Vacuum Infusion Processing of Self-Healing Composites with Reinforcement Bound Microcapsules

The objective of this work is to investigate a vacuum assisted liquid composite molding process which results in a uniform distribution of liquid filled microcapsules in glass fiber/epoxy composites. These microcapsules are designed to fracture when the composite structure is damaged in service, releasing a liquid healing agent and repairing the damaged region during cure. For this, the microcapsules have to stand the infusion process and may fracture yet when the epoxy matrix is being damaged. A binding agent which is soluble in the epoxy resin serves to anchor the microcapsules in place during resin infusion before being dissolved in the epoxy matrix, resulting in a composite with a high level of uniformly distributed microcapsules.

Erzeugung von mit selbstheilenden Mikrokapseln verstärkten Faserverbundkunstoffen in einem Vakuuminfusionsverfahren

In dieser Arbeit wurden Möglichkeiten untersucht, durch einen vakuumunterstützten „Liquid Composite Molding“-Prozess Mikrokapseln, die mit flüssigem Harz gefüllt sind, gleichmäßig in eine Glasfaser/Epoxidharz Verbundstruktur einzubringen. Die eingesetzten Mikrokapseln haben die Aufgabe, die während des Einsatzes der Verbundstruktur entstehenden Schäden (Mikrorisse) der Matrix zu heilen. Hierfür müssen die Mikrokapseln dem Verarbeitungsprozess standhalten und dürfen erst bei Eintritt einer Matrixschädigung aufbrechen, um das flüssige Harz freizugeben, welches die beschädigte Region durch Aushärten repariert. Dafür wurden unterschiedliche Varianten untersucht, die Mikrokapseln in einem Vakuum unterstützten Infusionsprozess in die Verbundstruktur einzubetten.
1 INTRODUCTION

Matrix microcracking in fiber-reinforced polymers is a long standing problem for applications ranging from aerospace to microelectronics. Microcrack damage in composite structures can be caused by low velocity impacts, high compression or shear loads, manufacturing defects, thermal expansion mismatch, and cyclic loading [1,2]. However, with the continuous growth of composite materials, there is a corresponding need for improved durability and service life [3,4]. To enhance durability, self-healing composite materials have been developed by several researchers [5,6]. One method employs microcapsules filled with a liquid healing agent (often a ring opening metathesis polymerization (ROMP)-based resin)[7,8]. The capsules are designed to fracture upon microcracking induced damage and release the liquid healing agent into the crack, which polymerizes through contact with a catalyst and seals minor cracks [9]. However, the majority of studies of self-healing materials have been small in scale and only focused on laboratory conditions [10,11].

The detection of microcracks is generally difficult, especially in structures with relatively thick and complex geometries [12]. Therefore, the goal of this research is to develop a process to manufacture microcapsule containing self-healing composites using a vacuum infusion process. Such liquid composite molding (LCM) processes are very efficient for mass production of structural components made with thermosetting resins. The main focus of the experiments was to characterize the distribution of the microcapsules relative to a range of manufacturing processing conditions, including the use of binding agents to anchor the microcapsules to the glass preform to reduce movement of the microcapsules during resin infusion.
2 EXPERIMENTAL PROCEDURE

2.1 Materials

A high-performance low-viscosity epoxy resin, Araldite LY 5052, and polyamine curing agent, Aradure 5052, obtained from Huntsman Advanced Materials (The Woodlands, TX) were used at the manufacturer’s recommended stoichiometric ratio (38 phr hardner) as the matrix system. Two different styles of glass fiber-reinforcement were obtained from Hexcel Corporation (Stamford, CT): a mock leno weave (style 7587) with an areal density of 695 g/m² and a double satin weave structure (style 7597) with a fabric weight of 1309 g/m².

The microcapsules comprised a gelatin shell and a core of red oil based dye for visualization. They were fabricated in a complex coacervation process by Thies Technology, Inc. (Henderson, NV). Three separate batches, labeled Batch A, B, and C were supplied with varying capsule diameters. A standard laboratory Leitz Aristomet microscope and Olympus image inspector software, Analysis Pro, were used to characterize the microcapsule size. The polydisperse capsule diameters are detailed in the histograms in Figure 1. It is seen that Batch B and C are relatively similar with a peak population of size of approximately 75-80 µm while the peak population for Batch A is 110 µm. In Figure 1, the bar graphs correspond to the measured population as a function of diameter while the line corresponds to a calculated Gaussian distribution for visualization purposes. It is seen that while the measured population generally follow a Gaussian distribution they are not true Gaussian distributions.
Figure 1: Size distribution of microcapsules for: (a) Batch A, (b) Batch B, and (c) Batch C.

A phenoxy resin, InChemRez Phenoxy PKHP-200, was obtained from InChem Corporation (Rock Hill, SC) as a free flowing powder with a particle size of approximately 110 to 200 µm. This resin is a polyhydroxyether based amorphous polymer with a high thermal stability and good adhesive and cohesive strength. Between 5 and 15% of the Phenoxy PKHP 200 was incorporated into the liquid epoxy resin to increase the resin viscosity and to toughen the matrix.
2.2 Experimental layup

All resin mixtures were vacuum degassed prior to infusion. Composite panels (400mm x 200mm) were manufactured with a vacuum infusion process shown schematically in Figure 2 and Figure 3. It is important to note that this is a cross sectional view of the experimental setup and the spiral tube extends the though the entire length.

![Figure 2: Standard infusion set-up for producing composite panels](image)

![Figure 3: Set up of the infusion and vacuum gate](image)

Two different flow media, obtained from Airtech International, Inc. (Huntington Beach, CA): Greenflow 75 and Lantor’s Soric® XF were used in separate experiments to study their effects on resin flow. As detailed by the manufacturer, 500g of the epoxy / hardener system was used in experiments with the Soric XF flow medium and 435g in combination with Greenflow 75. All resin infusion experiments were performed at a relative pressure of -94kPa.
2.3 Embedding techniques

Three different techniques (detailed below) were used for embedding microcapsules (Batch C) in composite samples; direct placement, direct infusion and preforming.

2.3.1 Direct placement

In direct placement, the microcapsules were manually distributed by hand by scattering them in a rectangular and a parallelogram pattern onto the top fabric layers prior to applying the vacuum, as detailed in Figure 4 and 5. Screening experiments were conducted to determine the proper amount of capsule placement (proportion of capsules to resin and fabric ratio), as well as location within the layers of glass fabric, in order to promote capsule movement during evacuation and resin transfer. Between 0.33 and 0.50 g of capsules were used and were placed between the last layers of fiber laminates. It was assumed that this location corresponded to the location where maximum capsule redistribution would be promoted during resin flow due to the fact that only one glass laminate is present to reduce microcapsule movement. As detailed in following sections, it was seen that the microcapsules did not move through the glass laminates.

![Figure 4: Details of the microcapsule distribution in a rectangle](image_url)
2.3.2 Microcapsule direct infusion

With direct infusion, the capsules were mixed with a stirring staff by hand into the resin prior to infusion. The mixture consisted of 2.5 wt % of microcapsules which corresponds to the amount of microcapsules used in the embedded technique assuming perfect distribution.

2.3.3 Bonding of the microcapsules (preforming)

In the preforming technique, the microcapsules were fixed to the fabric plies with Phenoxy PKHP-200 prior to the vacuum and infusion processes. Based on screening experiments the amount of binder was: 20 g/m² for the mock leno weave and 25 g/m² for the double satin fabric. This amount is a decade less of material compared to the amount of microcapsules.

The binding agent was activated by heating the coated fabrics to 140°C for 20 min. Heating was achieved by placing the fabric plies in a compression molding system where the platens were separated by a 1.5 cm gap. In selected cases, samples were heated under a relatively low pressure of 6.6E-4 MPa.

2.4 Analysis characterization

To characterize the movement of microcapsules through the fabric, specimens were cut from cross sections of selected samples and composite samples at selected locations. The samples were then mounted in a Heraeus Kulzer's Technovit 4000/4002 embedding resin and polished with standard techniques. The polished samples were examined by optical microscopy using a Leitz Aristomet microscope.
3 RESULTS

Figure 6 shows the typical distribution of the manually dispersed microcapsules. The distribution is not perfectly uniform due to human error, air drafts during the hand-scattering process and electrostatic forces. It is important to note that in this case, no resin is present at this stage of the experimentation.

Figure 6: Dispersion of microcapsules on dry glass fiber fabrics

In the initial test using the direct placement method it was observed that the microcapsules moved during the vacuum process. This result is displayed in Figure 7 where a parallelogram pattern (a) was elongated (b) in the direction of the air flow from the vacuum. In the early stages of the vacuum process the air flow promoted microcapsule movement. As the vacuum proceeded, the free volume with the glass fabric decreased as atmospheric pressure compressed the system, restricting movement later in the process.
Figure 7: Capsule movement induced by the air flow before resin infusion, (a) prior to vacuum (b) after vacuum. In both images no resin was present.

The movement of microcapsules was minimized by securing them with the binding agent. For example Figure 8 (b) and Figure 9 show that with no binder the microcapsules were shifted to the right in the circled areas (direction of air movement during the vacuum process). While this shift is minor there is evidence that the microcapsules did experience some movement. In contrast, in Figure 8 (a), when the binder was used prior to the vacuum process, the microcapsules remained in their original placement.
Figure 8: (a) Microcapsule distribution with binder and (b) without binder after vacuum infusion. In both images no resin was present.
When direct infusion was used (microcapsules in the resin) the microcapsules remained at the inlet gate near the edge of the fabric and were never transported to the part, as seen in Figure 10. It is believed that because of the vacuum which was applied prior to infusion of the resin microcapsule mixture, the limited free volume within the fabric caused the fabric to act as a filter preventing the microcapsules from flowing with the resin. This theory is supported by a cross sectional view of the gate, shown in Figure 11, where the microcapsules are concentrated between the fabric layers. Thus, it is seen that microcapsule movement is limited by the laminate’s permeability and by the compaction of the layer structure. It is seen that the laminate is compacted to a level that there are no voids large enough to allow the microcapsules with an approximate diameter of 100 µm, suggesting that the voids are less than 100 µm.
The microscopy results of microcapsules embedded in composite panels demonstrated that gelatin capsules are processable by the vacuum infusion techniques without being visibly damaged, as seen in Figure 12. In addition it was observed that capsules tended to migrate together which may be the result of static charges during deposition. These concentration differences are marked by red and yellow circles for higher and lower concentrations respectively.
A cross sectional microscopic examination of a panel prepared by the direct placement method also suggests that there is very little migration of the microcapsules between the plies, as seen Figure 13. Because the glass fabric prevented movement of the microcapsules between the plies, the movement of the microcapsules is only interlaminar, not intralaminar.

![Cross sectional image of composite with microcapsules](image)

**Figure 13:** Cross sectional image of composite with microcapsules

### 3 CONCLUSIONS

This paper details the possibility of using microcapsules in conventional vacuum infusion processes for manufacturing self-healing composite structures. It was demonstrated that gelatin microcapsules can be embedded in glass fiber/epoxy composite materials by a vacuum infusion process without visible damage of the microcapsules.

Microcapsules were embedded using three different techniques: a direct placement technique; a preformed direct placement technique coupled with a binding process to prevent microcapsules movement, and a direct infusion method.

It was theorized that the microcapsules would be displaced during the infusion of the resin by fluid drag, but this effect was not seen. Instead it was observed that the microcapsules were displaced only during the initial vacuum process, as the air vacated from the vacuum bag producing drag on the microcapsules. Binding the capsules to the fabric was important to prevent microcapsule movement only during the vacuum stage of processing. This unwanted effect
may be reduced by applying the vacuum slowly, however this would adversely affect processing time.

The direct infusion of the microcapsule did not allow the microcapsule to be transported through the fiber plies. Again, because of compaction and increased density of the fiber plies induced by the vacuum, the fabric acted as a filter, preventing microcapsule motion.

Future studies should include the characterization of the healing of damaged components. In these studies microcapsules would be filled with a ROMP-active monomer (such as dicyclopentadiene) and a corresponding initiator (such as Grubb’s catalyst) dispersed in the matrix. Microcapsules in varying composite structures of different compositions also merit a focused investigation. This work demonstrates that future applications of self-healing composite structures employing liquid filled microcapsules are possible through vacuum infusion processing.

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