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Improved simplified approach for the prediction of porosity growth during the curing of composites parts

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ABSTRACT

One of the major defects which may occur during the manufacturing of thermoset fiber reinforced composites is the creation of voids which are known to induce a severe degradation of mechanical performances. The modeling of porosities growth during curing is therefore of primary importance. This work proposes an improved void growth model taking into account the coupling between water diffusion, thermo-mechanical effects and matrix properties evolution, which are the assumed driving factors of the problem. In the idealized framework of the growth of a micro-bubble in a homogeneous surrounding medium, the existence of a boundary layer, taking into account moisture transfer modifications around the bubble, is proposed and added to the classical approach. This semi-analytical model is solved numerically and its predictions are compared to experimental observations on parts cured with different pressure, temperature and initial moisture contents. After identification of a single adjustable parameter, results prove to fit realistically experimental data.

1. Introduction

Carbon fiber reinforced epoxy matrix prepregs are nowadays widely used for the manufacturing of aeronautical parts, where a high quality is required. However, depending on the processing conditions, it is well known that voids may develop during the curing stage. It is now well known that above a certain critical volume content, voids induce a severe degradation of mechanical properties [1–5]. Porosities may induce damage, crack initiation and propagation [4,6] decrease the interlaminar shear strength and the flexural and compressive strength properties [1,3,4]. Some investigations showed also an impact of the presence of porosity on fatigue performances [2,5]. For the aircrafts manufacturers, this leads to production rates drops, excessive scraps, associated reworks and repair costs [7].

Despite those impact evidences, the mechanisms of void creation and development are still not well-understood and opposing views exist concerning the origin of voids. All the studies agree on the fact that voids are the result of microcavities, which are present in the material at the initial state and evolve under the effect of time, temperature, pressure, material polymerization degree and water concentrations. Some researchers [3,7–10] claim that dissolved volatile and especially moisture are the primary sources of microcavities. Some others [4,11–13] also mentioned the possible role of the air which can be mechanically entrapped during the lay-up, or eventually present inside the matrix after impregnation. Grunenfelder and Nutt [9] investigated the effects of moisture dissolved in the resin on the porosity by producing different composite plates in an oven only under vacuum, for which prepreg plies were beforehand humidity-conditioned at different relative humidity levels. This investigation showed that different initial dissolved moisture contents resulted in different final void volume fractions and validated the predominant effect of moisture dissolved in the resin on the porosity creation. Campbell et al. [7] gave an interesting explanation for this observation: since moisture is the most important volatile present in hot melt addition curing prepregs, the amount of absorbed water in the prepreg determines the resultant vapor pressure of volatiles generated during the cure cycle. Indeed, an increase in moisture content and temperature results in an increase of vapor pressure which leads to void growth if the latter exceeds the resin pressure (addition of vacuum and autoclave pressure) while the resin is in the liquid state. When the resin gelation occurs, voids are finally locked into the resin matrix. Besides, temperature accelerates water diffusion between

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the voids and the resin, that can also induce an increase of the internal void pressure. Conversely, when the resin hydrostatic pressure exceeds the internal void pressure, water is dissolved into the resin which leads to the porosity shrinkage [11].

Epoxy resin is known to be hydrophilic [14], but in practice, the environmental conditions are not always fully controlled during manufacturing and especially during the storage (room temperature and freezer) and the lay-up. It is to notice that the latter can last for a long time. Thus, there is an important risk for the material to absorb some water and then to develop porosity during curing. A numerical model which would be able to accurately predict the void development during the laminate cure, depending on its initial moisture content, would be of great practical interest and should lead to improve production costs.

While the governing phenomena at origin of voids development seem rather well identified, it is surprising to note that only few models were proposed for composites manufacturing in the literature. This is probably due to the traditional use of a high curing pressure in an autoclave that prevents the risk of water vaporization, so of moisture induced bubbles. The different models of the literature are based on the pioneering works of Epstein and Plesset [15] or Scriven [16], that described the growth of a single bubble of a gas surrounded by a saturated liquid. Retaining this idea, few authors proposed to apply these early theories to the growth of voids during processing of thermosetting matrix composites [8,11,17]. To this end, they considered and solved the problem of the growth of a spherical bubble induced by the diffusion of water coming from the surrounding resin, assumed in a viscous liquid state.

As visible from Fig. 1, when those models are utilized with typical material parameters obtained from one aeronautical epoxy resin, they indicate final bubble sizes of several millimeters, even bigger than the height of the composite layup. Among those three main models in this field, Ledru's model nevertheless seems to give the best results. Wood's model is not sensitive to the imposed pressure, whereas Kardo's model gives a huge bubble size and an instantaneous effect of the pressure changes.

Looking more precisely at the local morphology of real bubbles (Fig. 2) obtained on a sample especially designed to achieve an important initial moisture content, one can observe that their shapes are really complex and very far from the idealized spherical shape of the theory. They are mainly located at the interfaces between plies (Fig. 2(b)), though some of them can appear inside fiber tows. They have mainly a rather flat shape in the thickness direction, but show totally random shape in the plane direction. Predicting such kind of phenomenon would, if even possible, require huge computational efforts as well as the knowledge of some physical data at a very fine scale, that would explain the complex shape often observed.

Considering those two last remarks:

(a) inability of current models to predict reasonable porosities size,
(b) unaffordable complexity of the real growth phenomena at the micro-scale,

this paper proposes a rather simple but enhanced spherical growth model, ideally able to predict the effect of moisture content, temperature and pressure history on the final average size of bubble inside a thermosetting matrix composite. The leading ideas are twofold: (i) to better account for the complex moisture diffusion behavior using the recent experimental results of de Parscau du Plessix et al. [18] and (ii) to introduce the notion of an interphase layer in the vicinity of the growing bubble, that would induce a significative local slowdown of the water diffusion.

In the first section, the Dual-Fick diffusion model coupled to the polymerization kinetics identified by de Parscau du Plessix et al. [18] is reminded, as it is plays an important part in the present approach. The proposed bubble growth model is then detailed in the second section. Lastly, its predictions are compared to experimental observations of several composites panels that were manufactured under specific humidity conditions in order to produce a controlled porosity.

2. Material properties identification

The curing of thermoset matrix composite parts is a complex process which involves numerous phenomena that can affect porosity development. As explained above, cavities evolution depends on the diffusion of water molecules from the matrix to the bubbles, or conversely, but also on the properties of the matrix, that are well known to strongly evolve with the degree of cure [19–22]. The first step for a good prediction of bubbles growth is therefore a fine knowledge of those two properties for typical industrial storage and processing conditions.

2.1. Polymerization kinetics

The material under consideration is a typical aeronautic epoxy resin, that was already presented in [18], which includes all details about identification procedures. It was checked that the cure kinetics of this resin could be fitted by a Kamal and Sourour model [23] modified by diffusion factor (Eq. (1)), where α_{max} is the highest polymerization degree for a given temperature, k_1, k_2, $n1$, $n2$, $n3$ are constants and f is called the diffusion factor. This type of behavior is classically observed for epoxy resins.

$$\frac{\partial \alpha}{\partial t} = (k_1(1-\alpha)^{n1} + k_2\alpha^{n2}(1-\alpha)^{n3}) f(\alpha - \alpha_{max}(T)) \quad (1)$$

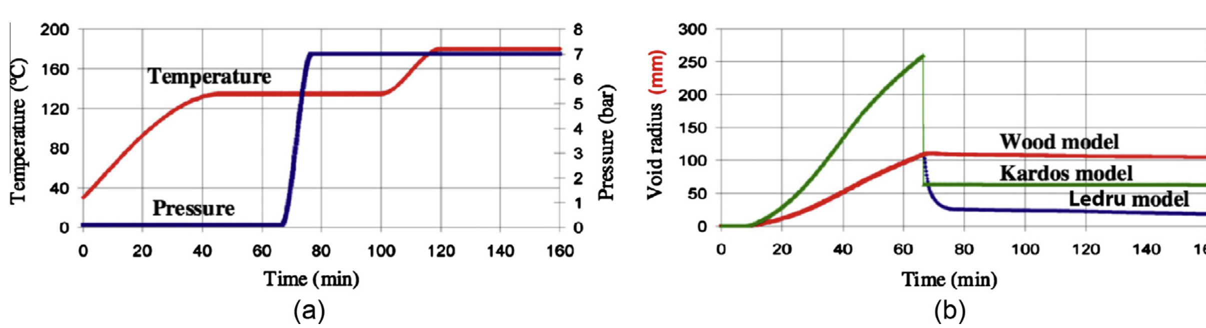

Fig. 1. Bubble size evolution in time for a given temperature and pressure cycle (a), typical from industrial autoclave curing as predicted by the models Kardos et al. [8], Wood and Bader [11] and Ledru [17] (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)