



Detection of dry rubber content in rubber cup lumps using electrical impedance spectroscopy

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Para rubber is one of the strategic crops in Thailand as it generates very high income and has made Thailand to one of the biggest exporters of Para rubber. At present, farmers commonly make rubber cup lumps from latex to add value to the latex. The cup lump can be further used to produce rubber blocks. The merchant evaluates the dry rubber content DRC by visual inspection which is a subjective method and depends on the experiences of the buyer. There has been no objective method to detect the DRC. Therefore, there is a need for a rapid and accurate method for assessment of the DRC in the cup lump.

Electrical impedance spectroscopy (EIS), which is a simple technique requiring no complex instruments, is one technique of interest in this regard as it can be used to assess the condition of plant tissue. Electrical impedance is related to the moisture content in the material and therefore can be applied to detect the DRC in the para cup lump. The EIS technique has been applied extensively for the evaluation of the internal quality of agricultural products. For instance, apple bruises were successfully evaluated for the extent of tissue damage (Jackson and Harker 2000). The ripening of fruit was also determined using EIS (Harker and Dunlop 1994, Harker and Maindonald 1994). In the study, the impedance spectrometry was reported to have capability in the characterization of raw and ripe mangos in the frequency range 1–200 kHz. Another related electrical technique using the resistance was also investigated to estimate fat content in beef carcasses (Bohuslavek 2000), with reactance in combination with other physical properties being used to develop a model which had high prediction accuracy.

There has been little research on the evaluation of the DRC in para cup lump. The current research focused on the application of EIS to develop a model for the estimation of the DRC and the selection of the optimal frequency for

use in the future development of a simple device. Fresh latex was harvested during 2017 from Para rubber trees in Eastern Thailand (13°14'32.6"N, 101°27'43.7"E). The initial DRC in the latex was determined by first pouring the latex with a thickness of about 2 mm into a Petri dish. The weight of the latex was measured and recorded and then 3% concentration of formic acid was added and stirred thoroughly to solidify the latex. Once the solidification was complete, the solid latex was oven dried at 70°C for 20 h. The dried latex was then weighed and the initial DRC was calculated from the initial weight and the dried weight. Upon production of the rubber cup lumps, the remaining latex was poured into cups of volume equal to 1000 mL up to two-thirds of the cup height, added with 20 mL of 3% concentration of formic acid and allowed to solidify. In total, 60 samples were prepared for further measurement.

EIS measurement: Each cup lump was weighed and cut into halves. EIS was performed by inserting two stainless steel needles into the cup lump to a depth of 4 mm and at spacing of 5 mm (Nakawajana *et al.* 2016). The change in capacitance was recorded using an LCR meter (3532-50, Hioki E E Corporation, Nagano, Japan) in the frequency range of 1–200 kHz using frequency steps of 1 kHz and a measuring voltage of 1 V. Data was analysed using the Hioki LCR-RS232C V4.01e software package (Nagano, Japan). During the course of 15-day storage, 10 samples were taken for EIS measurement every three days until all samples were measured.

Determination of rubber cup lump DRC: Each cup lump consists of fixed weight of the dry rubber and weight of water. The initial dry rubber weight of each cup lump was calculated as the weight of the cup lump multiplied by the initial DRC of the latex. During the storage water evaporated from the cup lump causing a reduction in the total weight of the cup lump while the weight of the dry rubber remained the same. The DRC (%) was calculated as a ratio of dry rubber weight to the total weight of cup lump multiplied by 100.

Partial least squares regression (PLSR) analysis was performed using the Unscrambler V9.8 program (Camo,

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Oslo, Norway) to develop a model to predict the DRC of the rubber cup lump. PLSR is multivariate data analysis that is used to avoid co-linearity. The validation of the model was achieved by means of full cross validation to select the optimal number of PLSR factors. The prediction performance of the model was evaluated from the correlation coefficient (r) and root mean square error of prediction (RMSEP).

The samples obtained from all treatments were combined and assigned into a calibration set (215 samples with averaged yellow pigment value of 7.16 mg/100 mL 3.10 mg/100 mL) and a prediction set (109 samples with averaged yellow pigment value of 7.23 mg/100 mL $\pm$ 2.77 mg/100 mL) on the basis of similar variances of the yellow pigment content. Spectral data used as independent variables and the yellow pigment value as the dependent variable of the calibration set were analyzed using partial least squares regression (PLSR) to create a calibration model (The Unscrambler v.9.8; Camo; Oslo, Norway). A cross validation technique was utilized to optimize the number of factors in the model. The predictive performance of the model was then determined in terms of the coefficient of correlation (r_p) and the root mean square error of prediction (RMSEP) using data from the prediction set.

Original spectra and pretreated spectra with one or more techniques of second derivative, standard normal variate and multiplicative scatter correction were used in building each PLSR model for comparison of the predictive performance.

Change in DRC with storage: During the storage water evaporated from the cup lump resulting in a reduction in the total weight of the cup lump whereas the weight of the dry rubber remained the same. This evaporation caused a decrease in DRC (%) of each cup lump. The average initial DRC of the rubber cup lump samples was 60%. The DRC was observed to increase over the 15-day storage period. During the first six days in storage, the increase was at a higher rate than for the remaining time in storage. The final DRC was 90.6% at the end of the storage.

Change in the capacitance as related to the DRC: Overall, the capacitance reduced with an increase in the frequency (Fig 1). The decrease in the capacitance was at a rapid rate up to a frequency of about 2200 Hz and then leveled off with higher frequencies. This trend in the reduction of the capacitance was in agreement with the reports using mangosteen (Nakawajana *et al.* 2016) and durian (KusonP and Terdwongworakul A 2013).

The capacitance decreased with an increase in the DRC or a reduction in the moisture content. Water molecules possess high dielectric properties and thus high moisture content causes greater electrical polarization and high capacitance

(Walstra P 2001). The effect of the DRC on the capacitance was the same for all measured frequencies. However, the effect was prominent in the frequency range 1–7 kHz. The relationship of the capacitance and the DRC was in partial agreement with the study by Benjakul *et al.* (2013) who reported that the capacitance of mangosteen rind with lower dry matter content or higher moisture content was higher than in rind with higher matter content or low moisture content.

Development of DRC predicting model

Selection of normal samples: Prior to the development of the DRC prediction model, the capacitance was plotted against the frequency and the plot was visually checked for outliers. Samples with an irregular reduction in the capacitance were removed from the analysis. Only the samples displaying a smooth, monotonic decrease in the capacitance were selected for further analysis. The cause of the abnormal samples might be due to the porosity of the samples, which prevented the continuous flow of the current through the sample (Samouelian *et al.* 2005). Furthermore, as the sample moisture content was the main factor involved in the measureable capacitance, the samples at the end of the storage were relatively dry and displayed abnormal changes in the capacitance against the frequency. Overall there were only 44 normal samples available for the analysis.

Prediction of DRC: The PLSR model based on the capacitance of all frequencies could predict the DRC with a correlation coefficient of 0.83 and an RMSEP equal to 2.53%. The prediction performance of the model was moderate. However, the EIS technique showed the possibility of measuring the DRC in the rubber cup lump with the advantages of simplicity and using a low cost instrument.

To simplify the model, a reduction in the predictors in the model was investigated. First correlation analysis was performed between the DRC and the capacitance at each frequency. The results showed that the correlation coefficient was between -0.297 and -0.419. Therefore the capacitance values at frequencies where the correlation coefficient was equal to or higher than -0.3 were used as predictors

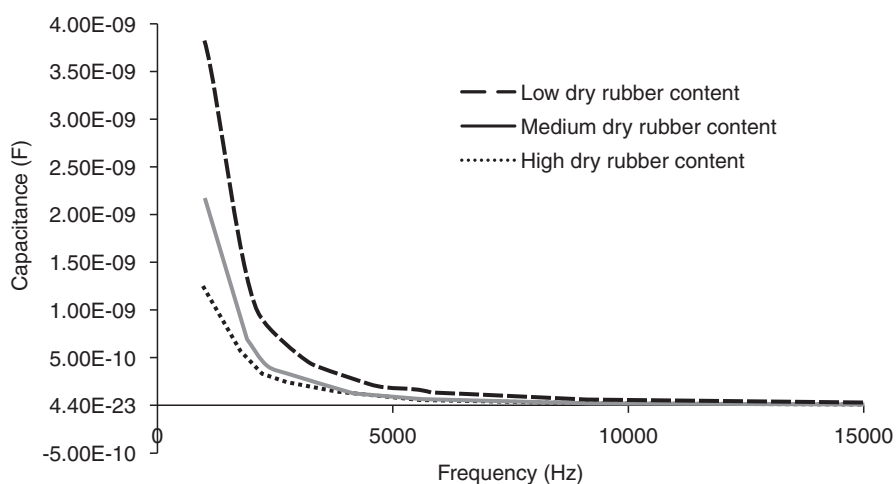


Fig 1 Capacitance of rubber cup lump samples as a function of frequency.

in developing a new predictive model. The best simplified PLSR model was found to be based on the capacitance at frequencies in the range 1–7 kHz. The new DRC prediction model had an r value of 0.80 and an RMSEP of 2.68%. The accuracy of the prediction was slightly lower than the PLSR model using all frequencies. However the model contained only seven predictors which consisted of the capacitance at frequencies of 1, 2, 3, 4, 5, 6 and 7 kHz. This implied that the device could be developed using only the capacitance from seven frequencies which would reduce the cost in manufacturing.

Evaluation of the DRC in rubber cup lumps was possible based on the capacitance at some selected frequencies. The accuracy of the DRC prediction was considered moderate based on the values of the correlation coefficient and root mean square error of prediction of 0.80 and 2.68%, respectively. However, the limitation of this EIS technique is that only samples with low porosity and high moisture content were measureable. The advantages of this technique are its simplicity and the low cost for development of the measuring device.

SUMMARY

The objective of this research was to apply electrical impedance spectroscopy for the detection of the dry rubber content in Para rubber cup lump samples prepared from rubber latex. The samples were collected during 2017 from eastern region of Thailand. Half-cut samples were measured for electrical parameters. The dry rubber content (DRC) of each cup lump was calculated as the weight of the cup lump multiplied by the initial DRC of the latex. A prediction model was developed using a partial least

squares regression technique. Results showed that the capacitance of the cup lumps tend to decrease with increase in the frequency and high rubber content in cup lumps was associated with higher capacitance. The prediction of the model was moderately accurate.

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