

Influence of Pretreatment Methods of the Spectra on the Calibration Model of the Precuring Degree

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ABSTRACT: In near infrared (NIR) spectra, there could be observed the baseline drift, background noise, scattering effects, and overlapped peaks. These errors can disturb the robustness and reliability of multivariate calibration models. Influences of spectral pretreatment methods on calibration model were studied. The partial least squares (PLS) were applied for developing model of the precuring degree. The multiplicative scatter correction gave the best values for R^2 and RMSEC. R^2 was 0.96,

RMSEC was 0.112, respectively. The method NIR and reference method were compared using Student's t test ($\alpha = 0.05$) for paired values, the result showed that there was no significant difference between the NIR method and the reference method. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1529–1533, 2012

Key words: near infrared spectroscopy; preprocessing; precuring degree

INTRODUCTION

Near-infrared (NIR) spectroscopy is a rapid and nondestructive method. It has been successfully applied in analysis of certain polymers.^{1–6} NIR spectra typically contain unselective, extensively overlapped bands. So it is necessary to use pretreatment methods for quantitative analysis.^{7,8} The selection of a suitable preprocessing of the NIR spectra is an important step in the model development.⁹ Preprocessing of the NIR spectra mainly include normalization, derivative, smoothing, and multiplicative scattering correction and so on.¹⁰ Multiplicative scattering correction is often used for the samples of the different particle size,¹¹ elimination of the stray light of the environment and correction of the scattering spectrum. It is applied in diffuse reflection spectrum also. Normalization fits the samples of different thickness and surface dispersion, the sample of prepreg has thickness disparity in the manufacture. To decrease or reduce the influence of the environmental noise in the manufacture, the baseline correction is used. Straight line subtraction is widely used in

the slant spectrum. Derivative is often used the first and second derivative,¹² which is applied in baseline correction and overlapping peaks.

A prepreg consists of a fiber reinforcement or fabric form, impregnated to a predetermined level with a resin matrix. It is the important intermediate material and greatly influences the properties of final composite products. Precuring degree is a determining step in manufacture of prepreg. The quality of prepreg is controlled to a great extent by the cure cycle parameters such as velocity, temperature and pressure in manufacture. To enhance the manufacture of final composite products, the ranges of precuring degree is 1.50–5.00% about.

The precuring degree is resin curing degree in manufacturing process of the prepreg. It is the key factor to ensure the quality of the prepreg. High curing degree will induce the crisp prepreg, whereas low curing degree will give the viscous prepreg. In this case, it is important to analyze the precuring degree as the manufacturing of the prepreg is difficult.

In our previous work, the prepreg quality was analyzed by NIR spectroscopy.¹³ The present study is the influence of pretreatment methods on the precuring degree models. To find a suitable preprocessing method, the impact of data preprocessing on the determination of precuring degree is studied. In turn, this would lead to an improved final calibration model, with an increased predictability and robustness. A comparison of the modeling power of partial least squares (PLS) is made using unprocessed spectra, derivative spectra, vector normalization, and multiplicative scattering correction spectra.

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TABLE I
Statistical Parameters of Calibration and Validation Set

Quality indexes	Range	Mean	Samples number
Calibration set	1.70–4.31%	2.97%	262
Validation set	1.92–3.91%	2.95%	35

EXPERIMENTAL

Preparation of samples and reference analysis

Reference methods are utilized to determine the precuring degree samples according to ASTM-Test Method C613. The analytical sample is divided into two equal parts A and B, and weighed separately to the nearest 0.0001 g to obtain the initial weight W_A and W_B . Part A is placed in an oven at 160°C for 10 min, cooled in a desiccator, and immediately weighed to obtain the weight W_{A1} . Part B is dissolved in acetone for 10 min, placed in the oven at 160°C for 10 min and weighed to obtain the weight W_{B1} , then is placed in a muffle furnace at 600°C for 20 min and weighed to obtain the weight W_{B2} . The volatile content ($V\%$) and the precuring degree ($C\%$) is calculated as follows:

$$V\% = (W_A - W_{A1})/W_A \times 100 \quad (1)$$

$$C\% = (W_{B1} - W_{B2})/(W_B \times (1 - V) - W_{B2}) \times 100 \quad (2)$$

The results obtained by the reference analysis method are recorded as the actual values and are used to model the relation with the NIR spectra.

Statistical characteristics of the calibration and validation sets are given in Table I. Two hundred and sixty-two prepreg samples from the different phases of the product line (size is $5 \times 5 \text{ cm}^2$) are used, it has considerable variability spread in weight and physical aspect, depending on manufacturing process of prepreg. The calibration set is composed of the distribution of precuring degree values (maximum, minimum, mean) and sample number in developing model. The maximum value of precuring degree is 4.31%, the minimum value is 1.70%, and the mean value is 2.97%. The range of the precuring degree confirms the wide diversity in the calibration sets. The maximum value of the precuring degree is 3.91%, the minimum value is 1.92%, and the mean value is 2.95% for the validation sets.

NIR spectroscopy and statistical analysis

NIR Spectrum is measured by a noncontact scanning FT-NIR spectrometer, which is operated in the NIR region from 4000 to 12,000 cm^{-1} . The resolution of the spectra is 8 cm^{-1} with average scanning of 16. The sample size is $5 \times 5 \text{ cm}^2$. The diffuse reflectance spectra of prepreg are recorded by the spectrometer.

Normalization, derivative, smoothing, and multiplicative scattering correction of the pretreatment

methods is used in developing model. The determination coefficient (R^2), root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) are calculated to evaluate the model. The linearity correlation coefficient is a measure of the consistency between the NIR prediction values and actual values for the calibration sets.

$$R^2 = \left(1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \right) \times 100\%; \quad (3)$$

$$\text{RMSEC} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}} \quad (4)$$

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^m (y_i - \hat{y}_i)^2}{m}} \quad (5)$$

where y_i is the actual value from the reference analysis for sample i , \hat{y}_i is the estimated value from the model for sample i , \bar{y} is the mean of the actual values for calibration samples, n is the number of calibration samples, m is the number of prediction samples.

RESULTS AND DISCUSSION

Precure process of the prepreg

Prepreg is manufactured in 110°C. The resin is precured in the glass cloth. Cure reaction of phenolic resin has the two processes in this temperature. First, the hydroxymethyl ($-\text{CH}_2-\text{OH}$) and active hydrogen ($-\text{H}$) reacts, after that two hydroxymethyls ($-\text{CH}_2-\text{OH}$) react by condensation. In this process, ethanol solvent and water (Cure reaction of phenolic resin generates the water) is volatilized. NIR spectrum of phenolic resin is shown in Figure 1.

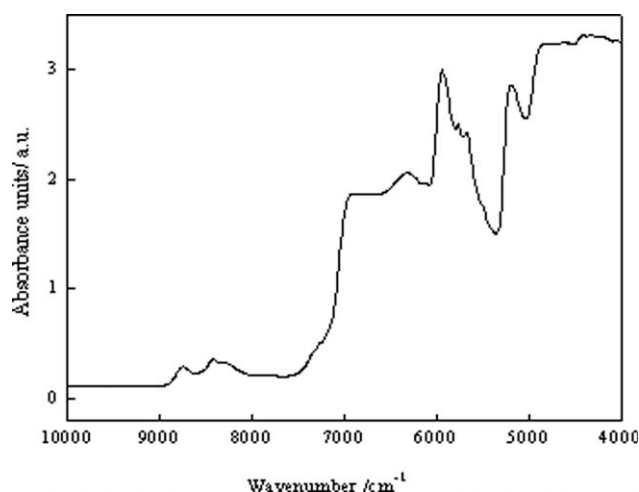


Figure 1 NIR spectrum of phenolic resin solution.

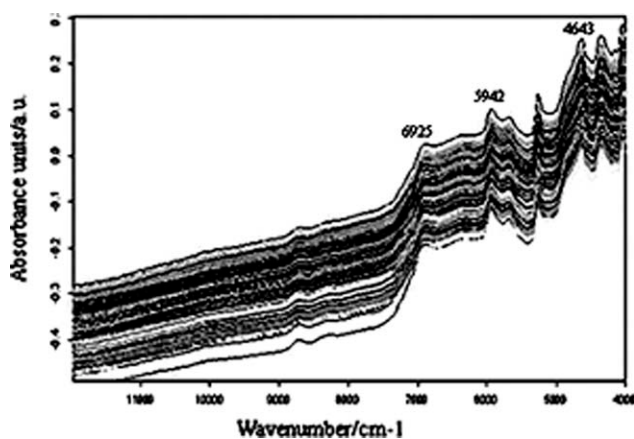


Figure 2 NIR spectra of glass cloth phenol resin prepreg.

Developing model

The precuring degree is resin curing degree during manufacturing process of the prepreg, NIR spectra of the precuring degree of prepreg shows characteristic peaks phenol resin in prepreg.

In Figure 2, a combination band of CH stretching and deformation mode of the benzene groups is at 4643 cm^{-1} , and the first overtone of CH stretching mode at 5942 cm^{-1} is associated with the aliphatic CH_2 . A first overtone of OH stretching mode of phenol and water is at 6925 cm^{-1} .

To eliminate variations in offset of samples and to ensure a good correlation between the spectral data and the concentration values, the several spectral

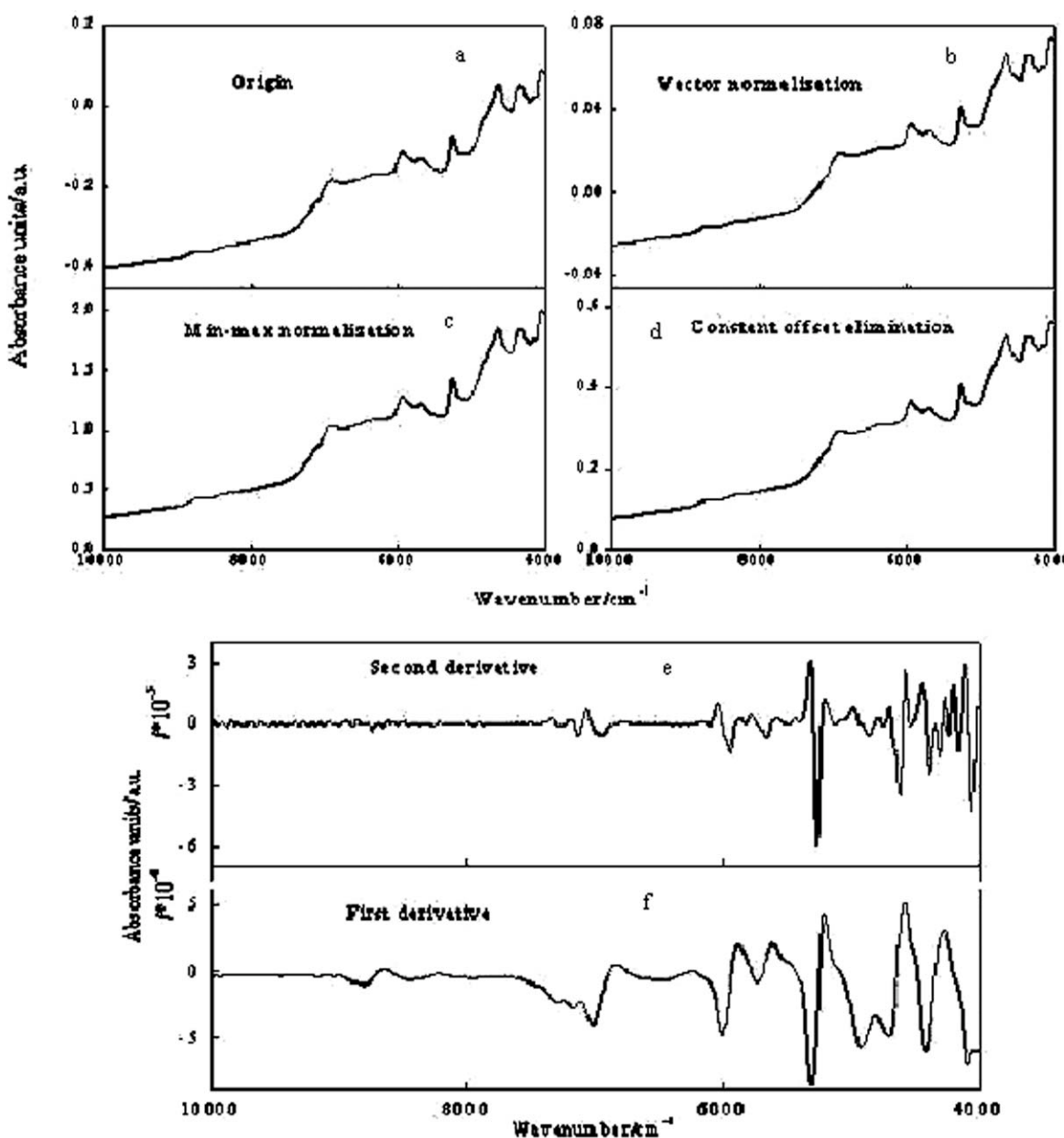


Figure 3 NIR spectra of various pretreatment methods.

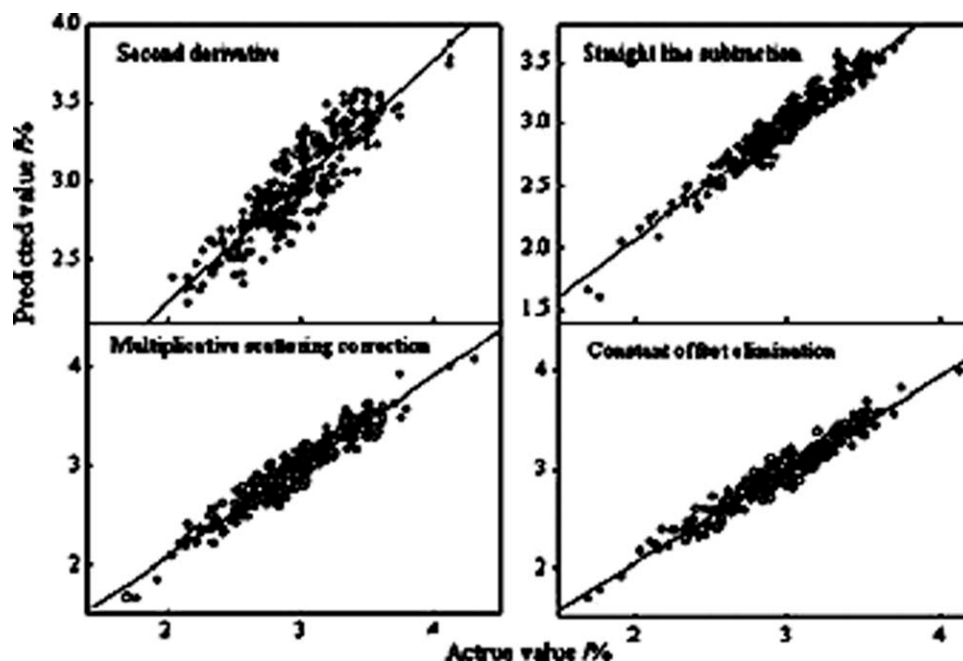


Figure 4 Correlation between predicted values and actual values.

pretreatments are employed and presented in Figure 3. As shown in Figure 3, NIR spectra did significantly change in origin, constant offset elimination, vector normalization, and min-max normalization pretreatment methods and also shows difference in first and second derivative from the macrography. There are five plots in Figure 3. It is suggested to label Figure 3(a–f) and explain each one how it is done and also clearly explain the first and second derivative from macrography.

Several data preprocessing methods are applied before calibration development to find models with the highest predictive power. Calibration model is developed by PLS. Full cross-validation is applied to optimize the calibration model. The influence of pretreatment methods on the precurving degree model is shown in Figure 4. Multiplicative scatter correction gave the best values for R^2 and RMSEC. The value of R^2 and RMSEC is 0.96 and 0.112, respectively. Eight PLS factors were used; the spectral range gave the best 12,000–7490 and 5453–4242 cm^{-1} . Because of NIR spectra are collected by the diffuse reflection in the manufacture. Multiplicative scattering correction suits the diffuse reflection spectrum and the different thickness; it can eliminate the stray light of the environment and correction of the scattering spectrum.

The worst value of R^2 and RMSEC is 0.95 and 0.118, respectively, which is obtained from second derivative. Two outliers are deleted from the calibration set and not used to develop to model. These outliers are samples whose deviation from the reference value is particularly large and statistically sig-

nificant. The second derivative is applied in overlapping peaks, but the needless information can show in the spectrum by second derivative. The interferential weak peaks are discovered in Figure 3(e). R^2 is 0.95 and RMSEC is 0.120 by straight line subtraction; R^2 is 0.95 and RMSEC is 0.118 by constant offset elimination.

The plot of the actual values against the NIR predicted values for calibration set is shown in Figure 4. The regression coefficient is 0.899, 0.957, 0.968, and 0.971 by second derivative, straight line subtraction, constant offset elimination and multiplicative scatter correction, respectively. Figure 4 shows a good correlation between the actual values and prediction values, the maximal predicted error of the

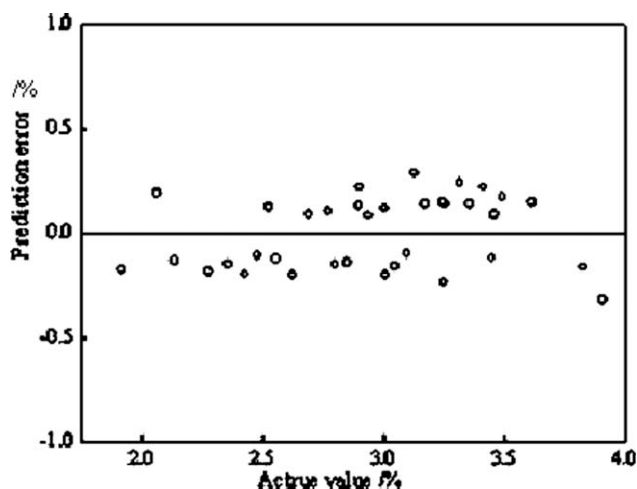


Figure 5 Predicted error of validation samples.

TABLE II
Results of the Paired *t* Test on NIR Prediction and Actual Values for the Validation Set

Maximal predicted error (%)	0.28
$t_{\text{experiment}}$	0.16
t_{critical}	2.03

calibration model was 0.27 by multiplicative scatter correction.

Validation

To further evaluate the reliability of the NIR method, 35 samples are collected randomly and analyzed by the reference method. RMSEP of the samples is 0.16, and Figure 5 shows that the maximal predicted error is 0.28. The NIR and reference method is compared using Student's *t* test ($\alpha = 0.05$) for paired values. The experimental *T* value given in Table II is lower than critical value *T*. The levels of significance obtained are 0.05; the result shows that there is no significant difference between the NIR and the reference method.

CONCLUSIONS

The above results show that NIR spectroscopy can detect the precuring degree; it is a reasonable accurate method. The preprocessing method of the NIR

spectra used the multiplicative scatter correction; it gave the best values for R^2 and RMSEC of the calibration model. The precuring degree of prepreg was analyzed once within less than 30 s without sample destruction. If the precuring degree of prepreg overflows the prescriptive ranges by NIR method, temperature, velocity, and solution concentration is rapidly adjusted. NIR method economizes time and material, enhances production efficiency.

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