Atmospheric argon-plasma treatment of maltodextrin: Changes in structure and physico-chemical properties

Khanh Son Trinh 1, *, Thuy Linh Nguyen 2

1Department of Food Technology, University of Technology and Education, Ho Chi Minh City, Vietnam
2Department of Fishery Processing, Nong Lam University, Ho Chi Minh City, Vietnam

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A B S T R A C T
Maltodextrin was modified using a dielectric barrier discharge (DBD) argon-plasma system. Under treatments, the color of maltodextrin samples was significantly changed and could be distinguished by human eyes; free acid content was 2.25-folded increased; DE value was 1.9-fold increased compared to untreated maltodextrin. The viscosity was strongly correlated to the treatment time. After modification, maltodextrin was depolymerized to reduce around 1.56-fold of its average molecular weight and degree of polymerization compared to untreated sample. The ratio of a-helix/amorphous structures was not dramatically changed. FTIR spectra showed that the depolymerization and cross-linking formation were processed at various level. A short time of treatment mainly resulted in the broken down of C-O-C bonds; whilst, new C-O-C linkage was created during a long time of treatment.

1. Introduction

Maltodextrin is a hydrolyzed starch product with a number of different properties compared to starch. Maltodextrin has the chemical formula (C_{6}H_{10}O_{5}) n.H_{2}O, similar to the chemical formula of starch but has a smaller molecular weight. Maltodextrin is an incomplete starch hydrolysate (by heat, acid or enzyme) with dextrrose (DE) equivalent of less than 20 (Chronakis, 1998; Kearsley and Dziedzic, 1995). Maltodextrin is water soluble and usually exists as a white powder or as a concentrated solution. Maltodextrin is recognized as a food additive (Chronakis, 1998). In food technology, maltodextrin is: (A) odor and flavor fixation; (B) structural changes and increased food sensitivities; (C) drying aids; (D) increase energy for dietary foods help foods to be dissolved, easily digested, and increase nutritional value (Chronakis, 1998). The properties of maltodextrin depend on the DE value and the degree of polymerization (DP). Maltodextrin with lower DE is less hygroscopic (Kearsley and Dziedzic, 1995).

Among the methods of denaturing materials derived from starch (starch, maltodextrin) by physical agents, the method of treating by cold plasma at atmospheric pressure (ACP, atmospheric cold plasma) is a new technique. It has many outstanding advantages, especially this processing technique is quite simple. In a plasma environment, with argon-conducting gas, a large number of high-energy electrons are formed from the discharge. These electrons can attach to argon atoms and transform them into excited or dissociated states for creating Ar+ and e-. Energy in the form of atoms, ions, electrons (Ar, Ar+, Ar2, e-) will affect the surface of materials derived from starch and alter the surface properties of the sample, leading to two main reactions during plasma processing: (A) depolymer reaction and (B) cross-linking reaction (Wongsagonsup et al., 2014). There have been many studies on the use of cold plasma to modify starch to change the transparency of the gel, heat resistance, rheology and digestibility (Wongsagonsup et al., 2014; Trinh, 2014).

In terms of chemistry, because maltodextrin is an incomplete hydrolysate of starch, changes in plasma on starch can completely occur on maltodextrin. However, until now, almost no published research has mentioned this issue. Therefore, the goal of our study is to investigate and evaluate the structural and physicochemical changes of maltodextrin under argon-plasma cold at atmospheric pressure.
2. Materials and methods

2.1. Atmospheric cold plasma treatment of maltodextrin

Maltodextrin treatment method with argon-plasma, basically based on the published method of Trinh (2014). Maltodextrin (5.0 g) (HiMedia Laboratories, India), spread evenly over a glass slide (19 cm×13 cm). Then, the sample was placed into the DBD plasma device, with the input parameters of the device: (A) 1 ampere, 120 voltages, 50 Hz; (B) argon gas flow rate of 5.0 l/min; (C) treatment time for one cycle was 2 minutes; (D) the sample was mixed well every 3 minutes; (E) treatment time of 0, 5, 10, 15 and 20 minutes (corresponding to MD0, MD5, MD15 and MD20 samples). DBD plasma device was manufactured by Plasma Technology and Environment Laboratory, Ho Chi Minh City University of Technology and Education. DBD plasma device were shown in Fig. 1.

Fig. 1: DBD plasma device

2.2. Color of maltodextrin

The color of maltodextrin was measured by colorimetric equipment (Minolta-CR400, Japan). The values of L∗, a∗, b∗ denote the white, red and yellow colors of the sample, respectively (Pimpa et al., 2007). The color differences between treated samples compared to untreated sample were determined by the formula (1): \( \Delta E^* = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \). The whiteness was determined by the formula (2): \( W_1 = 100 - \sqrt{(100 - L^*)^2 + a^2 + b^2} \) (Lanier et al., 1991).

2.3. Free acid content of maltodextrin (FA)

Free acid content was determined by the method of Sokhey and Chinnaswamy (1993).

2.4. Dextrose equivalent of maltodextrin (DE)

The dextrose equivalent of maltodextrin was determined by the method of Bernfeld (1995).

2.5. Fourier transform infrared (FTIR) spectrum of maltodextrin

FTIR spectra were used as a tool to quantify and describe changes in the structure of maltodextrin. Maltodextrin samples was scanned from 400-4000 cm\(^{-1}\) (Paulino et al., 2011). KBr (0.2 g) and sample (0.002 g) were put into the sample compressor and compressed at 8 bar for 10 minutes. The sample was then measured in the FTIR device (FTIR-8400S, Shimadzu, Japan).

2.6. Intrinsic viscosity (\( \eta_i \)), molecular weight (M) and degree of polymerization (DP)

The intrinsic viscosity of maltodextrin was measured according to the method of Dokic et al. (2004) and Harding (1997). Maltodextrin was diluted with distilled water into a range of concentrations of 5, 10, 15 and 20 g/ml. Then, the viscosity (\( \eta_i \)) was determined by Ostwald capillary viscometer (\( \theta=0.3 \) mm, Ref. No 509 03, Germany). Maltodextrin solutions were thermally stabilized in a thermostatic bath at a temperature of 30°C. The time flowing through the two marked lines of distilled water was 19.17 seconds. Kinematic viscosity (\( \eta_k \), m²/sec) was determined according to the formula (4): \( \eta_k = 0.004 \times t - 0.12/t \) (SI Analytics GmbH, 2014). The density of maltodextrin solution was determined by the formula (5): \( \rho = m/V \); where \( m \) was the mass (g) and \( V \) was the volume (ml). Relative viscosity (\( \eta_r = \eta_i/\eta_k \)) was determined by the following equations (6): \( \eta_r = \eta_i/\eta_k = t(t_0-\alpha)/t_0 \); where \( t \) was the flowing time (sec) of the sample, \( t_0 \) was the viscosity (m²/sec) of the distilled water, \( t_0 \) was the flowing time (sec) of water in the viscometer, \( \rho \) was the density of the sample solution at 30°C, and \( \rho_0 \) was the density of water at 30°C. Reduced viscosity (ml/g) was calculated by the formula (7): \( \eta_i = (\eta_i - 1)/c \); where \( c \) was the concentration of maltodextrin solution. The intrinsic viscosity (\( \eta_1 \), ml/g) of the sample was calculated by the formula (8): \( \eta_1 = \lim_{c \to 0} \eta_i \); From the intrinsic viscosity, the molecular weight (M, g/mol) of maltodextrin was determined through the Staudinger-Mark-Houwink formula (Dokic et al., 2004) to show the relationship between intrinsic viscosity and molecular weight (9): \( [\eta] = K \cdot M^a \); where, \( K \) and \( a \) were called Mark-Houwink coefficients that determined experimentally with coefficients in the range of 0.5<\( a <1.0 \). The relationships between dextrose equivalents (DE), degree of polymerization (DP), and intrinsic viscosity were expressed by the following equations (10): \( \eta_1 = K \cdot (\alpha + 18)^a \) and \( DP = \frac{111.1 \cdot \alpha}{DE} \); where, \( DP \) was the degree of polymerization. For DE in the range of 10-20, \( K=3.56 \times 10^{-3} \) and \( a=1 \) (Dokic et al., 2004).

2.7. Statistical calculation

All values were shown in the average ± standard deviation (n=3). The data were calculated differently by one-dimensional ANOVA calculation (\( P<0.05 \), Duncan’s multiple range test) using SPSS software.
(Released 2008, SPSS Statistics for Windows, Version 17.0, Chicago: SPSS Inc.).

3. Results and discussion

3.1. Color of maltodextrin

Color is one of the important factor in assessing the quality of material, product or consumer acceptance of the product. Moreover, the change in color also shows the change in composition, structure of materials and products. The changes in the color of the sample before and after the plasma treatment were shown in Table 1. Accordingly, the value of a’ (green-red) decreased from -2.04 to -2.14 after being treated during 20 minutes. b’ values (yellow-blue) between the maltodextrin samples under plasma treatment (MDS, MD10, MD15, MD20) did not change much. However, compared to untreated samples (MD0), these samples had higher b’ values. Thus, the longer the plasma treatment was, the more maltodextrin sample colors became green and yellow than the MD0 sample. The change in b’ value (yellow) was due to the caramelization reaction of monosaccharides obtained from the splitting of maltodextrin by plasma treatment. During treatment, maltodextrin was broken down into smaller sized molecules such as dextrin, sugar, and free radicals. Under the effect of temperature, caramelized sugar molecules change the color of maltodextrin. Besides, by increasing the treatment time, the L’ value (black-white) was reduced due to the influence of the change of the yellow (Kang et al., 1999).

This also corresponded to lower the whiteness (WI) of treatment samples compared to MD0 sample (Table 1). The ∆E’ value clearly showed that the plasma treatment of the sample had a marked change in color. The color difference was expressed in ∆E’ values of ≥ 4.89, indicating that the color differences between plasma treated samples and raw samples (MD0) were easily recognizable by the human eyes (Mokrzycki and Tatol, 2011).

### Table 1: Effects of DBD argon-plasma treatment time on color and the correlation between reduced viscosity (y) and maltodextrin content (x)

| Sample  | L’       | a’       | b’       | ∆E’     | WI       | y—a+b   |
|---------|----------|----------|----------|---------|----------|---------|
| MD0     | 98.45±0.01a | -2.04±0.00a | 2.48±0.00a | 0.00±0.00a | 96.43±0.00a | y=0.2751x+4.8552 (R²=0.9971) |
| MDS     | 93.67±0.02b | -2.16±0.00b | 3.49±0.00b | 4.89±0.00b | 92.46±0.02b | y=0.2476x+4.7064 (R²=0.9982) |
| MD10    | 93.06±0.00c | -2.19±0.00c | 3.60±0.01d | 5.51±0.00c | 91.88±0.00c | y=0.2614x+4.8191 (R²=0.9993) |
| MD15    | 93.49±0.01d | -2.15±0.00c | 3.26±0.01d | 5.02±0.00c | 92.41±0.01e | y=0.2750x+3.7572 (R²=0.9999) |
| MD20    | 93.07±0.00c | -2.14±0.00c | 3.24±0.02e | 5.43±0.00c | 92.06±0.01f | y=0.2996x+3.1194 (R²=0.9950) |

The values in the Table indicated the average value ± standard deviation (n=3). Letters in the same column with different symbols indicated statistically significant differences (P<0.05). MD0: Untreated maltodextrin; MDS, MD10, MD15, MD20: maltodextrin samples were treated with DBD argon-plasma for 5, 10, 15 and 20 minutes, respectively.

3.2. Dextrose equivalent (DE) and free acid content (FA) of maltodextrin

DE is an important indicator of maltodextrin because if the DE change, the functional and application properties of maltodextrin will also change (Lazaridou et al., 2007). The result (Table 2) showed the positive correlation between DE value and treatment time (t) was a linear (DE=0.585×t+12.744, R²=0.9311). Accordingly, the plasma treated maltodextrin for 20 minutes (MD20) had the highest DE value (around 1.9-folded higher than that of the untreated sample, MD0). The higher the DE index was, the higher level of depolymerization and the lower the molecular weight of maltodextrin were (Lazaridou et al., 2007). Besides, the free acid content (FA) indicated the acidity of maltodextrin. Thereby, it showed the application area of maltodextrin in industrial production. According to previous studies, plasma treatment could alter pH as well as the free acid content of starch-derived samples (Wongsagonsup et al., 2014). Table 1 showed a positive correlation between FA and treatment time (t) (FA=0.011x+0.258; R²=0.81618). Furthermore, maltodextrin which treated for 20 minutes (MD20) had the highest free acid content and its FA content was 2.25-folded higher than that of untreated sample (MD0). This result was similar to the previous study of Lii et al. (2003) on starch. This could be explained by the depolymerization of maltodextrin that takes place during plasma processing. This process led to the appearance of carboxyl (-COOH), carbonyl (aldehyde or ketone) or peroxide ((O-O=)), thereby increasing free acid content in the sample (Elshnash, 2010). The free acid content and depolymerization reactions of maltodextrin depend on the time of plasma treatment. Accordingly, the longer the treatment time was, the higher the degree of depolymerization and the higher the free acid content (FA) were (Lii et al., 2003).

3.3. Intrinsic viscosity (η_i), molecular weight (M) and degree of polymerization (DP) of maltodextrin

The results in Table 2 showed that the intrinsic viscosity (η_i) of samples change in turn with maltodextrin content in the solution. The characteristics of maltodextrin (size, volume, structure), maltodextrin concentration, pH, temperature interacted to others, then it made the viscosity change (Sokhey and Chinnaswamy, 1993; Deschreder, 1996). The results showed that the intrinsic viscosity of maltodextrin decreases with time (t) of treatment (η_i=0.0884×t+5.0082, R²=0.967). In which, MD20 sample had lowest viscosity. This result was similar to that of a published study on starch (Lii et al., 2003).
According to Sokhey and Chinnaswamy (1993), the decrease in viscosity occurred due to the structural and molecular weight changes of maltodextrin. During treatment, plasma could cause the depolymerization reaction that breaks maltodextrin to produce shorter polysaccharides leading to the reduction of viscosity (Deschreider, 1960).

The average molecular weight affected most of the physicochemical properties of maltodextrin. The average molecular weight (M) of maltodextrin decreased with the increasing time (t) of plasma treatment (M = -2.4836 × t + 1406.8, R² = 0.967). Similar result was reported by Lii et al. (2003) when treating plasma on starch. The average molecular weight reduction was caused by broken polysaccharides to produce smaller sized molecules (Elnashar, 2010).

According to Table 2, we found that the degree of polymerization (DP) of maltodextrin decreased linearly with plasma treatment time (t) (DP = -0.1518 × t + 8.4859; R² = 0.967). Similar result was reported by Pimpa et al. (2007). Along with the decrease in viscosity and DP, the DE index of maltodextrin increased (Dokic et al., 2004). Under the action of plasma with a high energy level, ionized maltodextrin molecules led to a decrease in intrinsic viscosity and average molecular weight (Pimpa et al., 2007).

Table 2: Effects of DBD argon-plasma treatment time on free acid content (FA), dextrose equivalent (DE), intrinsic viscosity (ηi), molecular weight (M), degree of polymerization (DP), α-helix/amorphous (H/A) ratio and absorption (Abs) FTIR at the peak of 1155 cm⁻¹ of maltodextrin samples

| Sample | FA     | DE     | ηi     | M      | DP    | H/A   | Abs    |
|--------|--------|--------|--------|--------|-------|-------|--------|
| MD0    | 0.20±0.00 | 13.58±0.79 | 4.86±0.00 | 1363.82±0.00 | 8.22±0.00 | 0.93±0.00 | 0.566±0.01 |
| MD5    | 0.35±0.00 | 15.83±0.33 | 4.71±0.01 | 1322.02±0.00 | 7.97±0.00 | 0.94±0.00 | 0.281±0.00 |
| MD10   | 0.40±0.00 | 17.12±0.64 | 4.18±0.00 | 1174.66±0.00 | 7.07±0.00 | 0.92±0.00 | 0.371±0.00 |
| MD15   | 0.40±0.00 | 20.63±2.11 | 3.76±0.10 | 1055.39±0.00 | 6.34±0.00 | 0.94±0.00 | 0.44±0.00 |
| MD20   | 0.45±0.00 | 25.90±0.00 | 3.12±0.01 | 876.24±0.00 | 5.24±0.00 | 0.96±0.00 | 0.59±0.02  |

The values in the Table indicated the average value±standard deviation (n=3). Letters in the same column with different symbols indicated statistically significant differences (P<0.05). MD0: Untreated maltodextrin; MD5, MD10, MD15, MD20: maltodextrin samples were treated with DBD argon-plasma for 5, 10, 15 and 20 minutes, respectively.

3.4. Structural properties

FTIR spectra in Fig. 2 showed that the spectral shape of maltodextrin samples before and after treatment were almost no different in shape, no appearance or loss of peaks. Water molecules were retained in the structure of maltodextrin by tightly and weakly linkages which were reflected at two peaks, respectively 1645 cm⁻¹ and 3363 cm⁻¹. The results obtained from the FTIR spectra showed that peak intensity (i) 1645 cm⁻¹ and (ii) 3363 cm⁻¹ of MD0, MD5; MD10, MD15, MD20 samples respectively were (i) 0.294, 0.190, 0.198, 0.230, 0.51 and (ii) 0.374, 0.247, 0.290, 0.280, 0.593. Thus, the samples treated with short time (from 5 to 15 min) had a peak intensity (–OH) lower than that of MD0 sample.

Meanwhile, 20 min-plasma treated sample (MD20) had higher peak intensity than that of MD0 and the others. It can be seen that, at the same time, there are two factors that affected the intensity of –OH peak in FTIR spectrum: (A) the depolymerization formed free water molecules and (B) the water vaporization process under the effect of temperature as well as the effect of argon gas flow (5 l/min) during plasma treatment (Wongsagonsup et al., 2014). The formed water molecules were unabsorbed in the α-helix helical structure, but they were absorbed in the amorphous region, which leads to an increase in the intensity of the –OH peak after plasma treatment (Wongsagonsup et al., 2014; Deeyai et al., 2013). The depolymerization reaction also depended on the time of plasma processing (Lii et al., 2003). At the same time, the formed water evaporated resulting in a decrease in the intensity of the –OH signal. The longer the treatment time was, the higher the level of depolymerization was (the increase in the intensity of the –OH signal) and level of water evaporation (the decrease in absorption intensity of the –OH group) were. Thus, at a short treatment time (from 5 to 15 min), the free water would be completely evaporated. On the contrary, for the 20 min-treated sample, the amount of water formed by the depolymerization reaction was more than that of evaporated water.

Using FTIR, structural analysis of maltodextrins showed that the peak at 1155 cm⁻¹ was corresponded to C-O-C asymmetric stretching glycosidic bond and the signal at 927 cm⁻¹ was referred to α-1,4 glycosidic linkage. Intensity of the C-O-C signal decreased after plasma treatment (from 5 to 15 minutes) due to depolymerization reaction during processing. This reaction broke the C-O-C linkages (Table 2) (Wongsagonsup et al., 2014). The MD20 sample had an increased in the intensity of C-O-C group compared to that of other treated samples (Fig. 2). This can be explained by the fact that, during the plasma treatment process, the following two reactions simultaneously occurred at different levels: (A) the depolymerization reaction and (B) the reaction formed cross-linkages (Wongsagonsup et al., 2014).

At a short plasma treatment time (from 5 to 15 minutes), the dominant depolymer process caused a fracturing of maltodextrin molecule to form a smaller molecular such as dextrins, glucose and water. At a long treatment time (20 minutes), between two glucose molecules of maltodextrin, a new glycosidic (C-O-C) bond could be formed, thereby increasing the intensity of the C-O-C peak compared to that of the non-plasma sample. However, more detailed analysis is needed to clarify this theory.
Starch or starch derivatives such as maltodextrin had a semi-crystalline structure including the α-helix region (double helix structure) and amorphous region. The ratio of the intensity of peak 1047 cm\(^{-1}\) (α-helix) and 1022 cm\(^{-1}\) (amorphous) indicated the level of orderly structure of a sample (Deeyai et al., 2013). The results of the α-helix/amorphous ratio of the samples were shown in Table 2. Treated samples had slightly increased α-helix/amorphous ratios compared to that of MD0 samples. However, this difference was very small and does not much meaning in terms of structural property.

4. Conclusion

Argon-plasma treatment techniques helped maltodextrin significantly reduce the level of polymerization and molecular weight, helped DE increase and reaching a value of 25.80 (12.22-folded higher compared to that of the original sample). This meant that maltodextrin is transformed into a product with a higher sweetness than that of the original maltodextrin. Especially, this product still remained in solid stage.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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