, utilizing Fourier Transform Infrared spectroscopy (FTIR) to study the changes in functional groups of riceberry brown rice (RB). A comparison before and after plasma treatment and thermal treatments.

2. Materials and methods

2.1. Rice samples

Rice cultivar in this study was riceberry rice (RB). The color of the RB rice is dark purple. The RB was procured from Rice Research Center, Kasetsart University, Thailand. They were supplied in the form of brown rice, i.e., the bran layer and germ part were still intact. The RB brown rice grain was milled to separate the bran (bRB) from its endosperm (eRB). The milling process was done prior to thermal treatment but after the plasma treatment. This is done to facilitate the other following process, and also with consideration that thermal bulk treatment should affect in the same fashion to the two parts as separated entity and the rice grain where the two parts were still intact as a whole. Normal brown rice, subject to no treatment, were labelled as UT. They were used as a control group.

2.2. Plasma treatment

The low-pressure inductively coupling argon plasma system (LP-ICP) in this study is the same as was used by Arworn *et al.* [9]. Briefly, a discharge tube was made of quartz with 38 mm diameter and 30 cm long. A 7-turns copper coil was mounted around the middle part of the discharge tube. The plasma was generated from argon by a 13.56-MHz RF-generator at 100 W. The plasma zone is about 7-cm in length.

Riceberry (RB) rice grain was loaded to the LP-ICP setup. The RB was admitted from the loading cell by their own gravity through the plasma discharge zone. The interacting time was a fraction of a second. The treated RB was collected and re-processed for 5 times. After plasma treatment, the RB was milled, ground and sieved through an #80 mesh. All ground samples were then packed in vacuum bags and kept away from light and labeled as plasma treated or PT.

2.3. Thermal treatment

The separated RB bran and endosperm were subject to thermal treatment in an oven under three conditions; 45°C, 60°C, and 75°C, and the holding time of 120 minutes. Then they were ground, sieved, stored, and labeled as thermal treated or TT.

2.4. Fourier transform infrared spectroscopy

FTIR was used to measure functional groups after the PT and the TT. FTIR spectra were recorded from 400 to 4000 cm^{-1} [7,10] in ATR mode by 64 scans and resolution of 4 cm^{-1} (ATR) mode (Nicolet 6700 FTIR spectrometer). All data were analyzed by OMNIC and Origin 8 software.

3. Results and discussions

Figure 1 shows FTIR spectra of the bran (bRB) from various conditions, while figure 2 shows those of the endosperm (eRB). The absorbance peaks at 922 cm^{-1} , 993 cm^{-1} , 1143 cm^{-1} , and 3000 - 3600 cm^{-1} are

the C-O-C skeletal mode of α -1,4 glycosidic linkage, C-O-C asymmetric stretching glycosidic bond, C-O-H bending, and the O-H stretching mode respectively. It can be observed that the control bran sample (UTbRB) have some peaks profoundly differing from the control endosperm counterpart (UTeRB), namely, in the FTIR bands range 1500 - 1750 cm^{-1} and 2800 - 3000 cm^{-1} . These peaks are understood to come from protein and fat which are present much more in the bran than in the endosperm.

Also shown along in figure 1 and 2 are FTIR spectra of the plasma treated, and thermal treated conditions, respectively. It can be seen that the plasma treated bran (PTbRB) have higher absorbance by the main functional groups than the normal bran (UTbRB); indicating an increasing amount of these functional groups after the plasma treatment. The same observation is also found in the case of the endosperm (figure 2). On the contrary, the thermal treated samples show the lower absorbance than the control condition; indicating the decreasing amount of these functional groups after the thermal treatment. Thus, the plasma treatment cause more complex changes than the thermal treatment alone could account for.

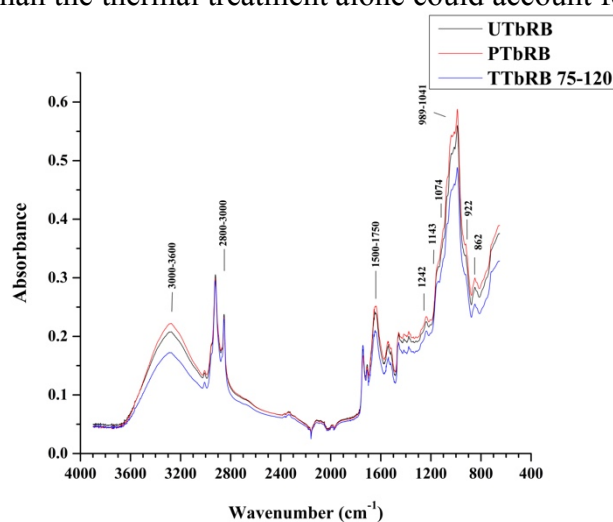


Figure 1. FTIR spectra of the bran of riceberry rice (bRB)

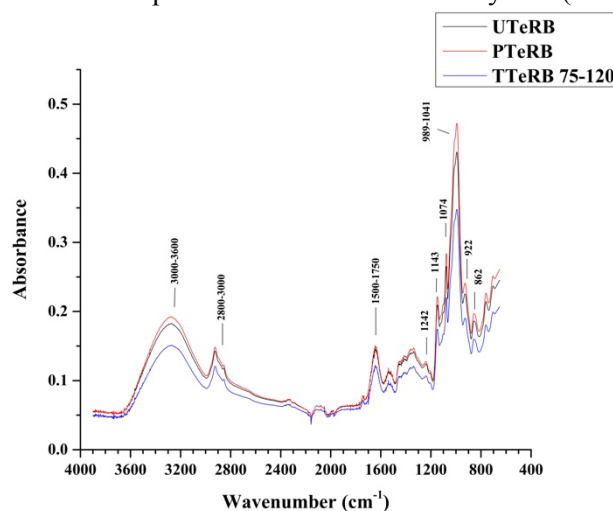


Figure 2. FTIR spectra of the endosperm of riceberry rice (eRB)

Wongsagonsep *et al.* [8] have related the 924 cm^{-1} absorbance to the glycosidic bonds and 1149 cm^{-1} to the cross-linking or depolymerization processes in starch. The higher absorbance means

the preference to cross-linking, while the lesser absorbance the preference to depolymerization. Thirumdas *et al.* [11] have referred this 993 cm^{-1} FTIR band to the C-O-H bending and the corresponding polymeric chain in starch molecules. The 3272 cm^{-1} FTIR band was referred as the O-H stretching mode by Deeyai *et al.* [7] with the connection to water in starch.

We have also varied temperatures for the thermal treatment to three conditions; 45°C, 60°C, and 75°C; each last for 120 minutes. The more elevated temperature the stronger the decrement.

The contrast changes after the plasma treatment in comparison to the thermal treatment are also highlighted in figure 3 and 4. We have observed more of the C-O-C skeletal mode of α -1,4 glycosidic linkage, C-O-C asymmetric stretching glycosidic bond, and the O-H stretching mode after plasma treatment; indicating more cross-linking process taken place after plasma treatment [10]. On the contrast the thermal treatment cause unbound water molecules to evaporate from the samples as commonly expected. The higher temperature the stronger the effect.

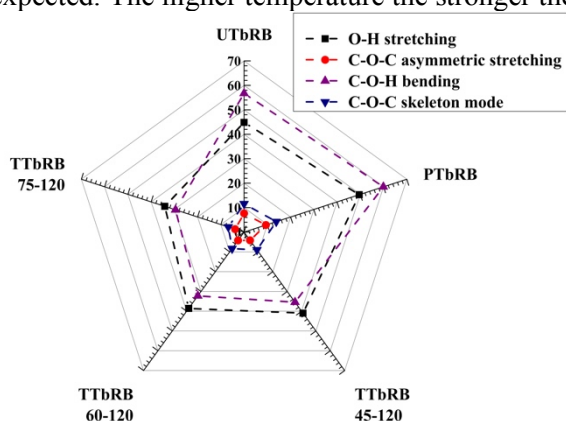


Figure 3. Relative amount of major functional groups in bran from various conditions.

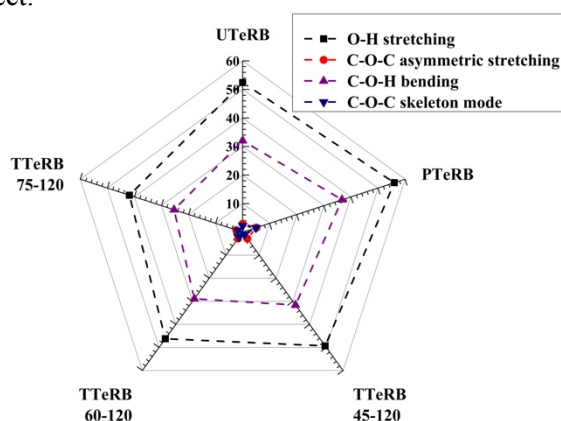


Figure 4. Relative amount of major functional groups in endosperm from various conditions.

4. Conclusion

This study has performed plasma and thermal treatment on the bran and the endosperm portion of the riceberry rice grain. FTIR analysis showed that plasma treatment caused distinct modifications in contrast to the thermal treatment. Therefore, plasma treatment has caused more complex effects which cannot be accounted for by the elevated temperature during plasma treatment alone.

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