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Direct and indirect observation of multiple local healing events in successively loaded fibre reinforced polymer model composites using healing agent-filled compartmented fibres

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ABSTRACT

Compartmented fibres containing liquid healing agents have been proposed as a new method to provide local healing in fibre reinforced polymer composites. The compartmented fibres do not contribute to the mechanical properties of the composite but only serve to locally distribute the sources of healing agent and to overcome the intrinsic problems associated with hollow fibres and spherical capsules as containers for the healing agent. In this work the intended multiple local release and healing functionality in a thermoplastic matrix is successfully demonstrated using X-ray micro-tomography and a modified three-point bending test. The results here presented further support the potential of this new concept for the development of self-healing composites.

1. Introduction

The intentional implementation of self-healing capabilities into engineering materials already focused at an early stage on composite materials. Dry demonstrated in the 90s that self-healing of concrete structures was possible by using embedded liquid adhesive-containing hollow glass fibres [1,2]. Since then a lot of attention has gone out to self-healing fibre reinforced composites. The prime reason for this early attention is the fact that composites, due to their excellent mechanical properties, are often used in demanding applications where failure due to uncontrolled propagation of small scale damage is totally unacceptable. The early work on self-healing composites by Bond and Trask [3–6] focussed on the use of hollow glass fibres filled with liquid healing agents similar to those encapsulated in previous studies with spherical capsules [7]. In later studies the hollow glass fibres were replaced by sacrificial fibres thermally removed to create hollow channels [8]. The continuous hollow fibre geometry is excellent for distributing larger amounts of healing agent to the damage site, but the unwanted continuation of the crosslinking reaction triggered at the damage site propagating back into the hollow fibre, generally means that each fibre can only be used for one repair event. As a consequence, the simple architecture of individual hollow fibres co-aligned with the reinforcing fibres (e.g. carbon or glass) and placed at delamination prone areas such as interply regions is being gradually abandoned in favour of more complex but also more versatile 3D continuous fibre networks with pressurised healing agent dosage solutions [9–11]. Mixing spherical capsules with the fibres or fibre tows was proposed as an alternative extrinsic healing route for fibre composites aiming at multiple healing events in one system. Nevertheless, this route was found to be not very successful as the capsule distribution was inhomogeneous and uncontrolled during the composite manufacturing process [12–13]. Recently Mookhoek et al. proposed new fibre architecture to store liquid healing agents in such a manner that multiple local healing events are theoretically possible and in a manner which is compatible with composite fibre production technology: the compartmented fibre concept [14]. In this concept the elongated fibres containing individual vacuoles each filled with the healing agent have no real contribution to the final mechanical properties of the composites as the fibre mechanical properties are intended to be at the level of the usual polymeric (e.g. epoxy) matrix in a fibre composite. While in our previous work [14] we demonstrate the feasibility of manufacturing compartmented fibres no experimental proof of their use in self-healing systems was shown. It is the aim of the present paper to demonstrate that multiple healing upon successive loading steps can be obtained by using compartmented fibres in a composite model system. To prove the concept compartmented alginate fibres containing *ortho*-dichlorobenzene (DCB) as healing

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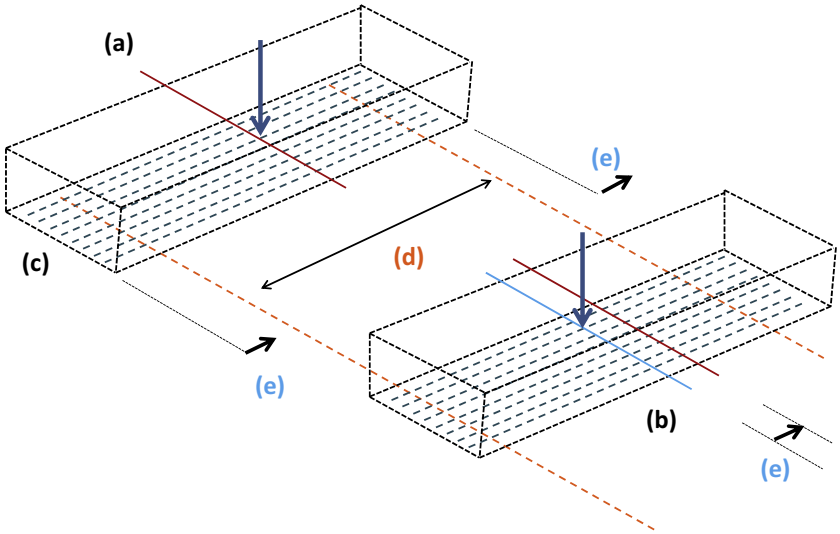

Fig. 1. Rationale of the off-axis three-point bending test showing the position of the PMMA composite beam during the first (a) and second (b) bending event; (c) shows the compartmented fibres aligned close to the beam surface loaded in tension (dashed blue lines); (d) is the span fixed in both bending events and calculated on the span to thickness ratio $L/h = 16$; (e) is the 2 mm shift of the bending axis for the second flexural event which was done after 2 h or 1 week healing time. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

agent were embedded in polymethylmethacrylate (PMMA) and used as the model composite system. In order to determine the potential of the compartmented fibre concept to undergo multiple local damaging and healing events involving the same set of fibres an off-axis bending test and X-ray computed tomography were employed.

2. Experimental

The self-healing composite system consisted of alginate fibres containing unconnected compartments (i.e. healing agent filled vacuoles) embedded in a PMMA matrix. The healing agent in the compartments was a dichlorobenzene/dibromobenzene/polymethylmethacrylate mixture (DCB/DBB/PMMA). This solvent mixture was selected based on the basis of preliminary lap-shear tests between two PMMA sheets [15]. A small portion of PMMA was added to the solvent mixture to enhance the contact between the two broken surfaces as observed in preliminary tests in thermoplastic welding in a kind of bridging concept [16].

2.1. Fibre manufacture

The compartmented fibres were spun from an emulsion of *ortho*-dichlorobenzene in a water solution of sodium alginate (ALG). To this aim a 6 wt.% solution of sodium alginate in de-ionized water was prepared. At the same time a 2.5 wt.% poly(ethylene-alt-maleic-anhydride) (PEMA) polymeric surfactant solution was prepared by dissolving the copolymer in water at 70 °C/60 min. The PEMA solution was then mixed with the sodium alginate solution using a high speed mixer at 2500 rpm for 2.5 min. Then an 86 wt.% DCB/12 wt.% DBB/2 wt.% low molecular weight (Mn ~ 50 kDa) PMMA solution as the healing agent was added while continuously stirring with a three-blade stirrer. In order to obtain two significantly different compartment geometries the emulsion was stirred at 300 rpm for 5 and 10 min. Short stirring time lead to the emulsion with larger droplets and subsequently to bigger compartments. Longer stirring time-produced emulsions with small droplets leading to compartments of small sizes as will be shown in the results section. The presence of PEMA in the alginate helped stabilizing the emulsion after stirring and prior to the spinning process. The composition of the final emulsion was as follows: the DCB-DBB-PMMA/ALG ratio was 1/4 and the PEMA/DCB-DBB-PMMA ratio was 1/50. It should be noted that DBB was mainly added to the DCB/PMMA healing agent to enhance the vacuole contrast in the X-ray tomographic recordings.

The emulsion was then spun with a plunger-based lab scale wet spinning line in a conventional wet spinning process [14,17] to form the healing-agent filled compartmented fibres. A spinneret containing one capillary of 0.25 mm diameter and 2 mm length was used. The extrusion rate was 38 μl/min and the take up speed was 1.3 m/min. The coagulation bath was 0.8 m long and contained a 0.45 M solution of $CaCl_2{\cdot}6H_2O$. Fibres were wound onto a pre-heated (40 °C) plastic bobbin. More details on the fibre preparation and spinning process can be found elsewhere [14]. All used chemicals were purchased from Sigma Aldrich, The Netherlands.

2.2. Scanning electron microscopy (SEM)

All the samples were gold coated by means of plasma sputtering (Balzer Union sputter coater model SCD 040) prior to SEM evaluation in a JEOL 7200 SEM microscope. Low accelerating voltage of 10 kV was used to limit the loss of surface detail in the micrographs resulting from excessive depth of penetration of the electron beam within the polymeric samples.

2.3. Single fibre tensile test

Spun fibres were tested in tension using a Zwick 1455 tensile testing machine with 10 N load cell and at a cross-head speed of 1 mm/min. Fibres (cut from a continuous filament of approximately 20 m long) were glued on supporting paper cards with a gauge length of 25 mm according to BS EN 1007-2004. After clamping the card in a testing machine, the sides of the supporting paper card were cut with a pair of scissors. The effective fibre diameter was determined gravimetrically. At least 25 fibres for each experimental group were tested successfully. Tensile strength distributions of the fibres were modelled with a two parameter Weibull distribution function. The fibre strain was measured from the machine cross-head displacement taking into account the system compliance.