

Use of Near-Infrared Spectroscopy for Online Quality Analysis of Armos Fiber/Prepreg Tape

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Received 7 April 2010; accepted 11 October 2011

DOI 10.1002/app.36358

Published online 27 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Near-infrared spectroscopy (NIR) was applied in manufacture of the Armos fiber/prepreg tape. The reinforced material, resin matrix, and prepreg were analyzed by NIR spectroscopy, the qualitative and quantitative method. The volatile content and resin content of the calibration models were developed by partial least squares. The analytical result showed that, it was a rapid,

nondestructive, and noncontact method for the simultaneous measurement of prepreg quality. This method enhanced the quality of prepreg. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2485–2488, 2012

Key words: prepreg; resin; NIR spectroscopy; fiber

INTRODUCTION

Near-infrared (NIR) spectroscopy is a very rapid, accurate, and nondestructive method for the simultaneous measurement on different constituents in various products. Nowadays, NIR spectroscopy has been applied in many fields such as the agriculture,¹ environment,² petrochemical,³ pharmaceuticals,⁴ food industry,⁵ and in the manufacture of certain polymers.⁶

A prepreg consists of a fiber reinforcement in unidirectional (aligned) or fabric (woven or multiaxial) 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. Therefore, study of prepreg quality was important. The volatile content and resin content are the important indexes of the Armos fiber/prepreg tape.

The classical methods are usually time-consuming, use large amounts of reagents, and produce waste. In fact, analysis times can range from a few minutes to several hours. This lengthens production cycles, raises costs, and lowers outputs.

Updating production processes entails improving their efficiency and productivity. This can be accomplished by using fast analytical techniques enabling effective, complete analytical control of the processes concerned. The instrumental analytical techniques are most frequently used to identify and characterize prepreg,^{7–9} which include gamma and beta ray,¹⁰ ultrasonic,¹¹ dynamic mechanical analysis,¹² differential scanning calorimeter,¹³ infrared, and photoacoustic spectroscopy.¹⁴

It has been developed for analyzing the volatile content, resin content, and precure degree of the prepreg. However, these methods measured one or two quality indexes of prepreg. The void content and the aging of prepreg have been studied.^{15–17} In previous work, NIR spectroscopy was applied in the glass and carbon cloth/prepreg.^{18,19} The aim of this study is to apply NIR spectroscopy technology in manufacture of the Armos fiber/prepreg tape. Since the Armos fiber/prepreg tape, glass, and carbon cloth/prepreg are different in raw materials and manufacture, the analytical methods are different for the Armos fiber/prepreg tape, glass, and carbon cloth/prepreg.

Additional Supporting Information may be found in the online version of this article.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50903025.

Contract grant sponsor: Research Fund for the Doctoral Program of Higher Education of China; contract grant number: 20092302120032.

Contract grant sponsor: KOTO innovation foundation.

Journal of Applied Polymer Science, Vol. 125, 2485–2488 (2012)
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EXPERIMENTAL

The manufacture of prepreg tape was given in Figure 1. The Armos fibers were pulled into the resin solution; it went through the press rollers to meter the fibers to solution ratio. The impregnated fibers then went into the oven where the excessive solvent was driven off. After the impregnated fibers were fed through the oriented rollers, it was wrapped around the take up mechanism.

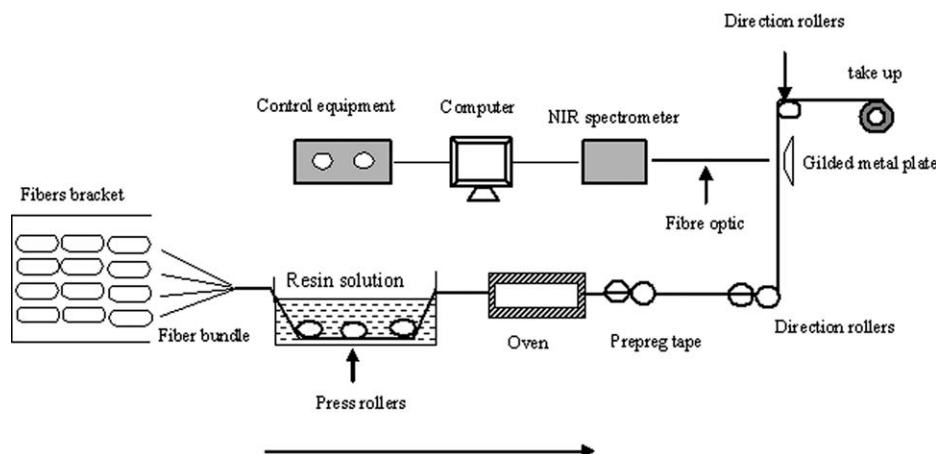


Figure 1 Schematic of quality analysis of prepreg tape in manufacture.

Online analysis equipment included NIR spectrometer (Bruker MATRIX-F, Equipment photo in Supporting Information) with fiber optic probes, whose diameter was 6 mm, gilded metal plate, spectrometer bracket, and computer.

The light from the sources NIR spectroscopy was focused on prepreg tape, from 12,000 to 4000 cm^{-1} . The resolution of the spectra was 16 cm^{-1} and the average scanning times was 8. The partial least squares (PLS) were used to develop the calibration models. Full cross-validation was applied to optimize the calibration models. Before starting the calibration, one sample was excluded from the entity of samples, which was used for the prediction. The determination coefficient (R^2) and root mean square error of calibration (RMSEC) were calculated to evaluate the calibration models.

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

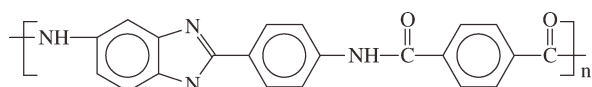
$$\text{RMSEC} = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}} \quad (2)$$

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, and n is the number of calibration samples.

RESULTS AND DISCUSSION

NIR information of the prepreg tape

The chemical formula of armos fibers components was shown below:



NIR spectra of armos fiber and prepreg tape were shown in Figure 2, which may be interpreted by assignment of the bands to overtones and combination of fundamental vibrations involving hydrogenic stretching and deformation modes. In NIR spectrum of armos fiber, the combination band of CH stretching mode was occurred at 4320 cm^{-1} , while the CONH group was located at 4661 cm^{-1} , and the first overtone of CO stretching was formed at 5230 cm^{-1} . On the other hand, the combination band of NH stretching mode and the first overtone of NH stretching mode were occurred at 5110 cm^{-1} and 6723 cm^{-1} , respectively. A first overtone of CH stretching mode given was located at 5997 cm^{-1} .

Figure 2 show that the NIR spectra between the prepreg tape and Armos fiber are similar, while epoxy resin solution was used in the Armos fiber prepreg. In NIR spectrum of the prepreg tape, the epoxy groups was at 4520 cm^{-1} , the absorb band was strengthened at 5230 cm^{-1} . The analytical spectral information mentioned above can provide the

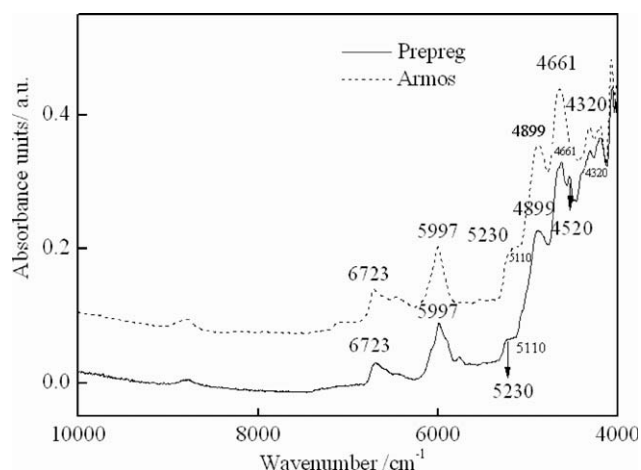




Figure 2 NIR diffuse reflectance spectra of the Armos/prepreg tape.

TABLE I
Band Assignments for Chemical Groups from NIR Absorption Spectra of the Armos Fiber and Prepreg

| Absorption band | Observes wavenumber (cm ⁻¹) | |
|--|---|---------------------------------------|
| | Armos fiber | Prepreg |
| —CO— | 5230 ^a | 5230 ^a |
| —NH— | 5110 ^b , 6723 ^a | 5110 ^b , 6723 ^a |
| —CONH— | 4661 ^b | 4661 ^b |
|  Epoxy groups | | 4520 ^b |
| Aromatic C—H | 4320 ^b , 5997 ^a | 4320 ^b , 5997 ^a |

^a Overtone band.

^b Combination band.

 Epoxy groups.

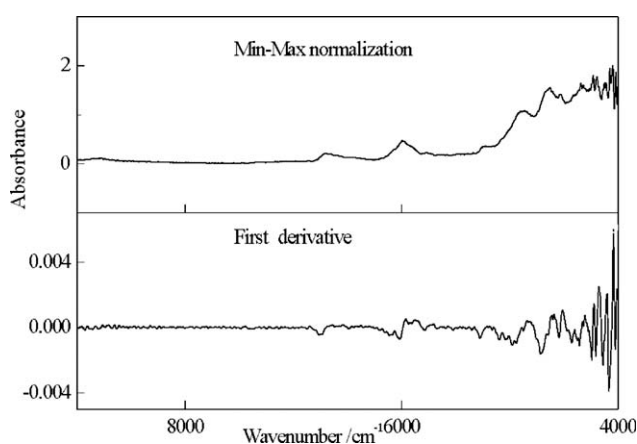


Figure 3 NIR diffuse reflectance spectral of the min-max normalization and first derivative pretreatments.

essential theoretical bases to help developing the models. The values of the absorption bands were shown in Table I.

NIR analyzed the prepreg tape

To eliminate variations in offset of samples and to ensure a good correlation between the spectral data and the concentration values, the min-max normalization and first derivative pretreatments were employed and presented in Figure 3.

About 74 samples were developed the calibrations models by PLS. The volatile was acetone and some small molecules, resin matrix included epoxy resin, curing agent, and accelerating agent. The spectral regions of developing model were 6800–4070 cm⁻¹

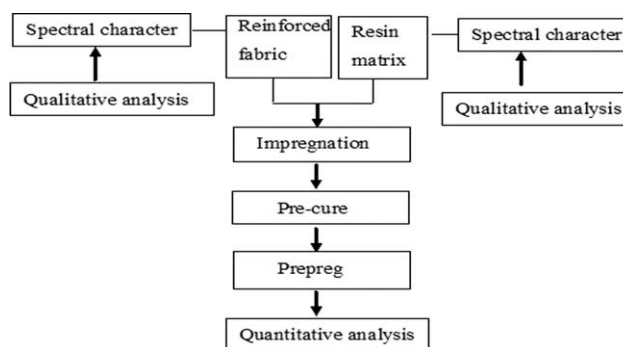


Figure 4 NIR Spectroscopy analyzed the quality of the prepreg tape in manufacture.

for the volatile content, which is included the information of prepreg. The calibrations models ranged from 0.62 to 3.52%, used the vector normalization preprocessing method and 8 PLS factors. R^2 and RMSEC of the evaluative indexes of models were 0.86 and 0.26, respectively. The parameters of the developing resin content models were shown in Table II also.

As it is observed from our study, RMSEC of resin content model was bigger. The resin content was analyzed by weight in the reference method. On the other hand, traditional analysis of resin contents was burn-off. The heat-resistant temperature of the Armos fibers was lower; thus the burn-off method has not been used for the Armos fibers prepreg. The weight of the Armos fibers was mean value in analytical process of prepreg. Hence, the veracity of resin content model was lower than volatile content model.

Above developing models of the resin content and volatile content were applied in manufacture of prepreg tape. Based on the NIR analysis, the prepreg tape quality could be controlled properly by adjusting of the processing parameters. The change of the concentration of epoxy resin solution and the distance of nip rollers could be used to control the resin content, while an increase or decrease of the concentration of solvent, temperature of oven, and the production speed could control the volatile content. Therefore, high quality prepreg was obtained and, at the same time, raw materials were saved.

Figure 4 shows the procedure of NIR spectroscopy in manufacture to evaluate the of prepreg tape

TABLE II
Statistical Results of Volatile and Resin Contents Models

| Quality indexes | Range | Mean | Preprocessing routines | Spectral range (cm ⁻¹) | PLS factors | R^2 | RMSEC |
|------------------|--------------|--------|------------------------|------------------------------------|-------------|-------|-------|
| Volatile content | 0.62–3.52% | 2.30% | Vector normalization | 6880–4070 | 8 | 0.86 | 0.26 |
| Resin content | 30.89–35.88% | 33.46% | First derivative | 6820–5720 5373–4351 | 3 | 0.72 | 1.13 |

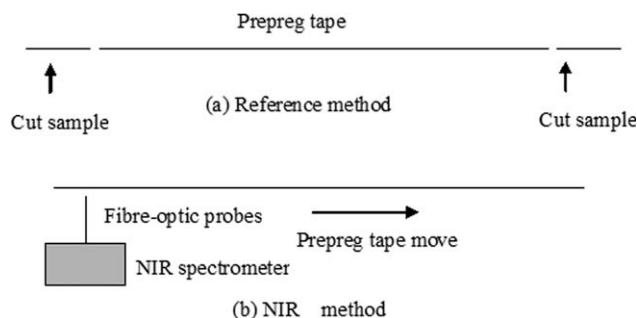


Figure 5 The comparison between NIR spectroscopy and reference method in prepreg tape.

quality. As it is seen from the Figure 4, the reinforced material, resin matrix, and prepreg were analyzed by NIR spectroscopy. Figure 5 showed the contrast between NIR spectroscopy and reference method in prepreg tape. To save the material and enhance the productivity, prepreg tape was cut from beginning and end by reference method, which destructively and interruptedly analyzed the quality of prepreg tape. The quality analysis of prepreg tape spends about 60 min by reference method. This method used the excessive solution and high temperature at oven; it expends the energy and contaminates the environment. NIR spectroscopy is a rapid and nondestructive method, it analyzes the quality of prepreg tape about 2 min. This method is green and clean.

CONCLUSION

The different NIR equipment analyzed the quality of prepreg tape. NIR spectra with PLS method were used for the calibration models of the volatile content and resin content. Based on the NIR analysis, the prepreg tape quality could be controlled properly by adjusting of the processing parameters. The

quality prepreg was enhanced; at the same time, raw materials were saved by NIR spectra. The analysis techniques introduced in this study showed that NIR spectroscopy is a rapid, nondestructive, and noncontact method for the simultaneous measurement of prepreg quality in manufacture. Study of this method can give a new direction on the quality analysis of prepreg.

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