



# Non-destructive and Rapid Analysis of Resin and Volatile Contents in Carbon Fibre/Epoxy Resin Prepreg Cloth by Near-infrared Spectroscopy

Bo Jiang, Yu Dong Huang\*, Wei Li, and Li Liu

Polymer Materials and Engineering Division, Department of Applied Chemistry,  
Harbin Institute of Technology, P.O. Box: 410, Harbin 150001, P.R. China

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## ABSTRACT

Near-infrared (NIR) spectroscopy has been applied for qualitative analysis of carbon fibre/epoxy resin prepreg cloth. A partial least square (PLS) calibration model for the prediction of the resin content and volatile content was developed using 104 samples for calibration and 30 samples for prediction, respectively. The calibration model for the resin content was obtained by using no spectral data preprocessing ( $R^2= 93.52$ , RMSEC= 0.60), and the volatile content was obtained by second derivation ( $R^2= 94.57$ , RMSEC= 0.129). RMSEP of the prediction model for the resin content is 0.81% and for volatile content is 0.237%. Sixteen samples were collected randomly and analyzed by chemical and NIR methods. The results of the paired t-test revealed that there was no significant difference between the NIR method and the standard method. The NIR spectroscopy method can be used to predict the resin content and the volatile content simultaneously. Besides, the prepreg could be analyzed one time within 30 s without sample destruction. The study indicates that the NIR analysis is sufficiently accurate and effective for quality analysis in carbon fibre/epoxy resin prepreg cloth.

## Key Words:

NIR spectroscopy;  
partial least square regression;  
volatile content;  
resin content;  
prepreg.

## INTRODUCTION

Thermosetting composite systems are emerging as potential materials in many engineering applications, such as aerospace, transportation, construction and automotives [1]. Many of these composites are made from prepreps. The prepreg is a semi-finished, machine-made

product in which a reinforcement material has been impregnated with a pre-catalyzed resin system [2]. Performance, material qualification and product consistency of prepreg have been considered to be significant requirements and renewable energy sectors. As the quality of the

(\*) To whom correspondence to be addressed.

E-mail: [huangyd@hit.edu.cn](mailto:huangyd@hit.edu.cn)

prepreg will greatly influence the properties of the composite products, it is important to monitor quality in the production of prepreg.

The prepreg contains volatile substance such as water, solvent and small molecule, a small volatile content which induces aging of the prepreg and low level of underproduction. Besides, a small resin content decreases the viscosity and fluidity, while a high resin content conduces to resin outflow and waste. In the manufacture of the carbon/epoxy resin prepreg, the resin content and the volatile content are the key factors to ensure the quality of the prepreg. Traditional analytical methods such as solvent extraction, weighing and burn-off are often used to measure the resin content and volatile content of the prepreg. However, these methods are not the best candidate for analyzing the quality of the prepreg cloth due to the excessive time required, agent wasted and specimen destructed.

The current analysis methods, which include the gamma-ray reflectance [3], ultrasonic [4,5], beta-ray transmission [6-8] and infrared spectroscopy techniques [9] are widely used to measure the resin content of the prepreg, but the volatile content cannot be measured by these methods.

Near-infrared (NIR) spectroscopy is an excellent alternative analytical method. It is a very rapid, accurate and non-destructive method for the simultaneous measurement of different constituents in various products [10-15]. NIR Spectrum contains information related polymer properties such as composition, conformation and crystallinity, therefore it can be widely applied for various polymer analyses in conjunction with chemometric calibration methods [16]. The applications of NIR in the above fields are combined with the chemometric calibration methods. However, NIR spectra typically contains unselective, extensive-

ly overlapped bands, so it is necessary to use multi-variate chemometric analytical tools such as partial least squares (PLS), principal components regression (PCR) or multiple linear regression (MLR) for quantification analysis. The aim of this study was to develop an analysis method for the instantaneous and simultaneous prediction of carbon fibre/epoxy resin prepreg cloth by diffuse reflection near-infrared spectroscopy. The calibration models about the resin content, and the volatile content were established separately by using partial least square (PLS), and several spectral pretreatments were tested in order to obtain the optimum models. After validation, a NIR method was established for analyzing the resin and volatile content of prepreg cloth in manufacture. The NIR spectroscopy method can be used to predict the resin content and the volatile content simultaneously. Besides, the prepreg could be analyzed one time within 30 s without sample destruction. The results of the paired t-test revealed that there was no significant difference between the NIR method and the standard method.

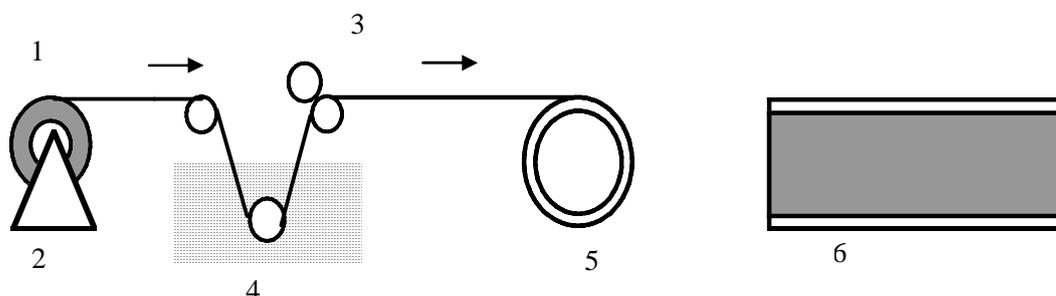
## EXPERIMENTAL

### Raw Materials

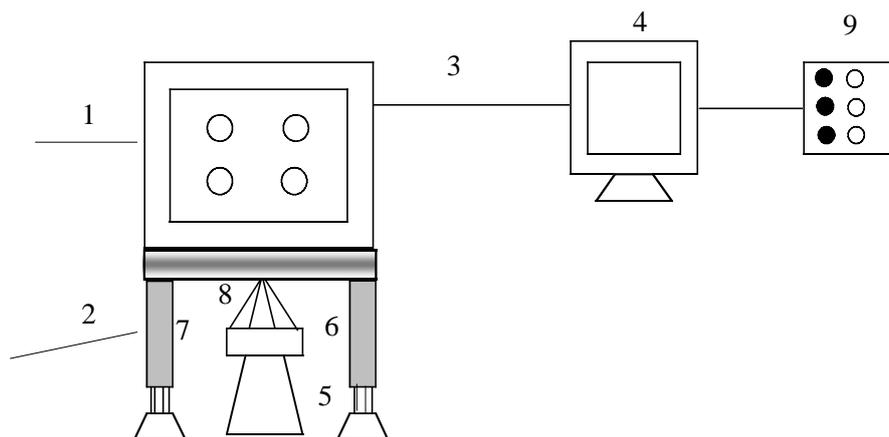
Epoxy resin systems were provided by Xi'an Research Institute of Airplane Corporation, China. Carbon fibre (T700) was obtained from Toray Industry, Japan. Acetone was purchased from Beijing Chemical Reagent Factory, China.

### Preparation of Carbon Fibre/Epoxy Resin Prepreg Cloth

The twist method was used to manufacture the carbon fibre/epoxy resin prepreg cloth. The procedure is



**Figure 1.** Schematic diagram of manufacture process of carbon fibre/epoxy prepreg cloth: (1) carbon fibre, (2) bracket, (3) nip rollers, (4) resin impregnation bath, (5) twister, (6) expanding prepreg cloth.



**Figure 2.** Schematic diagram of monitoring the quality of carbon fibre/epoxy prepreg cloth by near-infrared spectroscopy: (1) NIR spectrometer, (2) tailor-made bracket of spectrometer, (3) data line, (4) computer, (5) bracket, (6) gilded metal plate, (7) carbon fibre/epoxy prepreg cloth, (8) beam, and (9) annunciator.

being shown in Figure 1. First, the carbon fibre was passed into epoxy resin solution, and the excessive solution was removed off by the nip rollers [20], then the prepreg cingulum was wrapped to the twister. Finally, the prepreg was placed three days for the next analysis. The size of the prepreg cloth was 470 cm × 96 cm.

### Spectroscopic Techniques

NIR Spectrum was measured by a FT-NIR spectrometer (Bruker Matrix-E Germany). The qualitative analysis equipment of the carbon fibre/epoxy prepreg cloth is shown in Figure 2. NIR Spectrometric analysis of prepreg samples was conducted following the NIR standard procedures, including selection of calibration and prediction samples, and the standard data obtained by routine laboratory analysis.

NIR Spectral data were obtained by a non-contact scanning method, the light from the sources was focused on the prepreg cloth, and then the diffuse reflectance spectra from the prepreg cloth was recorded by the spectrometer. A gilded metal plate was placed under the prepreg cloth in order to enhance the diffuse reflectance effect. When the spectrometer completed a collection of spectrum, the corresponding piece was cut from the prepreg cloth exactly and it was regarded as one sample. The size of each sample was 5×5 cm. FTIR Spectrometer was operated in the near-infrared region from 4000 to 10000 cm<sup>-1</sup> using a tungsten light source and an indium gallium arsenide (InGaAs) detector, along with a CaF<sub>2</sub> beam-

splitter. The resolution of the spectra is 8 cm<sup>-1</sup> and the averaging scanning time is 8.

### Chemical Analysis

The resin content and volatile content of prepreg cloth samples were measured according to China Standard. The test specimen was divided into two equal parts, A and B, and weighed separately to the nearest 0.0001 g to obtain the initial weights of trawl, A<sub>1</sub> and B<sub>1</sub>. The total weights of trawl and samples were named A<sub>2</sub> and B<sub>2</sub>. Part A was placed in an oven at 160° for 15 min, and cooled in a desiccator, and then immediately weighed to obtain the weight A<sub>3</sub>. Part B was washed several times with acetone until no resin, then placed in the oven at 160°C for 10 min and weighed to obtain the weight B<sub>3</sub>. The volatile content (V%) and the resin content (R%) were calculated as follows:

$$V\% = (A_3 - A_1) / (A_2 - A_1) \times 100 \quad (1)$$

$$R\% = (B_2 - B_3) / (B_2 - B_1) \times 100 \quad (2)$$

The results measured by the chemical analysis method were regarded as the actual values and were used to model the relation with the NIR spectra.

### Statistical Analysis

PLS Regression was used to develop the calibration models for the resin content and the volatile content of the prepreg cloth. The samples were separated into a calibration set and a prediction set as described in all

**Table 1.** Statistics of calibration set of each parameter.

Quality indexes	Maximum	Minimum	Mean	SD	N
Volatile content	1.925	0.388	0.938	0.384	104
Resin content	44.255	35.451	39.687	2.057	104

N: number of samples; SD: standard deviation.

NIR calculations. Statistical characteristics of the calibration and prediction sets are given in Table 1. 104 Samples were developed for the calibration model. The maximal volatile content was 1.925%, the minimum volatile content was 0.383%, the standard deviation was 0.384; the maximal resin content was 44.255%, the minimum resin content was 35.451%, and the standard deviation was 2.057.

Full cross-validation was applied to optimize the calibration models. In the optimized process, the number of PLS factors was determined and the outliers were detected. Before starting the calibration, one sample was excluded from the entity of samples, which was used for the prediction. The remaining samples were used to calibrate the system. Spectral outliers were detected through the Mahalanobis distance. A spectrum with a Mahalanobis distance larger than the limit was marked as a spectral outlier. These outliers were samples whose deviation from the reference value was particularly large and statistically significant. The outliers must be deleted from the calibration set, which were forbidden to develop the models.

In order to be able to eliminate variations in offset or different linear baselines and instrument noise, to ensure a good correlation between the spectral data and the concentration values, several spectral pretreatments were tested such as straight line subtraction (SLS), vector normalization (VN), min-max normalization (M-MN), multiplicative scattering correction (MSC), constant offset elimination (COE), first derivative (1st deriv.), second derivative (2nd deriv.), 1st deriv.+SLS, 1st deriv.+MSC, 1st deriv.+VN, no general recommendation can be given if data preprocessing should be applied, or which method would be best suitable. It is best to compare several different spectral preprocessing methods to obtain the optimum result.

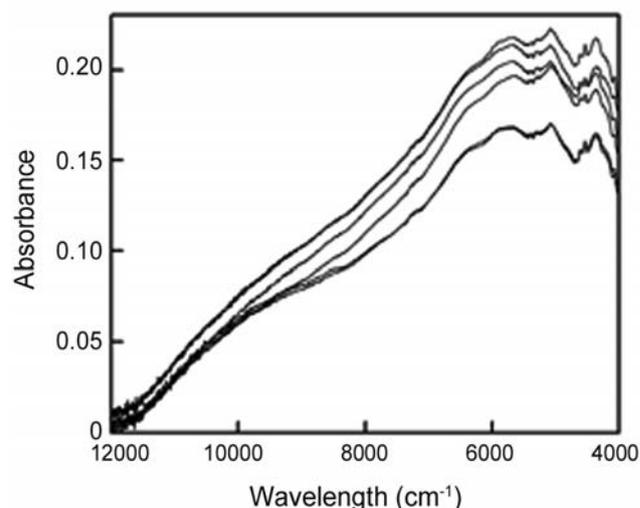
The performance of the model was evaluated according to the following criteria: the determination

coefficient ( $R^2$ ) gives the percentage of true component values present;  $R^2$  approaches 100% as the fitted values approach the true values. The RMSEC corresponds to root mean square error of calibration model, while the root mean square error of prediction model is RMSEP and the number of PLS vectors used.

## RESULTS AND DISCUSSION

### NIR Spectral Information of Materials

The prepreg samples comprise epoxy resin system, acetone and carbon fibre. There are many hydrogen-containing groups in the epoxy resin system and the acetone molecules, so the NIR spectrum of the prepreg contains information about the resin and volatiles. NIR Spectra of the different concentration prepreg cloth samples are shown in Figure 3, their differences could be observed. From this figure, characteristic peaks of the epoxy resin groups can be seen as follows: 4522  $\text{cm}^{-1}$  peak was combination band of epoxy group; weaker peaks at 5881  $\text{cm}^{-1}$  was the first



**Figure 3.** NIR Diffuse reflectance spectra of carbon fibre/epoxy resin prepreg cloth.

**Table 2.** R<sup>2</sup>, RMSEC and values for number of factors for different preprocessing routines of the resin content.

No	Preprocessing routine	No samples excluded	R <sup>2</sup>	RMSEC	RMSEP	Number of factors
1	No spectral data preprocessing (12000-7498 and 4601-4246) cm <sup>-1</sup>	1	93.52	0.60	0.81	7
2	No spectral data preprocessing (12000-7498 and 5453-4598) cm <sup>-1</sup>	2	93.16	0.63	0.90	8
3	Straight line subtraction (12000-7498 and 5454-4246) cm <sup>-1</sup>	1	93.23	0.62	0.85	6
4	Straight line subtraction (12000-6097 and 5454-4597) cm <sup>-1</sup>	2	92.70	0.63	0.98	5
5	Vector normalization (12000-4598) cm <sup>-1</sup>	1	87.2	0.82	1.13	7
6	Min-max normalization (12000-7498 and 6102-5450) cm <sup>-1</sup>	1	83.69	0.91	1.29	8
7	Constant offset elimination (12000-6097 and 4601-4246) cm <sup>-1</sup>	1	90.82	0.70	1.01	7

overtones of the fundamental CH<sub>2</sub> stretches; weaker peaks at 6070 cm<sup>-1</sup> was the first overtones of the fundamental CH stretches; 5068 cm<sup>-1</sup> peak was a combination band of a primary amine N-H [17-19].

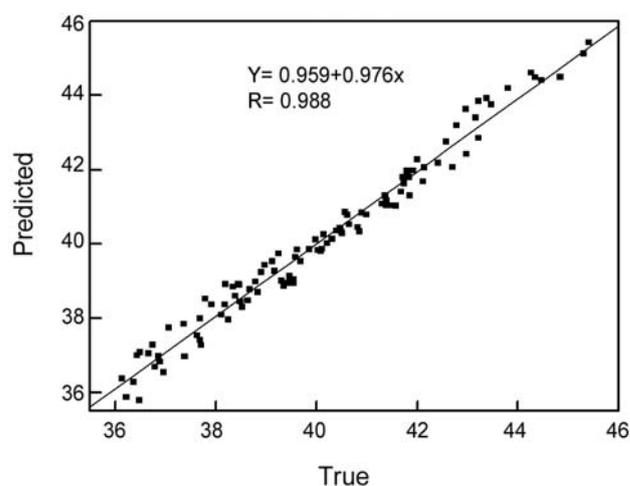
From the above analysis, NIR spectra contain abundant information of prepreg related with the resin content and the volatile content, a multivariate calibration method based on PLS could be used to obtain relevant analytical information and determine the quality indexes. The spectrometer can perform non-contact analysis of the product. In the test, the light from the sources was 17 cm far from prepreg cloth and the facular on it was 25 mm in diameter.

#### Model of Resin Content and Volatile Content

From Table 2, it is observed that no spectral data preprocessing method gave the best values for R<sup>2</sup>, RMSEC, and RMSEP. Also, the R<sup>2</sup> and RMSEC figures obtained using the same preprocessing technique (Table 2, -none, SLS, VN, M-MN, MSC, COE) were very dependent on the number of spectra used as internal test samples. This was explained by the fact that the cross-validation used the same set of samples for calibration and validation.

This model used 7 factors, achieving R<sup>2</sup> of 93.52, RMSEC of 0.60% and RMSEP of 0.81%, and one

sample was deleted from the calibration set. The plot of the actual values against the NIR predicted values for calibration set is shown in Figure 4; it has a linear trend curve with a slope of 0.976, a regression coefficient of 0.988 and an intercept of 0.959. Figure 4 shows a good correlation between the true concentration values, analyzed by standard method and the predicted concentrations, calculated from the near-infrared spectra using the multivariate calibration

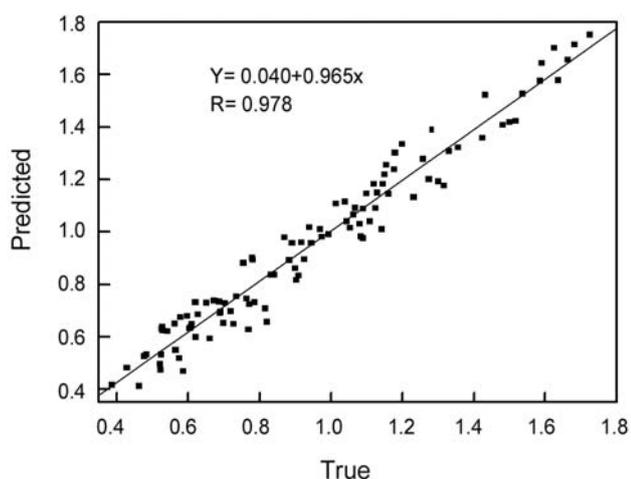
**Figure 4.** Correlation between predicted values and actual values for resin content.

**Table 3.** R<sup>2</sup>, RMSEC and values for number of factors for different preprocessing routines of the volatile content.

No	Preprocessing routine	No samples excluded	R <sup>2</sup>	RMSEC	RMSEP	Number of factors
1	No spectral data preprocessing (12000-6097 and 5454-4247) cm <sup>-1</sup>	1	92.81	0.149	0.263	9
2	Straight line subtraction (12000-7498 and 5454-4247) cm <sup>-1</sup>	1	93.01	0.136	0.259	5
3	Vector normalization (12000-6098) cm <sup>-1</sup>	1	91.05	0.203	0.263	6
4	Multiplicative scattering correction (12000-6097) cm <sup>-1</sup>	1	92.89	0.163	0.256	6
5	Second derivative (Smoothing points:17) (7500-6908 and 5454-4246) cm <sup>-1</sup>	2	94.57	0.129	0.237	5
6	Second derivative (Smoothing points:17) (7500-4246) cm <sup>-1</sup>	1	94.01	0.133	0.239	5
7	Constant offset elimination (12000-6097 and 6102-4598) cm <sup>-1</sup>	1	92.06	0.172	0.293	8

method.

From Table 3, it is observed that the models using the spectral pretreatments second derivation with smoothing points of 17 gave the excellent fitting effect. The model used factors, R<sup>2</sup>, RMSEC, and RMSEP is shown. From Figure 5, it is observed that the slope of the linear trend curve was 0.965, a regression coefficient of 0.978 and its intercept was 0.040. The NIR method and the standard method did not give

**Figure 5.** Correlation between predicted values and actual values for the volatile content.

significantly different results.

#### Analysis of Unknown Samples

The structural models of resin content and volatile content were put into the Opus/Process software (Bruker Co., Germany), so the NIR spectroscopy method can be used to predict the resin content and the volatile content simultaneously during the production process. The spectra of the prepreg were collected once less than 1 min without sample destruction. When the volatile and resin contents of the prepreg cloth were not within a certain scope, the change in time set could be used to control the volatile content, afresh manual infuse resin solution or solvent could be used to control the resin content.

In order to further evaluate the reliability of the NIR method, 16 samples were collected randomly and analyzed by the chemical method. The actual measured values and the predicted values are listed in Table 4. It was clear that the predicted values were closed to the actual values. The maximal predicted error and the standard deviation of the differences were 0.749% and 0.406% for the resin content, -0.169% and 0.083% for the volatile content. The method NIR and standard method were compared for the resin content and

**Table 4.** Comparison of the results between NIR method and standard methods for validation samples.

No	Volatile content (%)			Resin content (%)		
	Actual	Predicted	Error	Actual	Predicted	Error
1	0.688	0.730	0.042	36.853	36.717	0.136
2	0.941	0.974	0.033	38.758	39.079	-0.321
3	0.555	0.511	-0.044	37.811	37.262	0.549
4	0.643	0.708	0.065	41.912	42.316	-0.404
5	0.419	0.518	0.099	43.354	43.224	0.130
6	1.428	1.406	-0.022	42.216	42.535	-0.319
7	0.393	0.357	-0.036	42.571	42.903	-0.332
8	0.491	0.583	0.092	40.469	40.760	-0.291
9	1.507	1.596	0.089	41.359	41.046	0.313
10	0.851	0.838	-0.013	38.979	38.230	0.749
11	1.317	1.148	-0.169	40.594	40.457	0.137
12	1.232	1.213	-0.019	39.306	39.078	0.228
13	1.133	1.255	0.122	38.649	39.326	-0.677
14	1.048	0.976	-0.072	40.887	40.697	0.190
15	1.264	1.151	-0.113	39.879	39.531	0.348
16	1.062	1.000	-0.062	41.588	41.053	0.535
SD%		0.083			0.406	
t <sub>exp</sub>		0.024			0.601	
t <sub>crit</sub>			2.13			

SD: standard deviation

volatile content using Student's t-test ( $\alpha = 0.05$ ) for paired values. The levels of significance obtained were 0.05, the result showed that there was no significant difference between the NIR method and the standard method, so, the NIR technique was reliable for the measurement of the quality of the prepreg cloth. It may be concluded that the NIR method was helpful for the prepreg cloth production, and it can be used as a quality control analysis tool.

The above results indicated that the models developed for the resin content and the volatile content were accurate and reliable. It may be deduced that the NIR spectroscopy method is a very good alternative for the determination of resin content and volatile content of the prepreg cloth.

## CONCLUSION

It has been demonstrated successfully that the near-infrared spectroscopy combined with PLS methods is feasible for the qualitative analysis of the carbon

fibre/epoxy resin prepreg cloth. The results presented in this study showed that the near-infrared system could detect the resin content and the volatile content of the prepreg cloth. Moreover, it was a reasonable accuracy and precision. Thus the NIR spectroscopic method would be a perfect substitute of the traditional chemical analysis method as quality analysis tool for the carbon fibre/epoxy resin prepreg cloth.

## ACKNOWLEDGEMENTS

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