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Proposal for a long-fibre microbuckling scenario during the cure of a thermosetting matrix

Ch. Jochum [a,*], J.C. Grandidier [b], M. Smaali [a]

[a] *Laboratoire de Mécanique des Structures Navales-Ensieta 2, rue François Verny, F-29806 Brest, France*
[b] *Laboratoire de Mécanique et de Physique des Matériaux, UMR CNRS 6617-Ensma Téléport 2, 1 av Clément Ader, BP 40109, F-86961 Futuroscope Chasseneuil Cedex, France*

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Abstract

Recently, real-time video images of the appearance of undulations on a long T300 single carbon fibre during the curing of a LY556 epoxy matrix were proposed by Jochum et al. [Jochum Ch, Grandidier JC, Smaali M. Experimental study of long T300 carbon fibre undulations during the curing of LY556 epoxy resin. Compos Sci Technol 2007;67:2633–42]. The correlation of the fibre undulation with cure kinetics has established that undulations appear prior to glass transition. The present study presents a description of the evolution of the elastic and loss modulus during curing, which is correlated with cure shrinkage estimations and previous video results. The comparisons between these results lead to a clear proposal for a single long-fibre microbuckling scenario during the curing of an epoxy matrix. Novel results are that fibre instability is triggered at local heating rates higher than 3 °C/min and coincides with the maximal chemical shrinkage observed prior to glass transition. Similarly, the observation of the relaxation of partial fibre undulation relaxation is coherent with the viscoelasticity of the matrix during formation. The instability appears some time after exposure to a rubbery state. The analysis of single fibre undulation is an excellent indicator of cure quality and an appropriate testing structure for further chemical, thermal and mechanical models of the co-operative buckling of many fibres.

Keywords: A. Resins; A. Carbon fibre; B. Cure behaviour; B. Defects

1. Introduction

The use of composites in structural applications has become increasingly important in the industry. These trends have recently emerged in naval construction since the optimization of the structures became inevitable. Such use requires a highly accurate knowledge of material properties and of the internal state obtained at the end of the manufacturing process. For example, internal stresses are generated and several imperfections (bubbles, fibre waviness, etc.,) may appear during the curing of a composite, thus decreasing the mechanical performance of the final material. These phenomena constitute an important aspect in the manufacturing of thick composites with long fibres. In fact, the presence of regular undulating fibres in the plies can be observed at the end of the cure cycle. In thin composites, this phenomenon also seems to be active as suggested by the study of Paluch [1] into long carbon fibres. This author clearly showed that the fibres assume an undulatory form at the end of the cure. Unfortunately, it has been shown in practice that fibre undulation or waviness has a negative influence on the stiffness and strength of fibre-reinforced composites [2–9].

Several modelling approaches were used in order to determine this loss of strength. The quality of the predictions depends on the initial value of the wavelength and amplitude of the fibre, which results from the cure process [10–15]. Currently, no study exists for the prediction of a complete microscopic stress–strain distribution inside a composite after its cure. Existing models only solve the macroscopic strengthening of a composite, either by means

* Corresponding author. Tel.: +33 298 348 876; fax: +33 298 348 730.
E-mail address: jch@ensieta.fr (Ch. Jochum).

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of a parametric study of the description of fibre defects [12], kink band approaches [13], or the spectral density of waviness [14]. The literature does not take the behaviour of the matrix during the cure, fibre–matrix interaction and its consequences on the stress state of the matrix after the return to room temperature into account. The characteristics of fibre undulation at the end of the manufacturing process are seldom presented in the literature. The authors modelled fibre waviness with a single harmonic and therefore a range of imperfection angles are considered to determine the actual compressive strength of the material.

In order to compensate for this lack of real information about the description and understanding of fibre waviness, it was decided to first study a single fibre composite. The single fibre approach is a powerful tool for the simple observation and identification of the fibre instability mechanism that appears during the cure. In particularly, quantitative measurements of fibre undulations are possible on a single fibre composite, and are easy to correlate with the cure kinetics.

The single fibre approach is obviously questionable since the use of a single fibre involves local stresses that are certainly much different when the fibre volume fraction changes, however, on the other hand, the physics that triggers the instability would probably not change when the fibre volume fraction increases. Both in the case of a single fibre and a high volume fraction composite, the instability during the curing is generated by the same chemical shrinkage mechanism. The difference is examined from a structural point of view (single fibre or composite) but the mechanism that triggers the instability remains the same.

The shrinkage effect on fibre waviness was shown in a previous paper [16]. To obtain this result two experimental cure cycles were performed on an epoxy sample containing one single fibre. The first cure cycle was used to obtain slow cure kinetics and the second cure cycle to obtain fast cure kinetics. Both cure cycles used the same final cooling phase. Comparisons of the results clearly established that the instability appears during the heating phase of the cure and depends on the parameters of the cure schedule. An instability approach, which takes the evolution of the elastic behaviour of the matrix during the cure into account, was developed and confirms that chemical shrinkage can generate a higher level of stress than the critical level. However, the viscoelastic behaviour of the matrix was not taken into account and this point is critical.

Nonetheless, in a recent previous study [17] we presented the real-time monitoring of the undulation and description of fibres during the cure cycle of a T300 carbon fibre embedded in LY556 epoxy resin. The mass effects and the non-isothermal analysis were studied in order to gain more insight into the real cure conditions of laminates. Correlations with cure kinetics and glass transition have shown that fibre undulations appear prior to the crossing of the glass transition temperature (T_g) line during the rubbery state of the matrix.

The instability is generated by chemical shrinkage and many authors have described the evolution of the volume strain. Several techniques exist in the literature for strain measurements of a thermosetting resin. Russell et al. [18] used a pressure volume temperature (PVT) apparatus for the measurement of the volumetric shrinkage of epoxy resins. Kinkelaar and Lee [19] developed a dilatometer to measure the shrinkage of low-shrink unsaturated polyester resins. Li et al. [20] developed a technique to monitor Archimedes force variations by enclosing a small quantity of resin in a deformable bag plunged into an oil bath. Although these existing techniques examined small resin masses and volume shrinkage under isothermal conditions, indications are that chemical shrinkage is dependent on the degree of conversion.

The expounded single fibre strategy therefore offers an experimental method for the identification, characterization and validation of cure shrinkage models developed in association with the mechanical behaviour of the matrix during curing. Of course, the next step will focus on the fibre–matrix interaction in composite materials. However, this phenomenon should not be studied without models of matrix behaviour during the thermosetting reaction. An understanding of the basic mechanisms involved in a single fibre composite will lead to the improvement of models for the cure shrinkage of the matrix and its corresponding mechanical behaviour.

Moreover, the co-operative buckling of many fibres in a composite could be analysed as a consequence of compressive loading caused by the chemical shrinkage of the matrix during the cure. The same tools as those developed for the analysis of the strength of composite subjected to a macroscopic compressive load [12] can be used for the interaction between fibres and the gradient of properties and load gradient of the matrix.

The initial alignment imperfection of fibres (waviness) is a key element of the plastic microbuckling mechanism and provides highly strategic information for the development of composites for structural applications.

Therefore, the aim of this paper is to propose a scenario for the appearance of fibre undulation and growth during the cure based on the previous studies of the author. This information is required for the construction of efficient models to predict fibre defects and internal stresses that develop during the curing of composites. The second chapter of this paper presents essentials results obtained by real-time video images of the fibre undulation phenomenon. However, in order to understand the undulation mechanism, chemical, physical and mechanical aspects associated with the curing of a thermosetting epoxy are examined in the next chapters under the cure conditions provided by the video results. Cure kinetics and the corresponding state of the resin blend, either liquid, rubbery or glassy are evaluated in the third chapter. The impact of the phase change associated with the thermosetting reaction during the cure is analysed in the fourth chapter by determining the evolution of cure shrinkage in an epoxy matrix in correlation