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# The application of near infrared spectroscopy in the quality control analysis of glass/phenolic resin prepreg

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**Abstract** During the manufacture of glass/phenolic resin prepreg cloth, the feasibility of near infrared (NIR) spectroscopy as a technique for the quality control analysis of the resin content, the volatile content and the resin pre-curing degree has been verified. The partial least square (PLS) regression was used to develop the calibration models by utilizing several different spectral pretreatments. The optimum models had determination coefficients ($R^2$) of 98.29 for the resin content, of 99.50 for the volatile content and of 97.66 for the pre-curing degree, respectively. The root mean square errors of prediction (RMSEP) for the resin content, the volatile content and the pre-curing degree were 0.376%, 0.169% and 0.105%, respectively. The results of the paired *t*-test revealed that there was no significant difference between the NIR method and the standard method. In the manufacture process of the prepreg cloth, the NIR on-line monitoring results were used to be the instructions for the quality control.

## Introduction

Thermosetting resin matrix fiber composites have been employed in military and aerospace applications due to their high performance [1, 2]. Many advanced composites are constructed from the prepregs. A prepreg is a semi-finished, machine-made product in which a reinforcement material (fiber or fabric) has been impregnated with a pre-catalyzed resin system. Because the quality of the prepreg can greatly influence the properties of final composite products, it is important to do the quality control analysis accurately and quickly in the manufacture process of the prepreg. The resin content, the volatile content and the resin pre-curing degree are the three key factors to ensure the quality of the prepreg. Traditional analysis methods such as solvent extraction, burn-off and acid digestion are often used to measure the three factors. However, these methods are unsuitable for continuous measurement during the manufacture of prepreg due to the excessive time required and the destructive analysis of the specimen.

Hitherto, a series of investigation for on-line monitoring the quality of the prepregs have been proposed, in which the methods utilized include the gamma-ray reflectance [3], ultrasonic [4, 5], beta-ray transmission [6–8] and infrared spectroscopy [9] techniques. Although these methods overcome most shortcomings accompanied with the traditional analysis methods, they only monitor one or two of the three quality factors.

For the above reasons, NIR spectroscopy is ideally suited to the quality control analysis of the prepreg. NIR is a fast and accurate analysis technique, and it can be performed on the raw product to measure numerous analytes without destroying the sample. The wide applicability and potential of NIR spectroscopy for polymer analyses have been recognized [10–17]. NIR spectrum contains information related polymer

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properties such as composition, conformation and crystallinity [18], therefore it can be widely applied for various polymer analyses in conjunction with chemometric calibration methods.

The aim of the present study was to develop a quality control analysis method for glass/phenolic resin prepreg cloth by using diffuse reflectance NIR spectroscopy. In this objective, the calibration models about the resin content, the volatile content and the pre-curing degree were developed respectively by using PLS regression, and several spectral pretreatments were applied in order to obtain the optimum models. After validation, NIR method was compared to the conventional analysis method as the quality control analysis technique in the manufacture of the prepreg cloth to show its advantages.

## Experimental

### Samples and NIR measurement

The solution impregnation method was used to manufacture the prepreg cloth. The impregnation procedure is shown in Fig. 1. The resurrection glass cloth was preheated before it was pulled into the alcohol solution of phenolic resin. After the glass cloth was fed through the solvent bath, it went through the nip rollers to meter the cloth to solution ratio. The impregnated cloth then went into the dry tower where the excessive solvent was driven off.

The prepreg cloth was produced at the speed of 80 m/h, and the width of the cloth was 80 cm. A FT-NIR Systems model MATRIX-E spectrometer (Bruker Co., Germany) was assembled between the take up mechanism and the dry tower as shown in Fig. 1. The spectrometer can perform non-contact analysis of the product. In the test, the light from the sources was focused on to the moving prepreg cloth, and then the diffuse reflectance spectra from the prepreg cloth were 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 was regarded as one sample. The size of each sample was 16 × 8 cm. NIR spectra were collected over the 12000 to 4000 $\mathrm{cm}^{-1}$ with a resolution of 8 $\mathrm{cm}^{-1}$, each sample spectrum was obtained by averaging 4 scans. All the 105 samples were collected in two months.

### Chemical measurement

The reference measurement method used for the prepreg cloth samples is the standard method currently used for the quality control. 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 weight $G_A$ and $G_B$. Part A was placed in an oven at 160 °C for 10 min, cooled in a desiccator, and immediately weighed to obtain the weight $G_{A1}$. Part B was dissolved in acetone for 10 min, placed in the oven at 160 °C for 10 min and weighed to obtain the weight $G_{B1}$, then was placed in a muffle furnace at 600 °C for 10 min and weighed to obtain the weight $G_{B2.}$ The volatile content ($V\%$), the resin content ($R\%$) and the pre-curing degree ($C\%$) were calculated as follows:

$$V\% = (G_A - G_{A1})/G_A \times 100 \tag{1}$$

$$R\% = (G_B \times (1 - V) - G_{B2})/(G_B \times (1 - V)) \times 100 \tag{2}$$

$$C\% = (G_{B1} - G_{B2})/(G_B \times (1 - V) - G_{B2}) \times 100 \tag{3}$$

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

All the samples were divided into 79 samples for the calibration and 26 samples for the prediction set

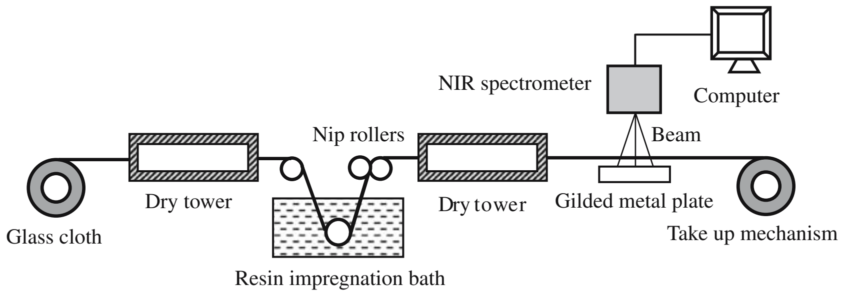

**Fig. 1** Schematic of manufacture process of prepreg cloth

according to the 3:1 ratio. The calibration set was used to build the models, and the prediction set was only used to test the models. The PLS regression was used to model the relation between every quality factor of the prepreg cloth and the NIR spectra. To enhance the accuracy of calibration, several spectral pretreatments were tested (constant offset elimination, COE; straight line subtraction, SLS; vector normalization, VN; min–max normalization, M–MN; multiplicative scattering correction, MSC; first derivative, D1; second derivative, D2; D1+SLS; D1+MSC and D1+VN).

Full cross-validation was applied to optimize the calibration models. In the optimize process, the number of PLS factors was determined and the outliers were detected. With full cross-validation, each sample is removed one at a time from the calibration set, a new calibration performed and a predicted value calculated for the sample removed. This procedure is repeated until every sample has been left out once.

The optimal number of PLS factors was selected by performing an $F$-test ($\alpha = 0.25$) on the root mean square errors of cross-validation (RMSECV). This F-test consists in searching the model with the lowest number of PLS factors and that gives a RMSECV, which is non-significantly different from the lowest error calculated on the first twenty factors.

The $F$ ratio value for each removed sample during cross-validation was used to detect the outlier [19]. The probability that a sample was considered to be an outlier was above 99%. The outliers must be deleted from the calibration set, which were forbidden to develop the models.

The performance of the model was evaluated according to the following criteria: high determination coefficient ($R^2$), low root mean square error of calibration (RMSEC), low root mean square error of cross-calibration (RMSECV) and low root mean square error of prediction (RMSEP).

$$R^2 = \left(1 - \frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}\right) \times 100 \tag{4}$$

$$\mathrm{RMSEC} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}} \tag{5}$$

$$\mathrm{RMSECV} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_{\backslash i})^2}{n}} \tag{6}$$

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{m} (y_i - \hat{y}_i)^2}{m}} \tag{7}$$

where $y_i$ is the actual value from the chemical analysis for sample $i$, $\hat{y}_i$ the estimated value from the model for sample $i$, $\bar{y}$ the mean of the actual values for calibration samples, $\hat{y}_{\backslash i}$ the estimated value for sample $i$ when the model is constructed with sample $i$ removed, $n$ the number of calibration samples and $m$ the number of prediction samples. The data analysis was accomplished by OPUS/QUANT-2 software (Bruker Co., Germany).

The model validation was executed by using linear regression and paired $t$-test on the prediction set. The linearity was tested by evaluating the slope and the $y$-intercept on the plot of predicted values by NIR versus values obtained with the standard chemical method. A paired $t$-test [20] was computed on the NIR prediction and actual values in order to know whether there was difference between the NIR method and the standard method.

### Quality control analysis

The NIR method was applied in the product line to analyze the quality of the prepreg cloth. With the aid of the OPUS/PROCESS software (Bruker Co., Germany), the diffuse reflectance spectra of the prepreg cloth were collected every 2 min and then were predicted to obtain the values of resin content, volatile content and pre-curing degree simultaneously. Based on the predicted values of the three quality factors, the relevant processing parameters were adjusted so as to control the quality of the prepreg cloth.

## Results and discussion

### Chemical analyses and spectral information

The means, standard deviations and ranges of the prepreg cloth samples for the three quality factors are summarized in Table 1. The results obtained for the calibration samples revealed a broad range of variability, which was important when searching for calibration equations to be used later in the prediction.

The raw spectrum of a prepreg cloth sample is shown in Fig. 2, which may be interpreted by assignment of the bands to overtones and combination of fundamental vibrations involving hydrogenic stretching and deformation modes [21]. The benzene groups gave a first overtone of CH stretching mode at 5922 cm$^{-1}$, a

**Table 1** Summary of the three quality factors of the prepreg cloth

| Quality factor | | Mean (%) | S.D. (%) | Min. (%) | Max. (%) |
|---|---|---|---|---|---|
| Resin content | Calibration set | 33.79 | 1.946 | 30.20 | 38.10 |
| | Prediction set | 33.62 | 1.586 | 30.54 | 36.78 |
| Volatile content | Calibration set | 5.270 | 0.942 | 3.922 | 7.541 |
| | Prediction set | 5.348 | 0.788 | 4.061 | 7.172 |
| Pre-curing degree | Calibration set | 2.131 | 0.543 | 1.198 | 3.218 |
| | Prediction set | 1.992 | 0.370 | 1.307 | 2.820 |

S.D.: standard deviation

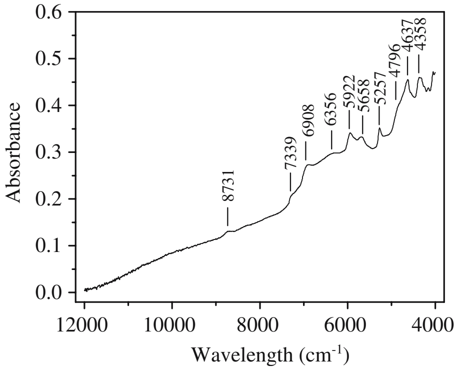

**Fig. 2** Raw spectrum of glass/phenolic resin prepreg cloth

second overtone at 8731 cm$^{-1}$, and a combination band of CH stretching mode and CH deformation mode at 4637 cm$^{-1}$. The methyl and methylene groups gave two combination bands of CH stretching mode and CH deformation mode at 4358 cm$^{-1}$ and 7339 cm$^{-1}$, a first overtone of CH stretching mode at 5658 cm$^{-1}$. The alcohol, phenol and methylol groups gave a combination band of OH stretching mode and OH deformation mode at 4796 cm$^{-1}$. The alcohol gave a first overtone of hydrogen bonding OH stretching mode at 6356 cm$^{-1}$. The water gave a first overtone of OH stretching mode at 6908 cm$^{-1}$ and a combination band of OH stretching mode and OH deformation mode at 5257 cm$^{-1}$.

## Calibration and validation

The purpose of developing models is to be able to predict an unknown sample property from its NIR spectrum as the sole raw data. For this reason the model must be accurate but also as robust as possible, which usually involves compromise. The models for the resin content, the volatile content and the pre-curing degree were calculated on full range spectra respectively. The results of the PLS calculation for resin content, volatile content and pre-curing degree using different spectral pretreatments are summarized in Table 2, 3, 4, respectively.

### *Resin content*

As shown in Table 2, the optimum model for the resin content was built from spectra pretreated with a first derivate followed by vector normalization. This model used 6 factors, achieving a RMSEC of 0.255% and a RMSEP of 0.376%, and two samples were deleted from the calibration set. The plot of the actual values against the NIR predicted values for prediction set is shown in Fig. 3, it has a linear trend line with a slope of 0.950 and an intercept of 1.67. The paired t-test ($\alpha$=0.05) was executed on the NIR prediction and actual values for the prediction set, the result (Table 5) showed that there was no significant difference between the NIR method and the standard method.

### *Volatile content*

From Table 3, it was known that the models using the spectral pretreatments D1+VN and D1+MSC gave the excellent fitting effect, but their prediction ranges were reduced because the sample with the maximum value (7.541%) was deleted from the calibration set as an outlier. The models obtained from the other spectral pretreatments gave the almost similar results except that the model using the spectral pretreatment D2 gave a relative large predicted error. The model with the lowest RMSEP was calculated from spectra pretreated with a first derivative. This model used 7 factors, achieving a RMSEP of 0.169%. Fig. 4 shows linearity between the NIR predicted values and the actual values on the prediction set, the slop of the linear trend line is 0.964 and its intercept is 0.249. From Table 5, it was known that the NIR method and the standard method did not give significantly different results.

### *Pre-curing degree*

From Table 2–4, it was seen that the second derivative gave the bigger prediction errors comparing to the other spectral pretreatments for all the three quality factors. By comparing the results listed in Table 4, it

**Table 2** Results of the PLS calculation for resin content using different spectral pretreatments

| | PLS number | $R^2$ | RMSEC (%) | Outlier number | RMSECV (%) | RMSEP (%) |
|---|---|---|---|---|---|---|
| None | 8 | 97.81 | 0.286 | 0 | 0.600 | 0.444 |
| COE | 8 | 98.06 | 0.266 | 2 | 0.529 | 0.477 |
| SLS | 6 | 97.30 | 0.301 | 1 | 0.567 | 0.481 |
| VN | 6 | 96.99 | 0.336 | 0 | 0.601 | 0.434 |
| M–MN | 7 | 96.60 | 0.357 | 0 | 0.606 | 0.491 |
| MSC | 6 | 96.99 | 0.335 | 0 | 0.601 | 0.434 |
| D1 | 6 | 97.44 | 0.309 | 0 | 0.616 | 0.452 |
| D2 | 6 | 97.71 | 0.293 | 2 | 0.910 | 0.835 |
| D1+SLS | 6 | 97.58 | 0.301 | 0 | 0.609 | 0.460 |
| D1+VN | 6 | 98.29 | 0.255 | 2 | 0.567 | 0.376 |
| D1+MSC | 5 | 97.45 | 0.311 | 1 | 0.626 | 0.384 |

**Table 3** Results of the PLS calculation for volatile content using different spectral pretreatments

| | PLS number | $R^2$ | RMSEC (%) | Outlier number | RMSECV (%) | RMSEP (%) |
|---|---|---|---|---|---|---|
| None | 10 | 99.71 | 0.0506 | 2 | 0.144 | 0.195 |
| COE | 11 | 99.69 | 0.0525 | 1 | 0.160 | 0.199 |
| SLS | 8 | 99.61 | 0.0587 | 2 | 0.156 | 0.205 |
| VN | 9 | 99.64 | 0.0560 | 1 | 0.161 | 0.195 |
| M–MN | 10 | 99.57 | 0.0615 | 1 | 0.172 | 0.212 |
| MSC | 9 | 99.64 | 0.0561 | 1 | 0.161 | 0.195 |
| D1 | 7 | 99.50 | 0.0668 | 1 | 0.156 | 0.169 |
| D2 | 9 | 99.71 | 0.0491 | 2 | 0.298 | 0.311 |
| D1+SLS | 7 | 99.49 | 0.0674 | 1 | 0.158 | 0.175 |
| D1+VN | 9 | 99.85 | 0.0354 | 4 | 0.125 | 0.188 |
| D1+MSC | 9 | 99.85 | 0.0357 | 4 | 0.126 | 0.186 |

**Table 4** Results of the PLS calculation for pre-curing degree using different spectral pretreatments

| | PLS number | $R^2$ | RMSEC (%) | Outlier number | RMSECV (%) | RMSEP (%) |
|---|---|---|---|---|---|---|
| None | 6 | 96.09 | 0.107 | 1 | 0.172 | 0.138 |
| COE | 7 | 96.99 | 0.0940 | 1 | 0.174 | 0.125 |
| SLS | 6 | 97.20 | 0.0907 | 1 | 0.175 | 0.107 |
| VN | 6 | 97.48 | 0.0862 | 1 | 0.165 | 0.111 |
| M–MN | 7 | 97.66 | 0.0829 | 1 | 0.161 | 0.105 |
| MSC | 6 | 97.48 | 0.0861 | 1 | 0.165 | 0.111 |
| D1 | 2 | 90.76 | 0.167 | 5 | 0.183 | 0.175 |
| D2 | 4 | 97.32 | 0.0865 | 5 | 0.189 | 0.255 |
| D1+SLS | 2 | 90.77 | 0.167 | 5 | 0.183 | 0.175 |
| D1+VN | 3 | 95.15 | 0.120 | 2 | 0.178 | 0.146 |
| D1+MSC | 3 | 95.16 | 0.119 | 2 | 0.178 | 0.146 |

was clearly known that the most accurate model for the pre-curing degree was built by using min-max normalization spectral pretreatment. This model had a RMSEC of 0.0829% and a RMSEP of 0.105%. The plot of the NIR predicted values against the actual values for prediction samples is shown in Fig. 5, the slop of the linear trend line is 0.985 and its intercept is 0.068. From Table 5, it was also known that there was no significant difference between the NIR method and the standard method.

NIR is a rapid quantitative analytical method once it has been validated. The above results indicated that the models developed for the resin content, the volatile content and the pre-curing degree were accurate and reliable. It may be deduced that the NIR spectroscopy method is a very good alternative for the determination of resin content, volatile content and pre-curing degree of the prepreg cloth.

## Quality control analysis

In the routine manufacturing process, the quality of the prepreg cloth is controlled by the adjustment of the processing parameters based on the analysis results of

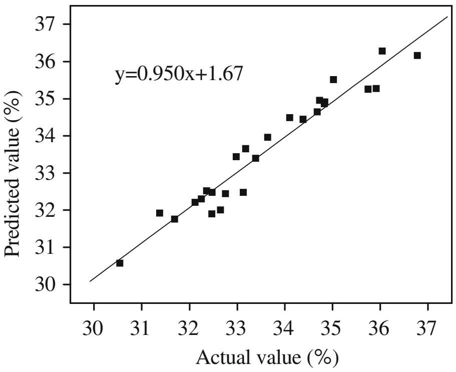

**Fig. 3** NIR predicted values against actual values of resin content for the prediction set

**Table 5** Results of the paired *t*-test on NIR prediction and actual values for the prediction set

| | Resin content | Volatile content | Pre-curing degree |
|---|---|---|---|
| Average difference, % | 0.011 | –0.055 | –0.038 |
| S. D., % | 0.384 | 0.163 | 0.100 |
| $t_{\text{experiment}}$ | 0.152 | 1.711 | 1.944 |
| $t_{\text{critical}}$ | | 2.060 | |

S.D.: standard deviation of the differences

the standard methods. For example, the change of the concentration of phenolic resin solution and the distance of nip rollers are used to control the resin content, and the adjustment of the dry tower temperature can control the volatile content and the pre-curing degree. However, this adjustment is delayed because the excessive time is spent on achieving the analysis results. Therefore, it is difficult to obtain the high quality prepreg cloth, and the waste is often produced. With the rapid analysis nature, NIR can be used on-line for a better understanding of the process.

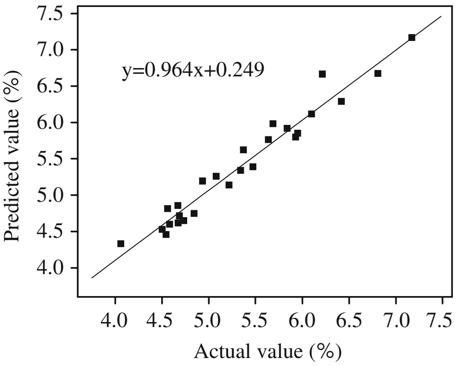

**Fig. 4** NIR predicted values against actual values of volatile content for the prediction set

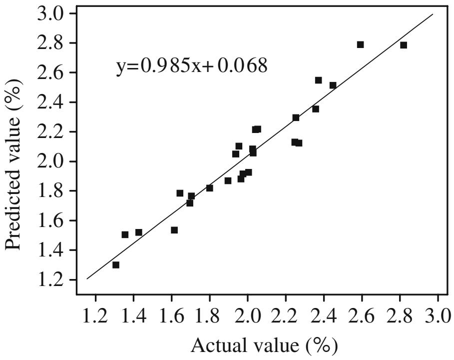

**Fig. 5** NIR predicted values against actual values of pre-curing degree for the prediction set

Fig. 6(a) illustrates the NIR on-line monitoring results of the three quality factors in the manufacture process of the prepreg cloth. It was clearly known that the prepreg cloth with low resin content was produced in a long period due to the delayed analysis results, and the variation range of resin content was rather wide. This result approved that it was almost impossible to produce the high quality of the prepreg cloth without the real-time analysis results as instructions.

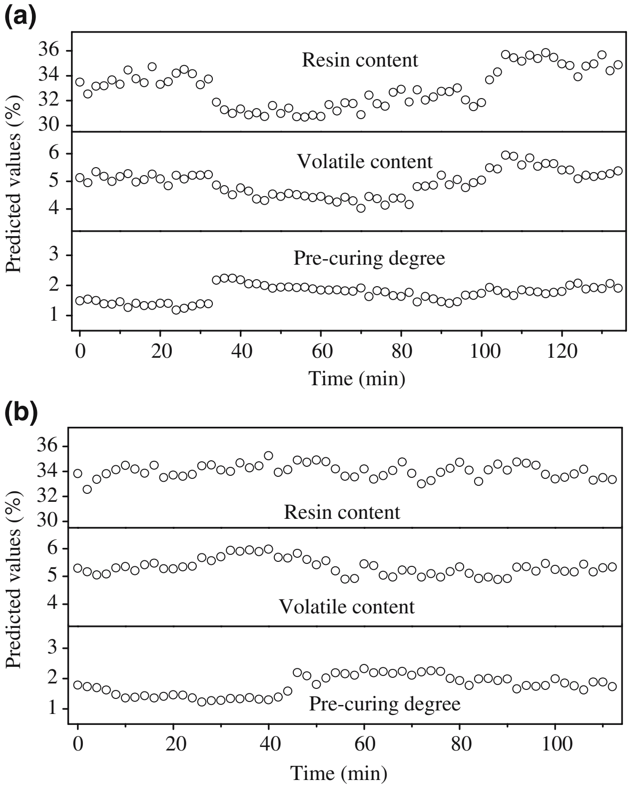

**Fig. 6** Change of the resin content, the volatile content and the pre-curing degree in the manufacture of the prepreg cloth (**a**) standard method as the quality control analysis tool; (**b**) NIR method as the quality control analysis tool

With the NIR monitoring results as the guide of adjusting the processing parameters, the change of the three quality factors was shown in Fig. 6(b). It was obvious that the values of the three quality factors were varied within the relative narrow ranges. It is concluded that the use of NIR method is helpful for the prepreg cloth production, and it can be used as a quality control analysis tool.

## Conclusion

NIR diffuse reflectance spectroscopy has been demonstrated to be a suitable technique for quality control analysis of the glass/phenolic resin prepreg cloth. Our study shows that the NIR method developed is capable of quantifying the resin content, the volatile content and the pre-curing degree of the prepreg cloth to a reasonable accuracy and precision. Therefore this method can be used in the product line to continuously monitor the values of the three quality factors, moreover, these on-line monitoring results is considered to be the reliable instructions for the quality control. With the rapid and non-destructive natures, the NIR spectroscopic method is a perfect substitute of the traditional chemical analysis method as quality control tool.

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