MANUFACTURING OF PREPREG WITH MICROCAPSULES FOR SELF HEALING COMPOSITES

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1 Introduction

Fiber-reinforced polymer composite materials with self-healing ability have attracted great interest because they can extend a product’s life and prevent catastrophic failure. Self-healing of the composite material can be activated by delivering a healing agent to the damaged zone [1-11]. One method to deliver a healing agent is to embed the healing agent in microcapsules which then release the agent upon capsule rupture\cite{1-6}. White \textit{et al.} \cite{1} first demonstrated self-healing in polymer composites using this approach by incorporating catalyst particles and microcapsules of a healing agent in epoxy. The healing agent was dicyclopentadiene (DCPD), a monomer that polymerizes when in contact with Grubbs’ catalyst. Epoxy specimens with this healing system demonstrated a recovery of fracture toughness after the generation of a crack resulted in capsule rupture, contact of DCPD and Grubbs’ catalyst in the crack plane, and polymerization of DCPD within the crack plane.

Caruso \textit{et al} \cite{3, 12} studied a healing chemistry of a solvent core microcapsule. Microcapsules with reactive cores are advantageous since they require only one type of microcapsule to heal damage. Full recovery of fracture toughness was achieved using microcapsules consisting of a nontoxic solvent ethyl phenylacetate (EPA) with a Di-Glycidyl Ether of Bisphenol F (DGEBF) epoxy resin \cite{12}. Blaiszik \textit{et al.} \cite{4} then successfully reduced the size of microcapsules to a sub-micron scale by applying ultrasonication during their manufacture. Microcapsules with a sub-micron scale were utilized to heal microcracks such as interfacial debonding between a fiber and a matrix \cite{13, 14}.

The use of microcapsules of sub-micron scale is advantageous for fiber-reinforced composites because they can allow for a high fiber volume fraction of the self-healing composite to be achieved. These microcapsules are small enough to fit into the interstitial spaces between single fibers. However, self-healing functionality of a fiber-reinforced composite with such microcapsules has yet to be demonstrated due to the difficulties of a sample preparation. One significant challenge is distributing the microcapsules uniformly within a fiber-reinforced composite. The minimal gap between single fibers makes it difficult for microcapsules to penetrate within the inner regions of fiber yarns. If inner fibers are not functionalized with microcapsules, the potential self-healing ability of the composite will be limited because the healing agent will only be able to reach a limited portion of the composite.

To create a composite with evenly distributed capsules, we propose the fabrication of a prepreg in which each single fiber is already functionalized with microcapsules. Microcapsules can be well attached onto a fiber yarn via a dip coating method before resin is introduced \cite{13}. Performing this dipping method during sonication leads to a good dispersion of microcapsules throughout the entire fiber yarn. Resin can then be impregnated after the microcapsules are introduced to the fibers.

In this research, a method to incorporate sub-micron sized microcapsules to E-glass/epoxy resin prepreg was developed. A lab scale prepregger was built to fabricate the prepreg with minimal damage to microcapsules. Prepreg with various microcapsule concentrations, fiber volume fraction, and fiber areal weight can be fabricated using the prepregger. The status of microcapsules in the prepreg was
successfully examined using confocal fluorescent microscopy.

2 Material and experimental

2.1 Microcapsule fabrication

Polyurethane (PU)/poly(urea-formaldehyde) (UF) microcapsules containing a mixture of EPA and DGEFB epoxy resin were prepared by a modified procedure of Caruso et al [15], as shown in Figure 1. Fluorescent dye Nile Red was mixed with the core material of the microcapsules to aid with confocal fluorescent microscopy. Prepared microcapsules were contained in deionized (DI) water with various microcapsule concentrations and used as a sizing agent.

DGEBA epoxy resin (EPON 862) was purchased from Miller-Stephenson and EPA, urea, formalin (37 % formaldehyde), resorcinol, Nile Red, and ammonium chloride were purchased from Sigma-Aldrich. Ethylene-maleic anhydride (EMA) copolymer powder (Zemac-400) was received from Zeeland Chemicals, and was used in a 2.5 wt% deionized water solution. PU prepolymer (Desmodur L 75) was purchased from Bayer Material Science and used as received.

2.2 Lab scale prepregger development

Building a prepregger was the primary step to fabricate a prepreg with microcapsules. The machine was required to have a fiber sizing system for the incorporation of microcapsules, a drying system, and a resin impregnation system. Figure 2 shows a 3D CAD model of the prepregger designed using SolidWorks. The use of 3D CAD helped to design the machine with all necessary systems held in a limited space.

A lab scale prepregger was then built as shown in Figure 3. The machine consists of a shelf to place the fiber bobbins, a fiber sizing system, a drying system, a resin impregnation system, and a take-up drum. The fiber sizing system is equipped with a sonication bath outside of a dip type bath which contains a sizing agent. The drying system consists of several heaters with a vertical fiber pathway. A drum type bath with a scraper was used for the resin impregnation system. The take-up drum was controlled with two motors which made it possible to rotate and to translate independently. The diameter of the drum was 0.78 m and it could rotate with a speed of 1 to 14 rpm while translating at 6 to 84 mm/min.

DGEFB epoxy resin EPON 862 and aliphatic amine EPIKURE 3274 were used as a prepreg resin system because of the system’s long pot life. EPON 862 and EPIKURE 3274 were mixed in the ratio of 100:48 parts by weight and degassed for 15 min in room temperature before being added to the resin bath.

E-glass fiber yarn (ECG150 1/0.7Z), which has 200 single fibers, were purchased from PPG Fiber Glass. EPON 862 and EPIKURE 3274 were purchased from Miller-Stephenson.

2.3 Prepreg fabrication

Prepreg of 180 mm wide was fabricated using the custom built lab-sized prepregger. The take-up drum was translated with a speed of 4.5 mm/min, fast enough to overcome the pot life of the resin system which is less than an hour. Rotation speed was varied according to desired fiber areal weight of the prepreg.

E-glass fiber yarn was first sized with the microcapsules using a sizing system. Eight fiber yarns were simultaneously dipped into a sizing agent in the sizing bath. Microcapsule concentration of the sizing agent was varied from 0 to 10 wt% by diluting the agent with deionized water. The sizing bath was sonicated to aid with the distribution of microcapsules within the fiber yarns. Water from the sized fiber yarns was then removed through the drying system. Drying conditions were controlled by the distance of the fiber travel path and the power of the heaters.

The microcapsule sized fiber yarns were then impregnated with resin using a drum type resin bath. In this bath, fiber tension combined with the resin’s viscous friction rotates the drum while a scraper removes excess resin. A constant amount of resin is impregnated within the fiber yarns as they move over the drum. The fraction of resin in the fiber yarns was controlled by the distance of the scraper from the drum. A wider gap between the scraper and drum leads to a thicker coat of the fiber yarns were gathered as one fiber bundle through several rollers after resin impregnation.

The fiber bundle was then continuously wound up to the take-up drum while being evenly distributed.
along the width of the take-up drum. The prepregging process was finished when a prepreg of desired width was fabricated. The prepreg was kept on the drum for at least 2 hours at room temperature to let the resin reach a b-stage. Allowing the prepreg to reach b-stage made it possible to handle the prepreg without deformation or warp. The completed prepreg was then used to manufacture consolidated composites by a layup process or stored in a refrigerator for later use.

2.4 Imaging analysis

Microcapsules on a fiber yarn without resin were examined using a field emission environmental scanning electron microscope (Phillips XL30, FEI). However, it is impossible to use SEM to see microcapsules embedded in a prepreg or consolidated composite without fracturing the sample. Microcapsules seen on a sample’s fractured surface gave limited information about the damage after a prepregging process due to induced damage from the fracture.

A confocal fluorescent microscope (TCS SP2, Leica) was used to analyze the status of microcapsules incorporated into a prepreg without fracturing the sample. The core of the microcapsules illuminate under a fluorescent light because of the fluorescent dye Nile Red. A laser of wavelength 488 nm was projected to the specimen and its fluorescent signature of a wavelength 626 to 667 nm was collected. The focal plane of the microscope was changed from 5 to 45 µm below the surface of the specimen to achieve a three dimensional configuration of the specimen. A field of view of 238 × 238 µm was wide enough for an E-glass fiber yarn with a diameter of approximately 150 µm.

3 Results and discussion

3.1 Characterization of the microcapsule

Microcapsules were sphere-shaped and had a smooth as shown in Figure 4. The size distribution of the microcapsules was analyzed by analyzing more than 300 microcapsules from SEM images. The average diameter of the microcapsule was 3.3 µm with a standard deviation of 1.4 µm.

The fluorescent signature of the microcapsules was examined using a specimen consisting of microcapsules embedded in epoxy resin. The microcapsules were incorporated into the epoxy resin after being lyophilized for 24 hrs and the epoxy resin was cured. Figure 5 shows a confocal fluorescent micrograph of the microcapsules in epoxy resin. Microcapsules are seen as an illuminated sphere in the micrograph because of the fluorescent core material.

The thermal stability and content of the microcapsules were studied using a thermogravimetric analyzer (TGA1, Mettler Toledo). Lyophilized microcapsules were heated from 25 °C to 500 °C with 10 °C/min heating rate in a nitrogen atmosphere as shown in Figure 6. The microcapsules were thermally stable until the temperature reached the boiling point of EPA. The fill content of the microcapsules was calculated to be around 80% using the sharp drop of mass at this temperature.

3.2 Characterization of the prepreg

Figure 7 shows a microcapsule sized fiber yarn after drying. The microcapsules were well adhered to the fiber yarn. It was seen that more microcapsules were attached to the yarns when higher microcapsule concentrations of the sizing agent were used.

The status of microcapsules in the prepreg was assessed from confocal fluorescent. Microcapsules that survived processing conditions were shaped as an intact sphere as shown in Figure 8a while ruptured microcapsules were distorted as shown in Figure 8b. Microcapsules tended to be ruptured if fiber tension was high during the prepregging due to poor lubrication of rollers. Fiber tension was reduced after changing the lubrication of rollers. Prepreg with a high microcapsule survival rate was eventually fabricated after adjusting fiber tension and drying conditions by trial and error.

However, to ensure complete microcapsule survival throughout the process, it is also desirable to develop a method to quantify damage of microcapsules in a prepreg rather than imaging alone. Analyzing glass transition temperature (Tg) of the prepreg is one suggested solution to measure microcapsule damage, since as released core material from the ruptured microcapsules plasticize the matrix, the Tg of the prepreg should decrease.

Sonication of the fiber sizing bath was seen to help microcapsule distribution throughout fiber yarns during prepregging. Figure 9a shows microcapsules
around a fiber yarn in a prepreg fabricated without sonication the sizing bath. Microcapsules were not able to penetrate into the interior region of the fiber yarn. However, as shown in Figure 9b, microcapsules were well distributed in the interior area of the fiber yarn after applying sonication to the sizing bath. This led to a higher overall microcapsule concentration in the prepreg since microcapsules were located both in interstitial spaces between single fibers and along the outside of the fiber yarn.

Microcapsule concentration of the prepreg was controlled by the microcapsule concentration of the sizing agent. Higher concentrations of microcapsules in the sizing agent led to higher microcapsule concentrations in the prepreg. To quantify microcapsule concentration in the prepreg, it is recommended to develop three dimensional visualization of the prepreg using multiple confocal fluorescent images with different focal planes. The volume fraction of microcapsules in the prepreg could then be calculated by counting voxels that illuminate under fluorescence.

## 4 Conclusions

E-glass/epoxy resin prepreg with microcapsules was successfully fabricated using a custom built lab scale prepregger. Submicron sized microcapsules were incorporated into the prepreg by applying a microcapsule yarn sizing before resin impregnation. Applying sonication to the sizing agent helped the microcapsules to penetrate into the interior regions of the fiber yarns. Confocal fluorescent microscopy was used to analyze the microcapsules in the prepreg without fracturing the specimen.

Future work will consist of quantification of properties of the prepreg such as X, Y, Z so that prepreg manufacturing conditions can be optimized. In addition, fiber-reinforced composites with microcapsules will be fabricated using the prepreg and their mechanical and thermal properties will be examined.

## 5 Acknowledgements

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## 6 References


FIG. 1. Microencapsulation protocol for the preparation of PU/UF microcapsules with reactive core.


Fig. 2. 3D CAD model of the lab scale prepregger using SolidWorks. The prepregger consists of a shelf to place the fiber bobbins, a fiber sizing system, a drying system, a resin impregnation system, and a take-up drum.

Fig. 3. Photograph of the custom built lab sized prepregger.
Fig. 4. SEM image of the PU/UF microcapsules. The microcapsules were lyophilized for 24 hrs and sputter coated with Au/Pd.

Fig. 5. Confocal fluorescent micrograph of microcapsules embedded in epoxy, taken 5 µm below the surface of the specimen. Microcapsules were visible inside of the resin due to the use of a fluorescent core and focal plane adjustment.

Fig. 6. TGA trace of the PU/UF microcapsules containing EPA and DEGBF epoxy. The heating rate was 10 °C/min. The sharp drop of mass corresponds to the boiling point of EPA.
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Fig. 7. SEM image of microcapsules on an E-glass fiber yarn after drying but before resin impregnation. The microcapsules were well attached to the fiber yarn.

Fig. 8. Confocal fluorescent micrographs of microcapsules in a prepreg. Images were taken 5 µm below the surface of the specimen perpendicular to the fibers. (a) Microcapsules that survived are seen as intact spheres while (b) damaged microcapsules show rupture and distortion.
Fig. 9. Confocal fluorescent micrographs of fiber yarns in a prepreg. Images were taken 5 µm below the surface of the specimen perpendicular to the fibers. (a) Microcapsules were located only on the exterior region of the fiber yarn without sonication while (b) microcapsules are well distributed throughout the entire fiber yarn after applying sonication.