Composites: Part B 47 (2013) 230–237

Contents lists available at SciVerse ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

Cure behaviour and void development within rapidly cured out-of-autoclave composites

S.L. Agius *, K.J.C. Magniez, B.L. Fox

Institute for Frontier Materials, Geelong Technology Precinct, Deakin University, Waurn Ponds, VIC 3217, Australia

ARTICLE INFO

Article history:
Received 10 July 2012
Received in revised form 7 November 2012
Accepted 22 November 2012
Available online 6 December 2012

Keywords:
A. Prepreg
B. Porosity
B. Cure behaviour
Out-of-autoclave

ABSTRACT

This study investigates the effect of slow and fast heating rates (1.5 and 10 °C/min) on the formation of voids during the out-of-autoclave curing process of an aerospace composite (HexPly 8552). The cure cycles were interrupted at pre-defined stages for each heating rate enabling the in situ behaviour of the resin, void content and growth of voids to be studied. It was found that the morphology and content of voids remained unchanged up to the second heating stage of the cure cycle, regardless of heating rate. Thereafter, differences to minimum resin viscosity for the faster heating rate (5.2 Pa s compared to 32.5 Pa s) and a higher gelation temperature (177 °C compared to 160 °C) caused a slight increase to void growth for the rapid curing conditions. The causes of voids were the result of moisture volatiles contained within the prepreg, identified by mass spectrometry. Overall, the faster heating rate reduced the cure cycle time by 32% without any effect on the final degree of cross-linking (88.4%) or overall void content, which remained below 2%.

1. Introduction

Mass reduction has a significant impact on fuel efficiency, which is why airline industries are demanding larger and more fuel efficient aircraft in order to remain competitive. As a result, advanced materials with excellent strength and stiffness to weight properties such as composites, are being widely adopted in the aerospace industry. Composite aircraft structures are predominately manufactured from pre-impregnated (prepreg) carbon fibre materials which are cured in autoclaves, using high pressures in order to produce high quality parts. Pressure aids in the collapse and removal of entrapped volatiles, thus reducing the void content and providing materials with high fibre volume fractions. However, autoclaves impose limitations on production rate due to long thermal cycles arising from slow heating rates (1.6–3 °C/min) [1]. This limitation, combined with an increasing demand for composite structures on aircraft has resulted in the shift toward new curing processes, known as out-of-autoclave (OOA).

The low capital investment, lower consumable costs and improved energy efficiency of OOA processes have added to their appeal. However, these methods use very low pressures and typically rely on vacuum bag pressure to consolidate the part, and as a result, the mitigation of voids has become an issue. In order to aid in the reduction of voids, labour intensive lay-up methodologies and long intermediate dwells are implemented to help remove entrapped volatiles from the prepreg composite. As a consequence, OOA processing can be just as long or longer than those found using an autoclave [2].

One method to reduce cycle times is via the use faster heating rates. Rapid OOA curing processes such as the Quickstep and microwave have been shown to offer significant savings in manufacturing time and tooling expenses [3,4]. Unfortunately, the low consolidation pressures also associated with these methods also pose challenges in producing void free parts [4,5].

Many attempts have been made to understand the development of voids within both autoclave and OOA composites [6–13]. However, the effect of heating rate on void development has not been widely adopted. In addition, measuring the exact cause/s of voids within prepreg composites has proven difficult and is highlighted by the speculation shown within the literature. Some suggest that voids arise from entrapped moisture [6,14] or solvents [15] within the prepreg; others claim entrapped air during lay-up [16] and many propose a combination of all these things [7,9,17].

This study investigates the effect of slow and fast heating rates (1.5 and 10 °C/min) on the void development of an aerospace composite, manufactured using OOA processes. In the first step of this work, thermo-analytical techniques allowed the effect of heating rate on cure behaviour to be determined which was critical in understanding any changes to void growth. Also, mass spectrometry was able to accurately determine the residual volatile components within the prepreg. A cure monitoring approach was followed, which allowed the development and morphology of water voids at critical regions within a pre-defined cure cycle to

* Corresponding author. Tel.: +61 3 5227 3420; fax: +61 3 5227 1103.
E-mail address: s.agius@deakin.edu.au (S.L. Agius).

1359-8368/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesb.2012.11.020

be investigated. This methodology was able to minimise and segregate all factors responsible for the growth of voids within the prepreg during cure.

The collective outcomes from this study shall provide a research tool to further explore the development of voids within composites, as well as advance the use of rapid manufacturing techniques within the composite industry.

2. Methodology and validation

2.1. Material

As mentioned in Section 1, the intention of this study is to investigate the effect of heating rate on void development within out-of-autoclave composites. A single factor which affected void development was studied. This was achieved by selecting a hot melt prepreg material, as literature has suggested these prepregs are susceptible to contain water volatiles [18]. HexPly 8552, a commercially available modified epoxy prepreg reinforced with IM7 fibres was used. This system contains multifunctional epoxies tetraglycidylmethylenedianiline (TGMDA) and triglycidyl-p-aminophenole (TGAP), hardened with diaminodiphenysulfone (DDS). The matrix is also toughened with poly (ether sulfone) (PES) thermoplastic.

2.2. Processing

Laminates were produced by stacking 16 plies of unidirectional prepreg tape of approximately 150 × 150 mm dimension in the 0° direction in an ambient environment containing 60% RH. De-bulking was conducted for each ply for 5 min, followed by an additional 16 h (overnight) prior to cure. This stringent approach was carried out to minimise the presence of air trapped between prepreg plies. The exact time required to achieve a sufficient de-bulk was outside the scope of this paper, and it was assumed that time used was more than adequate. Furthermore glass tape was positioned on the edges of the tool surface and top layers of the laminate to help create an air path for the removal of voids. Slow and fast heating rates (1.5 and 10 °C/min) were achieved by using two different curing processes, convection oven and Quickstep, respectively.

In comparison to the convection oven process, the Quickstep process cures composites within a fluid filled, balanced pressure and heated mould. The technology comprises of three fluid filled tanks, a hot, medium and cold (ambient) which are controlled via a user friendly interface. The tanks combined with a booster heater control any dwell temperatures while a variable speed pump controls the heat up rate. The process takes advantage of the increased heat transfer capacity of a fluid (poly alkaline glycol), resulting in heating rates of (5–10 °C/min). For both OOA processes, consolidation pressure was achieved via a vacuum bag, which was able to apply approximately 97 kPa of external pressure. However, it should be noted that an additional external pressure of approximately 5 kPa was also applied to the laminate within the Quickstep process, due to the pressure within the fluid filled bladders.

The curing parameters used were based on recommendations made by Hexcel composites. Hexcel recommend that the 8552 system be heated to 110 °C for 60 min, then to 177 °C for 120 min, before cooling back to 50 °C [19].

2.3. Preparation of DSC and rheology samples

Samples of resin were extracted from the prepreg using the authors methodology highlighted in [20], in order to conduct degree of cure and viscosity measurements. This process involved preparing a prepreg stack (150 × 20 mm) with the fibres orientated parallel to the width. The stack was placed between two layers of ETFE release film and inserted in a hot press. Using a platen temperature and pressure of 65 °C and 3 tonne, respectively, the resin was left to bleed for 30 min and collected from the laminate edges. Fig. 1a and b highlights the prepreg stack before and after extraction, respectively. It is shown that there is a significant amount of resin at the laminate edges which was then removed to conduct DSC and viscosity measurements. The rheology sample shown in Fig. 1c was created by rolling the resin between two metal rollers in order to achieve the desired sample thickness. It was then trimmed to the appropriate diameter of approximately 20 mm.

DSC was used to validate this method which showed that it did not affect the degree of cure of the resin. This was achieved by monitoring the residual heat flow (corresponding to the energy released from the sample per unit mass J/g) of the extracted resin, which quantifies the extent of reaction [21]. In this work, a mean total heat flow of 551 J/g (averaged on three scans) was measured from a dynamic scan from 30 to 300 °C at 10 °C/min. This heat flow is consistent with Hubert et al. [22], who reported a value of 554 J/g on neat resin samples directly obtained from The Boeing Company. In addition, the isothermal extraction conditions were simulated using prepreg material within the DSC which highlighted no exothermic behaviour during this time. It was therefore confirmed that the extraction method used in this work did not significantly interfere with the polymerisation of the resin.

2.3.1. Degree of cure

The degree of cure throughout the cure cycle for each heating rate was determined using a TA Instruments Q200 with a nitrogen flow of 20 ml/min. Resin samples weighing approximately 5–7 mg were sealed in aluminium pans for analysis. The cure cycles were sectioned into a number of points, where the residual heat reaction (ΔHr) for each point was evaluated (Table 1 and Fig. 2). Each cure cycle was also divided into three stages (Fig. 2). The symbols which correspond to each stage are referred to throughout this paper.

Stage 1 has been implemented to investigate the effect of heating rate on the degree of cure, viscosity and processing time of the resin when heated from ambient and held at 110 °C for 60 min. Changes to any of these parameters could potentially alter the morphology and removal of voids within the composite. Stages 2 and 3 have been employed to understand the effect of heating rate on gelation and viscosity of the resin when heated from 110 to 177 °C and held at 177 °C for 120 min. It is well known that these portions within cure cycles are designed to promote cross-linking which can consequently trap voids within the composite as well as encourage void growth [6,9,17].

After a particular point in the cure cycle was reached, the DSC sample was quenched using a cooling rate of 30 °C/min. This was followed by a dynamic temperature scan from 30 °C to 300 °C at 10 °C/min to determine the residual heat (ΔHr). Fresh (B-staged) material was also subjected to a dynamic temperature scan using the same parameters to determine the total heat reaction (ΔHt). The degree of cure (α) was then calculated using $\alpha = (\Delta Ht - \Delta Hr)/(\Delta Ht)$ [23].

2.3.2. Rheology

Rheology was conducted to investigate the effect of heating rate on viscosity and gelation of the resin. The extracted resin was used in a parallel plate controlled strain ARES (TA Instruments) rheometer. Cure cycles were simulated using the rheometer with a plate gap, frequency and strain of 1 mm, 10 rad/s and 1%, respectively. A strain of 1% was used as a strain sweep test indicated the linear viscoelastic range (constant G') for the resin occurred between