Electrical impedance spectroscopy analysis of eggplant pulp and effects of drying and freezing–thawing treatments on its impedance characteristics

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Received 27 July 2007; received in revised form 2 October 2007; accepted 2 December 2007

Available online 8 December 2007

Abstract

The electrical impedance characteristics of eggplant pulp were investigated; the effects of drying and freezing–thawing treatments on the pulp samples were discussed by means of electrical impedance spectroscopy analysis. Fresh eggplant pulp was subjected to vacuum drying, hot-air drying and freezing–thawing treatments respectively, the electrical impedance of the non-treated, partially dried and frozen–thawed pulp tissue was measured using a LCR tester over a frequency range of 42 Hz to 5 MHz; the impedance spectra were analyzed with two lumped element models and a distributed element model based on the Cole–Cole impedance equation; the circuit model parameters representing physiological properties of the tissue were calculated using non-linear regression analysis. Results showed that the impedance loci of the fresh as well as partially dried samples could be described by the models, and the distributed model fitted the experimental data significantly better than the two lumped models did. After drying, the impedance of the samples increased dramatically across the test frequency range due to the loss of moisture; the increase in the impedance of hot-air dried sample was statistically higher than that of vacuum dried sample under the present experimental conditions. After freezing–thawing treatment, the impedance spectrum of the sample lost its original character and became almost independent of the test frequencies, which verified that the membranes of the cells were severely damaged during the freezing process.

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Keywords: Electrical impedance spectroscopy; Equivalent circuit model; Cole–Cole equation; Drying; Freezing–thawing; Eggplant

1. Introduction

Electrical impedance spectroscopy (EIS) measures the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external electric field with the electric dipole moment of materials. EIS has been used extensively to characterize properties of solid materials (Pan et al., 2003; Prabakar and Mallikarjun Rao, 2007; Takashima and Schwan, 1965). Compared with other techniques of physiological investigation, EIS measurement is very simple and easy to be conducted, it has been widely used to estimate the physiological state of various biological tissues (Cole, 1932; Damez et al., 2007; Harker and Dunlop, 1994; Zhang and Willison, 1992; Żywica et al., 2005).

In the EIS study for biological tissue, it is of great importance to establish appropriate equivalent circuit model to relate the measured data to the physical and physiological properties or their changes of the tissue investigated, and thus explanations for the impedance spectra could be provided at the cellular level. Recent EIS studies suggest that the impedance spectra of plant tissue can be characterized by the equivalent circuit models composed of resistors and capacitors representing plant cell structures; several equivalent circuit models including lumped element circuits and distributed element circuits for describing the impedance characteristics of plant tissue have been reported. A lumped model consists of limited circuit elements, each element should correspond to a cellular
structure that affects the impedance characteristics of tissue. In a distributed model, the complicated cell structures such as membranes are simulated by transmission line, which can be seen as a multiple combination of many small circuit segments instead of limited elements. Among the equivalent circuit models reported in the literature, a three-element circuit model proposed by Hayden et al. (1969), and its adaptation (a five-element model) proposed by Zhang et al. (1990) have been widely applied to the EIS analysis of various plant tissues and have provided a lot of useful physiological information (Bauchot et al., 2000; Harker and Maindonald, 1994; Zhang and Willison, 1991; Zhang and Willison, 1992). Since both the lumped element models were proposed based on the assumption that the shape and size of cells as well as their distribution in the tissue is uniform, in those cases where the lumped models failed to satisfactorily reproduce or interpret the measured impedance loci of some highly heterogeneous tissue, using distributed element model was proved to be an effective means of EIS analysis. Presently, a distributed circuit model described by the Cole–Cole empirical equation has been applied to some EIS studies; using the distributed model associated with electrophysiological consideration also offered valuable information about the physiological properties of biological tissue (Damez et al., 2007; Repo and Zhang, 1993; Zhang et al., 1995).

Until now, most EIS studies of plant tissue have been focused on the natural physiological properties of the tissue as well as relevant issues such as ripening, aging and frost hardness etc. There are few reports available detailing the impact of artificial processes such as commonly-used food processing techniques on the electrical impedance characteristics of fruits and vegetables. The use of EIS analysis could provide a new approach to the evaluation of the freshness or quality of processed agricultural products due to its simplicity and effectivity. The objectives of the present study were as follows: (1) to analyze the impedance characteristics of fresh, partially dried and frozen–thawed eggplant pulp in reference to the lumped element models proposed by Hayden et al. and Zhang et al. as well as the distributed model based on the Cole–Cole impedance equation, (2) to evaluate the effect of drying and freezing–thawing processes on the eggplant pulp tissue in terms of the EIS analytical results.

2. Materials and methods

2.1. Sample preparation

Eggplants used in the study were purchased from a local market and stored at 8 °C in a refrigerator before the experiment started. The pulp of the fresh eggplants had an average moisture content of 94% (w.b.) according to the vacuum oven method (AOAC, 1995). Four rectangular-shaped pulp sample blocks, each of 45 × 15 × 6 mm (Fig. 1), were cut from the central part of an eggplant fruit. Two of the four samples were vacuum dried (30 °C, 2.5 kPa) and hot-air dried (80 °C) respectively to a target moisture content of 80% (w.b.) in a vacuum/hot-air drying system (the drying setup and processes were detailed in the paper of Wu et al. (2007) discussing the vacuum drying characteristics of eggplant pulp). Another fresh sample wrapped in plastic film was frozen at −40 °C in an air-blast freezer (SANYO, MDF-435, Japan), and then thawed at 25 °C in a constant temperature oven (DK600, YAMATO, Japan). The duration of the freezing–thawing treatment was predetermined using type T thermocouples embedded in the samples. The impedance of the dried and frozen–thawed samples were measured immediately after treatments.

2.2. Electrical impedance measurement

The EIS measurement for the above fresh and treated samples was performed at room temperature. A schematic diagram of the EIS measuring system used in this study is shown in Fig. 1. The impedance data of the samples were measured using a LCR tester with two parallel clip test probes spaced 10 mm apart (HIOKI, 3532-50, Japan, frequency range: 42 Hz ~ 5 MHz, frequency accuracy: <±0.005%, measurable impedance range:10.00 mΩ ~ 200.00 MΩ). The impedance, resistance, reactance

![Fig. 1. Schematic diagram of EIS measuring system, 1– eggplant pulp sample; 2 – clip test probe; 3 – LCR tester; 4 – computer.](image-url)
and conductance of the samples were measured at 50 frequency points (logarithmic frequency intervals) over the frequency range of 42 Hz–5 MHz under a measuring voltage of 1 V, and automatically recorded by a computer for analysis. The measurement for each sample was repeated three times at different positions along the long axis of the sample, comparisons between means were performed using Duncan’s multiple range tests at a significance level of 0.05 in SPSS 12.0 software (SPSS Inc.).

Since both test probes and tested material could contribute to the measured impedance, a preliminary study was conducted to separate the impedance of eggplant pulp sample from the electrode impedance according to the method used by Stout et al. (1987). Results showed that using the method conducted to separate the impedance of eggplant pulp samples in this study.

2.3. Equivalent circuit models and data analysis

The equivalent circuit models for eggplant pulp tissue were presented in Fig. 2. Model (a) proposed by Hayden et al. (1969) takes account of the resistance of cell walls (R1 in model (a)), the cytoplasmic resistance including vacuole (R2 in model (a)), and the resistance and capacitance of cell membrane (C3 in model (a), the membrane resistance was considered very large and omitted); Zhang et al. (1990) suggested that the capacitance of the tonoplast (C5 in model (b)) and the interior resistance of the vacuole (R4 in model (b)) contributed substantially to the total impedance, and should be added as independent elements in the equivalent circuit (in parallel with symplastic resistance R2 in model (b)). In the distributed element model (c), R1 and R2 stand for the extracellular and intracellular resistance of plant tissue, respectively, the membrane impedance with transmission line properties is represented by Z1.

However, for the convenience of using the Cole–Cole impedance equation (Grimnes and Martinsen, 2000):

\[
Z = R_\infty + \frac{R_0 - R_\infty}{1 + (j\omega \tau)^{\alpha}} \tag{1}
\]

where \( R_\infty \) and \( R_0 \) are the tissue resistance at extremely high and extremely low frequency (Ohm), \( \omega \) is the alternating current frequency, \( \tau \) is the time constant (s), and \( \alpha \) is a dimensionless factor (taking values between 0 and 1), circuit (c) is transformed into (d), which is the simplest equivalent circuit for Eq. (1), considering the following relationships:

\[
R = \frac{R_1 R_2}{R_1 + R_2}; \quad R_0 - R_\infty = \frac{R_1^2}{R_1 + R_2}; \quad Z_2 = \frac{Z_1}{(1 + \frac{R_2}{R_1})^2}
\]

The complex impedance \( Z \) or admittance \( Y \) of the circuit models as a function of AC frequency (\( \omega \)) was broken down into its real and imaginary parts:

\[
Z = R + jX \tag{2}
\]

or \( Y = G + jB \) \tag{3}

where \( R\)-resistance (\( \Omega \)), \( X\)-reactance (\( \Omega \)), \( G\)-conductance (\( S \)), \( B\)-susceptance (\( S \)).

For model (a):

\[
R = \frac{R_1 R_2 (R_1 + R_2) C_3^2 \omega^2 + R_1}{(R_1 + R_2)^2 C_3^2 \omega^2 + 1} \tag{4}
\]

\[
X = \frac{-R_2^2 C_3 \omega}{(R_1 + R_2)^2 C_3^2 \omega^2 + 1} \tag{5}
\]

For model (b):

\[
G = \frac{1}{R_1} + \frac{R_2 R_4 (R_2 + R_4) + \frac{R_2}{C_3 \omega}}{\left(\frac{R_2 R_4}{C_3 \omega} - \frac{1}{C_3 C_4 \omega} + \frac{R_2}{C_3 \omega} + \frac{R_4}{C_4 \omega}\right)^2} \tag{6}
\]

\[
B = \frac{(R_2 R_4)^2}{C_3 \omega} + \frac{R_2}{C_3 \omega} + \frac{R_4}{C_4 \omega} \tag{7}
\]

\[
R = \frac{G}{G^2 + B^2} \tag{8}
\]

\[
X = \frac{-B}{G^2 + B^2} \tag{9}
\]

Fig. 2. Equivalent circuit models used to analyze impedance characteristics of eggplant pulp tissue, (a) lumped model proposed by Hayden et al. (1969); (b) lumped model proposed by Zhang et al. (1990); (c) & (d) distributed models.
Since following transformation can be made according to de Moivre’s formula:

\[
(j \omega t)^{(1-z)} = \left( \omega t \cos \frac{\pi}{2} + j \omega t \sin \frac{\pi}{2} \right)^{(1-z)}
\]

\[
= \left( \omega t \right)^{(1-z)} \left[ \cos \left( \frac{(1-z)\pi}{2} \right) + j \sin \left( \frac{(1-z)\pi}{2} \right) \right]
\]

The impedance \( Z \) in Eq. (1) can be broken down into:

\[
R = R_\infty + \frac{(R_0 - R_\infty) \left( \left( \omega t \right)^{(1-z)} \cos \left( \frac{(1-z)\pi}{2} \right) \right)}{1 + \left( \omega t \right)^{(1-z)} \cos \left( \frac{(1-z)\pi}{2} \right)}
\]

\[
X = \frac{-(R_0 - R_\infty)(\omega t)^{(1-z)} \sin \left( \frac{(1-z)\pi}{2} \right)}{1 + \left( \omega t \right)^{(1-z)} \cos \left( \frac{(1-z)\pi}{2} \right)}
\]

The parameters representing different physiological structures in the three equivalent circuit models were obtained by fitting the above Eqs. (4), (6) and (11) to the measured resistance or conductance data using non-linear curve fit in OriginPro 7.5 software (OriginLab Corp.). The Eqs. (4), (5), (8), (9), (11), (12) and the fitted model parameters were used for the calculations of \( R \) and \( X \) values. The goodness of fit of the models to the experimental data showing the appropriateness of using the models was evaluated by the coefficient of determination (\( R^2 \)), the root mean square error (RMSE) and a mean relative deviation modulus \( P \) (%) defined by Eq. (8).

3. Results and discussion

3.1. Fresh eggplant pulp

Theoretically, for the relatively uniform undamaged tissue, the path of alternating current lies mainly in channels of the cell wall at very low test frequencies due to a very large membrane impedance, hence the apoplastic resistance is estimated over low frequency range. The capacitive reactance of membranes gradually decreases with the increasing frequency; the decrease in the reactance significantly affects the total impedance and causes a decrease in the impedance value of the tissue when the frequency rises above a certain level. If the frequency is sufficiently high, the effect of the capacitor elements in the models may be neglected and the impedance becomes independent of the frequency, accordingly the approximate symplastic resistance can be measured (Bauchot et al., 2000; Harker and Dunlop, 1994; Hayden et al., 1969; Zhang et al., 1990).

The impedance spectra of the fresh, partially dried and frozen-thawed samples are shown in Fig. 3. The impedance of the samples were plotted with respect to frequency in

![Fig. 3. Electrical impedance spectra of fresh and treated eggplant pulp tissue.](image-url)
Fig. 3a (semi-logarithmic scale), and the relationships between the real (resistance) and imaginary (reactance) part of the complex impedance of the samples are presented in Fig. 3b (also known as Cole–Cole plot). The results indicated that the impedance characteristics of the fresh eggplant pulp tissue generally agreed with the above postulations of the lumped models. Two obvious limiting impedance values indicating the apoplastic and the cytoplasmic resistance, respectively at low/high frequencies, and a drop in total impedance with the increasing frequency within a specific frequency range (about 1 KHz ~ 1 MHz) can be observed in the impedance locus; when plotting the measured reactance against resistance, the locus presented a fairly perfect semicircle showing the dielectric relaxation process.

By fitting the models to the experimental results, the model parameters as well as the goodness of fit indexes were evaluated, the results are shown in Fig. 4 and Table 1. From Fig. 4, the three models could, to different extent, describe the impedance spectrum of the fresh eggplant pulp. The calculated results using model (a) showed comparatively obvious deviations from the measured data over the whole frequency range (Fig. 4a), which indicated that the model could be too “general” to precisely characterize the impedance-related physiological structures of the tissue. According to the literature (Bauchot et al., 2000; Harker and Maindonald, 1994; Repo and Zhang, 1993; Zhang and Wilison, 1991), model (b) was able to satisfactorily describe the impedance spectra of some plant tissues such as potato, carrot, kiwifruit and nectarine etc. While in this study, model (b) did not fit the experimental data at low frequencies very well, it only provided a comparatively good fit within the frequency range higher than $3 \times 10^4$ Hz (Fig. 4b). This result exhibited that the components in model (b), possibly capacitive element, were inaccurate for simulating the complex tissue structure. Zhang et al. (1993) also reported that the lumped circuits (including model (b)) did not fit the measured impedance data from wood of Scots pine well on account of a wide range of cell size in the tissue. The poorer fitting results of the lumped models in the present study could be attributed to the heterogeneity of the eggplant pulp (e.g. seeds and air bubbles) that the lumped models could not fully account for. Model (c) interpreted the impedance characteristics of the tissue by combining lumped resistor elements with a circuit element having transmission line properties. The goodness of fit indexes in Table 1 showed that model (c), having the highest $R^2$ and lowest RMSE and $P$ values, gave a significantly better fit to the measured impedance data of the fresh tissue than the two lumped models did. The calculated results almost overlapped with the measured impedance locus (Fig. 4c). According to the transformation relationship between circuit (c) and (d), as mentioned in Section 2.3, the elements representing the physiological structures in model (c) could also be characterized using the fitted parameters of the circuit (d), the calculated extracellular and intracellular resistance of the fresh tissue are presented in Table 1.

3.2. Partially dried eggplant pulp

Previous studies showed that the apparent impedance of dried eggplant pulp samples increased markedly with decreasing average moisture content (Fig. 5). While since surface hardening during drying, which occurred in the second falling rate period (moisture content <80% for eggplant pulp), brought inconvenience to the impedance measurement, the samples were dried to the target moisture content of 80% in this study.
Fig. 3 demonstrated that the impedance values of the partially dried samples were significantly higher than the fresh sample, besides the measured values from the hot-air dried sample was statistically higher than those from the vacuum dried one. The shape of the impedance spectra of the partially dried samples was basically consistent with that of the untreated sample despite the increase in the total impedance values, which implied that the physiological structure of the cells in the tissue remained intact after the drying treatments as far as impedance characteristics were concerned; the semicircle loci for the dried samples in the Cole–Cole plot showed only slight deviation at lower frequencies. Fitting results indicated that the resistance values of the resistor elements in all the models increased while the capacitance values of the capacitor elements in model (a) and (b) decreased after drying; model (c) still gave the best fit to the experimental data among the models examined, as presented in Table 2a and b.

The study of Wu et al. (2007) indicated that both the vacuum and the hot-air drying under the present conditions took place in the “falling rate period”, in which the evaporation of water on the surface of the sample is faster than the moisture transfer from the interior to the surface. Hence, the remarkable increase in the impedance of dried samples could be explained by a decrease in the mobility of the electrolytes due to the severe loss of surface moisture (Zhang and Willison, 1992). According to preliminary experiments, the difference in the impedance spectra between the samples processed at different drying temperatures (hot-air 60–80°C) was statistically insignificant, therefore only 80°C hot-air drying with shorter processing time was discussed in this study. From the calculated results presented in Table 2, the extracellular resistance in model (c) (or the counterparts in model (a) or (b)) of the hot-air dried sample differed greatly from that of vacuum dried sample, whereas the difference in the intracellular resistance (or the counterparts) between them was not as significant. This implied that the difference in the total impedance between the hot-air and vacuum dried samples consisted primarily in the difference in their extracellular resistance, i.e. the hot-air drying treatment caused greater extracellular moisture loss, which consequently led to a more significant increase in the impedance values of the sample. Under the present experimental conditions, the physiological status of the vacuum dried tissue were closer to the fresh sample according to the EIS analytical results.

### 3.3. Frozen–thawed eggplant pulp

Unlike the fresh and partially dried samples, the impedance spectra of the sample subjected to freezing–thawing treatment exhibited little change over the test frequency range, the impedance value of the thawed sample was close to the limiting impedance value of the fresh tissue within the high (>1 MHz) frequency range (Fig. 3a). The Cole–Cole plot also presented a irregular spectrum instead of semicircle, the locus was even hard to identify in Fig. 3b due to very small and nearly constant values (close to the

### Table 2
Model parameters and goodness of fit indexes of 3 circuit models fitted to impedance data of partially dried eggplant pulp samples

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>$R^2$</th>
<th>RMSE</th>
<th>$P$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a: Hot-air dried sample</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a $R_1 = 15637$, $R_2 = 2747$, $C_3 = 4.24$</td>
<td>0.962</td>
<td>1201</td>
<td>30.9</td>
</tr>
<tr>
<td>b $R_1 = 13201$, $R_2 = 2273$, $R_3 = 1369$, $C_3 = 2.01$, $C_4 = 0.294$</td>
<td>0.993</td>
<td>1972</td>
<td>13.8</td>
</tr>
<tr>
<td>c $R_1 = 17337$, $R_2 = 703$, $R_3 = 17337$, $R_4 = 676$, $\tau = 0.00008$, $\alpha = 0.40$</td>
<td>0.999</td>
<td>85</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>b: Vacuum dried sample</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a $R_1 = 10238$, $R_2 = 2249$, $C_3 = 3.80$</td>
<td>0.964</td>
<td>738</td>
<td>20.7</td>
</tr>
<tr>
<td>b $R_1 = 9256$, $R_2 = 2164$, $R_3 = 1605$, $C_3 = 2.30$, $C_4 = 0.305$</td>
<td>0.993</td>
<td>977</td>
<td>10.5</td>
</tr>
<tr>
<td>c $R_1 = 11181$, $R_2 = 747$, $R_3 = 11181$, $R_4 = 700$, $\tau = 0.00005$, $\alpha = 0.39$</td>
<td>0.999</td>
<td>119</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Units: resistance ($R$) – ohm; capacitance ($C$) – $\times 10^{-9}$ farad; $\tau$ – second.
left end of x-axis, marked by “+”). This result proved that the physiological structure of the cells, especially the membranes with dielectric properties, was disrupted by the ice crystals formed during the freezing process. After thawing, electrolyte leakage from symplasm led to the substantial disruption of membranes caused the severe drip loss and deterioration of appearance and texture of the sample. Consequently, the investigation into the post-thawing impedance characteristics of products could help understand and control the quality deterioration in frozen foods.

4. Conclusion

The electrical impedance spectroscopy analysis was applied to the evaluation of the effects of drying and freezing–thawing treatments on the eggplant pulp tissue. The measured impedance data of the fresh and treated samples were analyzed with three equivalent electrical circuit models. Model fitting was performed by means of non-linear curve fit using a regular statistical analysis software. The results indicated that the distributed model based on the Cole–Cole impedance equation gave the best fit to the measured impedance data of the fresh sample among the models examined. Drying treatments significantly increased the total impedance but did not fundamentally change the impedance characteristics of the samples. The impedance spectra of the partially dried samples (moisture content: 80% w.b.) could still be best described by the distributed element model. Under the present experimental conditions, the impedance of hot-air dried sample was apparently higher than that of the vacuum dried sample with the same moisture content. An explanation for the variations in the impedance spectra of the partially dried samples were provided considering drying theory. Freezing–thawing treatment had a severe impact on the impedance characteristics of the sample, the impedance locus of the sample became almost frequency-independent after treatment. The result proved that the membranes of the cells possessing dielectric properties in the tissue were seriously damaged during freezing process which was considered the uppermost reason for the post-thawing deterioration in quality attributes of frozen products.

References


