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Measuring the negative pressure during processing of advanced composites

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ABSTRACT

Pre-impregnated sheets of advanced carbon fibers with highly viscous thermoset-based resin systems are commonly used in fabricating aerospace composite parts. As prepreg sheets are vacuum bagged and heated during processing, the resin slowly infiltrates in dry spots between fibers. Under vacuum condition, surface tension-induced capillary effects impose deep negative pressures on the liquid resin, leading to tensile stretching. A method is presented to quantify the capillary-induced negative pressure. During processing, samples are quenched to freeze the infiltration process before taking SEM images. Using image analysis and by invoking interfacial stress boundary condition, the pressure distribution is determined. Sub-micron radii of curvature at the resin interface were measured corresponding to local negative pressures up to several atmospheres and an average pressure of −10 to −50 kPa. Effects of negative pressures on the state of material and on defects such as resin phase separation are discussed.

1. Introduction

In 1660, in his landmark book *New Experiments Physico-Mechanical* [1], Robert Boyle reported an experiment where he unsuccessfully tried to observe capillary action in vacuum [2]. This was followed soon after by others including a demonstration by Francis Hauksbee in 1706 who showed that capillary rise of liquids in narrow glass tubes is the same in vacuum as under atmospheric pressure [3]. As an indication of liquids under negative pressure, this and other demonstrations have generated a great amount of interest [4]. Consider a glass tube which is brought in contact with a liquid as shown in Fig. 1a. At hydrostatic equilibrium, according to the Young-Laplace equation a pressure jump across the liquid interface is sustained [5]:

$$\Delta p_c = \sigma \times \kappa \tag{1}$$

where σ is the liquid surface tension and κ is the total curvature of the meniscus. For the concave meniscus in Fig. 1a, this can be rewritten on the basis of Jurin's law [5]:

$$p_{air} - p_{liquid} = \rho g h = \frac{2\sigma\cos\theta_s}{R} \tag{2}$$

where ρ is the liquid density, h is the height of capillary rise, R is the radius of the tube and θ_s is the contact angle at hydrostatic equilibrium. Naturally, it follows that for the test in vacuum ($p_{air} \approx 0$) the liquid pressure near meniscus must be negative (if cavitation is prevented):

$$p_{liquid} = -\frac{2\sigma\cos\theta_s}{R} < 0 \tag{3}$$

Pressure distributions for the cases of atmospheric pressure and vacuum are compared in Fig. 1. This shows an overall shift in pressure distribution to create a zone of negative pressure in vacuum.

Even though the notion of negative pressure might seem confusing, it follows the laws of thermodynamics [6,7]. In closed systems for which extensive properties can be expanded to infinity (e.g. volume of gases), thermodynamics prohibits passing the threshold of zero pressure. For condensed phases with an upper bound on volume, however, negative pressure is a possibility [6,7]. Putting it simply, at negative pressure liquid undergoes tensile stretching. As a metastable state [8], the negative pressures is sustained until it is released via cavitation [9] or the liquid reaches its so-called spinodal limit [8].

A more interesting observation in Eq. (3) is the inverse effect of radius on negative pressure. This implies that capillary action at micro or nanoscales has the potential to generate large negative pressures [10–12]. Processing of advanced composites is an important engineering field where capillary flow occurs in vacuum at the microscale. To fabricate aerospace composite parts, pre-impregnated sheets of advanced carbon fibers with thermoset resins (i.e. prepreg) are commonly used. For processing, prepreg sheets are vacuum bagged and heated to ensure proper curing. As resin infiltrates in dry spots between fibers with diameters of 5–10 μm, at near full vacuum, resin undergoes appreciable negative pressures. This raises concerns on the adverse effects of such a pressure on porosity, phase separation [13] and fiber

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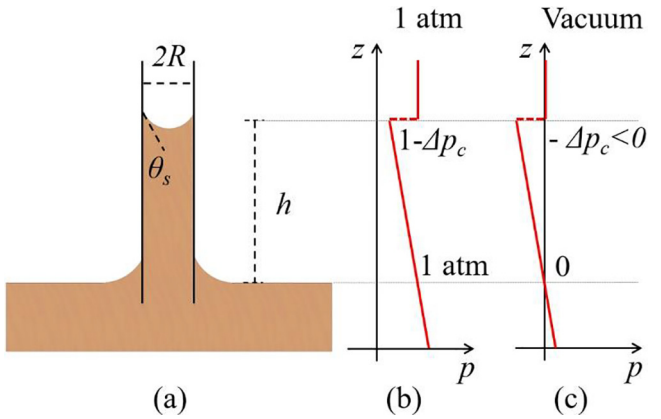

Fig. 1. (a) Capillary rise in a narrow tube, (b) liquid pressure distribution under 1 atmospheric pressure, and (c) liquid pressure distribution under vacuum.

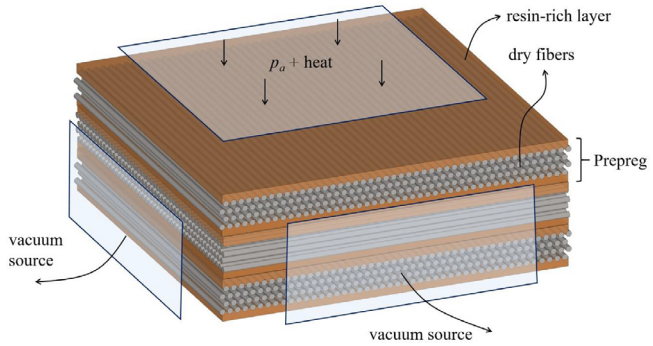

Fig. 2. Schematic of prepreg processing. Several prepreg sheets are stacked at different orientations and vacuum bagged before processing using external heat and pressure.

movement.

This study presents a novel method to quantify capillary-induced negative pressure during composites processing. While under vacuum, curing samples are quenched to freeze the hydrodynamic infiltration process. Scanning electron microscopy (SEM) images are taken and analyzed. By invoking interfacial stress boundary condition, pressure distribution is determined.

A summary of studies on capillary pressure during composite processing is presented. This paper focuses on the micro-level pressure distribution within a prepreg system. The method is presented to quantify the negative pressure through a combined experimental study and mathematical derivation. An aerospace grade carbon-epoxy prepreg, HexPly 8552, is used to demonstrate the application of the method. Effects of the negative pressure on the state of material and promoting/mitigating defects such as porosity, phase separation and waviness/wrinkling are discussed.

2. Background: capillary pressure during processing

Broadly speaking, processing of advanced composites can be divided into two categories:

- Resin Transfer Moulding (RTM) where dry fibers are placed on to a tool before injecting them with a low viscosity resin (usually less than 1 Pa.s) via an applied pressure gradient driven by the combination of inlet, outlet and capillary pressures [14].
- "Prepreg" processing where pre-impregnated (hence "prepreg") sheets of fibers with a highly viscous resin (usually beyond 10,000 Pa.s at room conditions) are used. Depending on the intended processing method, prepreg initially has a high void fraction mainly at its core. This void fraction is reduced below an acceptable limit by the end of production.

During prepreg processing, multiple layers are stacked at different orientations and vacuum bagged together as schematically depicted in Fig. 2. Usually using an oven or a pressurized autoclave, prepregs are convectively heated. This reduces the resin viscosity by several orders of magnitude to assist resin infiltration in dry spots of the prepreg. As curing advances, the thermoset resin undergoes three distinct phases [15]. Initially it is a viscous liquid. At gelation, it becomes a rubbery viscoelastic material and eventually transforms into a glassy solid [16–19]. Hence, gelation marks the end of resin infiltration.

The effect of capillary pressure on resin infiltration has been extensively studied for RTM processes [20–33] and to a much lesser extent for prepreg processing [34]. These studies cover a wide range of topics including evaluating capillary pressure, examining its effect on defects such as porosity and optimizing processing. The general approach is to correlate the speed of resin infiltration to total pressure gradient using closed-form solutions such as Darcy's law [20,21]. The average capillary pressure as part of the total pressure gradient is either experimentally measured [22], calculated using closed-form solutions [23] or numerically evaluated [24]. The experimental measurements usually involve infusing preforms under constant applied pressure or constant flow rate, and correlating the progression of infiltration to the pressure gradient [25,26]. Using this method, injection flow rate can be optimized to mitigate micro and macro void formations [26–28,22,29,30]. Usually an average negative capillary pressure is estimated if resin wets fibers with an angle less than 90° [28,33]. Variations of negative pressure and its effects on the state of material in RTM process are usually overlooked. In general, effect of capillary pressure for prepreg processing has been neglected. Considering new processing methods such as hot drape forming (HDF) [35] where the dry prepreg core promotes defects such as wrinkling, it becomes crucial to understand resin infiltration during prepreg processing.

3. Derivation of the negative pressure

Consider resin infiltration process in a prepreg under vacuum as schematically depicted in Fig. 3. A representative volume element of prepreg during processing is schematically shown in Fig. 3a and a close-up view of the resin infiltration front is shown in Fig. 3b. A macro view of the initial raw prepreg condition with resin-rich areas and dry spots is schematically shown in Fig. 2. In the initial state, prepreg exhibits fiber misalignments and variations of volume fractions. As such, the infiltration pattern is three-dimensional. For the sake of simplicity, however, only two dominant flow types are considered: flow perpendicular to the fibers (points *A* and *C* in Fig. 3) and flow parallel to fibers (point *B* in Fig. 3). The coordinate system is defined parallel to the flow directions to simplify the derivations.

We begin by invoking the interfacial stress balance based on the jump condition [36–39] while neglecting surface viscosities (i.e. ignoring Boussinesq-Scriven effect [40–43]):

$$\boldsymbol{n}\cdot(\boldsymbol{\Pi}_1-\boldsymbol{\Pi}_2) = \sigma\boldsymbol{n}(\nabla.\ \boldsymbol{n})-\nabla_s\sigma \tag{4}$$

In which $\boldsymbol{n}$ is the normal unit vector at the interface with positive direction as shown in Fig. 3 (i.e. pointing away from resin toward vacuum), $\boldsymbol{\Pi}_1$ and $\boldsymbol{\Pi}_2$ are total stress tensors on the concave side (near full vacuum) and on the convex side (resin) respectively, σ is the resin interfacial tension and ∇_s is the surface gradient operator:

$$\nabla_s \equiv \nabla-\boldsymbol{n}(\boldsymbol{n}.\ \nabla) \tag{5}$$

In Eq. (4), the first term on the right-hand side represents the surface tension effect similar to Young-Laplace equation [5] (Eq. (1)) while the second term represents the spatial variation of interfacial tension (i.e. Marangoni effect [38]). Assuming an isothermal condition and a surfactant-free surface, the Marangoni effect can be neglected (i.e.