Chapter

Rapid Evaluation of the Properties of Natural Rubber Latex and Its Products Using Near-Infrared Spectroscopy

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Abstract

The parameters including physico-chemical properties such as dry rubber content (DRC), total solids content (TSC), volatile fatty acid (VFA) number, alkalinity (ammonia content) and potassium hydroxide (KOH) number and physical properties such as viscosity and cross-link density are important to the trading and processing of natural rubber latex and its products. Traditionally these properties of field and concentrated latices and their products including thin and thick films are evaluated with chemicals and time-consuming methods and with the need of technical experts. The near-infrared (NIR) spectroscopy is a nondestructive, rapid, accurate and environment-friendly technique. It needs no chemical. This chapter describes the application of NIR spectroscopy on evaluation of the properties of natural rubber latex and its products.

Keywords: latex, thin and thick films, physico-chemical properties, near-infrared spectroscopy, ISO standards

1. Importance of physico-chemical properties of natural rubber latex and its products on trading and process control

Importance of physico-chemical properties of natural rubber latex and its products on trading and process control. The parameters include properties such as dry rubber content (DRC), total solids content (TSC), volatile fatty acid (VFA) number, alkalinity, potassium hydroxide (KOH) number, viscosity and cross-link density.

1.1 Historical background and introduction

The manufacturing of products directly from natural rubber latex takes place today in virtually every country of the world, and taken as a whole, the latex product industry is one of the most important non-tyre consumers of natural rubber.

Mankind has been making articles from natural latex for hundreds of years since Charles de la Condamine who made a journey across South America in 1736, reported the Amazonian Indians were producing shoes and bottles [1] from it. Nevertheless, a further 100 years had to pass before the beginnings of modern latex product industry can be discerned when in 1839 Charles Goodyear discovered

that the rubber samples after being baked in sulphur and white lead subsequently underwent little change through heat or cold [2]. This process was later coined as 'vulcanization' (from Vulcan the God of Fire) by Thomas Hancock.

The discovery of vulcanization was a milestone in the history of the rubber industry. As the demand for rubber increased and the supply of rubber from the wild *Hevea brasiliensis* trees of the Amazon Valley was unreliable, plantation rubber [2] began in Malaya in 1877, spreading to Southeast Asian countries and other tropical countries worldwide where millions of people's livelihoods depended on it.

Natural rubber latex is a stable colloidal dispersion of polymeric materials (latex particles) in an aqueous medium [3] containing no <60% by weight of polymer. Latex or rubber products, without vulcanization, suffer severely from poor physical properties, poor resistance to light and swelling in solvents and above all are susceptible to extremes of temperatures [4], becoming sticky in hot weather and hard when cold. The vulcanization process is brought about by the linking of macromolecules at their reactive sites. The cross-linking of rubber is also referred to as curing. During the progress of vulcanization [5], the modulus, hardness, elastic properties, resistance to swelling, etc. are considerably modified. In brief, vulcanization converts raw rubber molecules into a useful network by the formation of cross-links. The properties of vulcanized rubber are determined by the state of cure [6].

1.2 Types of natural latex concentrate

A range of natural latex concentrates is commercially available. The types of latex indicate the methods of concentration and the nature of the preservative systems. In all these latices, the polymer is the same, i.e. cis-1,4-polyisoprene; the differences lie in the quantity and the nature of the nonrubber substances present and the specific characteristics imparted by the preservatives.

The centrifuge-concentrated types of natural latex account for over 90% of total latex production, and of these the high ammonia (HA), low ammonia-TMTD/ZnO (LA-TZ) and medium ammonia (MA) types predominate. Centrifuged latices are used in virtually all latex processes, whereas other concentrates are used more selectively. Creamed latex, for example, is used almost exclusively for the production of extruded latex thread. Evaporated latex, which is characterized by a high solids content and by high stability, is used in processes where these properties are particularly desirable, e.g. in modifying bitumen or asphalt for road construction and as a binders or adhesives.

Latex particles are lighter than the serum in which they are suspended. There is a tendency to rise towards the surface (creaming). This movement is normally slow, and the rise of the rubber particles is covered by Stokes' law [2] as in the formula

$$V = \frac{2}{9} g \frac{(d - d_1)}{\eta} r^2$$

where V = rate of rise (mm/s)
g = acceleration due to gravity (cm/s/s)
d = density of serum (1.021 g/cc)
d_1 = density of rubber particle (0.91 g/cc)
r = radius of particle (av. 0.5 μm)
η = viscosity of medium (about 0.02 poises)

From Stokes' formula the rate of rise of a particle depends on the gravitational force, g. As g may be increased by some 2000–3000 times that of earth gravity using centrifuge, this method is used to concentrate the latex. If the rotating bowl is fed continuously with field latex, the concentrate (about 60% DRC) at the centre can

be withdrawn, while the dilute skim fraction is drained from the circumference. The ease and speed at which the field latex can be concentrated explains why the centrifugation is the preferred method commercially.

1.3 Properties of latex concentrates

It is appropriate to summarize here those properties of the major types of latex concentrate which may determine their use for any particular produce in **Table 1**.

1.3.1 HA-centrifuged latex

This is the most widely used form of concentrate and has the great advantage that the only preservative (ammonia) it contains is volatile. Consequently it may be used confidently in food applications and for medical or surgical goods. The disadvantages of HA latex are the strong odour of ammonia and the need for deammoniation in certain processes.

HA latex is the starting material for a wide range of products. It is used extensively for the manufacture of dipped products (e.g. examination gloves, household gloves, surgical gloves, industrial gloves, balloons, condoms, catheters) and in latex thread, latex foam, binder, adhesive and other miscellaneous applications. The level of ammonia is 0.6% minimum as specified in ISO 2004:2017 Natural rubber latex concentrate-centrifuged or creamed ammonia-preserved type specifications [8].

1.3.2 LA-TZ and MA-centrifuged latices

The LA-TZ latex is the most common of the LA types where tetramethylthiuram disulphide and zinc oxide are used as a secondary preservative. It is preserved with a blend of tetramethylthiuram disulphide and zinc oxide at ratio of 1:1. For MA, the amounts of preservatives (TZ and ZnO) used are intermediate between HA and LA-TZ.

Unlike HA latex, low ammonia (LA) latex contains ammonia not more than 0.29% (by mass); MA has ammonia between 0.30 and 0.59% (by mass) and has less objectionable odour. The disadvantage is that the presence of TMTD in LA and MA latices may result in the occurrence of nitrosamines and nitrosatable substances that are carcinogenic. As such manufacturers of baby teats, balloons and those products that are in contact with food avoid using LA-TZ or MA latices.

Type of latex concentrates	Preservatives
Centrifuged concentrate, min. 60% DRC	
High ammonia (HA)	0.7% ammonia 0.025% ammonium laurate
Low ammonia – tetramethylthiuram disulphide/zinc oxide (LA-TZ)	0.2% ammonia + 0.013% TMTD + 0.013% ZnO + 0.05% ammonium laurate
Medium ammonia - tetramethylthiuram disulphide/zinc oxide (MA)	0.5% ammonia + 0.006% TMTD + 0.006% ZnO + 0.04% ammonium laurate
All chemical additions are based on weight/weight of whole latex.	

Table 1.
Types of natural rubber latex concentrates [7].

1.4 Physico-chemical properties

1.4.1 Specified properties

Natural rubber latex concentrates are very highly specified materials, and a large measure of international agreement has been achieved regarding the limits to be imposed on their basic properties (**Table 2**). This international agreement is exemplified by the specifications published by the International Standards Organization (ISO) [7].

The natural rubber latex properties that are of chief significance to the users are total solids content, dry rubber content, nonrubber solids (NRS), alkalinity, volatile fatty acid number, mechanical stability time (MST), potassium hydroxide number (KOH no.) and magnesium content. The methods of measuring these properties have been established for many years in the ISO standards and are usually considered adequate.

1.4.2 Testing of latex

A brief description of each of the test procedure is given below. These details are not sufficient for practical use—the appropriate standards must be consulted.

The TSC is the weight percentage of all the solids (rubber plus nonrubber solids) present in the latex (ISO 124) [9]. It is determined by drying in a hot air oven at $70 \pm 5°C$ for 16 h or $105 \pm 5°C$ for 2 h a known weight of latex and weighing the dried rubber film thus produced. This is essentially a simple test to perform, and the reproducibility of the test between laboratories is normally very good. This is an important parameter as both VFA and KOH numbers are based on a quantity of latex containing 100 g of total solids (TS).

The DRC is the weight percentage of rubber hydrocarbon present in the latex. It is determined by coagulating a known weight of latex with dilute acetic acid, washing and sheeting the coagulum and then drying at $70°C$ for 16 h as in ISO 126 [10]. This test is time consuming, and it usually shows a high degree of reproducibility

Characteristic	Limits			Method of test
	Type HA	Type LA	Type MA	
TSC, min., % (by mass)	61	61	61	ISO 124
DRC, min., % (by mass)	60	60	60	ISO 126
Nonrubber solids, max., % (by mass)	1.7	1.7	1.7	TSC-DRC
Alkalinity (as NH_3), % (by mass)	0.60 min	0.29 max	0.30–0.59	ISO 124
MST, min, s	650	650	650	ISO 35
Coagulum content, max., % (by mass)	0.02	0.02	0.02	ISO 706
Cu content max., ppm of total solids	8	8	8	ISO 8053
Mn content max., ppm of total solids	8	8	8	ISO 7780
Sludge content, max., % (by mass)	0.06	0.06	0.06	ISO 2005
VFA no. max	0.06	0.06	0.06	ISO 506
KOH no. max	0.7	0.7	0.7	ISO 127

Table 2.
ISO specifications for centrifuged natural rubber latex [8].

between laboratories. This parameter is of extreme importance for commercial purpose as the prices depended on the dry rubber content.

The difference between the TSC and DRC values represents the weight percentage of NRS which comprises most of the nonrubber solids materials like proteins, fatty acid soaps and salts, together with a variety of other materials present in low concentrations. Hence, NRS is an indication of the cleanliness of the latex.

The VFA no. of a latex is the number of grammes of potassium hydroxide equivalent to the steam distillable fatty acids present in a quantity latex containing 100 g of total solids.

Fifty grams of latex coagulated with ammonium sulphate and the coagulum are removed. Twenty-five millilitre of serum is taken and acidified with sulphuric acid, and a 10 ml sample is steam distillated. The distillate is aerated with carbon dioxide-free air and titrated against barium hydroxide, phenolphthalein as indicator.

It has been found that majority of the volatile acid measures in the VFA test (ISO 506) [11] is acetic acid which is a by-product of bacterial activity in the latex. As such VFA no. is the primary measure of the state of preservation of the latex.

The alkalinity of the latex is the weight percentage of alkali present, determined by volumetric titration with a standard solution of dilute hydrochloric acid (ISO 125) [12]. As most natural latices are preserved with ammonia, the alkalinity is expressed as the percentage of ammonia present.

Five to ten grams of latex is weighed out to within 10 mg and diluted with about 200 ml of water to which a stabilizer solution has been added. This solution is titrated against 0.1 M hydrochloric acid with continual stirring, either electrometrically taking pH 6 as the endpoint or using methyl red indicator.

The ammonia added to the natural latices acts as a preservative, i.e. as a bactericide, to prevent the bacterial activity that would otherwise cause putrefaction.

The actual level of ammonia present in the latex is of significance in a number of latex processes where the control of pH is necessary.

The KOH no. is defined as the number of grammes of potassium hydroxide equivalent to all the acid radicals combined with ammonia in a quantity of latex containing 100 g of total solids. It is measured by potentiometric titration of the latex with potassium hydroxide solution and determining the inflection point in the titration curve (ISO 127) [13]. For a well-preserved latex, the KOH no. can be used as an indication of the age of the latex.

The viscosity, in centipoises (cps), of a latex sample is determined by Brookfield viscometer which measures the torque on a specific spindle at a constant rotational frequency and at a controlled rate of shear while immersed to a specified depth in the latex (ISO 1652) [14]. The latex test sample is diluted to 60% TSC and the viscometer set at 60 rpm using spindle no. 1.

Zinc-oxide viscosity tests may be useful in providing a qualitative indication of the chemical stability of the latex but not for quantitative measure. The principle of zinc-oxide viscosity tests is to determine the change in viscosity when the latex is compounded with zinc oxide under specific conditions. The smaller is the viscosity change, the more chemically stable is the latex deemed to be [3].

1.5 Maturation and vulcanization

In most latex processes, the compounded latices are either partially or completely matured and stored before use. Most compounded latices contain accelerators (dithiocarbamates) which can cause a measure of the rubber cross-linking during maturation. The extent of cross-linking depends largely on the nature and amount of curatives as well as on storage conditions. The prevulcanized latex production may be considered as a special form of maturation. Both processes require a

means of measuring the extent of latex vulcanization because of the influence it has on processing behaviour of latex product properties [15].

Toluene swell is universally used by rubber factories to measure the degree of cross-link of compound at different stages of production. The benefits of the toluene swelling tests are that the results are directly related to the cross-link density and are also quite reproducible. Its weak points are that it is relative slow procedure since reliable measurements can only be made at equilibrium. The time taken to reach equilibrium is largely dependent on the latex film thickness used. The total time for the test, including the film drying, is approximately 1 h or more [15]. The procedure requires a skilled technician and is time consuming.

2. Application of near-infrared (NIR) spectroscopy on evaluation of the properties of natural rubber latex and its products

2.1 NIR spectroscopy for quantitative analysis

NIR spectroscopy measures the interactions between the electromagnetic radiation in the NIR region and the materials, and the fundamental absorptions occurring in the infrared region extend down to lower wavelengths as overtones and combination vibrations [16]. The NIR region is located between the red band of the visible light and the mid-IR region as wavelength from 780 to 2500 nm ($12821–4000 \text{ cm}^{-1}$). The NIR spectroscopy is a rapid quantifying method with repeatability, reproducibility and accuracy equivalent to most reference methods and not prone to subjective operator errors. The NIR spectroscopy offers many benefits to research laboratory and quality control department in the factory. The method is environmentally friendly as no chemical is used. The instruments are simple to install and operate with little or no sample preparation and have the ability of evaluating many constituents at a time. According to Sirisomboon et al. [16], the instruments can be networked to use the same calibration, with their performance controlled from a single control centre.

Due to broad absorption peak and overlapping peak in NIR spectrum, NIR spectroscopy needs calibration modelling which relates to the absorbance vector, i.e. the inverse logarithm of the transmittance or the apparent absorbance vector which is the inverse logarithm of the diffuse reflectance (variable X) to the constituent vector (variable Y). The absorbance vector is obtained from NIR spectrometer, i.e. the spectra of calibration set samples. For example, the spectra of samples are scanned between 800 and 2500 nm ($12500–4000 \text{ cm}^{-1}$) by Fourier transform NIR (FT-NIR) spectrometer. The constituent vector is obtained from the reference measurement of the interested parameter for calibration set samples, such as the dry rubber content (DRC), TSC, viscosity and so on. The widely used calibration method is based on variable reduction where the principle is compressing the information in the whole spectrum into small number of variables. The most popular method is partial least squares regression and its diversified algorithms. In general, before the modelling, the spectral pretreatment is performed for noise suppressing, multiplicative scatter correction, baseline correction and spectral normalization. The pretreatment spectra may provide better model performance than that of raw spectra. After the model is developed, it has to be validated by either internal or external validation. The internal validation is used for the model that developed from a small number of samples (normally <100 samples), and the samples for calibration set and validation set are same. It can be by full cross-validation or segmented cross-validation. The external validation is used for more number of samples where the total samples are divided into calibration set and

validation set. The prediction performance of the model is indicated by the coefficient of determination (r^2), standard error of prediction (SEP), root mean square error of prediction (RMSEP), bias, ratio of prediction to deviation (RPD) and ratio of performance to interquartile (RPIQ). The r^2 is from 0 to 1. The higher r^2 indicates that the absorbance variable (variable X) can explain more the constituent variable (variable Y). The SEP is calculated from standard deviation (SD) of error in validation set. It indicates the precision of the model. The lower the SEP, the higher the model precision will be. The RMSEP is the error of validation set (without sign), while the bias is the error with plus or minus sign. The RMSEP and bias indicate the accuracy of the model. The RPD and RPIQ are the indicators for the model robustness. The model is acceptable if their value is more than 3. The RPD is used when the reference data are normal distribution, and RPIQ is used when the data are skewed distribution. The RPD is calculated from the ratio of standard deviation of reference value of prediction set to the standard error of prediction. For RPIQ, the SD of the prediction set in the RPD formula was replaced by the interquartile (Q3–Q1) where Q3 and Q1 were the value below which 75 and 25%, respectively, of the samples were found [17].

2.2 Near-infrared scanning of natural rubber latex and film

The scanning of rubber latex can be done in transmission, diffuse reflection and interaction modes. **Figure 1** shows the spectral measurement of latex in transmission mode using quartz cuvette with the size of 1 × 0.5 cm by UV-VIS-NIR spectrometer [AVA-Spec-2048-USB2, Avantes, Netherlands] at the wavelength range of 350–1100 nm with the 2.4-nm resolution. **Figure 2** shows the latex scanning using Fourier transform NIR spectrometer (NIRFlex solid, Buchi, Switzerland) in diffuse reflection mode over the wavenumber range of 4000–10000 cm^{-1} at 4-cm^{-1} resolution. The latex sample is placed in a Petri dish (25-mm depth and 150-mm diameter) at 3/4 of the dish depth. **Figure 3** shows a 200 mL latex sample in a glass beaker (250 mL) scanned by a portable NIR spectrometer (FQA-NIR GUN, Shizuoka, Japan) over the wavelength range of 700–1050 nm with a resolution of 2 nm and an integrating time of 15 ms. **Figure 4** shows the spectral scanning of latex in interaction mode using optic fibre probe dipped in a latex cup by UV-VIS-NIR spectrometer [AVA-Spec-2048-USB2, Avantes, Netherlands] at the wavelength range of 350–1100 nm with the 2.4-nm resolution.

According to Lim and Sirisomboon [18], for the scanning experiment of thin and thick films, the aluminium plates (90 × 220 × 0.5 mm) were dipped into the latex and dried. In the case of the thick film, the plate was dipped into 5% calcium chloride solution and dried prior to dipping into the latex compound. For thin film, it was a straight dipped, i.e. without the use of coagulant. Both thin and thick films were dried in an oven at 70°C for 5 min and 1 h, respectively. They were then subjected to NIR radiation using the FT-NIR spectrometer by placing on the integrating sphere window (2.3 cm in diameter).

The spectra could not be directly referred to the physico-chemical properties. It needs chemometric to analyse for the correlation.

2.3 NIR spectroscopy for chemical properties of natural rubber latex

2.3.1 Dry rubber content and total solids content

Cornish et al. [19] established an NIR spectroscopic method for the quick quantification of latex in both wet and dried *Parthenium argentatum* (guayule) homogenate and purified latex samples. The coefficients of determination (r^2) of
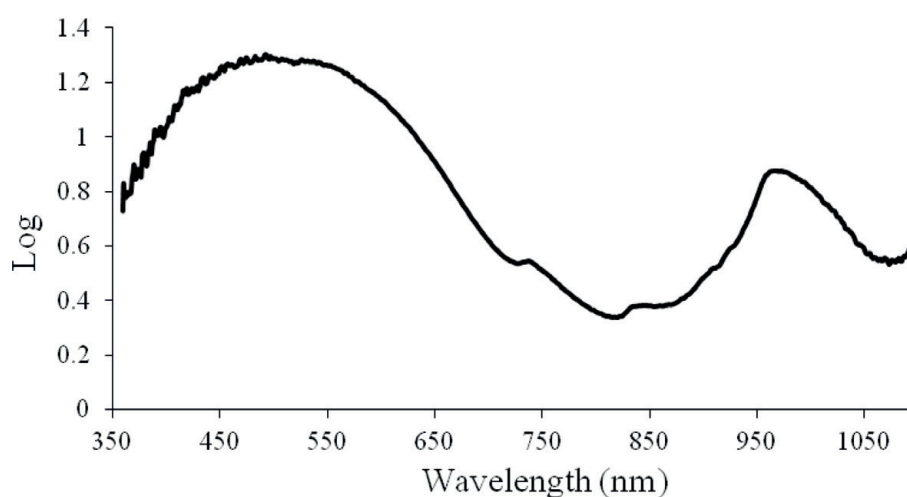
Figure 1.
Scanning of rubber latex in transmission mode and latex spectrum.

the measured rubber content and the predicted rubber content by NIR for the dry and wet samples were 0.92 and 0.83, respectively.

FT-NIR spectrometer in long wavelength between 1000 and 2500 nm (10000–4000 cm^{-1}) in diffuse reflection mode was applied to evaluate the DRC of field latex and concentrated latex from Para rubber and provided excellent prediction performance [16]. The result showed that the best model was established using the partial least squares regression (PLSR) from the spectra and corresponding DRC evaluated by reference method, which were the second derivative pretreated spectra, where the values of 0.997, 0.3398 and −0.0239% were the r^2, SEP and bias, respectively. The ratio of SD to SEP of the reference data in the prediction sample set (RPD) and the ratio of the range to the SEP of the prediction set (RER) were 18.18 and 74.4, respectively. The model was validated using unknown samples, and the prediction performance was good with an r^2, SEP and a bias of 0.999, 0.3898 and −0.0008%, respectively. Therefore, the NIR spectroscopy technique can be used as an accurate and quick method for estimating the DRC of both field and concentrated latices of Para rubber.

The shortwave NIR (700–1100 nm) spectroscopy was also used for the evaluation of DRC and TSC in Para rubber field and concentrated latices [20]. The transmittance spectra were obtained. There were 282 samples including 171 samples of field latex, 86 samples of concentrated latex and 25 of concentration-adjusted concentrated latex. The field latex and the concentrated latex had around 30 and 60% DRC, respectively. The concentration-adjusted concentrated latex was 55, 50,
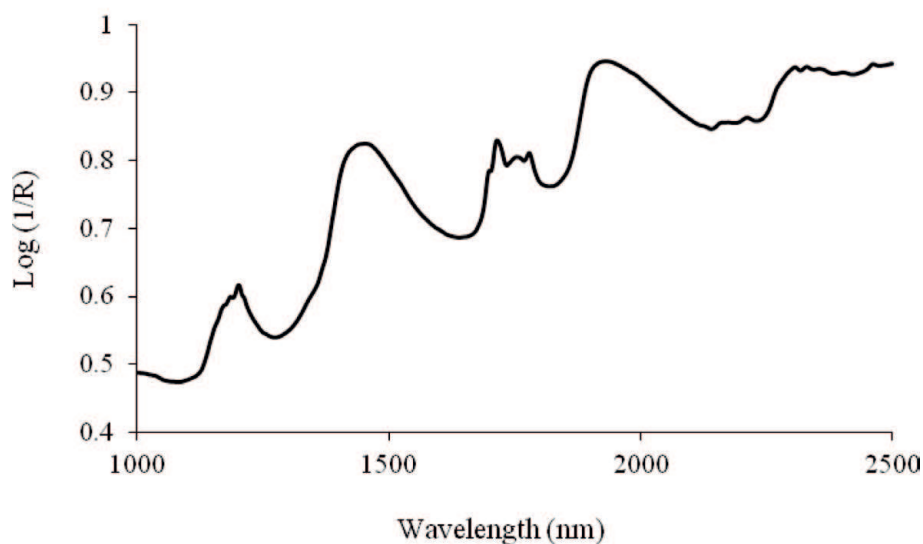
Figure 2.
Scanning of rubber latex in diffuse reflection mode and latex spectrum.

45, 40 and 35% DRC. The PLSR calibration models were developed using original and pretreated absorbance spectra. The model developed from smoothing and range normalization pretreated spectra in the wavelength range of 700–950 nm provided the best prediction accuracy for DRC, and the models using raw spectra in the same wavelength range gave the best results for TSC. The slope, offset, r^2, SEP and bias were 1.0154, −0.6286, 0.992, 1.1092 and 0.0321%, respectively, for the DRC prediction and 1.0084, −0.2332, 0.991, 1.3611 and 0.1456%, respectively, for the TSC prediction. The best models were validated using new unknown sample sets of 50 and 35 samples for DRC and TSC, respectively. The models provided an r^2, SEP, RPD and bias of 0.988 and 0.974, of 1.4296 and 2.1255, of 10.0 and 6.2 and of −0.6191 and 0.5476% for DRC and TSC, respectively. This work showed that the SW-NIR spectroscopy protocol in the evaluation of TSC had high accuracy for quality assurance and process control in the concentrated rubber latex factory. However, for prediction of DRC, the accuracy was still not acceptable for the latex factory because a bias of more than 0.01% can incur considerable profits or losses when large volumes of latex are involved.

Lim and Sirisomboon [21, 22] updated the above DRC and TSC models. The updated DRC model was done by adding the 180 samples merged into the 280 original samples. The slope, offset, r, SEP and bias were 1.0126, −0.3729, 0.9931, 1.2654 and 0.1103%, respectively. The updated TSC model was done by adding the
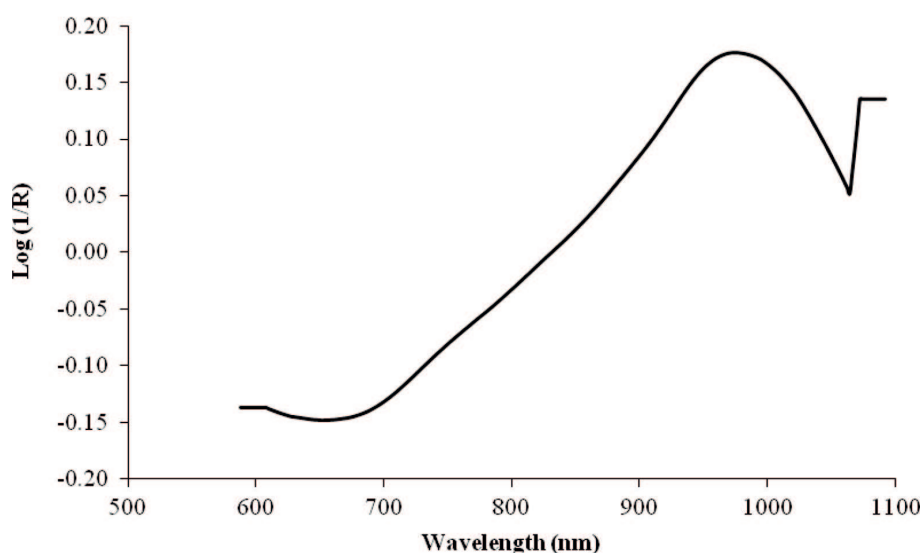
Figure 3.
Scanning of rubber latex in diffuse reflection mode using FQA-NIR GUN spectrometer and latex spectrum (Thanking Dr. Ronnarit Rittiron, Kasetsart University, Thailand, for the the photoes).

160 samples merged into the 280 original samples. The slope, offset, r, SEP and bias were 0.9795, 0.7150, 0.9834, 1.6186 and −0.0802%, respectively. Therefore, the more accurate, robust and faster updated model by NIRS technique was obtained for TSC of Para rubber latex, for both field latex and concentrated latex.

By the research conducted by Inagaki et al. [23], the ultraviolet-near-infrared (UV-NIR, 370–1085 nm) spectra of latex were measured in transmittance mode. Calibrations for TSC and DRC were developed using spectral data set of 57 samples with aid of PLSR. The latex UV-NIR spectra provided good regression models with r^2 for cross-validation of 0.96 and 0.97, for TSC and DRC, respectively. The PLS factors were 2 and 1, respectively. This study suggests UV-NIR spectroscopy with high-accuracy in-line quality control of latex. Inagaki et al. [23] also investigated the short-wavelength NIR spectra of bark which were scanned to check the feasibility of on-site evaluation of latex quality by measuring the NIR spectra of standing tree. This result suggested that the focal point should be on the outer part of bark to get the signal of latex when we measured the spectra of standing tree.

Three-fibre-based diffuse reflectance spectroscopy (TFDRS) was employed by Inagaki et al. [24] for the measurement of TSC in natural rubber latex samples. It was reported that TSC could be accurately predicted using the relative absorbance ratio even if the samples have significant variation in polyisoprene particle sizes (i.e. significant variation of reduced scattering coefficient). This group of researchers designed a user-friendly and inexpensive TFDRS system using a halogen light
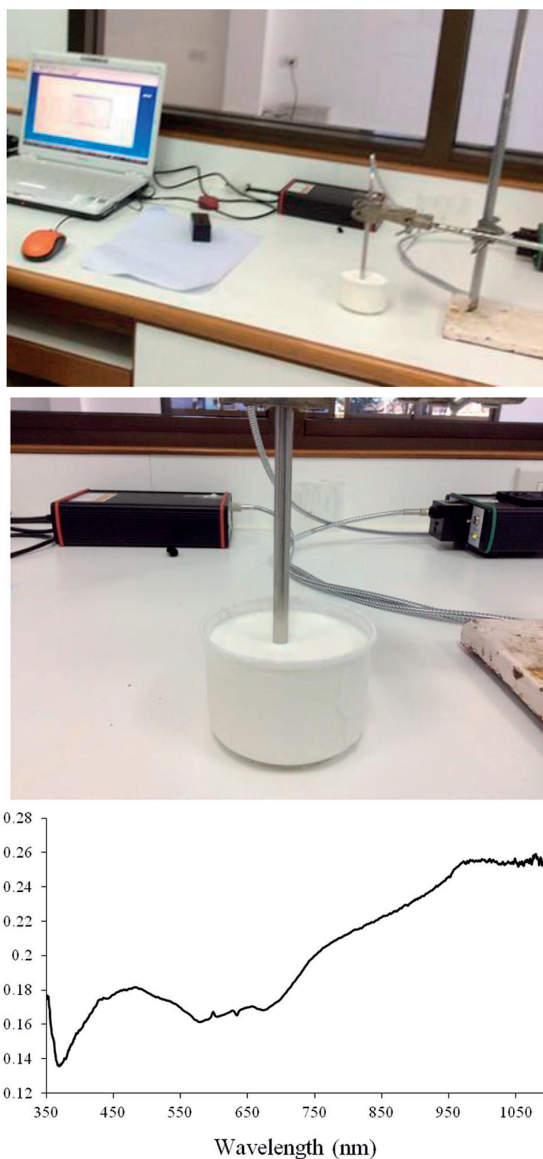
Figure 4.
Scanning of rubber latex in interaction mode and latex spectrum.

source and two spectrometers. Although compared to the Ti:Sapphire tunable laser system, the wavelength resolution was much lower. A strong relationship with r^2 of 0.97 was found between the relative absorbance ratio (970, 909, 849 nm) and TSC.

2.3.2 Volatile fatty acid number

Narongwongwattana et al. [25] reported that most factories analysed VFA number by the method in ISO 506:1992(E). However, the procedure was complicated, time and chemical consuming and also skilled technician required. Therefore, they applied NIR spectroscopy which is a quick, accurate and environment-friendly method to determine the VFA number in field and concentrated latex based on quantification and discriminant models. The standard normal variate (SNV) spectra provided the best calibration equation which was obtained from the region of 6109.7–5770.3, 4613.1–4242.9 cm^{-1} with correlation coefficient (r) of 0.832, standard error of cross-validation (SECV) of 0.036 and no bias. It was shown statistically that SECV and bias were low enough for practical use, and the predicted value was not different significantly from actual value at 95% confidence level. Moreover, discriminant model was established to separate good-quality latex from the deteriorated latex using VFA number at 0.06 as standard as in ISO 2004:2017(E). The model could

screen the latex with overall accuracy of 91.86% in validation set. Moryadee et al. [26] also used the FT-NIR spectrometer in diffuse reflectance mode in the wavenumber of 12500–3600 cm^{-1} for evaluation of VFA number. There were totally 168 samples including 117 field latex samples and 51 concentrated latex samples. The calibration models were developed by PLSR using original and pretreated absorbance spectra. By statistical analysis, the vector normalization (SNV) pretreated spectra provided the model in the wavenumber of 7506.0–4597.7 cm^{-1} and with the PLS factors of 10 provided the r^2, RMSEP, RPD and bias of 0.6044, 0.107, 1.650 and 0.029, respectively.

2.3.3 Alkalinity and potassium hydroxide number

Narongwongwattana et al. [27] reported that all factories monitor NH$_3$ content or alkalinity during processing and storage as it is an important parameter. Ammonia is a preservative for latex. Alkalinity is determined as a percentage (by mass) of ammonia by the standard analytical method, acid-based titration, as detailed in ISO 125:2011(E) Natural Rubber Latex Concentrate-Determination of Alkalinity. This method requires a skilled analyst and also the use of chemicals. The alkalinity predicting calibration equations were developed where the relationship between the latex absorbance spectra measured using a portable NIR and a Fourier transform NIR spectrometer and the alkalinity content of the latex was established. The best equation obtained using the portable and the FT-NIR spectrometers could be applied to evaluate the latex alkalinity with r^2, SEP and RPD of 0.63, 0.101% and 1.62 and 0.97, 0.027% and 6.07, respectively. From the statistic testing as recommended in ISO12099:2010, the NIR-predicted values were no different from actual values at the 95% confidence level. The best equation from the more reliable calibration obtained using the FT-NIR spectrometer was attributed to the longer wavelength range.

Sompiw [28] collected the samples of Para rubber-concentrated latex which were from the factory of the Thai Rubber Latex Corporation (Thailand) Public Company Limited in the Nong Yai District, Chonburi Province, Thailand. There were 220 concentrated latex samples. The experiment was conducted at 25 ± 2°C room temperature. A latex sample without bubbles was scanned in glass cuvette with the size of 1 × 0.5 cm (**Figure 1**) over the wavelength range of 359–1100 nm by a spectrometer in transmission mode. The Teflon with the thickness of 1 cm was used for scanning as the reference material. The samples were separated into calibration set and prediction set with the ratio of 3:1. The calibration model development was done using raw spectra by PLSR. The model developed provided the r^2, RMSEP, SEP, RPD and bias of 0.880, 0.070, 0.70, 2.980 and −0.00017 for alkalinity and of 0.422, 0.086, 0.086, 1.334 and −0.001 for KOH number, respectively. In addition, latex sample without bubbles was scanned in a glass Petri dish with the height of 1.5 cm and diameter of 9.5 cm over the wavenumber of 12500–3600 cm^{-1} by a FT-NIR spectrometer in a diffuse reflectance mode. The gold plate was used for scanning as the reference material. The samples were separated into calibration set and prediction set with the ratio of 1:1. The calibration model development was done by PLSR. The model developed provided the r^2, RMSEP, RPD and bias of 0.978, 0.030, 6.570 and 0.002 for alkalinity and of 0.862, 0.045, 2.71 and −0.005 for KOH number, respectively.

2.4 Near-infrared spectroscopy for physical properties of natural rubber latex and film

2.4.1 Viscosity

The FT-NIR spectroscopy in diffuse reflection mode was used to evaluate the apparent viscosity of Para rubber field latex and concentrated latex over the

wavelength range of 1100–2500 nm, using PLSR [29]. The sample in a Petri dish was scanned (**Figure 2**). The model with 10 PLS factors developed using the raw spectra accurately predicted the apparent viscosity with r, SEP and bias of 0.974, 8.6 and −0.4 cP, respectively. The RPD and RER of the predictive model were 4.4 and 16.7, respectively. Therefore, the model can be used for measurement of the apparent viscosity of field and concentrated latex in the factory for quality assurance and process control.

2.4.2 Cross-link density

The analysis of the cross-link density of prevulcanized natural rubber latex using near-infrared spectroscopy was conducted [30] using a FT-NIR spectrometer in diffuse reflection mode over the wavenumber range of 12500–3600 cm^{-1}. As the cross-link density is an indication of the cure degree, hence the properties of the latex products, the proposed method is useful for industrial purposes. For prevulcanized latex of 50% total solids content (i.e. PV50%) samples at 100% extension (prevulcanizate-relaxed modulus 100%), the best model was developed using the PLSR from the first derivative pretreated spectra, where the r^2, RMSEP and bias were 0.66, 6.06× 10^4 and 1.63 × 10^4 Nm^{-2}, respectively. The RPD was 1.8. This model could be used for screening. For samples at 300% extension (prevulcanizate-relaxed modulus 300%) for PV 50%, the best model was developed using spectra pretreated for scattering correction: r^2, RMSEP and bias were 0.88, 6.74 × 10^4 Nm^{-2} and 1.35 × 10^4 Nm^{-2}, respectively, and the RPD was 3.0. Hence, the near-infrared spectroscopy technique can be utilized as a rapid screening method for estimating the cross-link densities of prevulcanized natural rubber latex.

In addition, Lim and Sirisomboon [18] indicated that the toluene swell or equilibrium swelling is universally used by rubber factories to measure the degree of cross-link of their compounded or prevulcanized latices at different stages of production. They applied NIR spectroscopy for rapid and accurate quality control, spectral acquisition of prevulcanized latex and thin and thick films performed using a FT-NIR spectrometer in diffuse reflection mode across the wavenumber range of 12500–3600 cm^{-1}. For prevulcanized latex an effective model was developed using partial least squares regression with preprocessing (first derivative and straight line subtraction method). The r^2, RMSECV and bias of the validation set were 0.71, 3.93 and −0.005%, respectively. For the thin-film model, the r^2, RMSECV and bias were 0.65, 4.01 and −0.028%, respectively, whereas for the thick-film model, the r^2, RMSECV and bias were 0.70, 4.00 and −0.006%, respectively. Three models including prevulcanized latex and thin and thick films were validated by 23 unknown samples, providing SEP and bias of 5.357 and 2.494, 4.565 and 1.001 and 3.641 and −0.961%, for prevulcanized latex and thin and thick films, respectively. It was shown that the thick-film spectra model gave the best results.

3. Pros and cons of methods used

A NIR spectrophotometer is a computerized super-microscope. It sees past the surface of the material being scanned, through the cells or matrix of which the material is composed, and into the actual molecules of which the materials are made [31].

The advantages of NIR spectroscopy for rubber latex technology are summarized as follows:

The processing of field lattices to concentrates, compounding and control on production lines are hampered by the relatively cumbersome latex quantification methods of the ISO currently employed. Current methods, as specified in ISO 2004 on latex specifications [8], require several hours before analytical results can be obtained [19]. NIR spectroscopy once calibrated enables properties to be obtained in minutes with repeatability and reproducibility equivalent to most reference methods and not prone to subjective operator errors [18].

It is environmentally clean (no chemical is used) and flexible as many constituents can be tested simultaneously. Little or no sample preparation is required. They are stand-alone instruments and are easy and cheap to install. In addition, the measured cost per sample is cheap, and the samples to be tested can be many or every sample because the NIR spectroscopy is a nondestructive test.

There are also some disadvantages associated with NIRS technology. These include:

Separate calibrations are needed for every commodity and constituent, and the user has to monitor their performances. There is a need to monitor the accuracy and reproducibility including the reference analysis. The instruments are expensive to purchase. The lack of knowledge as to how to operate the instrument efficiently can affect the accuracy of their determinations.

4. Conclusions

From the review of NIR spectroscopy and its application on natural rubber latices (field latex and concentrated latex) and its products, i.e. thin and thick films, it is indicated that the technology is suitable for using in the quality, process control and assurance of the products in the factories.

NIR spectroscopy is rapid and reasonably accurate for determination of the various physico-chemical parameters of natural rubber field latex and concentrated latex and its latex products without chemicals. The developed calibration equation obtained from the NIR spectrometer is usable in most applications including quality assurance for coefficient of determination between 0.92 and 0.96 and excellent to use in any application for $r^2 > 0.98$ [31].

The latex products are prevulcanized latex and latex films. The thin and thick films are used to simulate the manufacture of condoms and gloves which are the two main dipped products made from natural rubber latex. The coefficient of determination of 0.66–0.81 means that this NIR spectroscopy method is usable for screening purpose and approximate calibration [31].

The rapidity of testing (<5 min/sample) by NIR would allow a factory to increase the frequency of monitoring the process resulting in improvement of the quality of the products being manufactured.

Consistency of properties of the latex became an important issue for the latex users. As such testing methods had to be devised in order to determine the property and quality of the latex raw material.

As consumers become more demanding, the importance grows of guaranteeing the quality of products. The employment of reliable testing techniques that assure the origin and characteristics of the inputs used by industry is a key factor in this respect.

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