

Rapid and Nondestructive Quantitative Analysis of Natural Rubber Blends Regardless of Geographical Origin and Harvest Time of the Natural Rubber

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ABSTRACT: Natural rubber (NR) blends are widely used in many industries because of their excellent integrated properties. However, a simple, easily operational, nondestructive, and accurate method for their quantitative analysis remains as a challenge. This has been always an important issue in the related industries, particularly for their daily quality control tests. One main reason is that NR ingredients vary according to their geographical origin and the harvest time, which renders it hard to set up a versatile analytical protocol for all NRs. Another reason is owing to the defects of the established methods themselves as having been revealed in those relying on TGA, Py-GC/MS, FTIR, and ATR-FTIR. In this study, a simple and feasible method based on near infrared spectroscopy combined with chemometric is proposed to solve this problem for the first time. NR/SBR (styrene-butadiene rubber) rubber blend, the most widely used NR blend, is selected as a typical research subject. Spectral calibration region, factor, and several different pretreatment methods are applied on the spectra data to optimize calibration models. The result shows the optimized calibration model provides a good accuracy (0.135 wt %), intraday precision (0.121 wt %) and interday precision (0.132 wt %) for 3 months. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41423.

KEYWORDS: blends; rubber; spectroscopy

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INTRODUCTION

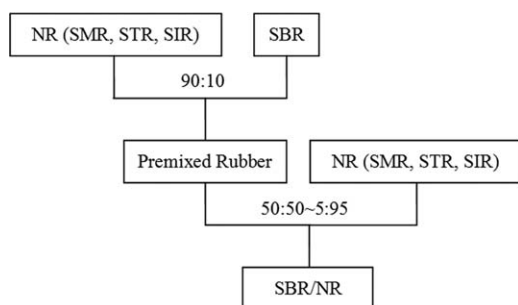
Rubber blends, usually multicomponents, are widely used in mechanics, electronics, chemical engineering, and new materials industries to obtain desirable physical and mechanical properties, processability, and durability, while neither component of the blends can supply.^{1–5} The properties of rubber blends are sensitive to slight variation in the amounts of their each component.^{6–9} It is therefore very important to control and to examine their composition for quality control.

To this end, a variety of analytical protocols have been developed to monitor rubber blend composition, such as TGA,^{9–16} Py-GC/MS,^{8,9,17,18} FTIR,^{8,12,19} and ATR-FTIR.⁶ However, sample preparation and testing are usually sophisticated and time-consuming, and the samples are destroyed through the testing in most of these methods, excluding the test by ATR-FTIR. However, the accuracy and precision in these methods are closely dependent on the homogeneity of the sample to be tested, which is an uneasy task. Other challenges to have reliable and accurate results are related to the instrumentation itself, the limited sampling amount, for instance. Allowed sampling amount in TGA and Py-GC/MS tests is usually limited to

10 mg, and so are those allowed in FTIR and ATR-FTIR testing^{20–22} owing to the limited diameter of the testing ray (usually <0.1 mm for ATR-FTIR) and the low penetration depth (usually <0.1 mm for both FTIR and ATR-FTIR).

Near infrared spectroscopy (NIR) is a fast, nondestructive and nonpollutant quantitative method with good accuracy and precision. Because the absorptivities of vibrational overtone and combination bands in NIR region are orders of magnitude lower than that of vibrational fundamental bands in infrared region, this can greatly increase penetration depth²³ (usually from 5 to 10 mm), and improve the accuracy and precision of the results. NIR has been used for quantitative analysis for plastic^{24–27} and single synthetic rubber,^{23,28,29} and SBR (styrene-butadiene rubber)/NBR (acrylonitrile-butadiene rubber) as well.⁶

However, up to date, little work has been reported on NIR analysis towards natural rubber (NR) blend. It is obvious that NR is quite different from synthetic rubber, simply composed of a group of homologues. NR, being a natural product, is natural complex. Besides polyisoprene, the main composition, it contains commonly protein, aliphatic acid, water, polysaccharide,



Scheme 1. Flow chart of sample preparation method.

sterol, and other minor components. Functional groups as C—H, N—H, and O—H adherent to the components are known to have their absorption in NIR region. It will greatly reduce the accuracy and precision of NIR in determination of polyisoprene content. However, the ingredients of NR vary according to the geographical origin and harvest time, which affect the availability and robustness of NIR.

The main aim of this study is to investigate the feasibility of NIR for accurate quantitative analysis for NR blends regardless of their geographical origin and harvest time of the NR. The technique is further applied for analysis of a blend of NR with SBR, the most widely used rubber blend.^{30–36} The availability of NIR quantitative analysis of rubber blend for a wide range of percentage content (0–100%, the interval is 10%) has been revealed in the literature, but the reported accuracy (2%) is not very desirable.⁶ Nevertheless, little work has been devoted to small percentage content. As mentioned above, it is very important to inspect the small variation of individual rubber content in several industries where the reliability is particularly important, such as spaceflight, aviation, and medical instrument. Therefore, this study mainly focus on accurate determination of low SBR content (0–5%) in NR/SBR rubber blends.

EXPERIMENTAL

Materials

Standard Malaysia Rubber (SMR20), Standard Thailand Rubber (STR20), and Standard Indonesia Rubber (SIR10) were selected as raw materials in this study. SBR1500 is a random copolymer with a styrene content of 23.5%. All the samples were kindly supplied by Entry-Exit Inspection and Quarantine Bureau of Shandong Province (EEIQB). Each NR sample lot has five samples with different harvest time, collected from different import corporations by EEIQB from March 2011 to April 2013.

Sample Preparation and Grouping

For sample preparation, NR was mixed with SBR in a mixing mill. To guarantee the uniformity and parameter accuracy of the rubber blends, following approaches were taken. First, each NR was mixed with the SBR into premixed rubber sample at 90/10 level. Second, each premixed rubber sample was mixed with respective NR at 50/50, 45/55, 40/60, 35/65, 30/70, 25/75, 20/80, 15/85, 10/90, and 5/95 levels. A flow chart of sample preparation method is shown in Scheme 1. The resulting samples are NR/SBR rubber blends with SBR contents of 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, and 0.5 wt %. The control group

was not mixed with the SBR, following the same mixing process. Therefore, there are three different NR (SMR, STR, and SIR) at eleven different levels (the control group can be regarded as 0/100 levels), result in 33 (3×11) groups of rubber blends. Each group has five samples. The five samples have same geographical origin and SBR content but different harvest time. Then four samples were randomly selected from the five samples of each group to establish a calibration set, while the rest were used to establish a validation set. Overall, there are 132 samples included in the calibration set and 33 samples included in the validation set. This grouping procedure ensured the calibration algorithm derived can ignore geographical origin and harvest time variations of NR, meanwhile; it ensured the representativeness of the validation set.

Equipment and Procedures

NIR spectra were acquired using a Thermo Antaris II FT-NIR spectrometer (Thermo Scientific) equipped with a spinner cup. The spinner cup was used to enlarge the effective sampling area to 829 mm^2 [$\pi(25 \text{ mm})^2 - \pi(19 \text{ mm})^2$] (The sketch is shown in Figure 1). Density of rubber blend is commonly between 0.92 and 1.00 mg/mm^3 , the effective sampling amount in NIR test can reach 3813.4 mg ($829 \text{ mm}^2 \times 5 \text{ mm} \times 0.92 \text{ mg/mm}^3$) at least, thus it make the accuracy and precision increase greatly. Each sample was scanned 32 times using integrating sphere reflectance. Before the test, to eliminate instrument drift, background corresponding to an accumulation of 32 scans was scanned. Spectral scanning region was from 4000 to $10,000 \text{ cm}^{-1}$ with resolution of 8 cm^{-1} . Moreover, TQ Analyst (version 8.0, Thermo Scientific) chemometric software was employed to construct calibration curves and perform data pretreatment.

Infrared spectra were recorded using Spectrum 400 spectrometer (Perkin-Elmer) equipped with a diamond crystal, using 16 scans acquired at 4 cm^{-1} resolution in the range of 4000 – 600 cm^{-1} . Omnic (version 8.0, Thermo Scientific) software was employed to calculate peak area of the infrared spectra.

Data Analysis

Partial least squares (PLS) method was used for data calibration. Furthermore, spectral modeling region and several pretreatment methods were investigated to find an optimal calibration model. The pretreatment methods include multiplicative scatter correction (MSC),³⁷ standard normal variate (SNV),³⁸ first derivative (first), second derivative (second), and Norris Derivative smoothing³⁹ (the number of data points per segment is 11 while the gap between segments is 5). In addition, full leave-one-out

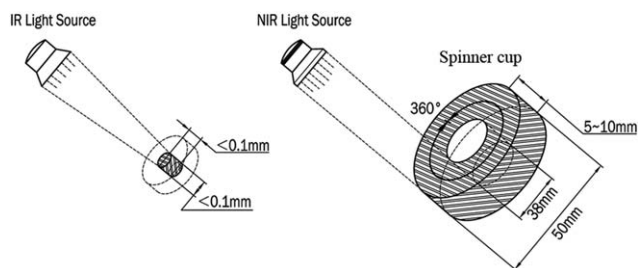


Figure 1. Scanning area of IR method (Left) and NIR method (Right).

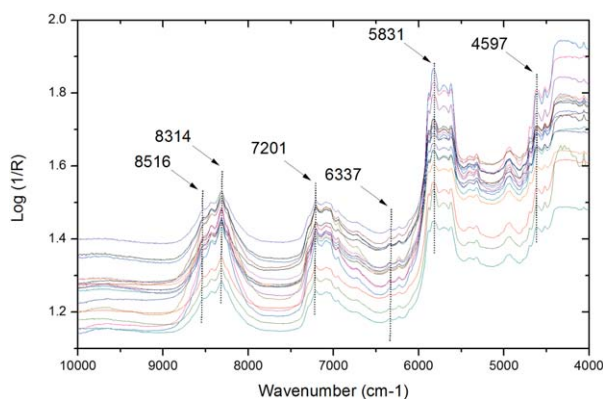


Figure 2. Raw NIR spectra of 18 typical rubber blend samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cross validation method and the validation set were used to evaluate models. The evaluation parameters include correlation coefficient of calibration set (R_C), correlation coefficient of validation set (R_P), correlation coefficient of cross validation (R_V), root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP), root mean squares error of cross validation (RMSECV) and prediction residual error sum of squares (PRESS). The RMSECV and PRESS were computed as:

$$\text{RMSECV} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}} \quad (1)$$

$$\text{PRESS} = \sum_{i=1}^m (y_i - \hat{y}_i)^2 \quad (2)$$

where, y_i is the reference component concentration; \hat{y}_i is the predicted component concentration; n is the number of spectra in the calibration set; and m the number of spectra in the validation set. Moreover, the relativity⁴⁰ between wavenumber of the spectra and sample identity was studied to find a suitable spectral region for calibration. It was computed as:

$$r_j = \frac{\sum_{i=1}^n \left(x_{i,j} - \frac{\sum_{i=1}^n x_{i,j}}{n} \right) \left(y_i - \frac{\sum_{i=1}^n y_i}{n} \right)}{\left[\sum_{i=1}^n \left(x_{i,j} - \frac{\sum_{i=1}^n x_{i,j}}{n} \right)^2 \sum_{i=1}^n \left(y_i - \frac{\sum_{i=1}^n y_i}{n} \right)^2 \right]^{1/2}} \quad (3)$$

where, x is absorbance vector corresponding to wavenumber; y is concentration vector of target parameter; n is the number of spectra in the calibration set; $j = 1, 2, \dots, m$; and m the total number of the wavenumber.

RESULTS AND DISCUSSION

Raw Spectra

Figure 2 shows raw near infrared spectra of some typical rubber blend samples. It can be seen that all the spectra look similar with respect to spectral band location and intensity. Since the main ingredient of NR is polyisoprene constituted by repeating unit $[-\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2-]$ and protein, there are mainly C—H and N—H overtones and combinations absorption peaks in the spectra. The absorption peaks include 8314 cm^{-1} corre-

sponding to methyl C—H stretching second-overtone vibration, 8516 cm^{-1} corresponding to olefinic =C—H stretching second-overtone vibration absorption peak, 7201 cm^{-1} corresponding to combinations of methyl C—H fundamental stretching vibration and methyl C—H fundamental bending vibration, 5831 cm^{-1} corresponding to methyl C—H stretching first-overtone vibration, 6337 cm^{-1} corresponding to N—H stretching first-overtone vibration, and 4597 cm^{-1} corresponding to N—H bending second-overtone vibration.⁴¹ The complexity of this overlap demands multivariate calibration techniques such as PLS regression to correlate the spectra and component concentration. In addition, as depicted in Figure 2, there are no obvious anomalies, noises and over absorption phenomena in all the spectra, so all the spectra can be used for calibration and validation.

Principal component analysis (PCA), a more elaborate method to compare spectra data,⁴² was used to compare the data of calibration and validation sets. Figure 3 shows a score plot set up from the first and second principal components of calibration and validation sets. Data input into the PCA method were spectra which are pretreated by MSC combined with second derivative smoothing. It can be seen from the PCA plot that the calibration and validation data are similar, which in turn provides a level of confidence that the calibration model will be able to predict component concentrations accurately in the validation set.

Spectral Modeling Regions Selection

Spectral modeling regions have great impact on the performance of calibration model. If the selected regions are too narrow, some effective information can be missed, and thus makes the applicability reduced. Otherwise, excessive noise information will be introduced, which will affect the accuracy. Figure 4 shows the relativity between each wavenumber of the spectra and concentration information. Regions for which the correlation coefficient is almost equal to one indicate a good correlation between the spectral absorbance and the sample identity.⁴³ It is noted that regions from 4000 to 9000 cm^{-1} have high correlation coefficients, while that from 9000 to $10,000 \text{ cm}^{-1}$ are mostly < 0.3 .

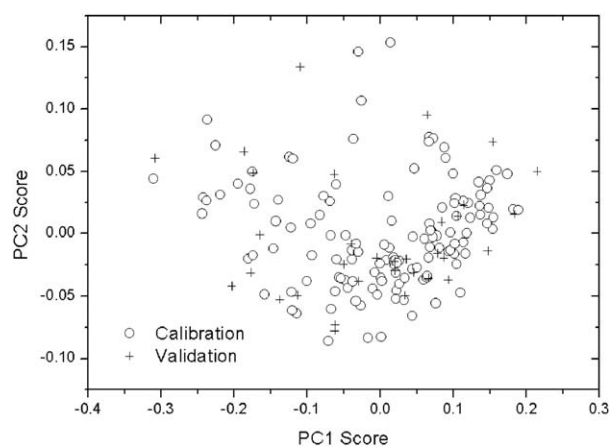


Figure 3. Principal component score plots of calibration set (O) and validation set (+).

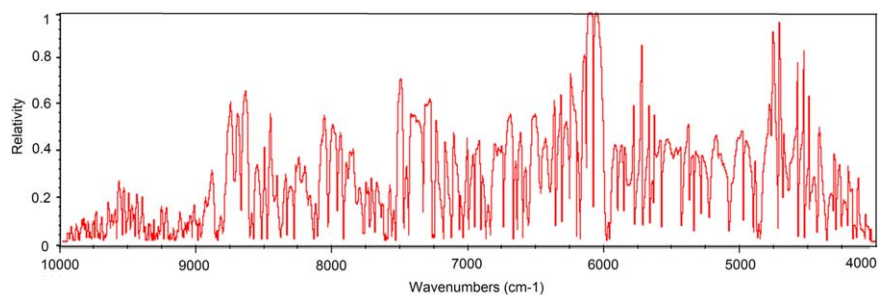


Figure 4. Relativity between each wavenumber of NIR spectra and concentration information. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In addition, differential treatment combined with smoothing, which can amplify the signal difference and make effective information easily to identify, can also be used as an effective tool for determining spectral modeling regions.^{44,45} Figure 5 shows some typical spectra of Malaysia, Thailand, and Indonesia rubber blends with SBR content of 2.5 wt %. These spectra were pretreated by first derivative combined with smoothing (Left) and by second derivative combined with smoothing (Right). It is noted that the spectral information is concentrated in the regions from 4000 to 9000 cm^{-1} , while regions from 9000 to 10,000 cm^{-1} are mainly for noise. Consequently, regions from 4000 to 9000 cm^{-1} were selected for PLS calculation finally.

Factor Selection

Factor is one of the most important indexes for NIR calibration model.⁴⁴ In a certain degree, the higher the Factor, the more effective information can be extracted from the spectra. But if the Factor is too high, too much noise information may be brought into the calibration model, causing overfitting, thus greatly reduce the accuracy of model. The optimal Factor is usually judged by PRESS and RMSECV.⁴³ In ideal conditions, with Factor increases, PRESS and RMSECV reduce quickly and then increase slowly. The Factor corresponding to the inflection point is optimal. But in actual conditions, PRESS and RMSECV are often against the rule. This is because sample homogeneity, sampling conditions, signal intensity, and spectral pretreatment

methods are always different, result in differences in extracting effective information from the spectra. However, models, which meet the rule, indicate that the representativeness of samples, sampling condition, and spectra data pretreatment methods are satisfactory.

Figure 6 shows the correlation between PRESS, RMSECV, and Factor of five typical models, which are established by raw spectra, by first, by MSC, by SNV and by MSC combined with second smoothing. It is observed that the change trends of PRESS and RMSECV are same, which indicated that the validation set is representative. Furthermore, it can be seen that the inflection points of the five models appeared at 9, 5, 12, 13, and 5. They can be used as the optimal Factor. Moreover, the models established by raw spectra, by first and by MSC combined with second smoothing generally meet the rule. But the models established by MSC and by SNV appeared glaring abnormal rising when the Factor are equal to 4 and 5, respectively. They do not obey the rule apparently. The results indicated using raw spectra or using MSC (or SNV) combined with differential smoothing to pretreat spectra data are desirable in the given application. However, using MSC or SNV alone to pretreat spectra data are not very desirable.

However, PRESS and RMSECV reduced abnormally when the Factor of the models established by raw spectra and by MSC combined with second smoothing are equal to 12 and 8, respectively. Differently, PRESS and RMSECV raised abnormally when

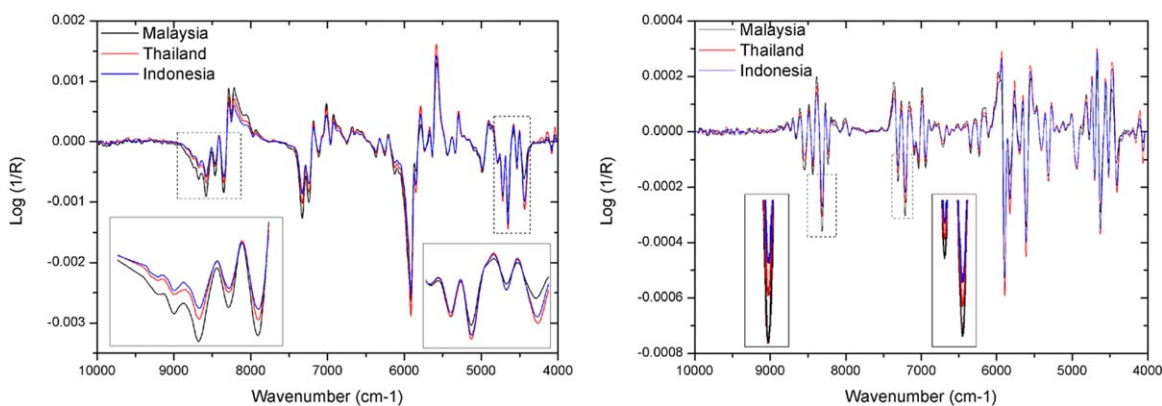


Figure 5. Spectra of Malaysia, Thailand, Indonesia rubber blends with SBR content of 2.5 wt %, which are preprocessed by first derivative combined with smoothing (left) and by second derivative combined with smoothing (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

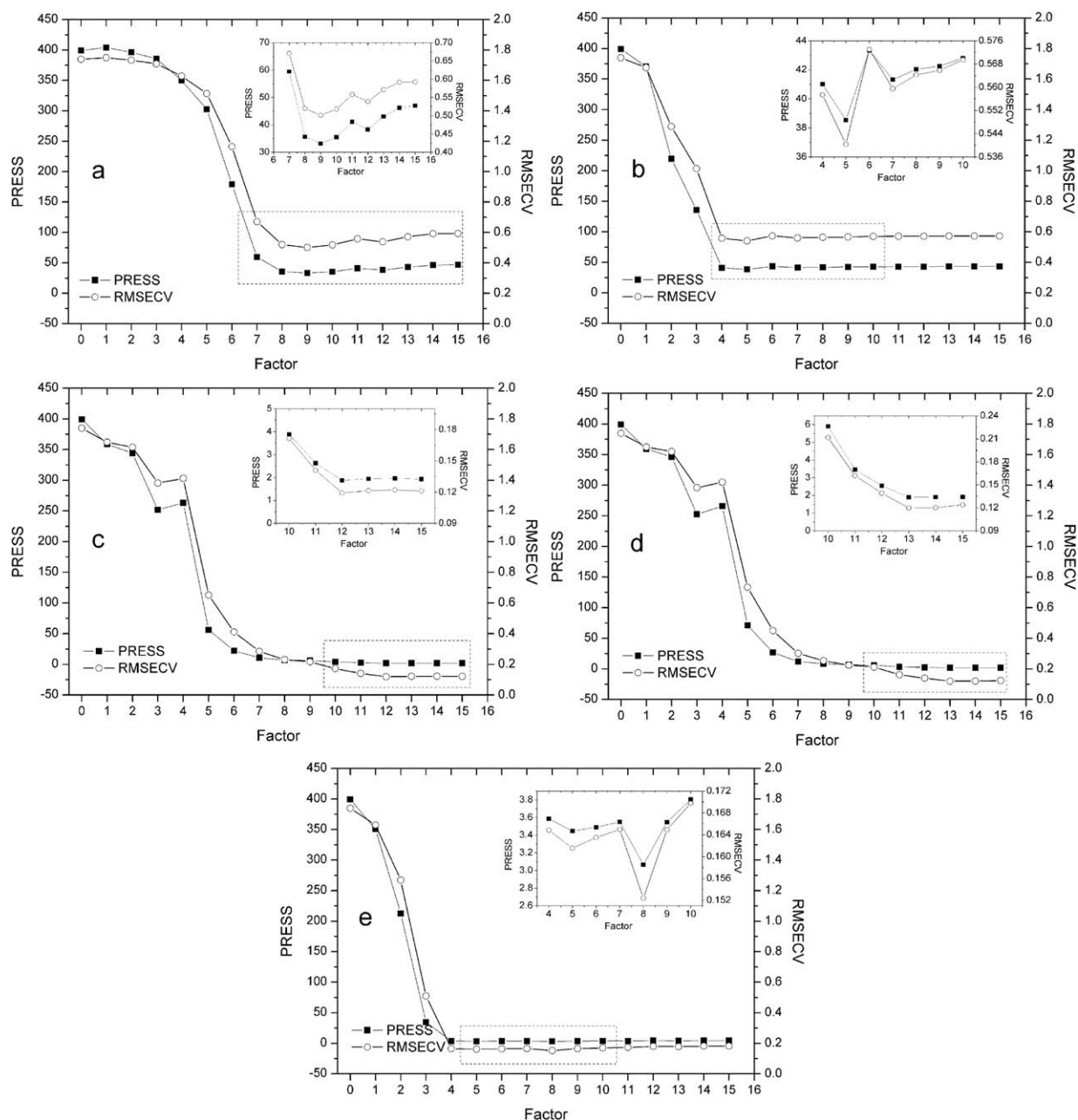


Figure 6. PRESS and RMSECV versus Factor of models pretreated by raw spectra (a), by first derivative (b), by MSC (c), by SNV (d), and by MSC combined with second derivative smoothing (e).

the Factor of the model established by first smoothing is equal to 6. This phenomenon can also be seen in several literatures.^{40,46,47} The reason for that could not be found, but may be able to find by mathematical study of PLS.

Results of Calibration Models

Table I lists performance of the models established by different pretreatment methods. The optimal model was chosen according to a low RMSEP and RMSECV, a low number of Factor, and a high R_c and R_p . As depicted in Table I, the model established by raw spectra represents poor performance. Although R_c and R_p are all higher than 0.97, RMSEP and RMSECV (key parameters to evaluate model) are 0.392 and 0.501, respectively,

which indicated that the accuracy of the model is poor. The reason may come from two aspects. First, the highest SBR content of all the rubber blend samples is only 5 wt %, so the spectral signal is relatively weak. Second, there are baseline drift and light scattering problems in the spectra data of rubber blends (common problems for solid samples), which make it difficult to extract effective information from the spectra data.

Derivative pretreatment can remove baseline drift and amplify signal differences. Judging from the result, although effective signals are amplified (embodies that the Factor reduced from 9 to 5), which is helpful to the model, the accuracy of these models are worse than that of the model established by raw spectra.

Table I. Results of Calibration Models Established by Different Pretreatment Methods

Pretreatment method	R_c	RMSEC/wt %	R_p	RMSEP/wt %	RMSECV/wt %	Factor
Raw spectra	0.9735	0.364	0.9705	0.392	0.501	9
First	0.9728	0.366	0.9519	0.508	0.540	5
Second	0.9999	0.027	0.6855	1.22	0.969	9
First + smoothing	0.9697	0.386	0.9621	0.461	0.497	5
Second+ smoothing	0.9721	0.371	0.9665	0.435	0.494	5
SNV	0.9989	0.074	0.9972	0.120	0.120	13
MSC	0.9989	0.076	0.9972	0.121	0.119	12
SNV + first + smoothing	0.9964	0.135	0.9966	0.132	0.171	5
MSC + first + smoothing	0.9961	0.140	0.9966	0.131	0.179	5
SNV + second + smoothing	0.9965	0.132	0.9963	0.136	0.160	5
MSC + second + smoothing	0.9965	0.132	0.9963	0.135	0.162	5

This is because when effective signal was amplified by derivative pretreatment, noise was also amplified. Although noise can be reduced by smoothing to a certain extent, which can improve the performance of the model (it is more obvious for second, the RMSEP decreased from 1.22 to 0.435 and the RMSECV decreased from 0.969 to 0.494), the accuracy is still worse than that of the model established by raw spectra.

MSC and SNV pretreatment can reduce light scattering of solid samples, which can improve model performances. Table I shows the performance of the models established by MSC or by SNV are better than that of the model established by raw spectra. Take the model established by MSC for example, the RMSEP and RMSECV reached 0.121 and 0.119, respectively. The results demonstrated light scattering is the main reason influencing the model performances.

When MSC (or SNV) and derivative smoothing are combined to use, the resulting RMSEP and RMSECV are worse than that of the models established by MSC (or SNV) alone. However, it is required to attention that the Factor (another key parameter to evaluate model) reduces from 12 (13 for SNV) to 5, which

indicate that the robustness of models improved greatly. Moreover, the RMSEP (0.135 wt %) and RMSECV (0.162 wt %) are close to that of the model established by MSC or SNV alone. This difference is acceptable for industry inspection. As we have discussed above, the Factor of the model established by MSC or SNV alone, appears abnormal rising at 4. It may lead to a potential risk of bad robustness. Therefore, MSC combined with second smoothing was selected as the optimal spectral pretreatment method ultimately.

Evaluation of the Optimal Calibration Model

Figure 7 shows linear correlation regression plots of calculated versus actual of the calibration model established by MSC combined with second smoothing and that of full leave-one-out cross validation. It can be seen that all the plots are uniformly distributed in the alignment of both sides, the R_c , R_p , RMSEC, RMSEP, and RMSECV are 0.9965, 0.9963, 0.132, 0.135, and 0.162%, respectively, which indicated that both linearity and prediction accuracy are satisfactory. The accuracy result 0.135 wt % is better than that of TGA (2–4 wt %), Py-GC/MS

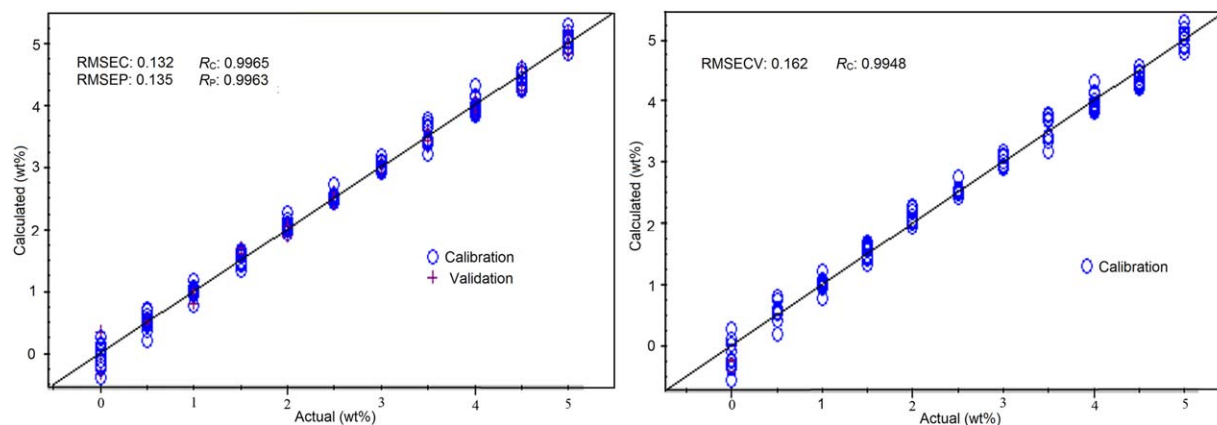


Figure 7. Linear correlation regression plots of calculated versus actual SBR content in rubber blends of calibration model (left) and cross validation model (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

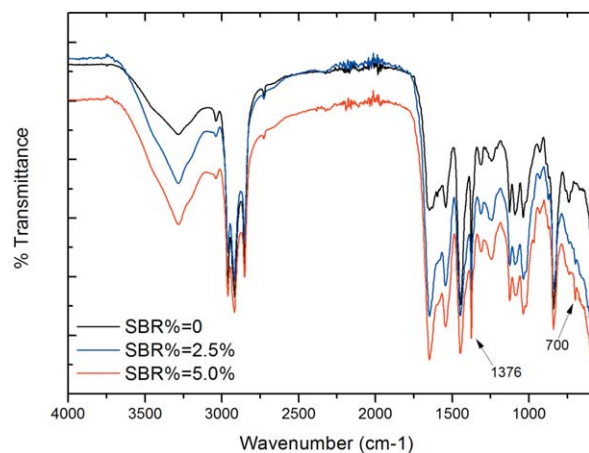


Figure 8. Raw infrared spectra of three typical rubber blend samples whose SBR content are 0, 2.5, and 5.0%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(1–2 wt %), FTIR (2–3 wt %), and ATR-FTIR (3–4 wt %), which have been reported in the literatures.^{6,8,12}

Intraday and Interday Precision of NIR Method

Considering the complexity and instability of NR composition, all validation set samples were measured three times every seven days by the optimal calibration model during three months. Then standard deviations between the predicted values and the reference value (calculated by the known weights ratio of raw material) of one day (intraday) precision and all days (interday) precision were calculated. The purpose is to evaluate the robustness of the optimal calibration model. The result shows averages of all the standard deviations are 0.121 wt % for intraday and 0.132 wt % for interday, which indicated a good robustness.

Predicted Result of NIR and FTIR for Validation Samples

Several literatures^{6,9,13} have revealed that FTIR is a useful analytical protocol for quantitative analysis of rubber blends. In this study, FTIR method was used for comparing with NIR method. Figure 8 shows raw infrared spectra of three typical rubber blend samples whose SBR content are 0, 2.5, and 5.0%.

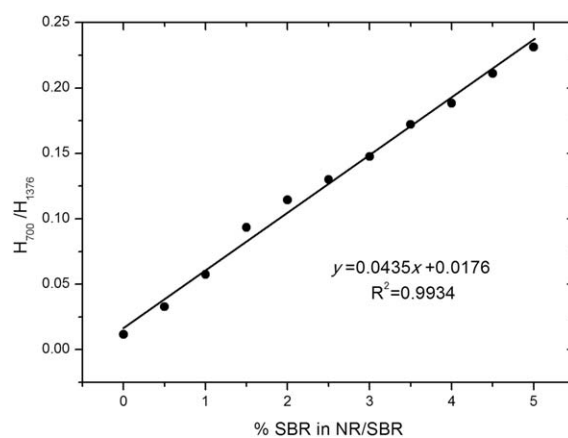


Figure 9. Plot of 700/1376 peak area ratio versus SBR content in NR/SBR blends.

The peak 1376 cm^{-1} corresponds to methyl C–H stretching vibration and the peak 700 cm^{-1} corresponds to C–H stretching vibration of benzene ring. The SBR content of NR/SBR blends can be determined from the peak areas ratio of the peaks at 700 and 1376 cm^{-1} , which correspond to NR and SBR, respectively.⁹ Figure 9 shows a plot of 700/1376 peak area ratio versus SBR content, which yielded an equation $y = 0.0435x + 0.0176$ with $R^2 = 0.9934$. The amounts of SBR in 10 typical validation samples whose SBR content range from 0.5 to 5.0%, were then determined by NIR method and FTIR method. The results are listed in Table II. It can be seen in Table II that the accuracy of NIR is generally better than that of FTIR.

CONCLUSIONS

The results obtained in this work indicate that NIR spectroscopy, in conjunction with multivariate calibration, can allow a fast, nondestructive, accurate quantitative analysis of NR blends regardless of geographical origin and harvest time of the NR. By appropriately choosing model parameters, one can accurately determine low rubber content in NR blends with good accuracy and precision. The test result is close to that of the existing methods such as TGA, Py-GC/MS, FTIR, and ATR-FTIR.

Table II. Predicted SBR Content in NR/SBR for Validation Samples

Sample	Calculated SBR (%)	FTIR		NIR	
		Measured (%)	Bias (%)	Measured (%)	Bias (%)
1#	0.5	0.20	−0.30	0.54	0.04
2#	1.0	0.73	−0.27	1.02	0.02
3#	1.5	2.33	0.83	1.61	0.11
4#	2.0	2.58	0.58	2.07	0.07
5#	2.5	2.92	0.42	2.60	0.10
6#	3.0	3.07	0.07	3.07	0.07
7#	3.5	3.46	−0.04	3.32	−0.18
8#	4.0	3.80	−0.20	3.89	−0.11
9#	4.5	4.41	−0.09	4.36	−0.14
10#	5.0	4.87	−0.13	5.02	0.02

Because of the rather limited range in the quantity and sources of the original samples, it is emphasized that further work in this area is to improve the method robustness, using a wider range of samples.

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