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Research Article

Qianfa Liu, Dan Li*, and Chiji Guan

Analysis of initiator content of prepreg by near-infrared spectroscopy

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Abstract: During the production process of some copper clad laminate (CCL), the content of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane in prepreg can affect the cross-linking and curing degree of resin directly, and thereby affect the properties of CCL. In this article, near-infrared (NIR) spectroscopy combined with partial least square regression using high performance liquid chromatography as a reference method were used for the determination of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane in the CCL production progress. 160 spectra of prepreg samples randomly formed the calibration set, and 50 spectra of prepreg samples formed the validation set. The value of the root mean square error of calibration (w/w) and root mean square error of prediction (w/w) were 0.011% and 0.013% for 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content (%, w/w), and the calculation and validation of the regression equation resulted in high correlation coefficients of 0.99 and 0.98, respectively. The scatter plot value of calibration set which was obtained from the root mean square error of cross-validation (w/w) was 0.015%, and the regression equation resulted in high correlation coefficient of 0.98. The results of the paired t-test revealed that there was no significant difference between NIR and HPLC method. Thus, the results obtained in this study reflect that NIR could be used as a rapid, accurate, and simultaneous technique to determine 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content of prepreg in the production process.

Keywords: copper clad laminate, prepreg, high performance liquid chromatography, near-infrared spectroscopy, partial least square regression

1 Introduction

Nowadays, copper clad laminate (CCL) is widely used for building electrical and electronic components, and play an important role in interconnection, insulation, and support for the printed circuit board (PCB). The quality of CCL has a great impact on the transmission speed, energy loss, and characteristic impedance of the signal in the PCB. Especially, with the rapid development of 5G communications, the requirement for CCL with high thermal stability, low dielectric constant, and dielectric loss are higher and higher [1,2]. Therefore, the process control in the manufacturing process is very important for CCL.

There were two steps in the CCL production process (Figure 1). First, the glass fiber or other reinforced material was impregnated with resin solution, and then placed in an oven in order to make the resins form three-dimensional net and drive away excessive solvent, then form the semi-finished prepreg. Lastly, the prepreg is coated with copper foil on both sides and formed CCL in the hot press control system [3,4].

3,3,5,7,7-Pentamethyl-1,2,4-trioxepane as a peroxide initiator is wildly used in the cross-linking and curing reaction of resins, whose content in the prepreg could affect the cross-linking and curing degree of resin directly, and affect the properties of CCL consequently. So, it was necessary to set up a suitable method to analyze the content of the initiator in the prepreg. If the content of the initiator in the prepreg was known, the resin formula and manufacturing parameters could be adjusted in time during the production process and avoid the wastage of materials and human resources simultaneously.

Many public literatures about the determination of peroxides using high performance liquid chromatography (HPLC) can be found. Caldwell and Perenich used HPLC technique to identify benzoyl peroxide and benzoic acid on exposed nylon carpet samples [5]. A direct and simultaneous HPLC/UV determination of methionine and methionine sulfoxide in enzyme-hydrolyzed milk proteins was described by Baxter and Lai [6]. Rui et al. developed and

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* **Corresponding author: Dan Li,** ShengYi Technology CO., LTD, National Engineering Research Center of Electronic Circuits Base Materials, 523808 Dongguan, Guangdong Province, China, e-mail: lid@syst.com.cn
Qianfa Liu, Chiji Guan: ShengYi Technology CO., LTD, National Engineering Research Center of Electronic Circuits Base Materials, 523808 Dongguan, Guangdong Province, China

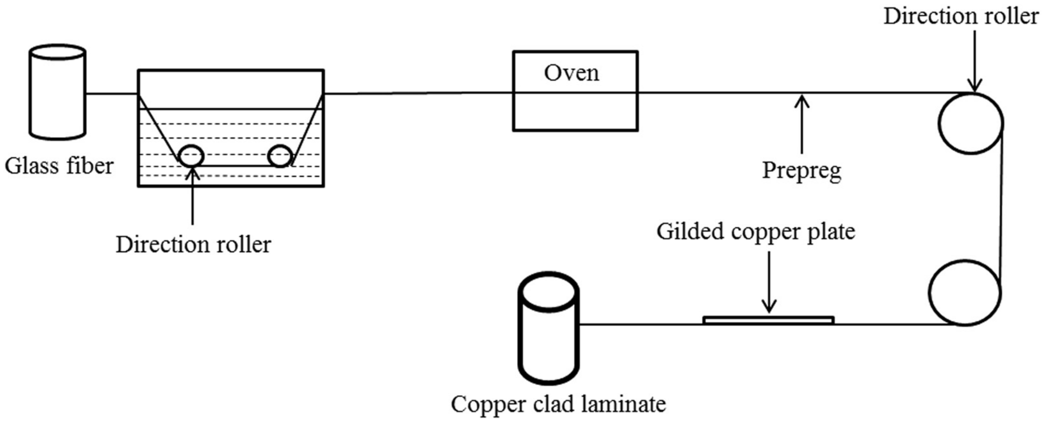

Figure 1: The production process of copper clad laminate (CCL).

validated 4-nitrophenol in aqueous solutions under the typical criteria for in-house pre-validations [7]. Zhang and Huang established a quick HPLC-UV method to detect peracetic acid and hydrogen peroxide in different water matrices [8]. So, we also established a HPLC method to detect the 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content of prepreg.

Nevertheless, necessary pretreatment is time-consuming and not suitable for rapid monitoring in CCL production process. For several years, near infrared (NIR) spectroscopy was commonly used to determine the value of an interest property of samples in a quick, clean, and effective manner for final product quality control during the production process in many research areas. They require multivariate regression models relating the matrix containing the spectral data of the samples with the vector containing the values of the polymer property, obtained using a reference method. After model building and validation, the properties can be monitored in new samples using only their NIR spectra [9–11].

In polymer fields, many literature reports have described NIR spectroscopy associated with HPLC as a reference method to have been used to research properties and components in different types of polymeric materials widely. Rácz et al. detected the quantitative caffeine content in energy drink [12]. Huck et al. established a method to obtain the content of alkaloids caffeine, theobromine and theophylline in roasted coffee [13]. Samira et al. reported the individual and total glucosinolates content of 12 new-bred open-pollinating genotypes of broccoli by using NIR spectroscopy associated with HPLC [14]. The active pharmaceutical ingredient content in escitalopram tablets and routine content uniformity analysis were researched by Solveig et al. [15]. Parika et al. established a non-destructive and reliable analysis method to determinate the b-carotene content in mango [16]. Garrido et al. monitored reactions of epoxy resins by using NIR spectroscopy and HPLC as a reference method [17]. Besides these applications, there were some others related to industry production process with NIR spectroscopy, such as NIR reflectance spectroscopy was evaluated as at-line technique by Marchi et al. to predict fatty acid profile of chicken breast directly at the slaughterhouse [18]. Lin et al. determined grain protein content in barley [19]. Kuda-Malwathumullage Chamathca and Gary used NIR reflectance spectroscopy to determine moisture content of polyamide 66 directly [20]. Guo et al. established the analysis method to determinate proteins in human serum [21]. The determination of ribavirin and moisture in pharmaceuticals was reported by Yang et al. [22]. Zhai et al. determined the SiAH content of hydrogen silicone oil by using NIR reflectance spectroscopy [23]. Lestander and Samuelsson predicted resin and fatty acid content of biorefinery feedstock by using NIR reflectance spectroscopy [24].

In this study, the goal of our work was to establish a time-saving method for quantitative determination of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane of prepreg using NIR spectroscopy. A HPLC method was developed to provide a reference method for the content of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane. This study has not been reported in the literature before.

2 Materials and methods

2.1 Samples and reagents

All the 210 prepreg samples were collected from factory of Shengyi Technology Co., Ltd. 3,3,5,7,7-pentamethyl-1,2,4-trioxepane was purchased from Akzo Nobel N.V. (Netherland).

Ultra-pure water (18.2 MΩ) was obtained from a Milli-Q system from Merck-Millipore (Milford, MA, USA). Acetonitrile were HPLC grade from Sigma–Aldrich (St. Louis, MO, USA).

2.2 Sample preparation

The prepreg is a kind of composition that contains the reinforced glass cloth and cross-linked polymer. First, the cross-linked polymer need to be separated from reinforced glass, then placed the polymer powder (1.00 g, accurate weight) into a 25 mL volumetric flask, treated with acetonitrile, adjusted to the mark, and placed at rest at room temperature for 6 h. Finally, the solution was filtered prior to HPLC.

2.3 HPLC

The HPLC system consisted of an Alliance e2695 pump (Waters Co., Ltd, USA) equipped with an Alliance e2695 sampling system and a 2998 photo diode array (PDA) detector. The system was governed by Empower software (Waters). 3,3,5,7,7-Pentamethyl-1,2,4-trioxepane was separated on a SunFire C18 column (5 µm particle size, 150 cm × 4.6 mm i.d., Waters Co., Ltd, USA). The volumetric flasks of 25 and 100 mL and a pipette of 10 mL were used (all instruments and glass apparatuses were calibrated previously). The wavelength of PDA detector was set at 220 nm in order to exclude influences of impurities in the retention window of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane. The SunFire nonporous stationary phase C18 column (5 µm particle size, 150 cm × 4.6 mm i.d., Waters Co., Ltd, USA) at ambient temperature (25°C), with a mobile phase water: acetonitrile (60:40, v/v) and the flow rate of 1.0 mL·min^{-1} was used. The injection volume for both standard solutions and sample extracts was 50 µL. The analysis time for standard solutions was 20 min, and for sample extract was 50 min. External calibration with peak area integration was used for the determination of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane in the prepreg samples. The points of calibration was as follows: 30, 60, 90, 120, 150, and 180 ppm. The content (%, w/w) of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane of all the 210 prepreg samples were determined by HPLC methods.

2.4 NIRS

All the 210 NIR spectra were scanned with a Fourier-transform near infrared (FT-NIR) spectrometer (Antaris MX, Thermo Fisher Scientific Inc, Waltham, MA, USA) in the range from 4,000 to 10,000 cm^{-1} wavelength with a resolution of 8 cm^{-1} and 32 scans in the diffuse reflection mode for one averaged spectra. The TQ software (Thermo Fisher Scientific Inc, Waltham, MA, USA) were used for data treatment and the establishment of quantitative models [25]. In modeling, all 210 resin powder samples were randomly divided into the calibration set and validation set with a ratio of 3:1, so that 160 samples formed the calibration set, and 50 samples formed the validation set. The samples with the lowest and the highest 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content were assigned to the calibration set.

2.5 Chemometrics data analysis

Chemometrics is a step-by-step methodology aiming to develop a calibration model relating the NIR spectral data to the reference characterization parameters. It involves the actual model development and its validation to guarantee effective predicting capabilities. The multivariate calibration technique uses the entire spectral structures instead of a single spectral data point to provide broader information, and thus detect even minute differences in the sample spectra [26]. Partial least-square regression (PLS) is one of the most commonly used multivariate regression techniques [12]. Usually, the prediction ability of the calibration is assessed by the root mean square error (RMSE) and coefficient of determination (R^2). RMSE is usually labeled as the root mean square error of calibration (RMSEC), root mean square error of prediction (RMSEP), and root mean square error of cross-validation (RMSECV) when applied to model development or final independent validation. All of them should be as low as possible. R^2 yields the percentage of variance present in the component values. Ideally, R^2 should be higher than 95%, but values above 90% are generally acceptable for qualitative studies [27]. Before the construction of the models, the presence of outliers was verified through the analysis of the influence graph (X and Y residual versus leverage). The PLS regression models were built using the mean spectrum of each sample. A number of preprocessing techniques were evaluated, such as Norris derivative smoothing associated with second derivatives [28]. The calibration model should be validated using full cross-validation, and the validation model also should be used to validate the actual prediction ability of the calibration model as an external test set.

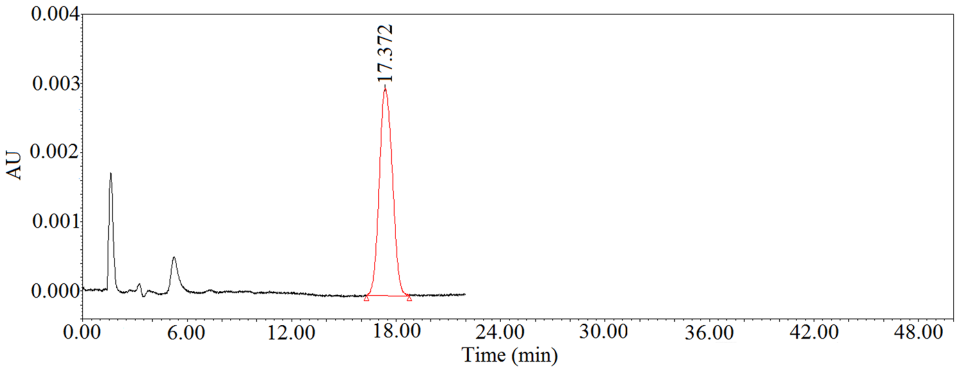

Figure 2: High-performance liquid chromatogram for the 3,3,5,7,7-pentamethy-l-1,2,4-trioxepane standard.

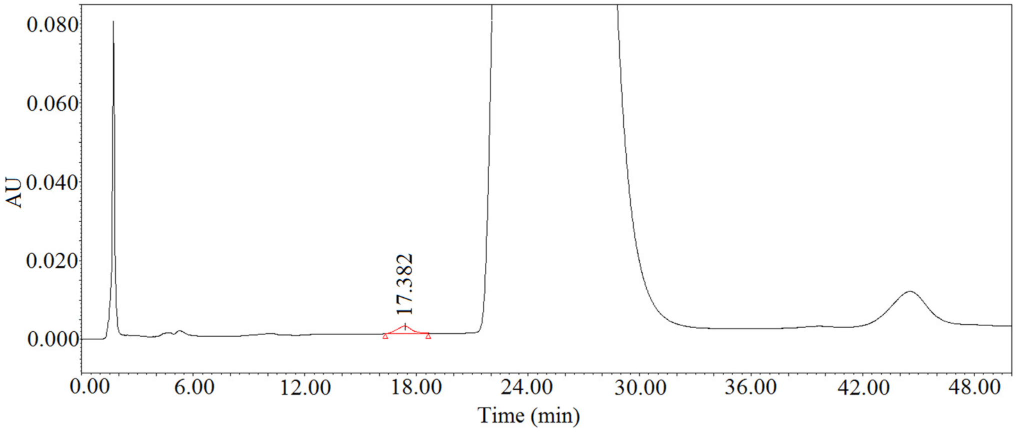

Figure 3: High-performance liquid chromatogram for the representative samples of prepreg.

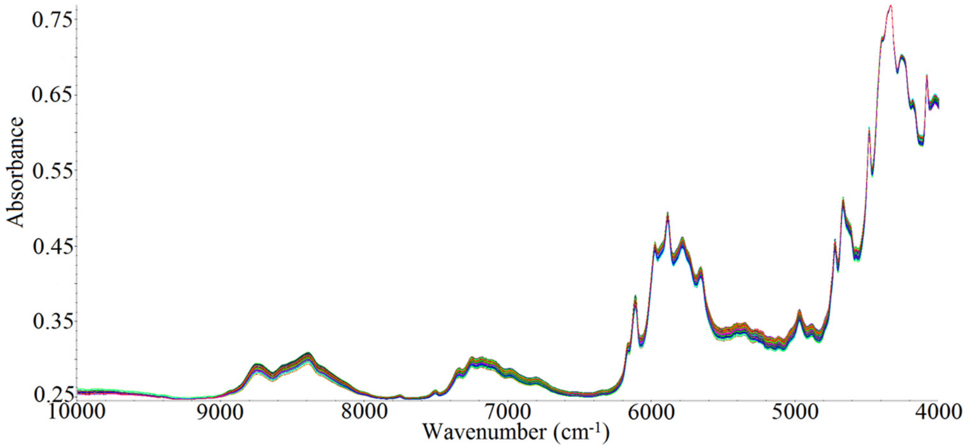

Figure 4: FT-NIR spectra of 210 prepreg samples.

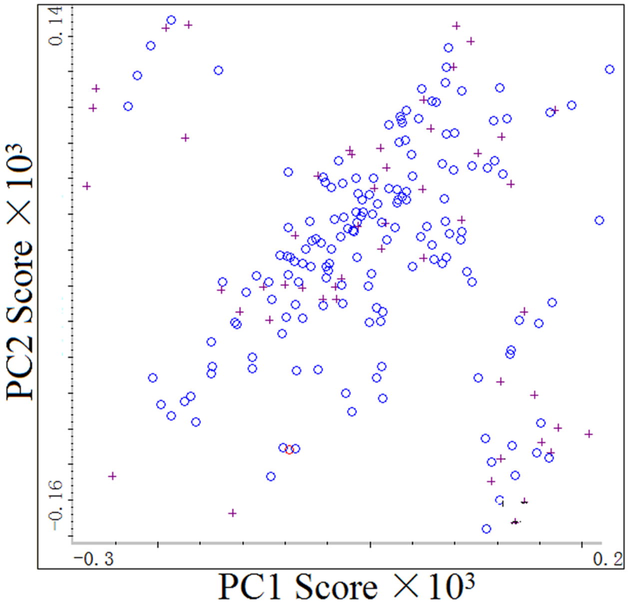

Figure 5: Scatter plot of the first two principal components of the prepreg samples. The blue circle and the red plus represented the calibration set and validation set, respectively.

3 Results

3.1 Determination of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane by HPLC

The HPLC chromatograms of the standard and representative prepreg samples are shown in Figures 2 and 3. The six-point calibration curves of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane were obtained by linear regression analysis and revealed high linearity with a correlation coefficient equal to 0.9999, which indicates that the reverse phase-C18 column facilitated accurate measurement of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane. The limit of detection and quantification of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane using the method were 20.10 and 50.25 ppm determined by the signal-to-noise (S/N) approach, defined at those levels resulting in S/N ratios of 3 and 10, respectively. The intra-day and the inter-day precision of the method were evaluated by analyzing 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content (%, w/w) of the same prepreg sample 6 times on the same day and on 6 different days, respectively. The inter-day relative standard deviation (RSD) value was 0.080%, and the intra-day precision RSD was 0.083%. Finally, the spiking of the prepreg samples with a standard allowed the determination of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane with 96.89% recovery. The content (%, w/w) of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane of all the 210 prepreg samples were calculated from the area under the chromatographic peak using a linear calibration curve with the range of concentration between 30 and 180 ppm.

3.2 NIRS

All the 210 prepreg samples were previously scanned by the diffuse reflection accessory and spectra were recorded in the range from 4,000 to 10,000 cm^{-1} with a resolution of 8 cm^{-1} and 32 scans per sample and displayed in terms of absorbance. 160 spectra of prepreg samples formed the calibration set, and 50 spectra of prepreg samples formed

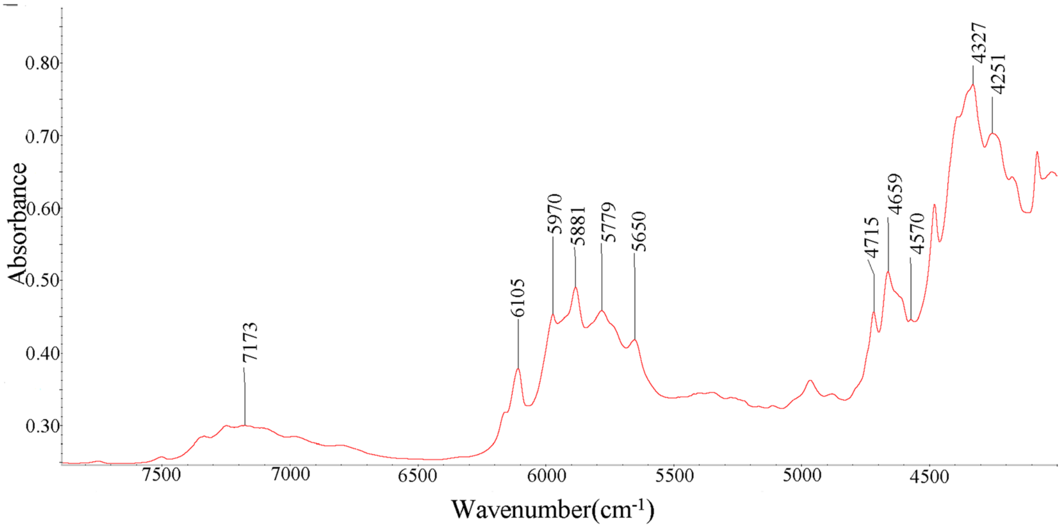

Figure 6: NIR spectra of the prepreg sample.

Table 1: Summary of NIR calibration model statistics

Data format	Pre-processing				Calibration		Validation		RMSECV (%)	R^2cv
	Savitzky–Golay filter Norris derivative filter				RMSEC (%)	R^2C	RMSEP (%)	R^2p		
	Data points	Polynomial order	Segment length	Gap between segments						
Spectrum	No smoothing				0.0133	0.9847	0.0170	0.9575	0.0175	0.9733
1st Derivative	No smoothing				0.0126	0.9861	0.0150	0.9677	0.0177	0.9728
2nd Derivative	No smoothing				0.0132	0.9848	0.0283	0.8773	0.0365	0.8936
1st Derivative	5	5	–	–	0.0126	0.9863	0.0152	0.9656	0.0182	0.9711
1st Derivative	–	–	5	5	0.0122	0.9871	0.0158	0.9634	0.0154	0.9794
2nd Derivative	5	5	–	–	0.0116	0.9883	0.0294	0.8678	0.0402	0.8668
2nd Derivative	–	–	5	5	0.0109	0.9896	0.0129	0.9756	0.0146	0.9815

the validation set randomly. The spectrum of all the samples are displayed in Figure 4. However, all the spectrum were similar both in band location and intensity. In order to research the variability of spectral, all the samples were evaluated by principal component analysis. The score plot of the first two principal components space corresponding to calibration and validation samples are displayed in Figure 5, the first and second component accounted for 47.2% and 23.7% of the raw spectral data, respectively. Totally, the first two components represented 70.9%. The PCA plot reveals that all the samples distributed equably in the calibration and validation set. So, the division of the samples was appropriate for NIR analysis.

4 Discussion

A calibration model was established by applying PLS regression using all the 210 FT-NIR spectral data and 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content (%, w/w) using HPLC method. The raw spectra usually contained baseline drift and noise, and in order to extract the useful information, different mathematical pretreatments were used for quantitative analysis through eliminating baseline shifts, resolving overlapping peaks, and reducing variability between replicates. The calibration's prediction ability was determined by the RMSEs and the correlation coefficient of the model. A model with higher correlation coefficient and lower RMSEs of calibration and prediction was optimal. If the RMSEC and RMSEP

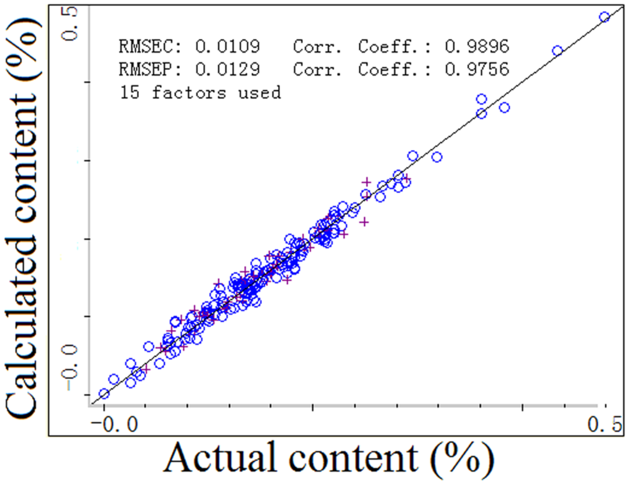

Figure 7: Predicted content versus actual content. The blue circle and the red plus represented the calibration set and validation set, respectively.

were smaller, the predictive ability of the mode was higher. The RMSEC must be smaller than the RMSEP in the same model, but there should be no significant differences between the two values [29].

In order to select the optimal wavelength range for the PLS model, simplify the model, and dispose of irrelevant or nonlinear variables, several targeted wavelength ranges should be carefully examined for the calibration of the model performance [30]. Figure 6 displays the NIR spectra obtained from the prepreg. Wide absorption at 7,173 cm^{-1} is attributed to the combination of $-CH_2-$ stretching and $-CH_2-$ deformation ($2 \times 2{,}860\ cm^{-1} + 1{,}460\ cm^{-1}$), the bands observed at 6,105 cm^{-1} is ascribed to the 1st overtone of terminal $-CH{=}CH_2$ stretching ($2 \times 3{,}053$), the bands detected at 5,970–5,650 cm^{-1} are due to aliphatic C–H stretching ($2 \times 2{,}985$, $2 \times 2{,}940$, $2 \times 2{,}889$, and $2 \times 2{,}825$), 4,715 cm^{-1} is ascribed to terminal $-CH{=}CH_2$, 4,659 cm^{-1} is due to the combination of benzene ring and *cis*-RCH=CHR, 4,570 cm^{-1} is due to the combination of $-CH_2$ asymmetry stretching and C=C stretching, 4,327 cm^{-1} is attributed to the combination of C–H stretching and C–H deforming, and 4,251 cm^{-1} is due to $-CH_2$ symmetry stretching and $=CH_2$ deforming [31,32]. The wavelength range from 4,200 to 7,500 cm^{-1} including important absorption bands was selected to be the optimum region for subsequent measures.

Table 1 summarizes the results achieved for seven different pre-processing approaches applied to the raw calibration spectra of prepreg samples in the same range of 4,200–7,500 cm^{-1}. Figure 7 shows the optimum model with the highest correlation coefficient and lowest RMSEC. The most suitable pre-processing methods for the 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content (%, w/w) were second derivative (Norris derivative) with five segment length and five gap size between segments. From Table 1, we can see that the other data pretreatments, e.g., calculation of the first derivative, resulted in worse statistical parameters compared to second derivative spectra. The robustness of the NIRS model was high, which was demonstrated in the similarity of the results for RMSEC and RMSEP, which were 0.011 and 0.013, for 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content, and the high correlation coefficient of calculation and validation are 0.99 and 0.98, respectively. Figure 8 shows the result of full cross-validation. The RMSECV was 0.015, and the high correlation coefficient was 0.98. So, the HPLC results agreed with NIRS on average.

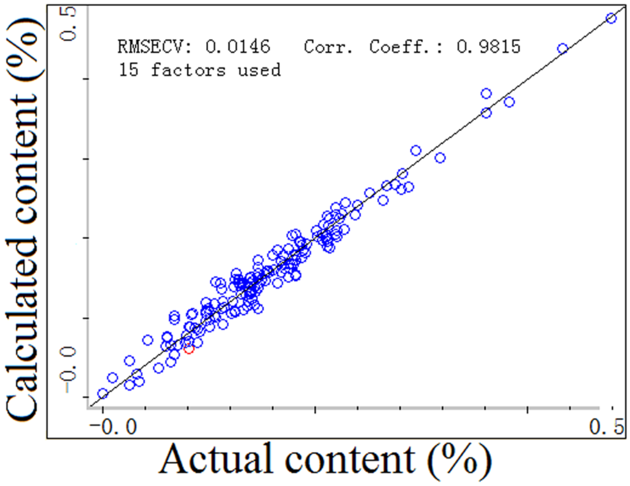

Figure 8: The results of full cross-validation.

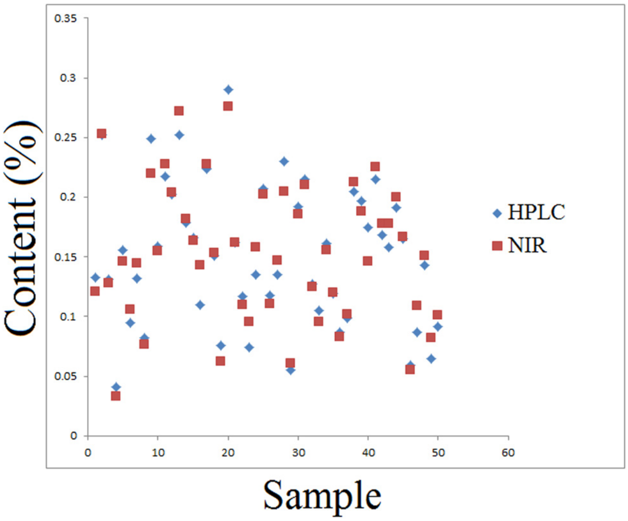

Figure 9: The reliability evaluation of NIR method versus HPLC method was used to calculate the student's *t*-test ($\alpha = 0.05$) for paired values.

Validation results showed that the robustness and reproducibility of the NIRS model for the determination of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane were high: the 50 external validation set samples were analyzed by the HPLC method. The statistical analysis paired *t*-test ($\alpha = 0.05$) was used to compare NIR and HPLC method. Figure 9 shows the reliability evaluation of NIR versus HPLC method, there was no obvious difference between the two methods (p-value > 0.05). The results clearly demonstrate that the model can be used to predict the content (%, w/w) of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane of prepreg in the production process.

5 Conclusion

In this study, NIRS associated with PLS was employed for the rapid, accurate, and simultaneous determination of

3,3,5,7,7-pentamethyl-1,2,4-trioxepane content of prepreg in the production process of CCL. The results demonstrated that NIR was a very powerful measurement technique which was stable, reliable, and suitable for the rapid determination of 3,3,5,7,7-pentamethyl-1,2,4-trioxepane content used in the quality control and quality assurance of CCL industry. Even though cost for the equipment was high and calibration process needed a lot of time, NIRS has the great advantages of reducing time and costs especially in combination with the HPLC method using nonporous C18 as a stationary phase. The total time for analysis was not more than 2 min for one sample, compared to over 50 min for the reference HPLC method. Because of the short analysis time of 2 min by NIR compared to 50 min by HPLC, a high production efficiency was guaranteed, and the prepreg quality could be controlled by adjusting the oven temperature and residence time in the oven.

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Author contributions: Qianfa Liu: writing – original draft and resources; Dan Li: correcting – original draft and project administration; Chiji Guan: methodology and formal analysis.

Conflict of interest: Authors state no conflict of interest.

Data availability statement: All data generated or analyzed during this study are included in this article.

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