UPDATED NEAR INFRARED SPECTROSCOPY MODELS FOR EVALUATION OF DRY RUBBER CONTENT AND TOTAL SOLIDS CONTENT OF PARA RUBBER LATEX

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ABSTRACT

The analysis of dry rubber content (DRC) of Para rubber latex including field latex and concentrated latex, using near-infrared spectroscopy was carried out by an ultra violet/visible/near-infrared (UV/VIS/NIR) Spectrometer in transmittance mode over the wavelength range of 350–1100 nm. The original model provided the best accuracy of prediction was developed using the partial least squares regression (PLSR) from the spectra which were pretreated by the smoothing and range normalization in the wavelength range of 700-950 nm. The slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0154, -0.6286, 0.9960, 1.1092% and 0.0321%, respectively. The updated model was done by adding the 180 samples merged into the 280 original samples. The slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0126, -0.3729, 0.9931, 1.2654% and 0.1103% respectively. Therefore, it is needed to make more robust updated model by NIRS technique for determining the DRC of Para rubber latex, for both field latex and concentrated latex.

As for the analysis of total solids content (TSC) of field latex and concentrated latex using the same technique and over the same wavelength, the slope, offset,

correlation coefficient (r), standard error of prediction (SEP) and bias of the original model were 1.0084, -0.2332, 0.9955, 1.3611% and 0.1456%, respectively. The updated model was done by adding the 160 samples merged into the 280 original samples. The slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 0.9795, 0.7150, 0.9834, 1.6186% and -0.0802%, respectively. Therefore, the robust updated model by NIRS technique was more accurate and faster method for determining the TSC of Para rubber latex, for both field latex and concentrated latex.

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LIST OF ABBREVIATIONS

ADS	Air dried sheet
DRC	Dry rubber content
FT-NIR	Fourier transform near infrared spectroscopy
HA	High ammonia latex
ISO	International Organization for Standardization
KOH	Potassium hydroxide number
LA	Low ammonia latex
MA	Medium ammonia latex
MST	Mechanical stability time
NIRS	Near infrared spectroscopy
NR	Natural rubber
NRC	Non-rubber content
PLSR	Partial least squares regression
r	Correlation coefficient (also termed coefficient of correlation)
r^2	Coefficient of determination
RSS	Ribbed smoked sheet
SD	Standard deviation
SEC	Standard error of calibration
SEP	Standard error of prediction
STR	Standard Thai Rubber
TSC	Total solids content
TSR	Technically specified rubber
USS	Unsmoked sheet
VFA	Volatile fatty acids number

CHAPTER 1

INTRODUCTION

1.1 General background

1.1.1 Historical introduction to plantation rubber.

It had been reported that Christopher Columbus, during his second voyage (1493-6) noticed that the natives of Haiti played games with rubber balls prepared from the gum of trees [1]. The elastic property intrigued subsequent travellers who brought samples back to Europe. In England, it was found that it could use as an eraser for removing pencil and ink and so the word "rubber" was derived. By 1800 rubber had limited application as it suffered from the disadvantage of being susceptible to changes of temperature, becoming sticky in hot weather and hard when cold. The breakthrough came when in 1839, Charles Goodyear discovered vulcanization with sulphur and zinc oxide and the rubber undergone chemical change with profound alteration in physical properties. In 1871, Sir Henry Wickham collected 70,000 rubber seeds of *Hevea brasiliensis* from the Amazon jungle in Brazil and brought back to Kew Gardens in London where the germinated seedlings were transferred to Ceylon (now Sri Lanka) and the then Malaya (now Malaysia) in 1877 where the whole vast plantation industry had grown in south-east Asia [1].

1.1.2 Rubber plant species

Natural rubber latex can be obtained from various plant species such as Guayule, Gutta-percha and Balata. But *Hevea brasiliensis* is the only rubber tree species now of technical and commercial importance as no other plant can compare in respect both of the quantity and quality of the rubber produced [1].

1.1.3 Conditions suitable for *Hevea brasiliensis*

Hevea brasiliensis flourishes well under tropical conditions at an average temperature of 27°C and an average annual rainfall of 200cm with good drainage e.g. on the slope. It grows satisfactorily in most types of soil but the clay-loam type of soil

with pH4.0-4.5 is preferred. Much of natural rubber in S.E. Asia is produced at latitudes less than 15° north of equator. Thus about 80% of the plantations in Thailand are found mainly in the south [2].

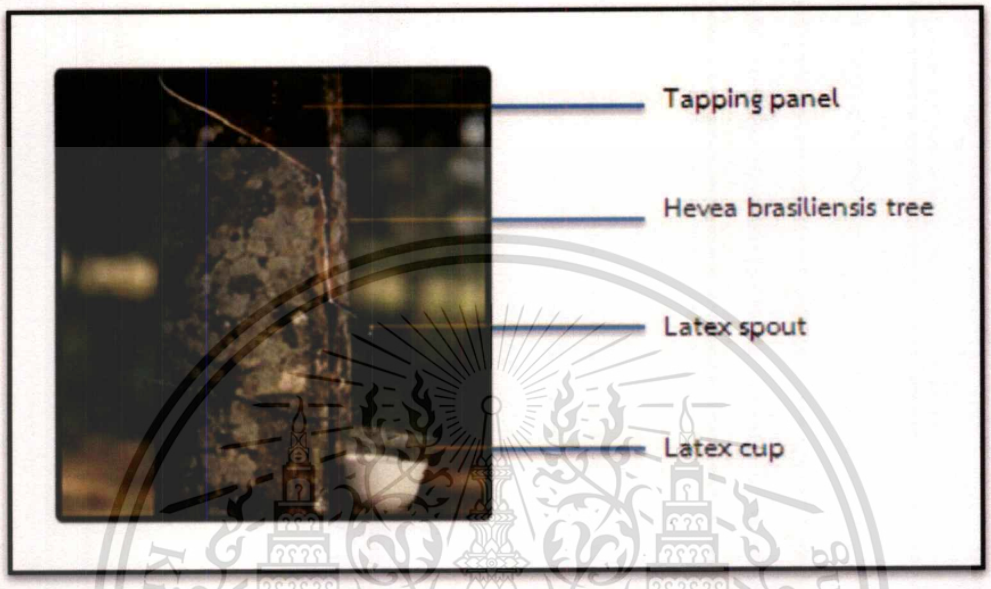


Figure 1.1 Latex being collected from a tapped Hevea tree

Hevea trees mature and ready for tapping about 6-7 years after planting. The trees are tapped, half spiral, (Figure 1.1) on alternate days so as to provide sufficient time for biosynthesis of latex in the trees to replenish the latex that has been harvested.

1.1.4 Supply of natural rubber

Thailand has been the largest producer of natural rubber in the world for many years. In 2012 it had a total of 3.01 million hectares under rubber cultivation with a total production of 3.611 million tons per year (Table 1.1) or 32.97 % of the world supply [3]. The top 5 producing countries, viz. Thailand, Indonesia, India, Malaysia and Vietnam make up 83 % of the world's natural rubber (NR) output (Figure 1.2).

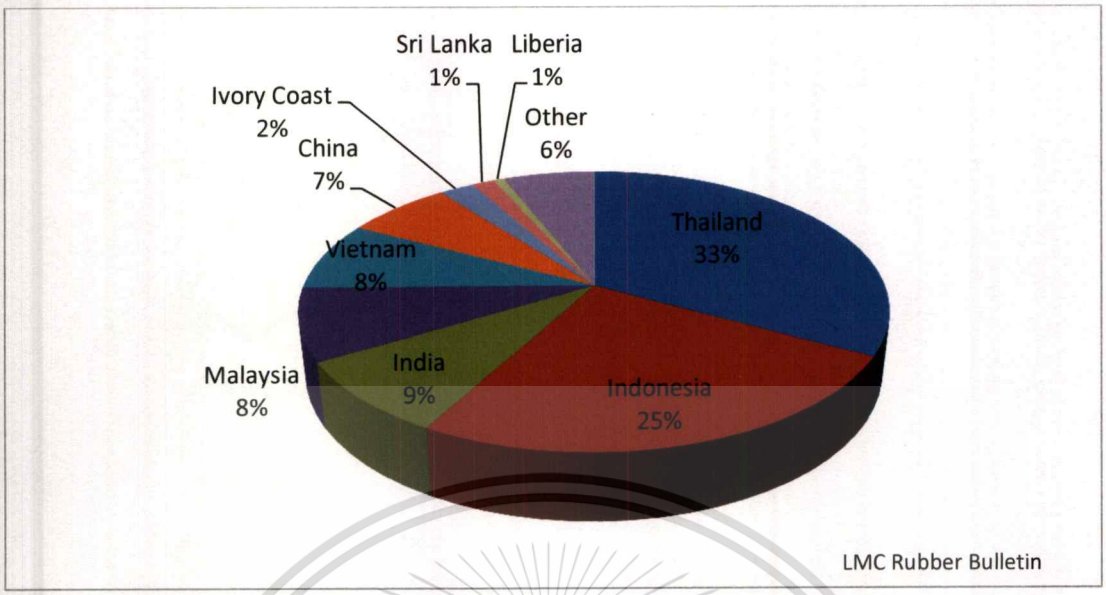


Figure 1.2 World NR production in 2012 by percentage [modified from 3].

Table 1.1 Production and consumption of NR in 2012

NR Production		NR Consumption	
COUNTRY	TONS (x 1,000)	COUNTRY	TONS (x 1,000)
Thailand	3,611	China	3,833
Indonesia	2,746	India	985
India	928	USA	934
Malaysia	910	Japan	731
Vietnam	873	South Korea	408
China	747	Other W Europe	402
Ivory coast	249	E Europe	280
Sri Lanka	159	Germany	271
Liberia	77	France	169
Other	651	Italy	96
Total	10,951	UK	66
		Other	2,435
		Total	10,610

Source: Anonymous (2013) [3].

1.1.5 Grades of dry rubber and latex

The field latex is processed into various grades of technically specified rubber (TSR) in blocks (e.g. STR 5, STR 10 and STR 20) and also various grades of sheet rubber (e.g. RSS, ADS and USS) as shown in Figure 1.3.

Concentrated latex is made into 3 common grades, namely, high ammonia (HA), low ammonia (LA) and medium ammonia (MA) latices.

Figure 1.3 STR 20 block rubber and ribbed smoked sheet

1.1.6 Uses of dry rubber and latex

The invention of pneumatic tyres by J.B. Dunlop in 1888 was one of the outstanding achievements in the field of rubber technology. Tyres still account for more than half of the total rubber consumption. Other uses are for automotive parts, footwear, fan and conveyor belting and equipment as in Figure 1.4.

Tyres Automotive parts Footwear & equipment

Figure 1.4 Dry rubber products [3]

The concentrated latex is the raw material used in factories worldwide in the manufacture of latex-dipped products like gloves, condoms, balloons, catheters, extruded latex threads, foam products like pillows and mattress, in casting products like toys and masks, adhesives and so on as shown in Figure 1.5.

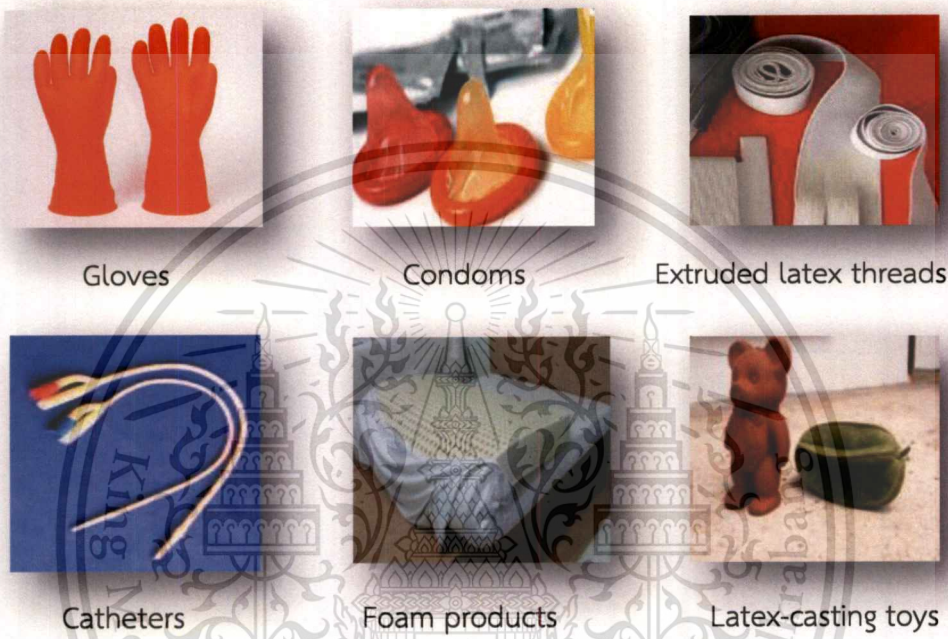


Figure 1.5 Various types of latex products

1.1.7 Importance of DRC and TSC determination

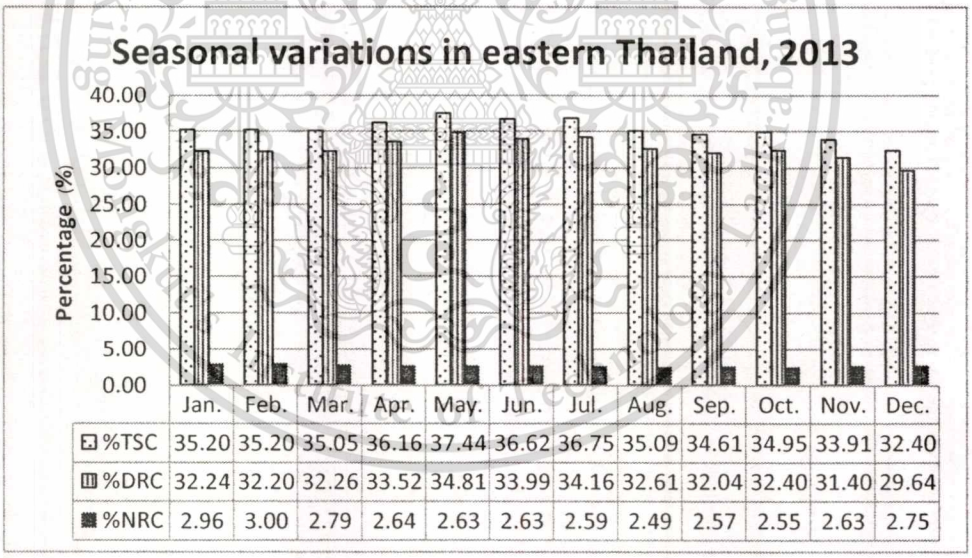
Dry rubber content (DRC) is an important parameter for natural rubber latex, which has to be measured quickly and accurately for various purposes for the rubber industry and so a reliable method for its determination is essential.

The dry rubber content (DRC) is defined as a percentage by the mass of the latex which is coagulated under specific conditions of colloidal destabilization [4].

The DRC of field latex may vary from 25-45% depending upon season, tapping system, weather, soil conditions, clone of the tree and environmental conditions. The concentrated latex is processed to 60% DRC. The DRC of Hevea latex is a familiar term to all in the rubber industry. It is probably one of the few properties of latex first recognized and widely used for trade and processing, ever since the commencement of

commercial exploitation of Hevea trees. The DRC of both field and concentrated latices is an essential parameter for ensuring fair prices for latex trading as well as process control [5].

The total solids content (TSC) of a latex is defined as the percentage by mass of the whole which is non-volatile under specified conditions of drying in an open atmosphere at an elevated temperature [4]. The TSC of both field and concentrated latex vary according to the yearly seasonal cycle as the results of the amount of non-rubber content (NRC) present in the latex. Thus NRC=TSC-DRC. There is a noticeable increase in NRC at year-end and the beginning of the new year as shown in Figure 1.6. The NRC is a good indicator of the cleanliness of the latex. The TSC is an important parameter on which the various parameters are based, namely, VFA number, KOH number, MST and Brookfield viscosity.



	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
%TSC	35.20	35.20	35.05	36.16	37.44	36.62	36.75	35.09	34.61	34.95	33.91	32.40
%DRC	32.24	32.20	32.26	33.52	34.81	33.99	34.16	32.61	32.04	32.40	31.40	29.64
%NRC	2.96	3.00	2.79	2.64	2.63	2.63	2.59	2.49	2.57	2.55	2.63	2.75

Figure 1.6 Seasonal variations of DRC, TSC and NRC

In latex factories, the DRC and TSC of field and concentrated latices are determined by the standard international methods, the ISO 126:2005 [6] and ISO 124:2011 [7] respectively. The procedures are destructive and take about 16 hours to

complete. They are tedious and time-consuming methods which also require skilled technicians to do.

1.1.7 Use of NIR to determine DRC and TSC

From [8] near infrared spectroscopy (NIRS) measures the interactions between the electromagnetic radiation in the NIR region (780–2500 nm) and the materials. The fundamental absorptions occurring in the infrared region extend down to lower wavelengths as overtones and combinations. The NIR spectroscopy technique can provide rapid results in seconds or continuously on-line, rather than in hours or days, with an accuracy and reproducibility equivalent to most reference methods. Other advantages of NIR include its low cost per test, low labour costs, no required chemicals to purchase or dispose of, great flexibility in sample presentation and the capability of testing many constituents simultaneously. The method is environmentally friendly because it requires no chemicals. The instruments are simple to install and operate and produce no emissions which need to be removed by drainage or exhaust. Little or no sample preparation is involved. Many instruments are of the stand-alone type and their durability allows them to work well for more than ten years. Instruments can be networked to use the same calibration, with their performance controlled from a single control centre. NIR spectroscopy has been applied to many types of agricultural products. However, there are few reports of its application to field and concentrated latices of Para rubber. Cornish *et al.* [9] developed and tested an NIR spectroscopic method for the rapid quantification of latex in both wet and dried *Parthenium argentatum* (guayule) homogenate and purified latex samples. The coefficients of determination (r^2) for correlations between the measured rubber content and the rubber content predicted by NIR were 0.92 and 0.83 for the dry and wet samples, respectively.

1.2 Objective

To update the existing models of NIRS to be more robust for the determination of dry rubber content (DRC) and total solids content (TSC) of the natural rubber (NR)

latex to facilitate the procurement of raw material and also for quality and process control in the factory

1.3 Scope

The use of short wave NIRS for the determination of TSC and DRC of the latices from the plantations near the Thai Rubber Latex Corporation (Thailand) Public Company Limited factory at Nongyai district in the province of Chonburi.

1.4 Expected results

The models will be more robust and accurate. There are 2 models, namely, the DRC and TSC models. The 2 models are expected to be used in the factories to save time and chemicals.

1.5 Flow chart of the research experiments

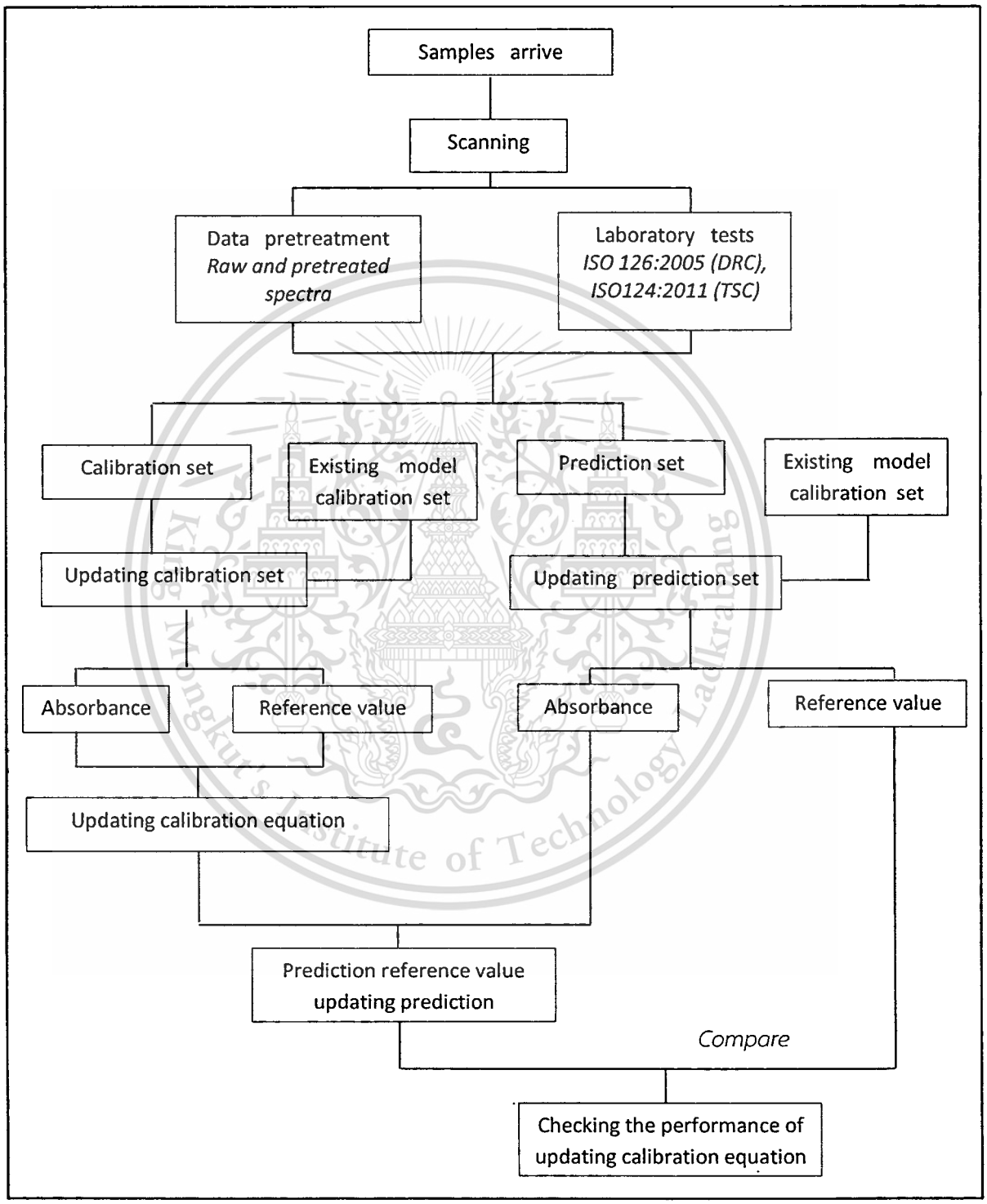


Figure 1.7 Flow chart of the research experiments

CHAPTER 2

LITERATURE REVIEW

2.1 Constituent of fresh natural rubber latex

Fresh natural rubber latex is the sap from the latex vessels of *Hevea brasiliensis.* It is a whitish fluid having a specific gravity in the range 0.975-0.980 and pH 6.0-7.0. Basically it is a colloidal dispersion of NR particles in an aqueous medium. Being a natural product, the composition of fresh natural rubber latex varies within wide limits. Like all plant materials, latex contains growth-related substances such as proteins, carbohydrates, and other organic and inorganic constituents. The rubber hydrocarbon particles comprise 25% to 45% of the latex system. The non-rubber substances constitute only a small percentage of the latex system. When subjected to ultracentrifugation at approximately 59,000*g*, latex can be separated into 3 principal fractions as in Figure 2.1

(1) rubber hydrocarbon particle phase;

(2) aqueous phase (C-serum) in which all latex particles are suspended; and

(3) bottom fraction of non-rubber particles, particularly lutoids. which contain yet another serum (B-serum) [10].

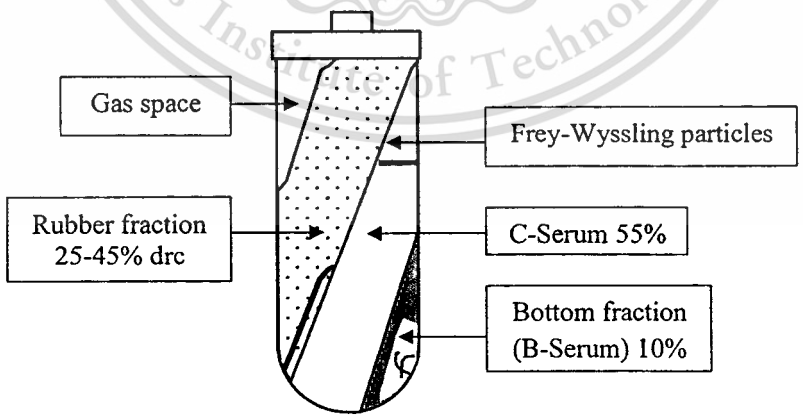


Figure 2.1 Fresh Hevea latex separated into its 3 main fractions on ultracentrifugation (Moir 1959) [11].

2.2 Rubber particles

Field natural rubber latex is composed of particles between 25-45% by volume. Rubber molecule is a polymer consisting of isoprene monomers connecting together into a long chain. At least 99% of its hydrocarbon are cis-1,4-polyisoprene as shown in Figure 2.2. In general rubber particles are spherical in shape (although some appear to be pear shape because of the thread attachment) having diameters approximately 0.02-3 μm covered with lipids and proteins. However NR rubber particles obtained from matured rubber trees are larger [12].

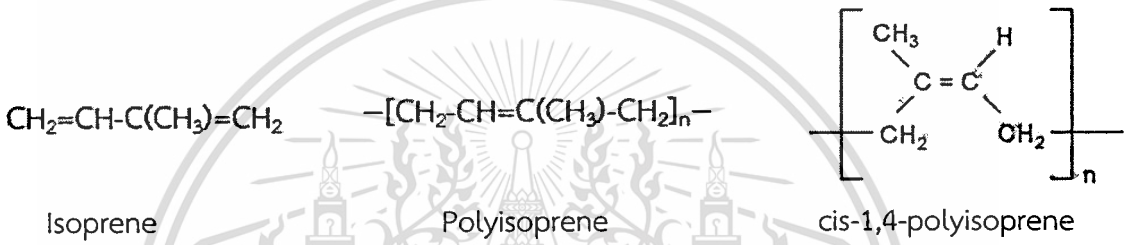


Figure 2.2 Chemical structure of natural rubber latex (cis-1,4-polyisoprene). The polymer consists of approximately 3,000-5,000 units

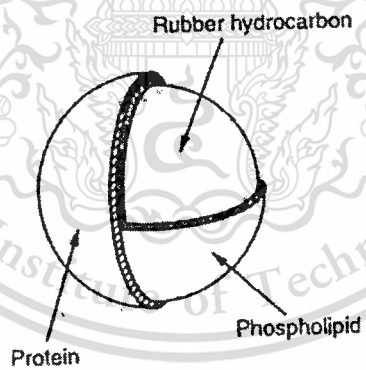


Figure 2.3 Rubber particle in fresh NR latex [2].

Figure 2.3 shows the rubber particle in fresh NR latex as comprising mainly rubber hydrocarbon, surrounded by an inner shell of phospholipid and an outer shell of protein.

2.3 Latex concentrates

The field latex has dry rubber content of around 25–45% and TSC about 2.5-3.5% above the DRC depending on clone, age, tapping methods, and seasons [13]. Concentrated latex is produced by reducing the water concentration of field latex to obtain 60% dry rubber content. There are several methods to produce concentrated latex, including evaporation, creaming, electro-decantation and centrifugal methods. The centrifugal method is the most popular method because it is fast and provides concentrated latex of higher purity [14].

In Thailand there are three common types of centrifuged concentrated latex, namely, high ammonia (HA), low ammonia (LA), and medium ammonia (MA). Ammonia gas is added to the latex to preserve the latex from bacteria action on carbohydrate producing volatile fatty acids resulting in coagulation. About 0.7% ammonia and 0.025% ammonium laurate soap are added to HA latex, 0.2% ammonia with 0.013% tetramethylthiuram disulphide (TMTD), 0.013% zinc oxide, and 0.06% ammonium laurate are added for LA [14] while 0.4–0.5% ammonia is added to MA with intermediate values of TMTD/ZnO and ammonium laurate as used in HA and LA.

Concentrated latex is the raw material for different kinds of rubber products including gloves, condoms, baby nipples, catheters, pillows and mattresses, latex thread for underwear, socks, brassieres, etc., rubber glue for shoes and other items such as dolls, masks, etc.

The field latex is centrifuged to produce latex concentrate. The factory purchases the field latex from numerous small holders based on the dry rubber content of the latex. Currently the dry content rubber of field latex can be determined quickly with using microwave method, spot DRC method, titration method or using a hydrometer [5] known as "Metrolac" which are inaccurate. The factory in which the trial is currently carried out, processes between 300,000-400,000 tons of field latex annually and even an error of 1 % can mean a gain or loss of tens of million baht.

In the concentrated latex factory, the latex concentrate is produced at 60 % DRC. The DRC is an important parameter for the purpose of trade for both field latex and latex concentrate. Other than this, DRC is required to calculate the non-rubber

content (NRC) as well as the volatile fatty acids number (VFA) of the latex using the standard laboratory method, ISO 506:1992 [15]. These are the other important process control parameters.

The TSC includes DRC and other solids matter called non-rubber content (NRC) in the latex. The non-rubber content is the indicator for the cleanliness of the latex. The lower the NRC, the cleaner is the latex. Thus NRC can be calculated by the difference between the TSC and the DRC of the latex. In addition, the TSC is an important parameter on which the various parameters are based, namely, VFA number [15], KOH number [16], mechanical stability time (MST) [17] and Brookfield viscosity [18].

Calculation of VFA and KOH numbers are:

$$VFA = \left[\frac{134.64\ cV}{m\ TSC}\right] \times \left[50 \times \frac{m(100\text{-}DRC)}{100p}\right] \qquad 2.1$$

$$KOH = \frac{561c \times V}{w_{ts} \times m} \qquad 2.2$$

where for VFA

c is the actual concentration of barium hydroxide solution

V is volume of barium hydroxide solution required to neutralize the distillate

m is mass of latex

p is density of serum

where for KOH

c is the actual concentration of KOH solution

V is the volume of KOH solution required to reach the end-point

w_{ts} is the total solids content of the latex

m is the mass of latex

Determination of VFA requires both DRC and TSC values whereas KOH no. requires only the TSC value. MST and Brookfield tests are carried out on latices at 55% TSC and 60 % TSC respectively and as such the TSC values of the samples have to be predetermined.

2.4 Near infrared spectroscopy

2.4.1 History and what is NIR

At the beginning of the 19th century, Sir William Herschel with his curiosity, regarding the colour within the visible spectrum that was responsible for the heat of the sunlight, did the experiment with thermometer and a glass prism to separate the colours of the sun's "white light". He moved the thermometer from one colour to the next , but not much had happened until he positioned it below the red end of the spectrum. In this location the temperature began to rise. Clearly, there was energy present beyond the red light, and because he could not see it, he named it "infrared" [19].

NIR Spectroscopy is the technique based on the measurement of NIR radiation absorbed by the analytes which are the components of a sample to be determined. The wave lengths are between 780-2500 nm and frequencies range from $3.84 \times 10^{14} - 1.20 \times 10^{14}$ hertz. NIR spectroscopy uses the technique of measurement and analysis of electromagnetic radiation that is absorbed or emitted by the materials. 906 nm is the absorption band of pure natural rubber [20].

2.4.2 NIR radiation and its effect on bond vibration of material

Why NIRS works comes down to chemistry. All agricultural and food materials are composed of molecules. Molecules consist of atoms and groups of atoms linked together by covalent bonds. In covalent bonds, electrons are shared between adjacent atoms in a molecule. All molecules are continually vibrating at various frequencies. Irradiation of materials by an energy source such as light causes some molecules to change their vibrations from one energy level to another. When transitions occur from one energy state to another, energy is absorbed. A NIR absorption occurs when the vibrations at a given frequency coincide with those of a molecular bond in the material being scanned. The absorptions of energy can be detected and measured by NIRS instruments. These are fundamental absorbers. These absorbers become repeated in the NIR region as overtones [19].

2.4.3 NIR spectroscopy modeling

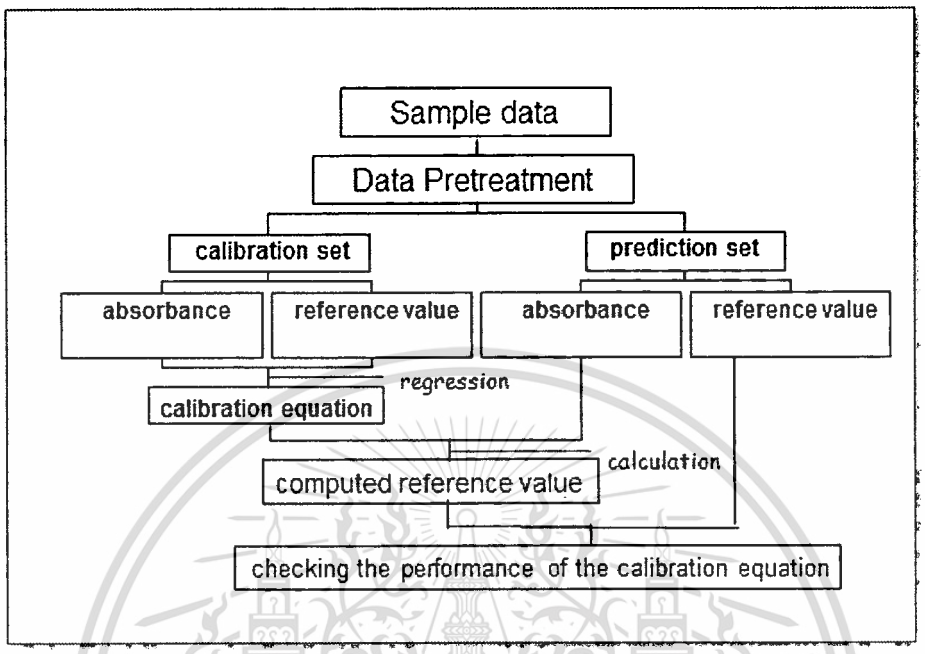


Figure 2.4 Flow chart of NIRS modeling

Sample data had two parts, the spectra (absorbance) and experimental results (reference value).

Before model development, the constituent reference data of all samples were checked for the presence of outliers. If the value of a sample satisfied Equation (2.3), the sample was considered to be an outlier:

$$\frac{x-\bar{x}}{SD} \geq \pm 3 \qquad 2.3$$

where X is the reference value, $\bar{X}$ is the average and SD is the standard deviation.

The NIR absorbance spectral data might be subjected to mathematical pretreatment, for example, by Savitzky-Goley smoothing and range normalization. Then the reference data were merged with all NIR absorption spectra. After sorting the samples in the order if increasing values the constituent content, the data will be divided into two sets as calibration and set prediction set in the ratio of, for example, 1:1, 2:1, 3:1, etc.

The absorbance and reference values were related to make equation (or model) by the computer software and use the equation for prediction. To test the accuracy of the equation, the absorbance values of the prediction set were substituted into the calibration equations, and they should be close to the reference values of the prediction set.

2.4.4 Spectra pretreatment

Chemometrics is the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods. The peak of interest is almost surely overlapped by one or more interfering peaks and the strong dependence of reflectance on the scattering properties of sample makes pretreatment of NIR spectra essential. Data pretreatments are in this study mainly done by 2 methods:

2.4.4.1 Smoothing – A method to reduce the noise occurred when an NIR spectrum was measured. Savitzky-Goley smoothing fits the spectrum in a wavelength interval with a polynomial by least square method. It is suitable for non-smooth with noise, original spectrum that has a lot of peak and need smooth spectrum but keep the same original shape of spectrum [19].

2.4.4.2 Normalization - A method to suppress unwanted sources of variability by making a group of spectra to have more features in common.

For example, there are the following normalization equations:

Mean Normalization $$x_{(i,k)} = \frac{x_{(i,k)}}{|Mean(x_{(i,*)})|} \quad (2.4)$$

Max Normalization $$x_{(i,k)} = \frac{x_{(i,k)}}{|Max(x_{(i,*)})|} \quad (2.5)$$

Range Normalization $$x_{(i,k)} = \frac{x_{(i,k)}}{Max(x_{(i,*)}) - Min(x_{(i,*)})} \quad (2.6)$$

where i = sample number k = absorbance wavelength point and * = all wavelength point.

2.4.5 Validation methods

There are 3 main methods of evaluation of calibration model. They are cross-validation, test-set validation and prediction of completely unknown samples. Cross-validation is preferred by many NIRS users, due mainly to the computation time saved. It involves elimination of the samples from the development of the equation The sample or a group of samples is then predicted using the equation that has been developed using the remaining samples and replace in the original sample set. A second sample or a group is then removed and the exercise repeated until all the samples have been used in development of the equations. Cross-validation (particularly one-out cross-validation) is theoretically satisfactory for the evaluation of any NIRS calibration equation.

Test set validation involves setting up calibration and validation sample sets. The validation set is the "test-set", and should be composed of samples of the same general type of commodity, but selected separately from the calibration sample set. Test-set evaluation has traditionally been achieved by using statistics coefficient of correlation (r), the coefficient of determination (r^2), standard error of prediction SEP, the bias and the regression coefficient or slope [19].

2.4.6 Parameters

Parameters used to determine the performance of the model are slope, offset, correlation coefficient (r), coefficient of determination (r^2) , standard error of calibration (SEC), standard error of prediction (SEP) and bias. The correlation coefficient (r) shows the degree to which 2 sets of data (NIRS and reference results) agree with each other. Perfect agreement with no differences at all between the 2 data sets will result in an r-value of 1.000. The formula for computing r is:

$$r = \frac{\sum(X^* Y)-[(\sum X^* \sum Y)/N]}{\left\langle\{\sum X^2-[(\sum X)^2/N]\}^*\left\{\sum Y^2-[(\sum Y)^2/N]\right\}\right\rangle^{1/2}} \qquad 2.7$$

where x = reference and y = predicted NIRS data, and can be positive or negative

N = number of samples.

The coefficient determination is given by r^2. It shows the proportion of variance in X data that can be explained by the variance in the Y data. r^2 is therefore the square of the value of r. The standard error of calibration (SEC) is the SD of differences between NIRS and reference sample in the calibration sample set. The standard error of prediction (SEP) is the standard deviation of differences between NIRS and reference values. The formula for its calculation is:

$$SEP = \left(\sum\left(X-Y\right)^2 - \left\{\left[\sum\left(X-Y\right)\right]^2 /N\right\}/N-1^{1/2}\right\} \quad 2.8$$

The bias is the mean difference between reference and NIRS data and is a measure of the overall accuracy of the calibration. In the real world of commerce and industry, the bias is one of the most important statistics [19].

The formula for calculating bias is

$$\left(\sum X /N\right)-\left(\sum Y /N\right) \quad 2.9$$

2.5 Near infrared spectroscopy researches related

Near infrared (NIR) spectroscopy is a rapid technique, accurate, and environmental friendly where there is no chemical use, no or less sample preparation and the parameter prediction model is developed from the relationship between the interested constituents and the NIR spectral data. This NIR spectroscopy technique has been applied to a few agricultural products similar to rubber latex. Takeno et al. [21] described the Fourier transform near infrared spectroscopy (FT-NIR) technique coupled with a partial least squares (PLS) regression model to quantify natural polyisoprene in *Eucommia ulmoides* leaves and the best PLS regression model was obtained with second derivative NIR spectra in the region between 4000–6000 cm−1 (r^2 =0.95). Marinho et al. [22] studied the application of NIR spectroscopy for analyzing the natural *trans*- and *cis*-polyisoprenes from *Ficus elastica* (*cis*-1,4-polyisoprene) and gutta-percha (*trans*-1,4-polyisoprene) and mixtures of these polymers.

NIR bands are generated from overlapping absorptions corresponding mainly to overtones and combinations of vibration of C–H, O–H, and N–H chemical bonds which are included in the biological materials. According to Huang et al. [23], in practice, the

common modes are transmittance, interactance, transflectance, diffuse transmittance, and diffuse reflectance, with the last two being most frequently used. Diffuse transmittance measurements are suitable for samples of 1-2 cm thickness using shortwave near infrared radiation (780-1100 nm).

It is reported that various agro-industries such as flour milling [24], soybean meal factory [25], bakery factory [26], etc. use NIR spectroscopy. There are a few research reported the application of NIR spectroscopy in rubber latex factory [20,8,14].

Sirisomboon et al., [8] applied the FT-NIR spectroscopy in the wavelength range of 1100-2500 nm in evaluation of dry rubber content of rubber latex and Sirisomboon et al.[20] used the short wave NIR spectroscopy in the wavelength range of 700-950 nm in evaluation of DRC and TSC. The work of Sirisomboon et al. [20] was tested to use in the concentrated latex factory. Therefore, the objective of our work was to study the ability of the short wave NIR spectroscopy and update the model developed by Sirisomboon et al. [20] for prediction of DRC and TSC of both field latex and concentrated latex of Para rubber, which were the materials used in the process of latex production, to facilitate the quality and process control in the factory.

CHAPTER 3

METHODOLOGY

3.1 Original model [20]

Samples of Para rubber field latex and concentrated latex were collected from the factory of the Thai Rubber Latex Corp. (Thailand) Public Company Limited, in the Nongyai District, Chonburi Province, Thailand. The samples for making the calibration models and for prediction were collected and immediately subjected to the experiment between 3rd and 28th October 2011. The 171 field latex samples were obtained from the latex that the farmers in the Chonburi and near-by provinces sold to the factory. The field latex had around 30% DRC. The 86 concentrated latex samples were obtained from the storage tanks of the factory. The concentrated latex had around 60% DRC. The 25 samples of concentration adjusted concentrated latex were prepared to have the levels of 55%, 50%, 45%, 40% or 35% DRC (five samples per level). The concentration adjusted was done by adding the calculated amount of water into the concentrated latex.

In total, there were 282 samples. The experiment was conducted at 25 ± 2°C room temperature. To validate the calibration model, a set of 50 samples was collected and subjected to the experiment on 24th May, 29th June, 7th September and 4th October 2012. There were 19 concentrated latex samples and 31 samples for field latex. The field latex samples were taken from 31 tanks (200 L drum or 1–2 ton tank car) sold from farms to the factory on the respective days. Concentrated latex samples were the samples submitted to the quality control section of the factory laboratory for analysis as routine samples. They came from different 100-ton storage tanks produced by the factory with different storage durations.

The model developed from smoothing and range normalisation pre-treated spectra in the wavelength range of 700–950 nm provided the best accuracy of prediction for DRC and the models using raw spectra in the same wavelength range gave

the best results for TSC. The slope, offset, coefficient of determination (r^2), standard error of prediction (*SEP*) and bias were 1.0154, –0.6286, 0.9960, 1.1092% and 0.0321%, respectively, for the prediction of DRC and 1.0084, –0.2332, 0.9955, 1.3611% and 0.1456%, respectively for the prediction of TSC.

3.2 Updated model samples

For DRC determination, samples of natural rubber field latex and concentrated latex for updating the model were also collected in the factory of the Thai Rubber Latex Corporation (Thailand) Public Company Limited in the Nongyai district, Chonburi province, Thailand. The samples were immediately subjected to the experiment during 24th-25th May, 19th, 25th and 29th June, 17th August, 7th September and 4th October 2012. The 159 field latex samples were obtained from the latex that the farmers in the Chonburi and nearby provinces sold to the factory. The 21 concentrated latex samples were obtained from the storage tanks of the factory. In total the adding samples were 180 samples. The experiment was conducted at 25 ± 2°C room temperature.

As for TSC determination, the source and the dates of collection of the samples were the same as for the DRC except fewer samples were used. Only 130 field latex samples and 30 concentrated samples were used, hence in total the adding samples were 160 samples. The experiment was also conducted at 25 ± 2°C room temperature

3.3 NIR Scanning

Each latex sample, without bubbles, was scanned in a quartz cuvette (Figure 3.2) with the light path length of 0.5 cm over the wavelength range of 350–1100 nm using a spectrometer (AVA-Spec-2048-USB2, Avantes, The Netherlands; www.avantes.com) in transmission mode with resolution 2.3 nm (Figure 3.1). The scanning was carried out on a sample with two replicates and five scans per replicate and the transmission spectra were transformed to be absorption spectra before analysis. Teflon specimen (Figure 3.3), with a thickness of 1 cm, was scanned as the reference material.

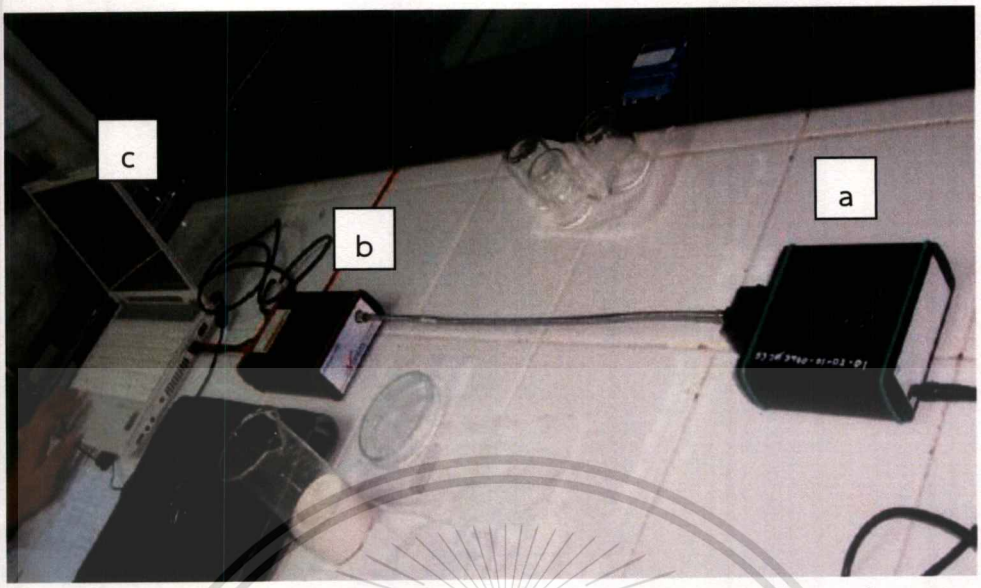


Figure 3.1 Shortwave NIR Spectrometer in transmission mode configuration (a) Light source, (b) Spectrometer and (c) Computer

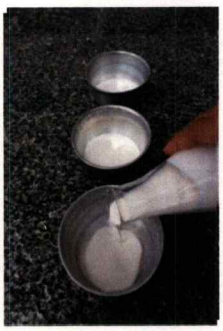
Figure 3.2 Cuvette (1x0.5cm)

Figure 3.3 T-shape Teflon (10mm thick) As reference specimen

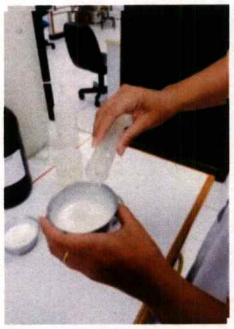
3.4 Standard laboratory method for DRC determination

This methodology follows the international standard method of ISO 126:2005(E): Latex, rubber, natural concentrate – Determination of dry rubber content [6].

1. Weigh latex



2. Put in dish



3. Coagulate with acid

4. Heat to complete coagulation

5. Sheeting sample

6. Dry in oven

7. Cool in desiccator

8. Weigh dry rubber

Figure 3.4 Determination of DRC

In Figure 3.4 the latex was poured into a conical flask and 10 g of latex was weighed into the dish by difference to the nearest 1 mg. Sufficient water was poured down the inside edge of the dish to reduce the solids content of the latex concentrate to 20 $\pm$ 1% (m/m). The dish was carefully rotated on a smooth surface to dilute the latex concentrate homogeneously.

For ammonia preserved latex, the acetic acid was added over a period of 5 min, 75 $\pm$ 5 cm^3 of the 20 g/dm^3 acetic acid solution, pouring down the inside edge of the dish and slowly rotating the dish while the acid was being added. The coagulated sheet of rubber was gently depressed below the surface of the acid. The dish was covered with a watch glass and heated on a water bath for 15 min. to 30 min. If the serum remains milky, 5 cm^3 of 95 % (v/v) ethanol was added. When the serum was clear, any small particles of coagulated rubber was collected by rubbing with the main bulk. The

coagulated rubber was soaked in several changes of water until the water was no longer acidic to litmus. The coagulated rubber was pressed to expel water and obtain a uniform sheet not exceeding 2 mm in thickness. The sheet was thoroughly rinsed in running water for at least 5 min. Allow the rinsed sheet to drip for a few minutes before transferring it to a drying oven. The sheet was dried at a temperature of 70 $\pm$ 2 °C until it had no white patches. If the sheet was dried on a large watch glass, it had to be carefully turned over two or three times during the first few hours of drying. The sample was allowed to cool in a desiccator for 30 min. and weighed.

The operations of drying, cooling and weighing were repeated until the loss in mass was less than 1 mg after heating for 30 min.

The dry rubber content (DRC) of the latex was calculated as a percentage by mass to the second decimal place from the equation 3.1:

$$DRC = \frac{m_1 \times 100}{m_0} \qquad 3.1$$

where

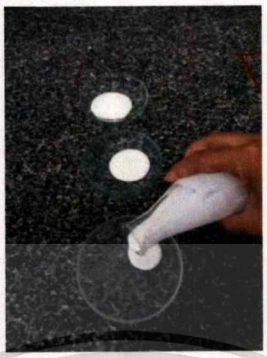
m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the dry sheet.

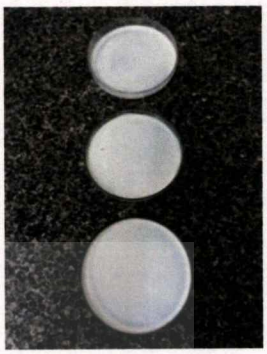
3.5 Standard laboratory method for TSC determination

This methodology follows the international standard method of ISO 124:2011(E): Latex, rubber – Determination of dry rubber content [7].

1. Weigh latex



2. Put in dish



3. Spread latex

4. Dry in oven

5. Cool in desiccator

6. Weigh dry rubber

Figure 3.5 Determination of TSC

The dish was weighed to the nearest 0.1 mg. The latex was put into a conical flask. About 2.0 ± 0.5g of the latex sample was weighed out by difference to the nearest 0.1 mg. (Figure 3.5). If desired, approximately 1 cm^3 of distilled water or water of equivalent purity might be added and mixed with the latex by swirling ensuring that the latex covered the bottom of the dish. The dish was placed in the oven so that it was horizontal, and heated it at 70 ± 2°C for 16 h or at 105 ± 5°C for 2 h or until the test portion had lost its whiteness.

The dish was removed from the oven and allowed it to cool at ambient temperature in a desiccator. The dish was removed and weighed. Return the dish to the oven for 30 min if the drying temperature used was 70 ± 2°C, or for 15 min if the

drying temperature was 105 ± 5°C. The drying procedure was repeated for periods of 30 min or 15 min, as appropriate, until the loss in mass between two successive weighings were less than 0.5 mg.

The total solid content (TSC) was expressed as a percentage by mass, using the equation 3.2:

$$TSC = \frac{m_1 X 100}{m_0} \qquad 3.2$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the dried material.

The results of the duplicate determinations shall not differ by more than 0.2% (m/m).

3.6 Model updating and data analysis

For DRC, the new reference data of 180 samples (5 spectra per sample) for model updating were merged with the corresponding 700-950 nm NIR absorption spectra. They were combined to the old data of 280 samples (1 average spectrum from 5 spectra per sample) of the original model. After sorting the added samples in ascending order of DRC, the samples were divided into a calibration set and a prediction set in the ratio of 7:3 for old data set and 8:2 for new data set. Then the updated model was developed by partial least squares regression (PLSR), using the calibration set, with spectral mathematical pretreatment (17 point S. Golay smoothing and range normalization). The updating of calibration model was done using Unscrambler 9.8 (Camo, Norway). The performance of the model was determined by the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias .

Similarly for TSC, the new reference data of 160 samples (5 spectra per sample) for model updating were merged with the corresponding 700-950 nm NIR absorption spectra. They were combined to the old data of 280 samples (1 average spectrum per sample) of the original model. After sorting the added samples in ascending order of TSC, the samples were divided into a calibration set and a prediction set in the ratio of 7:3 for old data set and 8:2 for new data set. Then the updated model was developed

by partial least squares regression (PLSR), using the calibration set, with spectral mathematical pretreatment (17 point S. Golay smoothing and range normalization). The updating of calibration model was done using Unscrambler 9.8 (Camo, Norway). The performance of the model was determined by the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Statistics of DRC and TSC in calibration and prediction sets

Table 4.1 shows the statistical values of DRC of field latex and concentrated latex of the calibration and prediction sets of updated model.

Table 4.2 shows the statistical values of TSC of field latex and concentrated latex of the calibration, prediction sets of updated model.

Table 4.1. Statistical values of DRC of field and concentrated latices of Para rubber of calibration set and prediction set of updated model.

Calibration Set					Prediction Set				
N	Mean	Max	Min	SD	N	Mean	Max	Min	SD
917	38.1514	63.9827	24.9845	10.8968	263	38.3053	61.8063	27.5900	10.5542

Remarks:

Calibration set: 917 spectra (Old set=197 samples; new set=72 samples with duplicate)

Prediction set: 263 spectra (Old set=83 samples; new set=18 samples with duplicate)

Table 4.2. Statistical values of TSC of field and concentrated latices of Para rubber of calibration set and prediction set of updated model

Calibration Set					Prediction Set				
N	Mean	Max	Min	SD	N	Mean	Max	Min	SD
847	38.8164	64.3857	27.0958	9.6037	233	38.8633	62.8061	29.8000	8.9126

Remarks:

Calibration set: 847 spectra (Old set=197 samples; new set=65 samples with duplicate)

Prediction set: 233 spectra (Old set=83 samples; new set=15 samples with duplicate)

4.2 Results of updating PLSR models

4.2.1 DRC model

The PLS regression updated models for DRC and TSC were developed. For DRC, the results show that the optimal number of factors of the model was 4 factors (PLS vectors), for which the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0126, -0.3729, 0.9931, 1.2654% and 0.1103%, respectively (Table 4.3). Williams [19] suggested that with the r of 0.99 or more the model was excellent and usable in any application including quality assurance. Comparing with old model where the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0154, -0.6286, 0.9960, 1.1092% and 0.0321%, respectively, it could be seen that the performance of the updated model was slightly lower than that of the old model. Therefore, there is the need to add more samples to the present model to make a new update to make a more accurate model where the wide variation of sample matrices will be covered. However, by those performance parameters obtained according to Williams [19] the model still can be used for the process control in a factory.

Figure 4.1 shows the linear correlation plots of measured versus predicted DRC. Figure 4.2 and 4.3 shows the regression coefficient plot and x-loading weight plots, respectively, of PLSR model for DRC of the latex. The signal at about 904-907 and 916-922 nm appeared to have a strong effect on the model and 906 and 922 nm are the natural rubber bands [20].

Table 4.3. Performance of updating PLSR model

Constituent	Wavelength range (nm)	Calibration				Prediction		
		Pretreatment	PC	r	SEC	r	SEP	Bias
DRC	700 – 950	Smoothing and range normalization	4	0.9857	1.3018%	0.9931	1.2654%	0.1103%
TSC	700 – 950	Smoothing and range normalization	4	0.9756	1.5004%	0.9834	1.6186%	-0.0802%

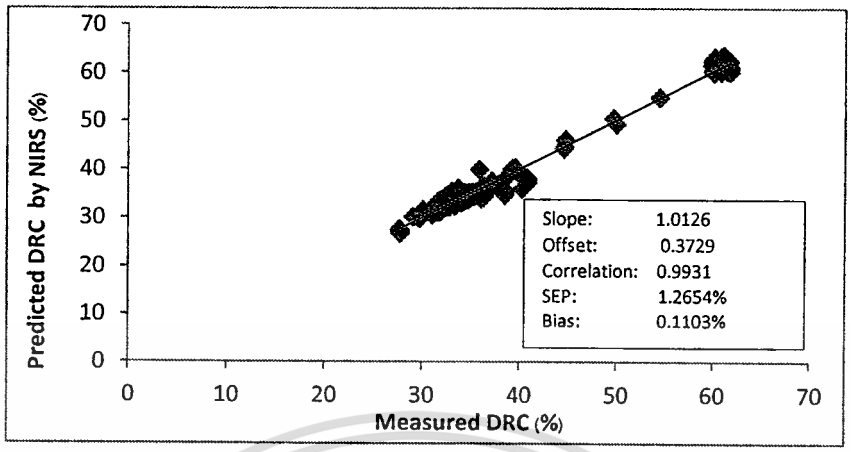


Figure 4.1. Linear correlation plots of measured versus predicted DRC of Para rubber of field latex and concentrated latex of updated model.

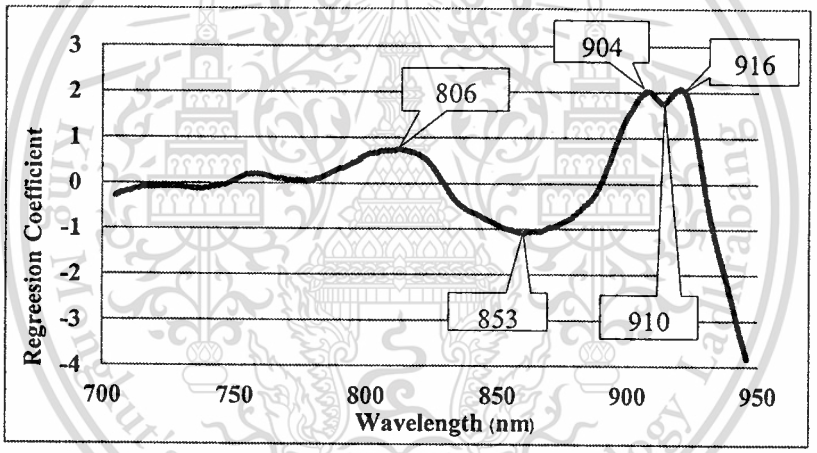


Figure 4.2. Regression coefficient plot of PLSR updating model for DRC of the latex.

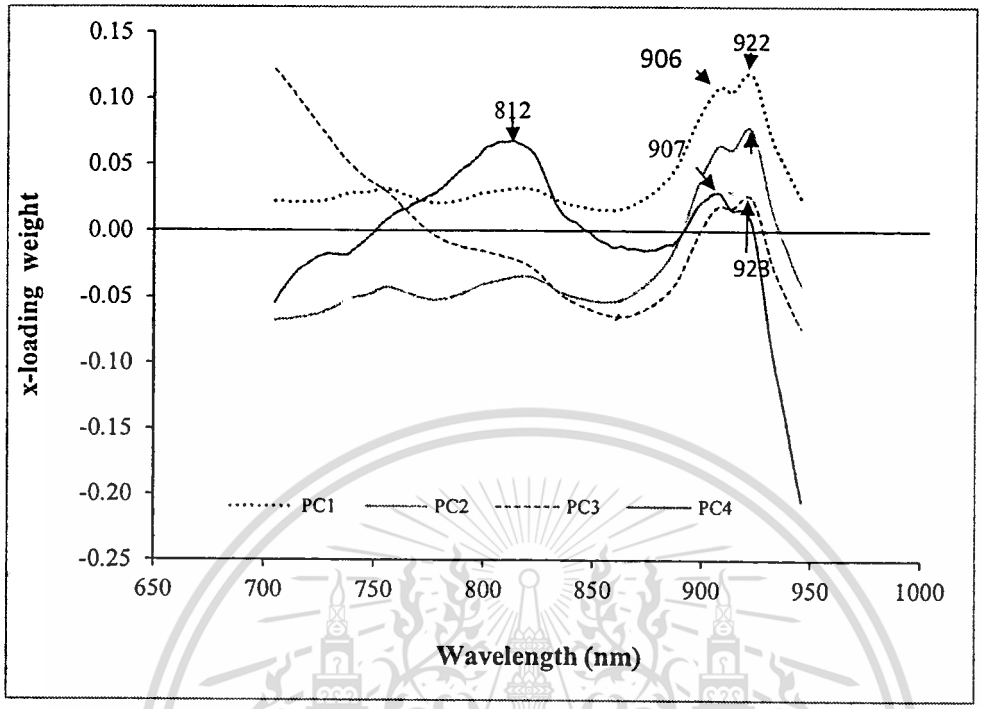


Figure 4.3. x-loading plot of PLSR updating model for DRC of the latex

4.2.2 TSC model

For TSC, the results show that the optimal number of factors of the model was 4 factors (PLS vectors), for which the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 0.9795, 0.7150, 0.9834, 1.6186% and -0.0802%, respectively. Williams [19] suggested that with the r between 0.96-0.98 the model was usable in most application including quality assurance. Comparing with old model where the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0084, -0.2332, 0.9955, 1.3611% and 0.1456%, respectively, it could be seen that though the r value of the updated model was not higher than that of the old model but the bias was much lower by 0.2258%. These proved that the model can be used for the process control in a factory.

Figure 4.4 shows the linear correlation plots of measured versus predicted TSC. Figure 4.5 and 4.6 show the regression coefficient plot and x-loading weight plots of PLSR model for TSC of the latex. The signal at about 905-909 and 918-922 nm

appeared to have a strong effect on the model and 906 and 922 nm is the natural rubber band.

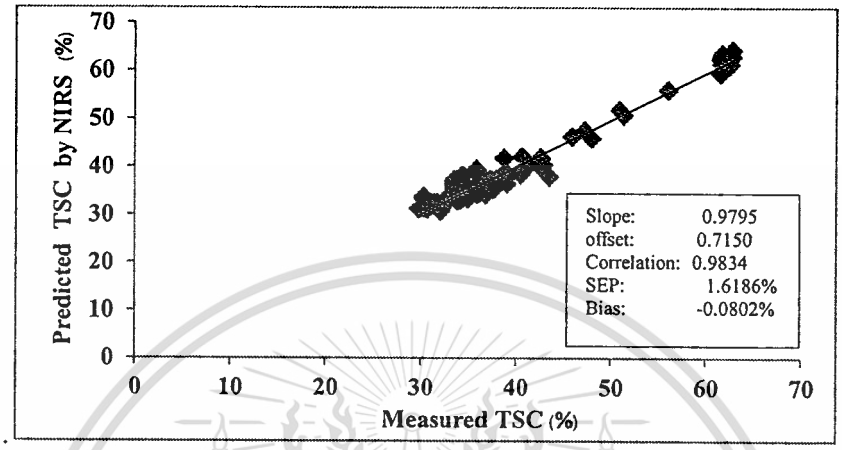


Figure 4.4 Linear correlation plots of measured versus predicted TSC of Para rubber of field latex and concentrated latex of updating model.

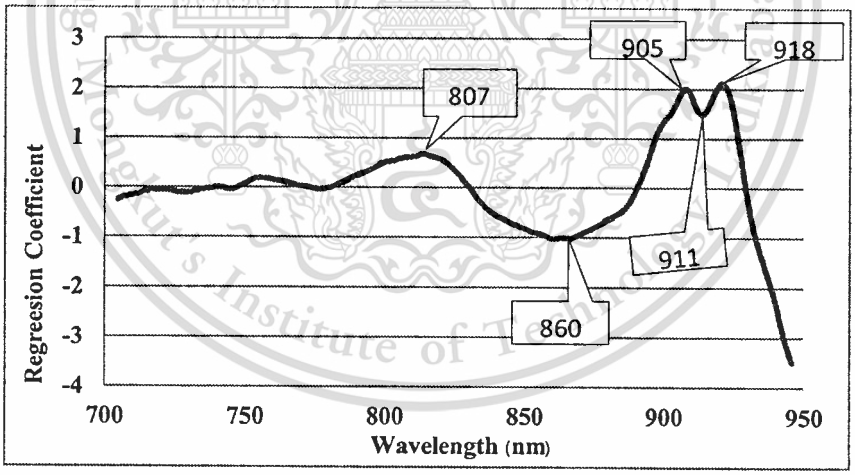


Figure 4.5 Regression coefficient plot of PLSR updating model for TSC of the latex.

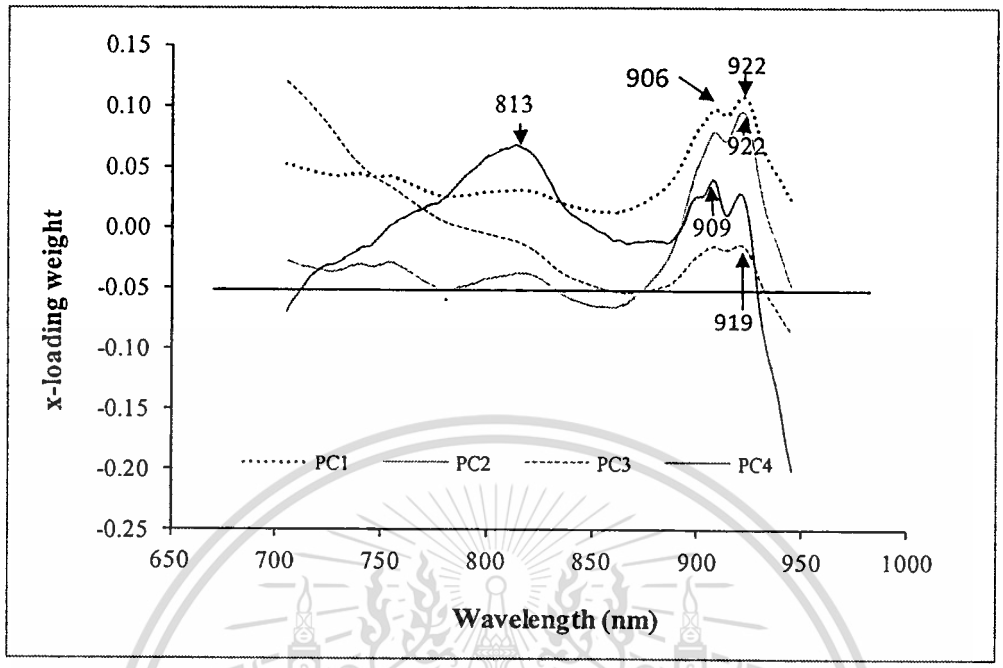


Figure 4.6. x-loading plot of updating PLSR model for TSC of the latex

CHAPTER 5

CONCLUSIONS

The near infrared spectroscopy technique developed for measuring the dry rubber content and total solids content of field latex and concentrated latex using shortwave near infrared (SW-NIR) spectrometer shows its high performance and this could be done within 2-3 minutes per sample. With the short wave near infrared technology, the investment and operating costs may be high compared to the standard ISO method, but the return of investment is relatively fast as the operating cost per sample is very low and rapid.

The results of original model for DRC determination for slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0154, -0.6286, 0.9960, 1.1092% and 0.0321% respectively whereas those of updated model were 1.0126, -0.3729, 0.9931, 1.2654% and 0.1103% respectively. There is a need to improve the updated model.

As for TSC the results of original model for slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.008, -0.2332, 0.9955, 1.3611% and 0.1456% respectively whereas those of updated model were 0.9795, 0.7150, 0.9834, 1.6186% and -0.0802% respectively. As such, the updated model was accurate.

The overall results did not show a significant improvement as the number of samples tested were not large.

Perhaps the methodology has to be changed from the present use of cuvette (use transmission mode) to the probe-dipping method (use reflectance mode) which is more practical in the factory environment. A fibre-optic probe dipping into a latex sample would be much easier to handle and clean than a delicate quartz cuvette.

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APPENDIX A

DRC AND TSC OF PREDICTION SAMPLES

Sample name/no.	DRC
CL1	60.087
CL14	60.15
CL25	60.177
CL28	60.249
CL29	60.312
CL33	60.033
CL34	60.098
CL4	60.182
CL43	59.971
CL45	60.897
CL5	60.156
CL52	60.194
CL57	60.004
CL61	60.082
CL62	60.242
CL63	60.488
CL64	60.443
CL65	60.16
CL67	60.24
CL68	60.9
CL69	60.29
CL70	61.27
CL71	60.3
CL76	60.57
CL78	60.91
CL83	61.208
CLA10	33.761
CLA12	50.049
CLA13	44.712
CLA19	39.6
CLA21	54.551
CLA25	33.789

Sample name/no.	DRC
CLA7	49.741
FL103	30.28
FL109	36.41
FL111	37.84
FL118	44.78
FL119	38.27
FL122	44.66
FL124	30.19
FL13	36.44
FL131	40.37
FL133	33.4
FL139	32.44
FL140	30.91
FL142	35.29
FL144	32.59
FL145	31.68
FL15	30.08
FL150	33.4
FL159	29.12
FL16	34.43
FL164	35.38
FL168	32.44
FL19	34.47
FL2	31.87
FL30	30.91
FL31	35.94
FL32	40.33
FL34	36
FL37	29.15
FL45	31.06
FL49	27.68
FL5	35.99

Sample name/no.	DRC
FL51	33.08
FL57	32.58
FL59	33.04
FL62	33.09
FL63	32.57
FL64	29.2
FL65	33.43
FL67	32.34
FL69	31.75
FL72	34.38
FL73	36.46
FL79	31.32
FL8	27.59
FL83	31.33
FL87	35.22
FL92	37.86
FL94	31.33
FL95	27.87
FL99	33.79
NEW0086	31.973
NEW0087	31.973
NEW0088	31.973
NEW0089	31.973
NEW0090	31.973
NEW0116	34.799
NEW0117	34.799
NEW0118	34.799
NEW0119	34.799
NEW0120	34.799
NEW0146	33.762
NEW0147	33.762
NEW0148	33.762

Sample name/no.	DRC
NEW0149	33.762
NEW0150	33.762
NEW0151	33.762
NEW0152	33.762
NEW0153	33.762
NEW0154	33.762
NEW0155	33.762
NEW0196	61.728
NEW0197	61.728
NEW0198	61.728
NEW0199	61.728
NEW0200	61.728
New0481	34.882
New0482	34.882
New0483	34.882
New0484	34.882
New0485	34.882
New0496	27.774
New0497	27.774
New0498	27.774
New0499	27.774
New0500	27.774
NEW0550	36.086
NEW0551	37.199
NEW0552	37.199
NEW0553	37.199
NEW0554	37.199
NEW0555	37.199
New0561	31.958
New0562	31.958
New0563	31.958
New0564	31.958

Sample name/no.	DRC
New0565	31.958
New0566	30.139
New0567	30.139
New0568	30.139
New0569	30.139
New0570	30.139
New0576	27.836
NEW0576	36.086
NEW0577	36.086
New0577	27.836
NEW0578	36.086
New0578	27.836
NEW0579	36.086
New0579	27.836
New0580	27.836
New0591	32.859
New0592	32.859
New0593	32.859
New0594	32.859
New0595	32.859
New0621	31.524
New0622	31.524
New0623	31.524
New0624	31.524
New0625	31.524
New0636	32.863
New0637	32.863
New0638	32.863
New0639	32.863
New0640	32.863
New0661	36.405
New0662	36.405

Sample name/no.	DRC
New0663	36.405
New0664	36.405
New0665	36.405
New0686	40.872
New0687	40.872
New0688	40.872
New0689	40.872
New0690	40.872
New0721	37.133
New0722	37.133
NEW0723	37.133
NEW0724	37.133
NEW0725	37.133
NEW0746	32.463
NEW0747	32.463
NEW0748	32.463
NEW0749	32.463
NEW0750	32.463
NEW0751	32.463
NEW0752	32.463
NEW0753	32.463
NEW0754	32.463
NEW0755	32.463
NEW0806	34.372
NEW0807	34.372
NEW0808	34.372
NEW0809	34.372
NEW0810	34.372
NEW0811	34.372
NEW0812	34.372
NEW0813	34.372
NEW0814	34.372

Sample name/no.	DRC
NEW0815	34.372
NEW0851	29.78
NEW0852	29.78
NEW0853	29.78
NEW0854	29.78
NEW0855	29.78
NEW0866	34.056
NEW0867	34.056
NEW0868	34.056
NEW0869	34.056
NEW0870	34.056
NEW0871	34.056
NEW0872	34.056
NEW0873	34.056
NEW0874	34.056
NEW0875	34.056
NEW0886	39.276
NEW0887	39.276
NEW0888	39.276
NEW0889	39.276
NEW0890	39.276
NEW0896	31.649
NEW0897	31.649
NEW0898	31.649
NEW0899	31.649
NEW0900	31.649
NEW0966	61.806
NEW0967	61.806
NEW0968	61.806
NEW0969	61.806
NEW0970	61.806
NEW0976	61.559

Sample name/no.	DRC
NEW0977	61.559
NEW0978	61.559
NEW0979	61.559
NEW0980	61.559
NEW1026	38.487
NEW1027	38.487
NEW1028	38.487
NEW1029	38.487
NEW1030	38.487
NEW1086	32.602
NEW1087	32.602
NEW1088	32.602
NEW1089	32.602
NEW1090	32.602
NEW1091	32.602
NEW1092	32.602
NEW1093	32.602
NEW1094	32.602
NEW1095	32.602
NEW1121	31.789
NEW1122	31.789
NEW1123	31.789
NEW1124	31.789
NEW1125	31.789
NEW1126	31.789
NEW1127	31.789
NEW1128	31.789
NEW1129	31.789
NEW1130	31.789
NEW0936	60.035
NEW0937	60.035
NEW0938	60.035

Sample name/no.	DRC
NEW0939	60.035
NEW0940	60.035
NEW0941	60.142
NEW0942	60.142
NEW0943	60.142
NEW0944	60.142
NEW0945	60.142

Sample name/no.	TSC
CL1	61.52
CL14	61.7
CL25	61.77
CL28	61.82
CL29	61.84
CL33	61.66
CL34	61.86
CL4	61.81
CL43	61.65
CL45	62.54
CL5	61.63
CL52	61.71
CL57	61.63
CL61	61.64
CL62	61.78
CL63	61.94
CL64	61.97
CL65	61.54
CL67	61.7
CL68	62.3
CL69	61.79
CL70	62.75
CL71	61.73
CL76	62.1
CL78	62.23
CL83	62.81
CLA10	34.62
CLA12	51.38
CLA13	45.91
CLA19	40.66
CLA21	56.03
CLA25	34.62

Sample name/no.	TSC
CLA7	50.95
FL103	34.2
FL109	39.15
FL111	40.4
FL118	47.27
FL119	40.91
FL122	48.02
FL124	32.76
FL13	39.17
FL131	42.92
FL133	37.01
FL139	34.43
FL140	33.6
FL142	38.6
FL144	35.36
FL145	34.81
FL15	32.94
FL150	36.66
FL159	31.77
FL16	37.34
FL164	39.08
FL168	35.06
FL19	36.91
FL2	34.13
FL30	34.06
FL31	38.72
FL32	43.53
FL34	38.42
FL37	31.72
FL45	33.89
FL49	30.73
FL5	38.51

Sample name/no.	TSC
FL51	35.84
FL57	35.97
FL59	36.17
FL62	35.29
FL63	35.33
FL64	31.75
FL65	36.36
FL67	34.85
FL69	34.22
FL72	37.03
FL73	39.21
FL79	33.86
FL8	29.8
FL83	33.78
FL87	37.48
FL92	40.46
FL94	34.22
FL95	31.4
FL99	36.95
NEW0056	34.38
NEW0057	34.38
NEW0058	34.38
NEW0059	34.38
NEW0060	34.38
NEW0091	34.92
NEW0092	34.92
NEW0093	34.92
NEW0094	34.92
NEW0095	34.92
NEW0121	36.84
NEW0122	36.84
NEW0123	36.84

Sample name/no.	TSC
NEW0124	36.84
NEW0125	36.84
NEW0126	36.84
NEW0127	36.84
NEW0128	36.84
NEW0129	36.84
NEW0130	36.84
NEW0141	35.75
NEW0142	35.75
NEW0143	35.75
NEW0144	35.75
NEW0145	35.75
New0481	37.95
New0482	37.95
New0483	37.95
New0484	37.95
New0485	37.95
New0506	37.98
New0507	37.98
New0508	37.98
New0509	37.98
New0510	37.98
NEW0521	30.33
NEW0522	30.33
NEW0523	30.33
NEW0524	30.33
NEW0525	30.33
New0541	32.99
NEW0541	35.87
New0542	32.99
NEW0542	35.87
New0543	32.99

Sample name/no.	TSC
NEW0543	35.87
New0544	32.99
NEW0544	35.87
New0545	32.99
NEW0545	35.87
NEW0546	35.87
NEW0547	35.87
NEW0548	35.87
NEW0549	35.87
NEW0550	35.87
New0566	32.89
New0567	32.89
New0568	32.89
New0569	32.89
New0570	32.89
New0601	31.98
New0602	31.98
New0603	31.98
New0604	31.98
New0605	31.98
New0616	35.98
New0617	35.98
New0618	35.98
New0619	35.98
New0620	35.98
New0621	34.96
New0622	34.96
New0623	34.96
New0624	34.96
New0625	34.96
New0626	32.09
New0627	32.09

Sample name/no.	TSC
New0628	32.09
New0629	32.09
New0630	32.09
New0656	34.4
New0657	34.4
New0658	34.4
New0659	34.4
New0660	34.4
New0691	33.5
New0692	33.5
New0693	33.5
New0694	33.5
New0695	33.5
New0696	33.5
New0697	33.5
New0698	33.5
New0699	33.5
New0700	33.5
NEW0766	36.01
NEW0767	36.01
NEW0768	36.01
NEW0769	36.01
NEW0770	36.01
NEW0781	42.43
NEW0782	42.43
NEW0783	42.43
NEW0784	42.43
NEW0785	42.43
NEW0861	35.62
NEW0862	35.62
NEW0863	35.62
NEW0864	35.62

Sample name/no.	TSC
NEW0865	35.62
NEW0866	37.64
NEW0867	37.64
NEW0868	37.64
NEW0869	37.64
NEW0870	37.64
NEW0871	37.64
NEW0872	37.64
NEW0873	37.64
NEW0874	37.64
NEW0875	37.64
NEW0886	42.64
NEW0887	42.64
NEW0888	42.64
NEW0889	42.64

Sample name/no.	TSC
NEW0890	42.64
NEW1066	30.28
NEW1067	30.28
NEW1068	30.28
NEW1069	30.28
NEW1070	30.28
NEW1121	35.22
NEW1122	35.22
NEW1123	35.22
NEW1124	35.22
NEW1125	35.22
NEW1126	35.22
NEW1127	35.22
NEW1128	35.22
NEW1129	35.22

Sample name/no.	TSC
Sample name/no.	TSC
NEW1130	35.22
NEW1151	35.1
NEW1152	35.1
NEW1153	35.1
NEW1154	35.1
NEW1155	35.1
NEW1156	35.1
NEW1157	35.1
NEW1158	35.1
NEW1159	35.1
NEW1160	35.1

APPENDIX B

PUBLISHED PAPERS

Updated Model for Fast Dry Rubber Content Determination in Natural Rubber Latex Using Shortwave Near Infrared Spectroscopy

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ABSTRACT.

The analysis of dry rubber content (DRC) of Para rubber latex including field latex and concentrated latex, using near-infrared spectroscopy was carried out by a ultra violet/visible/near-infrared (UV/VIS/NIR) Spectrometer in transmittance mode over the wavelength range of 350–1100 nm. The original model provided the best accuracy of prediction was developed using the partial least square regression (PLSR) from the spectra which were pretreated by the smoothing and range normalization in the wavelength range of 700-950 nm. The slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0154, -0.6286, 0.9960, 1.190% and 0.0322%, respectively. The updated model was done by adding the 180 samples merged into the 280 original samples. The slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0126, -0.5729, 0.9931, 1.2654% and 0.1103%, respectively. Therefore, it is needed to make more robust updated model by NIRS technique for determining the DRC of Para rubber latex, for both field latex and concentrated latex.

Keywords: Natural Rubber Latex, Dry Rubber Content, Shortwave, Near Infrared Spectroscopy

INTRODUCTION

Dry rubber content (DRC) is defined as a percentage by mass of the latex which is coagulated under specified conditions of colloidal destabilization [1].

At present determination of DRC is carried out by the international standard method as in ISO126:2005 [2] which involve coagulating the rubber with acid, separating the rubber solids from the serum, pressing the rubber solid and heating the coagulated sample for over 16 hours at 70 °C in a convectional oven. Hence this method is time consuming and unsuitable for a factory producing large quantities of centrifuged latex for production.

Natural rubber latex is the raw materials for manufacture of various types of dipped and extruded latex products such as gloves, condoms, baby teats, catheters, latex thread etc.

The field latex is centrifuged to produce latex concentrate. The factory purchases the field latex from numerous small holders based on the dry rubber content of the latex. The dry content rubber of field latex can be determined quickly with hydrometer known as "Metrolac" which is instantaneous but inaccurate

In the concentrated latex factory, the latex concentrate is produced at 60 % DRC. DRC is an important parameter for the purpose of trade for both field latex and latex concentrate. Other than this, DRC is required to calculate the non-rubber solids content (NRC) as well as the volatile fatty acids number (VFA) of the latex using the standard method, ISO 506:1992 [3]. These are the other important process control parameters.

Near infrared (NIR) spectroscopy is a rapid technique, accurate, and enviromental friendly where there is no chemical use, no or less sample preparation and the parameter prediction model is developed from the relationship between the interested constituents and the NIR spectral data. This NIR spectroscopy technique has been applied to a few agricultural products similar to rubber latex. Takeno et al. [4] describe the Fourier transform near infrared spectroscopy (FT-NIR) technique coupled with a partial least squares (PLS) regression model to quantify natural polyisoprene in *Eucommia ulmoides* leaves and the best PLS regression model was obtained with second derivative NIR spectra in the region between 4000–6000 cm^{-1} (R^2, 0.95). Marinho et al. [5] studied the application of NIR spectroscopy for analyzing the natural *trans*- and *cis*-polyisoprenes from *Ficus elastica* (*cis*-1,4-polyisoprene) and gutta-percha (*trans*-1,4-polyisoprene) and mixtures of these polymers. Sirisomboon et al., [6] applied the FT-NIR

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spectroscopy in the wavelength range of 1100-2500 nm in evaluation of dry rubber content of rubber latex and Sirisomboon et al.[7] used the short wave NIR spectroscopy in the wavelength range of 700-950 nm in evaluation of dry rubber content and total solids content. The work of Sirisomboon et al. [7] was tested to use in the concentrated latex factory. Therefore, the objective of our work was to study the ability of the short wave NIR spectroscopy and update the model developed by Sirisomboon et al. [7] for prediction of dry rubber content of both field latex and concentrated latex of Para rubber, which were the materials used in the process of latex production, to facilitate the quality and process control in the factory.

MATERIALS AND METHODS

Samples

Samples of Para rubber field latex and concentrated latex for updating the model were collected in the factory of the Thai Rubber Latex Corporation (Thailand) Public Company Limited in the Nongyai district, Chonburi province, Thailand. The samples were immediately subjected to the experiment during 24-25 May, 19, 25, 29 June, 17 August, 7 September and 4 October 2012. The 159 field latex samples were obtained from the latex that the farmers in the Chonburi and nearby provinces sold to the factory. The 21 concentrated latex samples were obtained from the storage tanks of the factory. In total the adding samples were 180 samples. The experiment was conducted at 25± 2°C room temperature.

NIR Scanning

The NIR scanning was conducted as in Sirisomboon et al. (in press). A latex sample without bubbles was scanned in a quartz cuvette with the size of 1X0.5 cm over the wavelength range of 350–1100 nm by a spectrometer (AVA-Spec-2048-USB2, Avantes, The Netherlands) in transmission mode. The scanning was done on a sample with two replicates and 5 scans per replicate, and the transmission spectra were transformed to be absorption spectra before analysis. The Teflon with the thickness of 1 cm was used for scanning as the reference material.

Dry Rubber Content (DRC) Measurement

The dry rubber content of rubber latex was measured following the standard method used by the factory which followed the ISO 126:2005 Natural rubber latex concentrate – Determination of dry rubber content [2].The description of the dry rubber content measurement according to the ISO standard is in Sirisomboon et al.[6].

Model updating and data analysis

The new reference data of 180 samples for model updating were merged with the corresponding 700-950 nm NIR absorption spectra. They were combined to the old data of 280 samples of the original model. After sorting the added samples in ascending order of dry rubber content, the samples were divided into a calibration set and a prediction set in the ratio of 8:2. Then the updated model was developed by Partial least squares regression (PLSR), using the calibration set, with spectral mathematical pretreatment (17 point S. Golay smoothing and range normalization).

The updating of calibration model was done using Unscrambler 9.8 (Camo, Norway). The performance of the model was determined by the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias.

RESULTS AND DISCUSSION

Table 1 shows the statistical values of DRC of field latex and concentrated latex of the calibration and prediction sets. The PLS regression updated model was developed. The results show that the optimal number of factors of the model was 4 factors (PLS vectors), for which the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0126, -0.5729, 0.9931, 1.2654% and 0.1105%, respectively. Williams [8] suggested that with the r of 0.99 or more the model was excellent and usable in any application including quality assurance. Comparing with old model where the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0154, -0.6286, 0.9960, 1.190% and 0.0322%, respectively, it could be seen that the performance of the updated model was slighly lower than that of the old model. Therefore, there is the need to add more samples to the present model to make a new update to make a more accurate model. However, by those performance parameters obtained according to Williams [8] the model still can be used for the process control in a factory.

Figure 1 shows the linear correlation plots of measured versus predicted DRC. Figure 2 shows the regression coefficient plots of PLSR model for DRC of the latex. The signal at about 904 and 916 nm appeared to have a strong effect on the model and 906 nm is the natural rubber band [7].

CONCLUSIONS

The near infrared spectroscopy technique developed for measuring the dry rubber content of field latex and concentrated latex using shortwave near infrared spectrometer shows its high performance and this could be done within 2-3 minutes per sample. With the short wave near infrared technology the investment cost may be high compare to the standard ISO method, but the return of investment is relatively fast as the operating cost per sample is very low and rapid. The technique now is tested for the real use in the concentrated latex factory in Thailand.

Table 1. Statistical values of dry rubber content (DRC) of field and concentrated lattices of Para rubber of calibration set and prediction set.

Data set	N	Mean	Max	Min	SD
Calibration Set	144	36.1514	63.9527	24.9545	10.5965
Prediction Set	36	38.3053	61.9063	27.5900	10.5542

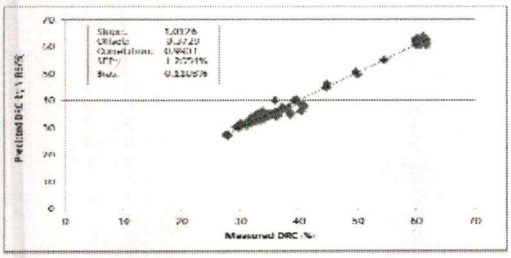

Figure 1. Linear correlation plots of measured versus predicted dry rubber content (DRC) of Para rubber of field latex and concentrated latex.

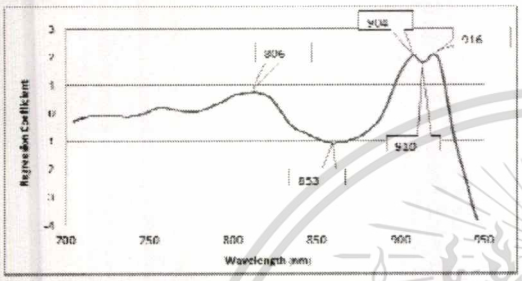

Figure 2. Regression coefficient plot of PLSR model for dry rubber content (DRC) of the latex.

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Lim Chin Hock graduated in rubber technology at London School of Polymer Technology, University of North London. He worked as a researcher at Tun Abdul Razak Research Centre in UK and RRIM in Malaysia before joining the present Company in Thailand in the R&D of latex production.

Updated Model for Fast Total Solids Content Determination in Natural Rubber Latex Using Shortwave Near Infrared Spectroscopy

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ABSTRACT

The analysis of total solids content (TSC) of Para rubber latex including field latex and concentrated latex, using near-infrared spectroscopy was carried out by a ultra violet/visible/near-infrared (UV/VIS/NIR) Spectrometer in transmittance mode over the wavelength range of 350–1100 nm. The original model provided the best accuracy of prediction was developed using the partial least square regression (PLSR) from the spectra which were pretreated by the smoothing and range normalization in the wavelength range of 700-950 nm. The slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0084, -0.2332, 0.9940, 1.3611% and 0.1456%, respectively. The updated model was done by adding the 160 samples merged into the 280 original samples. The slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 0.9795, 0.7130, 0.9834, 1.6186% and -0.0502%, respectively. Therefore, the robust updated model by NIRS technique was more accurate and faster method for determining the TSC of Para rubber latex, for both field latex and concentrated latex.

Keywords: Natural Rubber Latex, Total Solids Content, Shortwave, Near Infrared Spectroscopy

INTRODUCTION

The total solids content (TSC) of a latex is defined as the percentage by mass of the whole which is non-volatile under specified conditions of drying in an open atmosphere at an elevated temperature [1].

Natural rubber latex is the raw materials used for the manufacture of various latex products such as gloves (both examination and household), condoms, baby teats, catheters, foam products, latex thread for undergarments, adhesives for various applications and cast products like toys etc.

The TSC includes dry rubber content and other solid matter called non-rubber solids content (NRC) in the latex. The non-rubber content is the indicator for the cleanliness of the latex. The lower the NRC, the cleaner is the latex. Thus NRC can be calculated by the difference between the TSC and the DRC of the latex.

In addition, the TSC is an important parameter on which the various parameters are based on, namely, VFA number, KOH number, MST and Brookfield viscosity.

NIR spectroscopy uses the electromagnetic radiation absorption at wavelengths range of 780–2500 nm. NIR bands are generated from overlapping absorptions corresponding mainly to overtones and combinations of vibration of C–H, O–H, and N–H chemical bonds which are included in the biological materials. According to Huang et al. [2], in practice, the common modes are transmittance, interactance, transflectance, diffuse transmittance, and diffuse reflectance, with the last two being most frequently used. Diffuse transmittance measurements are suitable for samples of 1-2 cm thickness using shortwave near infrared radiation (780-1100 nm) while long wavelength (1100-2500 nm) could be applied to thinner samples. The diffuse reflectance measurement, where most of the incident radiation is reflected, is suitable for thicker samples. NIR spectroscopy is a rapid, accurate, non destructive, less or no sample preparation, no chemical, enviromental friendly and can be applied off line, at line, in line or online for quality assurance and process control.

It is reported that various agro-industries such as flour milling [3], soybean meal factory [4], bakery factory [5], etc. use NIR spectroscopy. There are a few research reported the application of NIR spectroscopy in rubber latex factory [6,7,8] and there is still a need for further research for the real application in the factory. Therefore, the objective of our work was to update the shortwave near infrared spectroscopy model developed previously [6] for fast total solids content determination in natural rubber latex production factory to facilitate the quality and process control.

MATERIALS AND METHODS

Samples

Samples of Para rubber field latex and concentrated latex for updating the model were collected from the factory of the Thai Rubber Latex

Corp. (Thailand) Public Company Limited in Nongyai district, Chonburi province, Thailand. The samples were immediately subjected to the experiment during 24-25 May, 19, 25, 29 June, 17 August, 7 September and 4 October 2012. The 131 field latex samples were obtained from the latex that the farmers in the Chonburi and near-by provinces sold to the factory. The 13 concentrated latex samples were obtained from the storage tanks of the factory. In total the samples were 144 samples. The experiment was conducted at 25± 2°C room temperature.

NIR Scanning

The NIR scanning was conducted followed Sirisomboon et al. (in press) [6]. A latex sample without bubbles was scanned in a quartz cuvette with the size of 1×0.5 cm over the wavelength range of 350–1100 nm by a spectrometer (AVA-Spec-2048-USB2, Avantes, The Netherlands) in transmission mode. The scanning was done on a sample with two replicates and 5 scans per replicate, and the transmission spectra were transformed to be absorption spectra before analysis. The Teflon with the thickness of 1 cm was used for scanning as the reference material.

Total Solids Content (TSC) Measurement

The total solids content of rubber latex was measured following the standard method used by the factory following the ISO 124:2011(E) Latex, rubber – Determination of total solids content [9]. The description of the total solids content measurement by the ISO standard is in Sirisomboon et al., in press [6].

Model updating and data analysis

The new reference data of 144 samples for model updating were merged with the corresponding 700-950 nm NIR absorption spectra. Then they were combined to the old data of 280 samples of the original model. After sorting the added samples in ascending order of total solids content, the samples were divided into a calibration set and a prediction set in the ratio of 8:2. Then the updated model was developed by Partial least squares regression (PLSR), using the calibration set, with spectral mathematical pretreatment (17 point S. Golay smoothing and range normalization).

The updating of calibration model was done using Unscrambler 9.8 (Camo, Norway). The performance of the model was determined by the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias.

RESULTS AND DISCUSSION

Table 1 shows the statistical values of TSC of field latex and concentrated latex of the calibration, prediction sets. The PLS regression updated model was developed. The results show that the optimal number of factors of the model was 4 factors (PLS vectors), for which the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 0.9795, 0.7150, 0.9854, 1.6186% and -0.0802%, respectively. Williams [10] suggested that with the r between 0.96-0.98 the model was usable in most application including quality assurance. Comparing with old model where the slope, offset, correlation coefficient (r), standard error of prediction (SEP) and bias were 1.0084, -0.2332, 0.9940, 1.3611% and 0.1456%, respectively, it could be seen that though the r value of the updated model was not higher than that of the old model but the bias was significantly lower by 0.2258%. These proved that the model can be used for the process control in a factory.

Figure 1 shows the linear correlation plots of measured versus predicted TSC. Figure 2 shows the regression coefficient plots of PLSR model for TSC of the latex. The signal at about 905 and 918 nm appeared to have a strong effect on the model and 906 nm is the natural rubber band [6].

CONCLUSIONS

The near infrared spectroscopy technique developed for measuring the total solids content of field latex and concentrated latex using shortwave near infrared spectrometer shows its high performance and this could be done within 2-3 minutes per sample. With the short wave near infrared technology the investment cost and operating cost will be tremendously low compared to long wave technology. The technique now is tested for the real use in the concentrated latex factory in Thailand.

Table 1. Statistical values of total solids content (TSC) of field and concentrated lattices of Para rubber of calibration set and prediction set.

Data set	N	Mean	Max	Min	SD
Calibration Set	144	38.8164	64.3857	27.6938	9.6037
Prediction Set	36	38.8633	62.8061	29.8000	8.9126

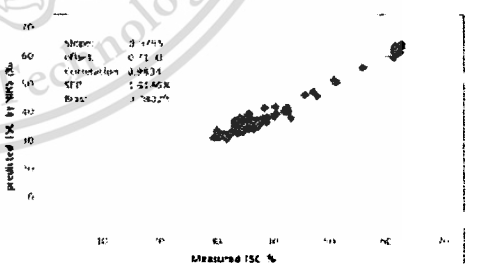

Figure 1. Linear correlation plots of measured versus predicted total solids content (TSC) of Para rubber of field latex and concentrated latex.

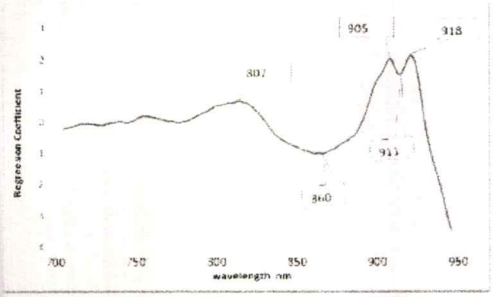

Figure 2.Regression coefficient plot of PLSR model for total solids content (TSC) of the latex.

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Since 2006, he has been in the technical committee for Thailand in ISO/TC45 – Rubber and Rubber Products and has helped to update existing international standards as well and introducing new standards for the natural rubber industry.

As a project leader, to date, he had revised 5 existing international standards and introduced 2 new international standards for natural rubber latex, viz:

Existing international standards:

(1). ISO2004:2010 Natural rubber latex concentrate – Centrifuged or creamed, ammonia-preserved type – Specifications.

(2). ISO124:2011 Latex, rubber – Determination of total solids content.

(3). ISO125:2011 Natural rubber latex concentrate – Determination of alkalinity.

(4). ISO127:2012 Rubber, natural latex concentrate – Determination of KOH number.

(5). ISO124:2014 Latex, rubber – Determination of total solids content.

New international standards:

(1). ISO11852:2011 Rubber – Determination of magnesium content of field and concentrated natural rubber latex by titration. (Jointly with Malaysia).

(2). ISO19043:2014 Rubber latex – Determination of total phosphate content in latex by spectrophotometric method.

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