Deakin Research Online

This is the published version:


Available from Deakin Research Online:

http://hdl.handle.net/10536/DRO/DU:30003687

Every reasonable effort has been made to ensure that permission has been obtained for items included in Deakin Research Online. If you believe that your rights have been infringed by this repository, please contact drosupport@deakin.edu.au

Copyright : 2006, Technomic Pub
Characterization and Analysis of Delamination Fracture and Nanocreep Properties in Carbon Epoxy Composites Manufactured by Different Processes

J. Zhang* and B. L. Fox

Victorian Centre for Advanced Materials Manufacturing
School of Engineering and Technology
Deakin University
Pigdons Road, Geelong, VIC 3217, Australia

Received March 3, 2005
Accepted June 22, 2005

ABSTRACT: Delamination resistance and nanocreep properties of 2/2 twill weave carbon epoxy composites manufactured by hot press, autoclave, and Quickstep™ process are characterized and analyzed. Quickstep is a fluid filled, balanced pressure heated floating mold technology, which is recently developed in Perth, Western Australia for the manufacture of advanced composite components. Mode I and Mode II interlaminar fracture toughness tests, and nanoindentation creep tests on matrix materials show that the fast ramp rate of the Quickstep process provides mechanical properties comparable to that of autoclave at a lower cost for composite manufacturing. Low viscosity during ramping process and good fiber wetting are believed to be the reasons that this process produces composites with high delamination and creep-resistant properties. Nanocreep properties are analyzed using a Kelvin–Voigt model.

KEY WORDS: manufacturing, interlaminar fracture toughness, nanocreep, CFRP, fast ramp rate.

INTRODUCTION

Woven fabric composites are widely used nowadays due to their ease of handling and shaping and uniform strength in both warp and weft directions [1,2]. The high degree of laminar geometry of fiber composite implies that delamination is one of the most serious damage modes to limit the application life. Mode I and Mode II interlaminar...

*Author to whom correspondence should be addressed. E-mail: jzh@deakin.edu.au


0021-9983/06/14 1287-13 $10.00/0 DOI: 10.1177/0021998305057438 © 2006 SAGE Publications
fracture toughness tests are very effective methods to quantify the delamination resistance of fiber-reinforced composites [3–7].

Indentation tests have been increasingly used for material characterization in recent years [8–11]. Indentation nanocreep tests have advantages over conventional uniaxial creep tests due to the simplicity of the experimental procedure, especially when the material cannot be firmly clamped to prevent slippage [12]. One of the major concerns about advanced polymer composites in their structural applications is their dimensional stability and durability as a result of the viscoelasticity of the polymer matrix [13]. Long-term creep behavior is normally extrapolated from short-term data by using a prediction model. Nanoindentation creep test on the polymer matrix gives valuable information at the nanoscale to aid the understanding of the time-dependent mechanical behavior of fiber polymer composites.

In this study, a woven carbon epoxy composite MTM56/CF0300 was cured by hot press, autoclave, and Quickstep. The autoclave process is a well-established and proven technology, which is widely employed in the aerospace industry for producing high quality composite components. The hot press process involves using heat from a hot platens for a single laminate-to-core application. Quickstep works by suspending a rigid mold between an upper and lower bladder, which contains an industrial heat transfer fluid (HTF) such as polyalkylene glycol, circulating in a low pressure environment. Since liquids can be heated or cooled much faster than air, Quickstep provides a much faster cure cycle for components than the autoclave process. Balanced pressure combines with vibration within the HTF to remove the trapped air and compact the laminates. To investigate the potential of the Quickstep process to supply advanced composite components to the aircraft and automotive industry, the composite laminates fabricated by this process are evaluated by comparing with those manufactured by the hot press and the autoclave processes, which are widely used in industries these days.

EXPERIMENTS

Materials Processing

Laminates were manufactured at Deakin University (Quickstep cure and hot press cure) and the Australian National University (autoclave cure). ACG (the Advanced Composites Group) MTM56/CF0300 prepreg was employed to produce carbon epoxy laminates. It is based on a 120°C curing epoxy matrix resin designed for component manufacture.

The Quickstep technology is briefly described here. A complete Quickstep production capable unit consists of three separate tanks, a curing chamber, a pumping system, and a control system (Figure 1). Heat transfer fluid is applied in the production of chemical cure reactions due to the fact that the fluid contains thousands of times the heat energy per volume of gas and the heat transfer rate is much higher. For example, water contains 2500 times the energy of air per volume and results in 25 times the heat transfer rate. The fluid is stored in a hot tank, a medium tank, and a cold tank. The pumping and recycling of the HTF can be completed in minutes to realize high ramp rates for heating and cooling. The cure temperature is maintained by the HTF in the pressure chamber. A vibrator on top of the chamber works by vibrating the HTF inside the chamber to disperse air bubbles and minimize the residual stresses during processing. The composite laminates
are cured inside the rigid mold, which floats between the upper and lower bladder using its proper cure cycle.

The prepregs were cut into sheets, laid up as laminates, and vacuum bagged for curing. Fiber glass tape was stuck along the edges of the laminate to stop the resin flow during the cure. The typical cure cycles for three processes are displayed in Figure 2. Figure 2(a) is the autoclave cure cycle for MTM56/CF0300. The ramp rates were 3°C/min for heating and 2°C/min for cooling. The cure temperature was held at 120°C, +5/−0°C and 620 kPa (inert gas pressure) for 10 min. The whole process took 83 min. Figure 2(b) is the cure cycle for Quickstep. The average ramp rates were 9°C/min for heating and 12°C/min for cooling. The Quickstep cure was completed in 27 min. It saved 67% of the processing time compared to the autoclave cure. Only vacuum was applied during the Quickstep cure which was −97.47 to −97.76 kPa. The hot press parameters for a cure cycle are illustrated in Figure 2(c). The autoclave and hot press cure cycles were chosen according to the manufacture recommendations from the material data sheet of ACG MTM56. The Quickstep cure was modified to utilize the fast ramp rate of the HTF of Quickstep for these reasonably thin laminates.

Experimental Procedure

The interlaminar fracture toughness tests (Modes I and II) were performed on a LLOYD 30 K universal tester by referring to the protocol of the European Structural Integrity Society [14]. A 15 μm thick aluminum foil was treated with a release agent (Frekote 44NC) and was inserted between the center layers prior to processing to provide the initial midplane delamination crack. The dimensions of the double cantilever beam (DCB) specimen were 175 × 20 × 4 mm³. Aluminum blocks measuring 25 × 20 × 13 mm³ with a loading hole of 6 mm in diameter were bonded on the precracked end to allow unrestrained rotation for the Mode I DCB test. The Mode II end notched flexure (ENF) specimen measuring 175 × 20 × 4 mm³ was positioned in a 100 mm span three-point bending fixture with the crack initiation edge 25 mm from the bottom support. Five specimens were tested for each type of tests. The crosshead speed for both tests was 1 mm/min. The Mode I critical energy release rate GIc and the Mode II critical energy release rate GIIc were calculated by the modified beam theory derived by
Figure 2. Cure cycles for three processes: (a) the autoclave cure: 89 kPa/min pressure build-up; 3°C/min heat-up; 10 min hold at 120°C; 2°C/min cool-down; 102 kPa/min pressure release; (b) the Quickstep cure: on average 9°C/min heat-up; 10 min hold at 120°C; 12°C/min cool-down; constant vacuum ~97 kPa; (c) the hot press cure: 3°C/min heat-up; 10 min hold at 120°C; 3°C/min cool-down; and constant vacuum ~98 kPa.

Hashemi et al. [15] (refer Appendix). The fracture surface was observed by a LEO 1530 scanning electron microscope (SEM).

Nanocreep tests were performed by using the ultra-Micro indentation system (UMIS). A conical indenter with radius 0.7 μm was employed. Creep tests were implemented on the epoxy matrix of composite specimens at room temperature. A 20 mN load was applied and the indentation depth was measured over a period of 1000 s.

Dynamic mechanical thermal analysis (DMTA) tests were performed using a Polymer Laboratories MK2 machine. Two samples were tested for each type at the single cantilever bending mode. The oscillating frequency used was 1 Hz as the temperature was scanned from 80 to 200°C at a constant heating rate of 2°C/min.

RESULTS AND DISCUSSION

Delamination Resistance of MTM56/CF0300 Manufactured by Different Processes

MTM56/CF0300 composites manufactured by hot press, Quickstep, and autoclave are simplified as HP, QS, and AC, respectively. The load and corresponding crack length versus crack opening displacement (COD) curves of DCB tests are shown in Figure 3.
The applied load increased linearly to the maximum value with a small load drop corresponding to the initiation of the crack propagation. With the growth of the crack, the load experienced several load drops until the complete delamination of the DCB specimen. The critical load and the crack length were recorded at the onset of the crack propagation, which caused the corresponding sudden load drop. At the initiation point, loads for three composite systems were comparable. However, the load for HP dropped dramatically with the increasing crack length. At a given crack opening displacement, the HP experienced longer crack length than the QS and the AC. The load–deflection curves of ENF tests are shown in Figure 4. The applied load increased linearly at the initial stage to a certain point and then became nonlinear. The AC experienced a sudden load drop before the load reached its peak value.

A comparison of average $G_{IC}$ and $G_{HIC}$ values for three composite systems is shown in Figure 5. The $G_{IC\text{-mean}}$ for the AC and the QS were 49 and 38% higher than that for the HP. The $G_{HIC\text{-mean}}$ for the AC and the QS were 25 and 20% higher than that for the HP, respectively. The $G_{IC\text{-mean}}$ value for the QS was 92% of that for the AC and the $G_{HIC\text{-mean}}$ value for the QS was 96% of that for the AC. Interlaminar fracture toughness comparable to that of autoclave products was achieved by using Quickstep. The values of $G_{IC}$ are dependent on the mechanisms of delamination growth, which are affected by several factors, such as the fiber–matrix adhesion, the interlaminar bonding strength, and the extent of fiber bridging [4]. The scanning electron micrographs for the DCB and the ENF fracture surface are presented in Figure 6. It can be seen from the DCB fracture surface that the HP was interfacial failure dominated leaving fiber imprints and gaps between smooth fibers. By comparison, the QS and the AC showed extensive matrix failure. The ENF fracture surface for the HP was a brittle fracture [16] due to the fact that small shear bands scattered between clean fibers. As the $G_{HIC}$ increased, the fracture surface became more plastic. Large shear bands closely spaced between fibers on the AC and the QS fracture surface. The major matrix failure indicated that the AC and the QS had stronger fiber–matrix adhesion than the HP. The good fiber–matrix adhesion for the QS was believed to be caused by the good fiber wetting of the Quickstep process. Low viscosity of
matrix resin before curing was achieved as a result of the fast heat-up rate, which made polymer resin flow better and react more completely.

**Dynamic Mechanical Thermal Analysis**

The DMTA spectra are shown in Figure 7. The glass transition temperature $T_g$ for the HP, the AC, and the QS was 113, 123, and 131°C, respectively. Quickstep produced composites with the highest $T_g$ among three manufacturing methods. DMTA has been
used to investigate the fiber–matrix adhesion by Afaghi-Khatibi and Mai [17]. They believed that the $T_g$ and storage modulus are lower for composites with poor interphase adhesion than those with strong interfacial bonding due to the increased mobility of polymer chains in composites with poor adhesion. The QS composites were believed to have strong fiber–matrix adhesion from these results.
Figure 7. DMTA tan δ curves for MTM56/CF0300. (HP – peak area: 10.011°C, peak width: 22.5°C, peak height: 0.378; AC – peak area: 7.688°C, peak width: 22.5°C, peak height: 0.254; QS – peak area: 9.747°C, peak width: 22.6°C, peak height: 0.349).

Figure 8. Indentation depth as a function of time on matrix material from three composite systems.

Creep of Epoxy Matrix under Conical Nanoindentation

Figure 8 presents the indentation creep plots for epoxy matrix from three composite systems. For both the HP and the QS, an essential part of the indentation depth increase happened within the first 300s after the onset of loading. Further rises were relatively
small within the remaining time. The AC experienced a longer interval before the indentation depth gradually became more stable. This change of indentation depth is believed to be due to a loss of stiffness in the material with time [18].

The indentation plots were analyzed using the Kelvin–Voigt model [19–21] as illustrated in Figure 9. This model represents materials, which undergo an initial elastic response and then a time-dependent nonlinear deformation. The equation for creep under a constant applied stress can be written as:

\[ \varepsilon(t) = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2} \left[ 1 - \exp\left( -\frac{t}{\tau_i} \right) \right] \]

(1)

\[ \tau_i = \frac{\eta}{E_2} \]

(2)

where \( \varepsilon(t) \) is the time-dependent strain, \( \sigma_0 \) is the constant stress, \( E_1 \) represents the complex modulus of the first spring element, \( E_2 \) represents the complex modulus of the second spring element, \( \tau_i \) is the time for a retarded elastic response, and \( \eta \) is the viscosity of the dashpot. The hydrostatic compression of indentation loading caused the modulus here involve both shear and tension components; therefore, the complex modulus represents a mixture of shear modulus and elastic modulus. For this constant load indentation using the conical indenter, the creep equation can be substitutively expressed as:

\[ h^2(t) = \frac{\pi}{4} P_0 \cot \theta \left\{ \frac{1}{2E_1} + \frac{1}{2E_2} \left[ 1 - \exp\left( -\frac{2E_2}{\eta} t \right) \right] \right\} \]

(3)

where \( h(t) \) is the indentation depth, \( \theta \) is the semi-angle of the conical indenter, and \( P_0 \) is the constant load. The viscoelastic properties were extracted by nonlinear Levenberg–Marquardt curve fitting of experimental data to the analytical solutions and are shown in Table 1. \( R^2 \) is the reliability value. The resistance of the resin to plastic deformation can be represented by \( \eta \). Comparing the analyzed results, we can see that the QS resin was more creep resistant than the others under a 20 mN constant load.
Figure 10. Creep compliance curves for matrix material from three composite materials.

The time-dependent creep property is usually characterized by the creep compliance $J(t)$ which is defined as the creep strain $\varepsilon(t)$ divided by the creep stress, as shown in Equation (3). The inverse of the creep compliance is the creep modulus $E_c(t)$, effectively representing creep behavior and is preferred for design data [18].

$$J(t) = \frac{\varepsilon(t)}{\sigma(t)}$$

(4)

$$E_c(t) = \frac{1}{J(t)}$$

(5)

To assess the indentation response of polymer material, assumption of quasi-static contact between a rigid axisymmetric indenter and a viscoelastic solid was used [22]. $J(t)$ was calculated by Equations (6) and (7) [23] for a conical indenter.

$$J(t) = \frac{A(t) \tan \theta}{P_0}$$

(6)

$$A(t) = \pi h(t)^2 \tan^2 \theta$$

(7)

where $A(t)$ is the contact area. Creep compliance curves were plotted as log–log plots, which are shown in Figure 10. $J(t)$ increased gradually with the retardation time. The QS and the AC had lower $J(t)$ than the HP indicating that these two systems were more creep resistant than the HP matrix.

CONCLUSIONS

The delamination resistance and nanocreep properties of MTM56/CF0300 produced by hot press, Quickstep, and autoclave were investigated. The Mode I and Mode II
interlaminar fracture toughness results showed that the Quickstep process provided comparable delamination resistance to the laminates manufactured by autoclave. The AC was 49% stronger and the QS was 38% stronger than the HP in terms of Mode I interlaminar fracture toughness; for Mode II interlaminar fracture toughness comparison, the AC was 25% higher and the QS was 20% higher than the HP. The $G_{\text{IC-mean}}$ value for the QS was 92% of that for the AC and the $G_{\text{IIIC-mean}}$ value for the QS was 96% of that for the AC. The delamination fracture surface showed mainly interfacial failure for the HP; however, extensive matrix failure was found on the fracture surface for the AC and the QS indicating stronger fiber–matrix adhesion for these two composite systems.

The QS was found to have the highest glass transition temperature which also implies the strong fiber–matrix adhesion of this material. This was believed to be caused by the fast ramp rate of this process, which made the matrix resin have low viscosity before curing so that the carbon fibers are wetted more completely. The rapid heating and cooling process saved 67% of the autoclave processing time and 25% of the hot press processing time. There is very low inert gas pressure and low gas consumption needed for the Quickstep process, which reduces the cost of the autoclave-manufactured products.

The three-element Kelvin–Voigt model was employed to analyze the nanocrep properties of three composite systems. Both the analytical result and the creep compliance curves showed that the QS was more creep resistant than the AC and the HP.

ACKNOWLEDGMENTS

This research is funded by Deakin University and Victorian Centre for Advanced Materials Manufacturing (VCAMM).

APPENDIX

Calculation of Mode I and Mode II Critical Strain Energy Release Rates

Mode I critical strain energy release rate ($G_{\text{IC}}$) was calculated using the following Equation (14):

$$G_{\text{IC}} = \frac{3P\delta}{2b(a + |\Delta|)} \frac{F_1}{N_1}$$  \hspace{1cm} (8)

where $P$ is the applied load, $\delta$ is the crack opening displacement, $b$ is the specimen width, $a$ is the crack length, and $|\Delta|$ is the crack length correction factor, which is determined to be the $X$-axis intercept of the plot of the cube root of compliance $C_1 (= \delta/P)$ versus the crack length. $F_1$ is the correction factor for large displacement and $N_1$ is the correction factor for loading block.

$$F_1 = 1 - \frac{3}{10} \left( \frac{\delta}{a} \right)^2 - \frac{3}{2} \left( \frac{\delta d}{a^2} \right)$$  \hspace{1cm} (9)

$$N_1 = 1 - \left( \frac{L' \sqrt{a}}{a} \right)^3 - \frac{9}{8} \left[ 1 - \left( \frac{L' \sqrt{a}}{a} \right)^2 \right] \frac{\delta d}{a^2} - \frac{9}{35} \left( \frac{\delta}{a} \right)^2$$  \hspace{1cm} (10)
where $d$ is the distance from the center of the loading pin to the midplane of the specimen arm to which the block is attached and $L'$ is the half-length of the loading block.

Mode II critical strain energy release rate $G_{II}$ was calculated using

$$G_{II} = \frac{9P_c^2a^2}{16b^2E_0e^3} \frac{F_{II}}{N_{II}}$$  \hspace{1cm} (11)

where $P_c$ is the maximum load, $E_0$ is the modulus measured during the compliance calibration for $a=0$, and $e$ is the half-value of the specimen thickness. $F_{II}$ is a correction for the moment arm and $N_{II}$ is a correction for the compliance. $E_0$, $F_{II}$, and $N_{II}$ can be calculated as:

$$E_0 = \frac{L^3}{4bC_{II}e^3}$$  \hspace{1cm} (12)

$$F_{II} = 1 - 0.6099 \left( \frac{\delta}{L} \right)^2$$  \hspace{1cm} (13)

$$N_{II} = 1 + 0.3766 \left( \frac{\delta}{L} \right)^2$$  \hspace{1cm} (14)

where $1/C_{II}$ is the initial slope of the load–displacement plot, ignoring any initial nonlinearity of the curve.

REFERENCES


