

Moisture content in raw rubber sheet analyzed by transfectance near infrared spectroscopy

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Moisture content is an important trait for rubber sheet trading system. Therefore, a calibration equation for predicting moisture content was created by near infrared (NIR) technique in order to develop a more fair trading system in Thailand. Spectra were recorded in two systems. One was measurement on each rubber sheet and the other was on a pile of sheets. Both were measured by a handheld NIR spectrometer in the short wavelength region (700–1100 nm) in the transfectance mode using Teflon as a diffuse reflector. The spectra showed the peak at about 900 nm which belongs to isoprene, the major component of rubber sheet. Pretreatment with second derivative was applied to remove baseline shift effect occurring due to thickness differences on each rubber sheet. From validation results, moisture contents predicted by single sheet system were more accurate than a pile of sheet system with standard error of prediction (SEP) = 0.39% and bias of –0.07%, and they were not significantly different from the actual values at 95% confidence. As a result, determining moisture content in each rubber sheet by a handheld NIR spectrometer provided accurate values, easy and rapid operation.

Keywords: NIR; quality; rubber sheet; trading system; handheld near infrared spectrometer.

1. Introduction

Rubber is an important material for multiple applications, particularly in the expanding of automobile industry. Thailand is the world's number one natural rubber producer and exporter. In 2012, its production volume was approximately 3.6 million tons,¹ of which 68% were exported and the rest was distributed domestically.

In Thailand, by the current system for trading raw rubber sheet, the price paid to rubber farmers depends on the moisture content. The rubber moisture content is randomly approximated by the visual method and by touching raw rubber sheets by the examiner. The result can be affected by environmental factors, and by the personal expertise of the examiner (trader). This places the

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rubber farmers at a possible disadvantage. For example, based on the total volume of rubber sheet produced annually in Thailand, 1.8 billion baht (about \$55 million) will be lost from farmers or trader if the trader over or underestimates the moisture content by only 1%. Therefore, an accurate and rapid moisture measurement system is required to make a fair trading for both traders and farmers.

As a possible alternative, near-infrared spectroscopy (NIRS) is widely used for quantitative analysis of moisture content. The technique has been used, for example, on triticale,² brown rice kernels,³ corn kernels,⁴ wheat and barley.⁵ Therefore, NIRS is a suitable method for quantifying trace amounts of moisture in raw rubber sheet, due to the strong combination absorption bands for water at around 1940 nm and the first, second and third overtones at 1450, 970 and 760 nm, respectively. This study presents the development of a NIRS method for measuring moisture in raw rubber sheet, and the comparison of the accuracy of spectrum acquisition systems, between using a single sheet, and a pile of sheets.

2. Materials and Methods

2.1. Raw rubber sheet

Raw rubber sheets were provided by Northeast Rubber Company, Buriram Province, Thailand. By their moisture contents measured conventionally, spectra of raw rubber sheet were manually separated into calibration (140 samples) and validation sets (125 samples) by an odd–even method with transfer first three and last three samples into calibration set to ensure range of calibration set covers one of validation set. Statistical characteristics of the samples used are given in Table 1.

2.2. Spectral acquisition

Spectra of raw rubber sheets in calibration set were recorded in two systems, one was measurement on each single sheet with thickness from 2.1 to 3.6 cm, and the other was measurement on a pile of sheets with height of 90–100 cm. For the latter method, only the uppermost rubber sheet was measured for spectrum. A handheld NIR spectrometer (FQA-NIRGUN, Fantec, Japan) was operated in the short

Table 1. Characteristics of calibration and validation sample sets of raw rubber sheet used.

Items	Calibration set	Validation set
Number of samples	140	125
Min	0.58	0.59
Max	9.67	6.51
Mean	1.95	1.72
Standard deviation	1.57	1.08
Unit	% w/w dry weight basis	

wavelength region (700–1100 nm) with spectral resolution 2 nm in the interactance mode, where the field of view of the detector is separated from the illuminated surface by a light seal in contact with the rubber sheet surface. One spectrum was measured per sample and a reference measurement of a teflon was performed after three samples. The calculation time used in this experiment was 6 ms because trying on 10, 20 and 30 ms of calculation time showed over-absorption.

2.3. Moisture content analysis

After obtaining spectra, rubber samples were collected from each sheet for single sheet system, and from only the uppermost sheet for a pile of sheet system. Rubber sheets were cut to weight about 10 g and put in zip lock bags before keeping in a desiccator. Moisture content was determined by drying rubber pieces in a hot air oven at 100°C for 10 h. Moisture content was reported as percent dry basis (%db) calculated from Eq. (1).

$$\begin{aligned} & \% \text{ moisture content (db)} \\ &= \frac{\text{weight before drying} - \text{weight after drying}}{\text{weight after drying}} \\ & \times 100. \end{aligned} \quad (1)$$

2.4. Calibration equation development

Prior to developing a calibration, the spectra were pretreated with the second derivative (segment size 16 points and derivative size 12 points). CA maker software (Shizuoka Shibuya Seiki, Hamamatsu, Japan) was used to perform multiple linear regressions (MLR). Predictive variables in the equations were chosen by the stepwise method.

3. Results and Discussion

3.1. Spectral acquisition testing

Spectra acquisition system of raw rubber sheet was tested by placing a measuring head in direct contact with the surface of the sheet, using one sheet for single sheet system and several sheets for a pile of sheets system. Due to the translucent property of the rubber sheet, and the power of the light source, the light reflecting to detector was too weak, and the handheld spectrometer in the interactance mode was not able to measure a spectrum of single sheet effectively. Therefore, the measuring system was modified to transreflectance mode using a material serving as diffuse reflector for reflecting energy to the detector.

For this purpose; Teflon, a material having a constant optical property and practically no absorption in NIR region, was selected. The curved Teflon block, designed especially for use with raw rubber sheet, and the FQA-NIRGUN, was built with a smooth surface and a radius of 4.5 cm, in order to make the measuring head perfectly fit to the rubber sheet. It was placed under a single rubber sheet before measuring the spectrum as shown in Fig. 1(a). For measuring the spectrum of a pile of rubber sheets, the measuring head was pressed adjacently on the uppermost rubber sheet [see Fig. 1(b)].

3.2. NIR spectra of raw rubber sheet

Baseline shifts occurred (see Fig. 2) due to the differences in each rubber sheet thickness. The peak of isoprene, the major component of rubber sheet, could be observed around 900 nm, which is the absorption of CH_3 and CH_2 third overtones of isoprene.⁶ Consequently, the spectra were pretreated with second derivatives to remove the baseline shift effect. For single sheet system, segment size and smooth size were 16 and 12 points, while in the case of pile system these values were 20 and 18 points, respectively. After pretreatment, the spectra were close to each other showing that the effect of baseline shift had been removed (see Fig. 3).

3.3. Calibration equation development

The result of calibration equations of moisture content was shown as scatter plots (see Fig. 4). Dots scattered close to the target line (diagonal line)



(a)



(b)

Fig. 1. Spectral acquisition system of single sheet with Teflon under a rubber sheet (a) and a pile of sheets (b).

indicate that the predicted values were close to the actual ones. In the single sheet analysis, the multiple correlation coefficients (R) and the standard error of calibration (SEC) were 0.97 and 0.37%db,

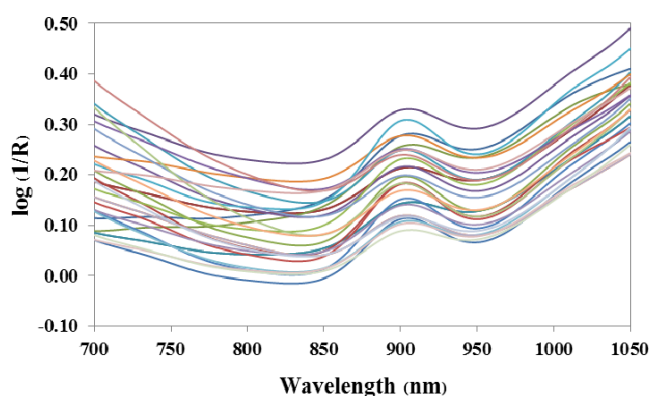


Fig. 2. Original spectra of raw rubber sheet in the short wavelength region.

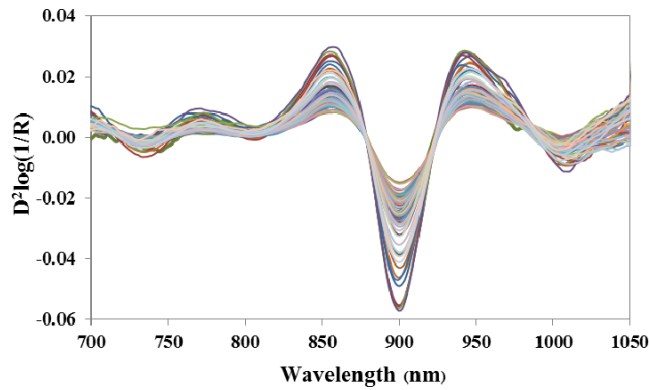
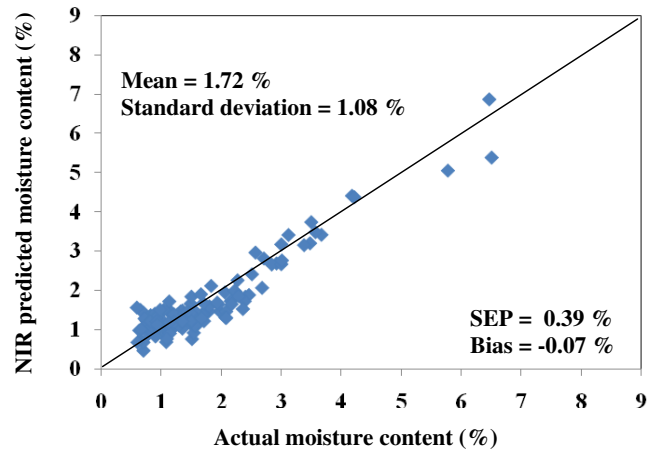
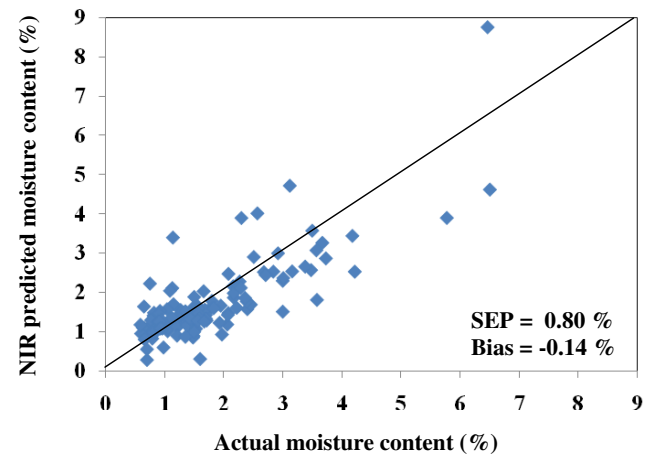


Fig. 3. Second derivative spectra of raw rubber sheet in the short wavelength region.

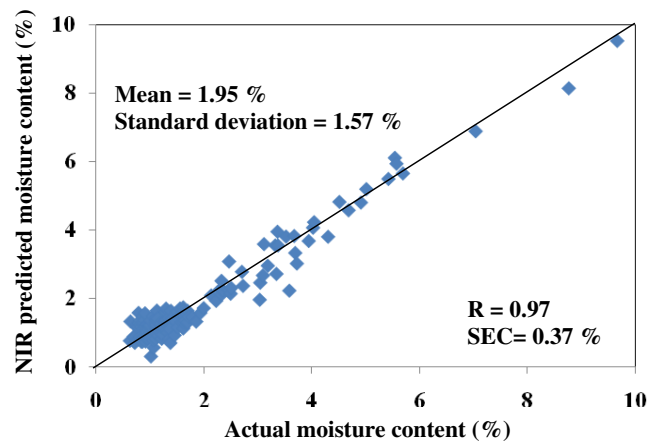


(a)

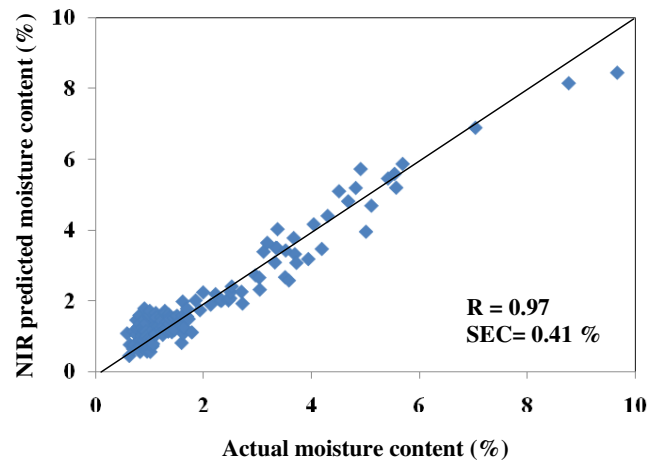


(b)

Fig. 5. Scatter plots of single sheet system (a) and a pile of sheet system (b) in the validation set.



(a)



(b)

Fig. 4. Scatter plots of single sheet system (a) and a pile of sheet system (b) in the calibration set.

respectively, while they were 0.97 and 0.41%db in a pile of sheet analysis.

Validation was performed on validation sample set to test the accuracy of both calibration equations. The result in Fig. 5 revealed that moisture content predicted by single sheet system was more accurate than a pile of sheet system with standard error of prediction (SEP) = 0.39% and bias of -0.07% . Using the paired t -test of calibration equation in the single sheet system, moisture contents predicted by NIR were not significantly different from the actual values at 95% confidence. For a pile of sheets system, SEP indicating standard deviation of difference and bias showing average of difference between actual values and NIR predicted values were significantly high.⁷

As the translucent property of rubber sheet in a pile of sheets system, an NIR spectrum was an average absorbance of 4–5 sheets including a top sheet while moisture content of the top sheet only was measured and used for calibration development. Figure 6 showed a measurement result of NIR spectra of a raw rubber sheet measured five times with single sheet system and a pile of sheets system, which changed the sheets piled below every time. It was noticed that spectra acquired by the single sheet system were essentially constant compared with that extremely varied from beneath pile sheets by a pile of sheet system. Therefore, the spectrum collected from a pile of sheets did not correspond to the moisture content which was analyzed only in the uppermost sheet. In the single sheet system, there was Teflon under each sheet, so a spectrum was collected from only one sheet and the absorbance of that sheet was used to predict moisture content. Finally, an MLR moisture calibration equation developed by single sheet analysis was as Eq. (2);

$$\begin{aligned} \text{Moisture (\%db)} &= 0.7637 - 60.3342A_{728} + 384.8081A_{860} \\ &\quad - 342.9129A_{956} - 126.3390A_{984} \\ &\quad + 55.1054A_{1040} \end{aligned} \quad (2)$$

where, A is the second derivative of an absorbance at the subscript indicated wavelength of x nm.

From the above equation, all predictive variables are necessary to predict moisture content in raw rubber sheet accurately and the most important

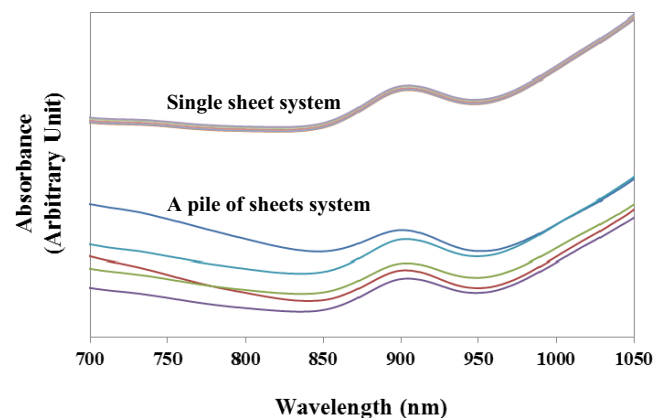


Fig. 6. Comparison of NIR spectra of a raw rubber sheet measured 5 times with single sheet system and a pile of sheets system.

variable in the equation is second derivative absorbance at the wavelength of 956 nm which is related to water absorption.⁸

4. Conclusion

A handheld NIR spectrometer could be used as a moisture content analyzer. To predict moisture content accurately for price determination for raw rubber sheet trading, a spectral acquisition system of a single sheet should be used.

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References

- Office of Agricultural Economics, 2013, Database of agriculture goods production: Rubber, Available at: <http://www.oae.go.th/download/prcai/farmcrop/rubber.pdf> (October 7, 2013).
- B. Igne, L. R. Gibson, G. R. Rippke, A. Schwarte, C. R. Hurburgh, "Triticale moisture and protein content prediction by near-infrared spectroscopy (NIRS)," *Cereal Chem.* **84**, 328–330 (2007).
- R. Rittiron, S. Saranwong, S. Kawano, "Useful tips for constructing a near infrared-based quality sorting system for single brown-rice kernels," *J. Near Infrared Spectrosc.* **12**, 133–139 (2004).
- E. E. Finney Jr., K. H. Norris, "Determination of moisture in corn kernels by near-infrared transmittance measurements," *Trans. ASAE* **21**, 581–584 (1978).
- P. C. Williams, K. H. Norris, D. C. Sobering, "Determination of protein and moisture in wheat and barley by near-infrared transmission," *J. Agric. Food Chem.* **33**, 239–244 (1985).
- B. G. Osborne, T. Fearn, P. H. Hindle, *Practical NIR Spectroscopy with Applications in Food and Beverage Analysis*, 2nd Edition, John Wiley & Sons, Inc., New York (1993).

7. International Standard, ISO 12099: Animal feeding stuffs, cereals and milled cereal products-Guidelines for the application of near infrared spectrometry, Switzerland (2010).
8. P. C. Williams, K. H. Norris, Qualitative applications of near-infrared reflectance spectroscopy, in

Near-Infrared Technology in the Agricultural and Food Industries, Chap. 15, P. C. Williams, K. H. Norris, Eds., p. 246, Am. Assoc. Cereal Chemists Inc., Minnesota, USA (1987).