SELF-HEALING COMPOSITES FOR MITIGATION OF LOW-VELOCITY IMPACT DAMAGE

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Fiber-reinforced composites with polymeric matrices are extensively used in many structural applications. Despite successful implementation, their susceptibility to damage due to transverse impact loads remains a major limitation. Low-velocity or ballistic impact events can create significant matrix damage that is often hidden and difficult to repair. In this study, fiber-reinforced composites with self-healing, polymeric matrices are investigated for mitigation of low-velocity impact-induced damage. The self-healing components described by White et al.1 and Rule et al.2-urea-formaldehyde microcapsules containing dicyclopentadiene (DCPD) liquid healing agent and paraffin wax microspheres containing 10 wt% Grubbs’ catalyst- are incorporated in a woven S2 glass reinforced epoxy composite using a hand lay-up technique. Low-velocity impact tests reveal that self-healing materials are able to repair large portions of delaminations. Fluorescent labeling of damage regions combined with image processing shows that total crack length per imaged cross-section is reduced by 51% upon self-healing. Closer inspection of damage with scanning electron and optical microscopy also shows clear evidence of damage repair.

Keywords: self-healing, composites, impact damage

Abbreviations: DCPD: dicyclopentadiene

1 Introduction

Because of their excellent in-plane properties and high specific strength, fiber-reinforced composites with polymeric matrices have found many uses in structural applications. Despite this success, they are particularly prone to both low-velocity and ballistic impact damage. In many cases, damage is subsurface or barely visible, making it difficult to detect.3 This type of damage can be enlarged by subcritical loads normally encountered in the lifetime of the composite part and eventually lead to structural failure. One solution to manual repair impact damage is the employment of self-healing materials.1
Initial studies on the recovery of mechanical properties in self-healing materials focused on monotonic fracture testing and fatigue of polymer composites without fiber reinforcement. In further work, Kessler et al. demonstrated recovery of Mode I interlaminar fracture toughness of a self-healing structural composite. However, the current study represents the first attempts to demonstrate self-healing of impact damage. The aim of the work presented here is to establish, by damage visualization and quantification, the feasibility of self-healing low-velocity impact damage.

2 Experimental

2.1 Materials

Self-healing functionality was incorporated in glass fiber-reinforced composites by utilizing components described in the work of White et al. and Rule et al. Distilled endo-DCPD filled microcapsules were manufactured by in-situ poly(urea-formaldehyde) microencapsulation using the method described by Brown et al. To promote both even distribution of microcapsules and delivery of adequate amounts of DCPD healing agent to crack planes, two different sizes of capsules were employed. Microcapsules of 35 μm number average diameter were used to ensure even distribution, while microcapsules of 180 μm number average diameter were used to provide a large supply of healing agent for delivery to damaged regions.

Wax-protected catalyst microspheres were made using the method described by Rule et al. Microspheres for self-healing specimens were made with 10 wt% first generation Grubbs’ catalyst (freeze-dried from benzene), while wax microspheres for control specimens were made by leaving out the catalyst phase. Microsphere size is also controlled by agitation rate, but plain and catalyst-containing wax microspheres made at the same agitation rate do not yield the same average size. Matching the size distribution between plain and catalyst-loaded wax microspheres was not possible, so the number density of microspheres in the final composite was maintained. Agitation rates of 1000 rpm and 600 rpm were used for catalyst-loaded and plain wax microspheres respectively, resulting in microspheres of approximately 135 μm in size.

Composite panels for low-velocity impact were approximately 100 × 100 × 4 mm and consisted of 4 plies of 810 g/m² 5×5 yarns-per-inch plain woven S2 glass fabric (Owens Corning Knytex SBA240F) in an Epon 862 and Epi-cure 3274 matrix (100:40 weight ratio). The self-healing panels of Group SH were made with a 2:1 ratio of ~35 μm to ~180 μm DCPD-filled microcapsules, as well as catalyst-containing wax microspheres of 135 μm average diameter. Control panels of Group C-II were made identical to those of Group SH, except they contained plain wax microspheres. In addition, a set of plain composite panels (Group C-I) and a set of microcapsule-only panels containing 2:1 ratio of ~35 μm to ~180 μm microcapsules (Group C-II) were fabricated as additional controls. Table 1 summarizes the composite panels tested. Panels were fabricated using a hand lay-up technique with self-healing components mixed into the liquid epoxy by hand prior to lay-up. The samples were cured for 24 hours at room temperature, followed by 48 hours at 35°C. Additionally, appropriate compaction force was used to yield a final composite thickness of ~4 mm and a fiber content of ~30%.
Table 1: Summary of tested composites

<table>
<thead>
<tr>
<th>Group</th>
<th>Microcapsules*</th>
<th>Wax Microspheres**</th>
<th>Total Crack Length per Imaged Edge (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-I</td>
<td>None</td>
<td>None</td>
<td>70 ± 12</td>
</tr>
<tr>
<td>C-II</td>
<td>35 μm and 180 μm</td>
<td>None</td>
<td>70 ± 10</td>
</tr>
<tr>
<td>C-III</td>
<td>35 μm and 180 μm</td>
<td>135 μm, no catalyst</td>
<td>90 ± 12</td>
</tr>
<tr>
<td>SH</td>
<td>35 μm and 180 μm</td>
<td>135 μm, w/ catalyst</td>
<td>45 ± 12</td>
</tr>
</tbody>
</table>

* Estimated 14 wt% of matrix after compaction
** Estimated 4 wt% of matrix after compaction

2.2 Testing

2.2.1 Low-Velocity Impact Testing

Impact testing was conducted on an Instron Dynatup 8200 instrumented drop weight impact tester with the sample circularly clamped (76.2 mm diameter) and a spherically shaped impact head of 25.4 mm radius of curvature. Samples were impacted with 7.43 kg from 0.60 m (44 J of impact energy). All impacted self-healing panels were given 48 hours to heal before further testing.

2.2.2 Damage Imaging and Quantification

To image impact damage, tested panels were sectioned through the point of impact into four quarters. The exposed delaminations and matrix cracks were marked by a fluorescent dye penetrant (Zyglo ZL-37) using a technique demonstrated by Kuboki et al. Figure 1a shows a typical image of highlighted damage under UV illumination. For each panel four separate images were obtained, one for each sectioning cut.

The total crack length per imaged edge was used to visually quantify the degree of damage. First, cracks were manually traced with a pencil tool in Adobe Photoshop CS2. The resulting images were thresholded to yield just the crack tracings, which were in turn skeletonized using a Fovea Pro photo analysis plugin (Fig. 1b). Finally, the total length of the skeleton was then computed using the same plugin software. Thus, a measure of total crack length per image was obtained.

![Image](image.png)

Figure 1: Cross-sectional images of impact damage in self-healing composites. (a) Image under UV illumination of fluorescently marked damage. (b) Skeletonization of marked cracks
3 Results and Discussion

Results for panels of the self-healing Group SH show a 51% decrease in total crack length per imaged edge when compared to the corresponding full control system of Group C-III (Table 1). Closer inspection with optical microscopy and SEM (Fig. 2) revealed large tracts of poly-DCPD-filled delaminations with only small unfilled regions, confirming this large reduction in total crack length. In addition, unfilled cracks were predominantly limited to surface cracks and transverse cracks located in regions devoid of self-healing components.

![Figure 2: (a) Optical image and (b) SEM micrograph of a cross-section of a healed delamination region from a panel from group SH. The dotted lines indicate the path of the delamination across the images](image)

Plain composite panels (Group C-I) and microcapsule-only panels (Group C-II) were tested to observe the effects of self-healing components on damage resistance. As seen in Table 1, there is a negligible increase in total crack length per imaged edge when Group C-II is compared to Group C-I, indicating that the addition of the microcapsules had little effect on impact damage resistance. However, when Group C-III is compared to Group C-II, a significant jump in total crack length per edge is seen, suggesting that wax microspheres have a detrimental effect on damage resistance. This trend was clearly apparent in some samples in Group C-III that had delaminations that propagated to the clamped edge. Additionally, self-healing panels of Group SH show a considerably smaller total crack length per edge than impacted plain composite controls, indicating that self-healing may be able to overcome the decrease in damage resistance imparted by the inclusion of wax microspheres.

4 Conclusions and Future Work

This study provides visual confirmation of self-healing of low-velocity impact damage to composite materials. Fluorescent labeling of damage regions combined with image processing shows a significant decrease in observed crack length when comparing impacted self-healing panels to impacted control panels. Furthermore, it was observed that the addition of microcapsules to the matrix of the composite had little effect on damage resistance. Incorporation of wax microspheres, on the other hand, increased impact damage considerably. Work is ongoing to identify an alternative method of incorporating the catalyst phase with less effect on global mechanical properties. Additionally, future work will focus on developing a protocol to evaluate the recovery of mechanical properties after healing of impact damage.
ACKNOWLEDGEMENTS

Funding for this project is provided by the Army Research Lab. The authors would also like to thank John D. Williams and the Materials Testing Instructional Laboratory at the University of Illinois for use of the drop weight impact tester. Other facilities used at the University of Illinois include the Composites Manufacturing Laboratory and Beckman Institute. Electron microscopy was carried out in the Center for Microanalysis of Materials, University of Illinois, which is supported by the US Department of Energy.

REFERENCES


