EFFECTS OF CURE PRESSURE ON VOID CONTENT AND ULTRASONIC ATTENUATION COEFFICIENT OF CARBON FIBRE REINFORCED COMPOSITE

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1 Introduction
The manufacture procedure of carbon fibre reinforced composites has decisive effects on the quality of the end product[1-4]. Cure pressure is considered as a key factor to influence the formation and growth of voids, to which the ultrasonic attenuation of composite laminates is quite sensitive. Numerous works have been undertaken on describing the relevance between cure pressure and voids in composite laminates[5-9]. A systematic research that established a pressure-temperature-humidity stability map was conducted by Kardos et al.[5], in order to identify conditions for void growth or dissolution. Many authors found an exponentially decrease of void content in the ordinary laminates along with the increase of cure pressure[6-8]. Jong et al.[9] suggested an increase of the void content in the early stage of the pressure increasing in carbon/phenolic laminates, which resulted from the gas products generated during the cure reaction. However, there have not been such studies on carbon/benzoxazine(BBZ) laminates. On one hand, the cure reaction of benzoxazine does not generate gas products, which is similar to the ordinary resin. On the other hand, benzoxazine was synthesized by phenols and formaldehyde, which is similar to phenolic resin. Many experimental methods have been taken by researchers in consideration of the relationship between the void and ultrasonic attenuation[3][10-14]. Almeida et al.[3] presented a fracture criterion correlating the ultrasonic attenuation to the strength of composite laminates, which aimed at determining the maximum allowable ultrasonic attenuation of a composite laminate for a specific loading condition. An easily operable and potentially useful method which was developed by Stone and Clarke[10], built a bi-linear relationship to describe the variation of attenuation with void content. Efforts were also taken by several authors to establish acceptance levels for the attenuation level in the ultrasonic inspection of composite laminates[11-12]. Further, an ultrasonic spectroscopic method was applied to broadband through transmission measurements in composites with voids by Jeong et al.[13] [14]. Nevertheless, it requires a large number of tests for the complete and reliable data from any experimental method and the result varies widely according to the composite system. Void features, such as size, shape and distribution, also have significant impact on the ultrasonic attenuation of laminates. Several authors agreed on a major range in size from 0.01mm to 1mm [4][15-16]. On the other hand, there have been several different opinions about the void distribution. Chambers et al. [15] suggested that the percentage of voids present for a certain aspect ratio range remain relatively constant and are independent of the total void content. David et al. [17] found a Gaussian distribution through plotting the percentage of voids against the natural logarithm of void length. Hernandez et al. [18] identified a void concentration in sections which were distributed periodically along the laminate width. Yet none of them has developed a comprehensive principle to describe the void distribution well.
By means of changing cure pressure, laminates with various void contents were fabricated by T300/BBZ prepreg. The chemical composition that may generated gas products was characterized by infrared spectroscopy (IR) and gas chromatograph - mass spectrometer (GCMS). Meanwhile, the influence of cure pressure on void size, shape and content of T300/BBZ composites were investigated as well as on the ultrasonic attenuation coefficient. Finally, plots of void content and ultrasonic attenuation coefficient of T300/BBZ laminates as exponential functions of the cure pressure were built.
2 Experimental procedure

2.1 Fabrication of the specimens

The material used in this study was a T300/BBZ prepreg purchased from Hexcel. Laminates with different porosity levels were produced through curing pressure varying [1][7]. Square (350×200 mm2) panels following the quasi-isotropic stacking sequence and 1.5 mm nominal thickness were manufactured by autoclave processing. The cure temperature was raised up to 185°C and kept for three hours; all the heating and cooling ramps were carried out at the same rate of 2.5°C/min. Laminates with intentionally different void levels were produced through the procedure during which the autoclave pressure was set as 0.1, 0.2, 0.3, 0.4 and 0.5 MPa. The pressure inside the vacuum bag was kept 0 MPa throughout the entire cycle.

2.2 FT-IR analysis

Spectral acquisition was performed on solid samples using a FT-IR spectrometer (A Nicolet 6700 from Thermo Nicolet Corp.). The spectra were recorded in the 650–4000 cm\(^{-1}\) region by a computerized system attached to a monitor and a printer.

![Figure 1. Temperature and pressure cue cycle used to process T300/BBZ composite prepreg](image)

2.3 GCMS analysis

GCMS analysis was performed on a Shimadzu 2010plus GC-MS. BBZ resin was separated from prepreg as the test sample. Chemical components of resin were separated by gas chromatograph in the mixed sample by column. The sample was evaporated in an injector heated at about 200 to 300°C, and then separated into each component during moving. These ions were separated according to their m/z value by a mass analyzer. An electron multiplier was also used as a detector on a mass spectrometer. The peaks of target compounds in

![Figure 2. The IR spectrum of T300/BBZ composite prepreg](image)
sample were identified by comparing the retention times of target peaks between standard sample and test sample. The GCMS spectrum of BBZ resin in prepreg was shown in Fig. 3.

<table>
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<th>R.Time</th>
<th>I.Time</th>
<th>F.Time</th>
<th>Area%</th>
<th>Height%</th>
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</tr>
</tbody>
</table>

|   | 100.00 | 100.00 |

Fig. 3. The GCMS spectrum of T300/BBZ composite prepreg

### 2.4 C-scan ultrasonic inspection

The ultrasonic attenuation coefficient was measured by ultrasonic echo immersion bottom reflection technique. The laminates were placed above a glass plane which enhanced the testing sensitivity and separated the ultrasonic back echoes. A flat immersion probe was transported by GE-USIP40 ultrasonic flaw detector. It generated a c-scan signal record of the plate with the frequency of 5MHz. Then quantized maps were drawn to represent different attenuation levels of the laminates.

Ultrasonic attenuation coefficient of the composite panels at each point on the quantized map was calculated by the equation below.

$$\alpha = \frac{n - m + 10 \log \frac{80}{2d}}{x} \quad (1)$$

In the equation, $\alpha$ (dB/mm) is the ultrasonic attenuation coefficient of the picked point, $d$ (mm) is the thickness of the plate, $n$ (dB) and $m$ (dB) are the signal gains when there is a sample and otherwise,
and $x$ is the extracted amplitude value. The average value of the ultrasonic attenuation coefficients in the selected area stands for the ultrasonic attenuation coefficient of the sample.

![Diagram](image)

(a) Abridged general view of detection

(b) Picture of detection procedure

Fig. 4. Pictures of ultrasonic echo immersion bottom reflection technique detecting the T300/BBZ laminates

### 2.5 Void content measurement

After c-scan inspection, the center of each laminate was cut off as specimens to evaluate the void content. The void content was measured by matrix digestion in a crucible according to the ASTM D2734-09 and D2584-11 standard tests. The sections of some specimens were also polished to achieve a high quality surface and pictured for a better assessment of void distribution and shape. The images were all captured and saved by VHX-900 optical microscope.

### 2.6 DSC test

Different resin contents were observed in different location of one piece of prepreg tape, as the impregnation of fibers was inhomogeneous. The middle area of prepreg was considered uniform and chosen to be the sample-selected area. The sample of DSC test was T300/BBZ prepreg cutting into square pieces of 1mm×1mm. The DSC test was performed from 25 °C to 300 °C at the rate of 10 °C/min on a differential scanning calorimeter (Mettler Toledo DSC-1). The rate of heat generation was plotted versus temperature as shown in Fig.7.

![Diagram](image)

Fig. 5. The process of void feature assessment of T300/BBZ composite laminates

### 3 Results and discussion

#### 3.1 Compound characterizations

As mentioned, there are two variation trends between cure pressure and voids in composite laminates. This depends on the existence of compounds that may generate gas products when curing. BBZ resin is a kind of modified phenolic resin synthetized by phenols and formaldehyde, the remaining of which can generate water and result in the formation of voids. FT-IR was chosen to qualitatively detect the existence of hydroxyl in
T300/BBZ prepreg. For further conformation, GCMS analysis was performed to give a list of compounds that consisted of the prepreg. It was obvious that hydroxyl was little in the prepreg as there was no peak in the range of 3650-3200 cm\(^{-1}\) in Fig. 2. However the aldehyde group was proved in the sample from the IR spectrum. It could be confirmed initially that the BBZ resin was high pure material with little raw materials remained. GCMS analysis in Fig. 3 showed that benzamide was the major compounds of BBZ resin, and phenols and formaldehyde did not remain in the sample. Therefore, the conclusion could be drawn that there was no such gas products as the carbon/phenolic laminates, and the relationship between cure pressure and void content in the T300/BBZ composite laminates was exponentially decreasing with the increase of cure pressure.

### 3.2 Effects of cure pressure on void content

Fig. 6 shows that the cure pressure has a significant influence on the size, shape and amount of voids. The void content varies from 0.6% to 1.4% owing to the cure pressure change. It is clear that resin-rich regions between the layers have a larger thickness when decreasing the curing pressure, which leads to a higher void amount and a greater void size and void aspect ratio.

![Fig. 6 Micrographs of laminates conditioned under different cure pressures](image)

The void formation and transportation can be explained through Fig. 6. Void formation may occur during the compaction before the curing. When the temperature rose up to 185 °C, the cure reaction became drastic and the trapped void cannot be released from the plies. Void dissolution might occur if the changes in temperature and pressure caused an increase in solubility in the resin[5]. The void content of each type of laminate is plotted against cure pressure in Fig. 8. It shows an exponential relationship between the void content and cure pressure. Therefore, an applied autoclave pressure is needed to accommodate the manufacture process by reducing the void content down to a certain level, which depends on the accuracy requirement of laminate quality[1][20]. So, an appropriate curing pressure can be determined according to the Fig. 8 when the other process parameters of cure cycle remain unchanged.
3.3 Effects of cure pressure on ultrasonic attenuation

The distinctions between laminates on different porosity levels could also be revealed by ultrasonic C-scanning as Fig. 9 shown. The acquirement of ultrasonic attenuation coefficient is normally started with the extraction of echo amplitude data from the central area of the examined composite, where we polish and observe through the optical microscope later. A laminate cured on larger pressure has a more regular distribution of colors owing to more types of void shape, size and location. Thus the relationship between the attenuation and the porosity could be fitted as the following Fig. 10, which is the same as the predicted after FT-IR and GC/MS analysis.

Fig. 7. Heat of reaction as a function of temperature

Fig. 8 Measured void contents as a function of cure pressures

Fig. 9 C-scan of laminates with different cure pressure

Fig. 10 Measured ultrasonic attenuation coefficients as a function of cure pressures

5 Conclusions

A manufacturing method is established through controlling cure pressure to produce various void contents from 0 to 1.4%. Exponentially decreasing relationships are obtained between the void content, cure pressure and ultrasonic attenuation coefficient. An appropriate cure pressure should be applied during the cure cycle according to the acceptable void levels for quality control.

References


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