Injection repair of carbon fiber/bismaleimide composite panels with bisphenol E cyanate ester resin

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Abstract

Resin injection of bisphenol E cyanate ester, a low viscosity resin that cures into a high temperature thermoset polymer, is investigated as a reliable repair method to restore strength and stiffness in delaminated carbon fiber/bismaleimide composites used in aircraft panels. The influence of temperature on the viscosity of the uncured resin was measured to optimize the injection conditions for high resin infiltration into the delaminations. The repair efficiency of the resin was evaluated by varying the panel thickness and the method by which the delamination damage was created in the composite specimens. Ultrasonic scanning (C-scan), flash thermography images, and cross-section analysis of repaired panels revealed excellent resin infiltration into the damaged region. Evaluation of mechanical repair efficiency using both bending stiffness and in-plain compressive strength of the composite panels as the repair metrics showed values exceeding 100%.

Keywords

- A. Polymer–matrix composites (PMCs);
- A. Adhesive joints;
- B. Thermomechanical properties;
- B. Impact behavior;
- D. Ultrasonics
1. Introduction

In recent years, the aerospace industry has dramatically increased the use of polymer matrix composites (PMCs) as structural materials, replacing their heavier metal counterparts [1]. Carbon fiber reinforced PMCs, in particular, are recognized as advanced structural materials because of their high stiffness to weight ratios and excellent fatigue resistance [2]. Although carbon fiber based PMCs are currently experiencing rapid growth in structural applications, their multi-layer laminate structures make them highly susceptible to defects and damage in the form of interlaminar fracture, or delamination. This type of damage can drastically reduce the strength and functionality of the part [3]. Delamination damage in PMCs may be caused from pre-existing manufacturing defects or by sudden impacts or high static loads in service; however, once delaminations are present, the material’s structural integrity is significantly compromised.

Repairs of delamination damage often must meet several conditions, including being aerodynamic, durable, and environmentally friendly [4]. There are two major methods for repairing a delamination in composite panels: scarf/bonded patch repairs and injection repairs. During a bonded patch scarf repair, material is removed or “scarfed” from the damaged area and a matching composite piece is bonded to the area using a suitable bonding adhesive [5]. Though fairly effective, this method is not suitable for structures that provide only limited access to the damaged area, such as corners or edges. The injection repair is an alternative, simpler method useful in structural repair applications. Here, resin is directly injected into the damaged area where it infiltrates the delaminated layers. Subsequently, the composite part will undergo a curing step to harden the injected resin, thus healing the damaged area internally.

A successful injection repair depends on the choice of resin, for which several requirements were specified by Russell and Bowers [6]. The resin should exhibit both good wettability on the composite surface and low viscosity to assure effective infiltration between the delaminated layers after injection. It should develop excellent adhesive strength between the delaminated surfaces to restore the mechanical strength of the composite after repair. The cured resin should have a glass transition temperature and thermal degradation temperature closely matching those of the composite panel and it should have matching service temperature limits. Finally, since the injection repair is typically done manually, the resin should not release significant amounts of volatile organic compounds (VOC) to meet EPA/OSHA workplace safety regulation during repair operations. Although epoxy resins were used in the past for injection repairs, their relatively low $T_g$’s and high moisture sensitivity created the need to identify alternative resins for repairing high temperature composites, such as bismaleimide (BMI) matrix based [7].

The present work focuses on bisphenol E cyanate ester (BECy), a resin that cures into a thermoset polymer with good thermal stability and mechanical properties [8]. Other properties such as high adhesive strength and low moisture absorption make cyanate ester polymers good replacements for epoxies in many applications [9] and [10]. In contrast to most thermoset polymer resins, BECy cures into a network with a high $T_g$ of ca. 270 °C, yet the monomer has a very low viscosity (90–120 cP at room temperature), a combination that makes the resin a unique candidate for injection repairs [9] and [11]. The resin also offers excellent compatibility and wettability with the bismaleimide/carbon fiber composites (BMI-cf) used as pristine specimens in this study [12].
In the present work, the injection repair process was developed and optimized to achieve high repair efficiencies on unidirectional carbon fiber–bismaleimide composite panels that are commonly used on advanced aerospace structures. The success of the repair is determined using ultrasonic C-scans and thermography, and the repair efficiencies are quantified based on the stiffness and strength of pristine, delaminated, and repaired panels. Through the investigation, we examine the influence of specimen thickness on reparability by examining specimens with two different thicknesses. Similarly, the influence of the type of delamination damage (static load method or impact load method) on the repair efficiency is also explored.

2. Experimental

2.1. Materials

The BMI-cf panels with 32 and 24 plies were manufactured by hand lay-up of Cytec IM7/5250-4 unidirectional prepreg material, provided by Cytec Engineering Materials, Tempe, AZ.

A quasi-isotropic layup [45/90/−45/0]s was used for preparing the specimen panels. Each panel was processed using standard autoclave processing with the manufacturer’s recommended cure cycle. Specimens measuring 4 × 6 in dimensions were machined from the autoclaved panels.

The repair resin was prepared by adding a small amount of liquid phase organometallic-based catalyst (3 parts per hundred of EX-1510-B, Tencate Technologies, Almelo, The Netherlands) to bisphenol E cyanate ester (BECy, Tencate Technologies, Almelo, The Netherlands). The mixture was stirred for 10 min with a magnetic stir bar, followed by degassing at 25 mm Hg vacuum for 20 min to eliminate absorbed air. Repaired PMCs were cured at 180 °C for 2 h in a convection oven, applying a temperature ramp of 1 °C/min.

2.2. Pre-damaging of panels

The specimens were pre-damaged by two different methods. The first method used an Instron 5569 tensile testing machine (Norwood, MA) to apply a static load to a pristine specimen, see Fig. 1. The specimen was secured between two steel plates (both with a 5.08 cm (2-in) diameter circular hole in the center) acting as a clamp and centered under the load cell. A steel ball bearing was placed at the center of the specimen to apply the load. Each sample experienced an initial static load of 200 N prior to applying the load necessary for delamination. A compressive load was applied at a rate of 1 mm/min until 4 mm extension was reached for creating delaminations in the samples. The method consistently generated a circular delaminated area of ca. 50.8 mm in diameter, as shown in Fig. 2. With the second method, a drop tower was used to introduce the delamination damage. The impact energy was varied depending on specimen thickness by increasing the height and weight from which the impact load was dropped. The 24-ply and 32-ply specimens were struck with impact energies of 20.60 J and 29.24 J, respectively. Fig. 2 shows that the delamination damage was inconsistent and the damaged area varied significantly among samples. This is explained by the fact that rapid delamination may have caused microcracks that were randomly initiated and propagated, rather than the slow, systematic damage propagation initiated by the static loading method.
2.3. Injection repair setup and procedures

After damaging the specimens, an injection hole and vent holes with 3.175 mm (1/8 inch) diameters were drilled into the composite panel. Based on the C-scan images of the pristine, the injection hole was drilled in the center of the delaminated area with six evenly spaced vent holes placed just on the edge of the delaminated area. Holes were drilled approximately 3/4 of the way through the panel. Before the repair, specimens were air blasted and flushed with acetone to remove debris from the microcracks and vent holes and to determine their connectivity with the delaminated layers. The panels were dried overnight at approximately 100 °C to eliminate any absorbed moisture. The injection repair setup developed in this work is schematically shown in Fig. S1 of supporting information along with detail description of various steps involved in the repair procedure.

2.4. Rheology of repair resin

The rheological behavior of BECy was characterized using a rheometer (Model AR2, TA Instruments, Inc., New Castle, DE). Temperature sweep tests were carried out between 25 and 175 °C at a frequency of 1 Hz, strain amplitude of 2%, and at a heating rate of 3 K/min. The temperature of sample was controlled by using environment chamber. The temperature sweep tests were conducted in two different steps. First, the resin was heated from 25 to 50 °C,
followed by a second heating step from 50 to 175 °C after a 90 min holding time between the two temperature sweep tests.

2.5. Nondestructive evaluation

Ultrasonic scanning was performed on pristine, delaminated, and repaired specimens to determine both the extent of delamination as well as the effectiveness of resin infiltration after the repair. Water immersion scans were performed using an Olympus 5077PR square wave pulser/receiver and a Sonda 007 CX ACUT system. A 6.35 mm (0.25 in) diameter, 10 MHz transducer was used to transmit and intercept the signals (Model V312, Serial Number 172643). Flash thermography was performed using Ecotherm flash thermography system (Thermal Wave Imaging, Inc., Ferndale, MI). An FLIR IR camera with a capture rate of 90 frames per second was used to provide thermal imaging of the samples.

2.6. Cross-section analysis

Static load delaminated samples were sectioned diagonally through the center injection hole to evaluate the cross-section by optical microscopy. The cross section surface was finely polished with 1200 grit sandpaper prior to microscopic imaging. Delaminations, microcracks, and air voids in the samples were traced to analyze resin infiltration into the delaminated areas.

2.7. Compression after impact testing (CAI)

The CAI tests on pristine, delaminated and repaired specimens were performed according to ASTM Standard D 7137 with a CAI test fixture. The fixture and specimen were loaded on an MTS universal testing machine and tested at a cross-head speed of 1.25 mm/min until a sudden drop in the load–displacement curve was recorded. A static load of approximately 10% of the maximum fracture load was applied and the deformation of the specimen from either side of the panel was measured using pre-mounted surface strain gauges on the samples. The difference in these strain values was balanced by adjusting the sample position and to confirm proper alignment of sample during the actual test.

3. Results

3.1. Influence of repair temperature on the rheological properties of the resin

Strain controlled oscillatory shear rheology tests were conducted as a function of temperature on the pre-cured resin to study its temperature dependent viscosity profile before onset of the cure reaction. Determining the temperature dependent viscosity of the pre-cured resin was important to identify the optimum temperature necessary for effective resin infiltration during injection repair. The viscosity profile of the resin from 25 to 50 °C shown in Fig. 3a reveals a decrease in viscosity with increase in temperature. After holding the temperature at 50 °C for 90 min the viscosity remained constant (data not shown here) at 0.05 Pa s. On further increase in temperature above 50 °C, the viscosity remained low until the onset of cure reaction in the resin. Fig. 3b shows that the viscosity of the resin remained below 0.05 Pa s between room temperature and 135 °C with a slight drop in viscosity at 90 °C (change in viscosity profile between 50 and
140 °C is shown in the inset of Fig. 3b). The temperature at which the resin exhibited its lowest viscosity was considered the optimum resin temperature for effective infiltration during injection repair.

![Fig. 3](image)

Fig. 3: Rheological behavior of BECy monomer; (a) change in resin viscosity with increase in temperature from 25 to 50 °C; (b) change in resin viscosity with increase in temperature from 50 to 175 °C after holding for 90 min at 50 °C.

Above 140 °C, the viscosity of the resin increased sharply revealing the onset of cure reaction caused by cross-linking of the resin. Because the optimum repair temperature (90 °C) was very close to the cure temperature (140 °C), the temperature of the resin and the substrate was reduced to 70 °C to avoid potential cross-linking of the resin during repair.

### 3.2. Evaluation of repair efficiency

For all repaired samples, repair efficiency was determined based on the post-repair stiffness of the specimen evaluated by through thickness static load tests. With increasing stiffness, the load bearing capacity of a composite specimen increases when deformed within the linear viscoelastic regime. A static load was applied through the thickness of the pristine, delaminated and repaired specimens and the low strain response was used to measure the repair efficiency. Mechanical stiffness was quantified using the slope of the compressive load versus the compressive extension curve as shown in Fig. 4. The slope was taken between 0.35 and 0.45 mm of compressive extension and the repair efficiency was measured by using Eq. (1).

\[
\text{Repair Efficiency (%) = } \frac{\text{Slope}_{\text{repaired}} - \text{Slope}_{\text{delam}}}{\text{Slope}_{\text{pristine}} - \text{Slope}_{\text{delam}}} \times 100
\]

The resulting value indicated the percent of panel stiffness recovered through the injection repair. A value of 100% indicates that the injection repair recovered the full, through thickness stiffness of the original panel.
3.3. Influence of delamination method on repair efficiency

The C-scan images (Fig. 5) showed that delaminations created by both the static bending method and the dynamic drop tower method resulted in repairs with adequate resin infiltration. Almost all severe delaminations, indicated by red, orange and yellow in Fig. 5, were eliminated. Interestingly, in the repaired specimens the delaminated area was reduced, indicating good resin infiltration. However, in some repaired samples, traces of small delaminations still existed. These may be attributable to the presence of isolated microcracks that were not connected with the delaminations network, and therefore could not be filled by the resin.

High repair efficiencies were achieved with both delamination methods, reflected by the infiltrations shown in the C-scans. The repair efficiency measured for static load and impact load delamination modes are listed in Table 1. For the static loading mode, repair efficiencies of 91%, 102%, and 126% were calculated for the investigated samples. The high repair efficiencies reveal the effectiveness of the repair in restoring the original stiffness of the specimens. The higher repaired stiffness than pristine specimens is possibly due to the influence of the higher
mechanical and adhesive properties of the infiltrated BECy polymer relative to the BMI polymer matrix of the composite [10].

<table>
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<th>Table 1. Comparison of repair efficiencies based on delamination mode and composite thickness.</th>
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<td>Sample</td>
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However, the drop tower specimens showed lower repair efficiencies compared to the static load damaged specimens (Table 1). The sudden impact load caused discrete rather than the well-connected delaminations achieved by static load. Therefore, the delaminated layers being less connected, made complete resin infiltration more difficult. The drop tower delamination repairs may require longer resin injection times or additional injection holes to increase the repair efficiency.

3.4. Influence of specimen thickness on repair efficiency

To investigate the influence of specimen thickness on repair efficiency, two batches of samples with different thicknesses were repaired using the injection repair setup. Both sample batches were delaminated using the impact loading method. The thickness of the composite specimens was changing from 4 mm to 3 mm by changing the lay-up from 32-ply to 24-ply. The C-scan images of delaminated and repaired 32 ply specimens are shown in Fig. 5 and those of 24 ply composite specimens are shown in Fig. 6, with a clear variation in color between the scans. As the scanner settings were kept constant between the two sets of specimens, the travel distance of the signal through the composites was shorter in the thinner panels, rendering the color for the 24-ply specimens lighter compared to the 32 ply specimens.
A comparison of the C-scan images of repaired specimens from both batches showed that the 24-ply specimens exhibited better resin infiltration than the 32-ply specimens. Here, the scans showed complete infiltration of the resin, leaving no traces of damage. The high resin infiltration in 24-ply composite specimens was also confirmed by measuring the mechanical repair efficiencies of 24-ply and 32-ply sample batches, see Table 1. The repair efficiencies for 32-ply specimens varied between 70% and 85%, while the repair efficiencies for 24-ply composites were above 100%. The measured values confirmed that resin infiltration is key for high repair efficiency. However, the nature of the delaminations may have had significant influence on resin infiltration. The delaminations in a thicker panel were expected to be more random and less interconnected than thinner panels resulting in limited resin infiltration in 32-ply composites compared to 24-ply composites.

3.5. Damage detection and screening resin infiltration by flash thermography

Flash thermography is another unique technique used to identify defects and damage in composite materials. It allows the detection of subsurface delaminations without directly contacting the specimen surface. This technique can also be used when only one side of the composite is accessible [12]. It provides quantitative information on how far the defect reached into the specimen from the surface using thermal diffusivity data from the damage zone. Defect detection by flash thermography is based on time dependent response of the temperature on the sample surface to a thermal impulse. A flash heating component was used to quickly transmit heat through the specimen and an infrared camera was used to monitor the surface temperature. In pristine samples, a uniform and fast surface heat distribution from the surface through the thickness of the sample is expected, resulting in a homogeneous heat distribution pattern from the surface of the composite panel when observed under an infrared camera. In samples with subsurface defects, a significant increase in surface temperature above the defect was observed,
which was attributed to the impedance to heat flow when passing through the delaminated layers. Here, the heat dissipated more slowly, revealing “hot spots” on the surface [13] and [14]. In the present work, flash thermography was used to reconfirm repaired resin infiltration into the delamination of the composite specimens. Fig. 7a shows the images of pristine, delaminated, and repaired 32-ply composite specimens taken at different time intervals after exposing the specimen surfaces to a flash thermal impulse (frames 70, 100, 130, and 160 from the video taken by IR camera). Fig. 7a shows the mechanical repair efficiency for 32-ply samples and Fig. 7b shows the C-scans of the specimens before and after repair. The decrease in brightness of the bulk samples with increase in time can be attributed to the decrease in surface temperature of the panel caused by the gradual flow of heat from the surface into the specimen thickness. For delaminated specimens, the bright spot on the surface corresponds to the sub-surface delamination caused by the applied impact load. The size of the delamination determined by thermography was in agreement with the damage observed in the C-scan image (Fig. 7b). After repair completion, the damage zone diffused the surface heat in a similar way to the pristine sample, showing only minor defects as indicated by the arrow in Fig. 7a. The dark spots around the repair area represent the vent holes drilled before repairing the specimens.

Fig. 7: Flash thermography images of pristine, delaminated and repaired 32 ply composite panels damaged by impact load; (a) flash thermography images, and (b) C-scan images.

3.6. Cross section analysis on repaired composite specimens

Cross-section analysis of a repaired specimen was performed to analyze the extent of resin infiltration into the delaminations. A 32-ply composite specimen repaired after static load delamination was selected for cross-section analysis. The C-scan images of the specimen before
and after repair are shown in Fig. 8a. The mechanical repair efficiency determined by stiffness measurements was 91% for the investigated sample. The specimen was sectioned along the line shown in the C-scan image of the repaired specimen (Fig. 8a), which connected the injection hole and two vent holes. The overall cross-section surface images taken with an optical microscope are shown in Fig. 8b. The dark grey lines stretching from the injection hole to the vent holes in the overall cross-section image represent the delaminations that were filled with resin during repair. The black areas correspond to unfilled delaminations. The high magnification images of the left side of the cross-section clearly show good resin infiltration, see Fig. 8(b1). The large unfilled delamination shown in Fig. 8(b2) may have been caused by the fact that the path of delamination was blocked by either carbon fiber debris or by the presence of air inside the fine cracks before resin reached the delaminations. This unfilled delamination can also be observe from the C-scan image marked with dotted circle. Such unfilled delamination may also have been caused by poor connectivity with other delaminations. Resin infiltration was also observed in fine delaminations present under the injection hole and the vent holes in Fig. 8(b1) and (b3). Resin infiltration in delaminations that were not connected to the injection hole may be attributed to the presence of an inter-connected network of delaminations in the damage zone.

![Fig. 8: Cross-section analysis of repaired 32 ply specimen damaged by static load; (a) C-scan images of the specimen taken before and after injection repair, and (b) microscopic images of cross-section of repaired specimen (1, 2, 3 correspond to the high magnification images of areas of particular interest on in the cross-section surface).](image)

3.7. Compression after impact testing (CAI)

The in plane mechanical strength of the specimens repaired after impact damaged was tested to evaluate the damage tolerance of the specimens under compressive load. CAI testing is commonly used to characterize the impact performance of composites by measuring the degradation in the compressive strength after prior impact loading [15] and [16]. CAI testing is typically not performed on pristine samples as the test fixture design does not adequately constrain the specimen edges resulting in incorrect failures at these locations (edge crushing). However, in this work to provide a relative comparison of the repair success using a standard test method, CAI tests per ASTM 7137 were performed on 32 ply repaired and pristine specimens.
The residual compressive strength of repaired specimens corresponding to the repair efficiency is measured in reference to the pristine and delaminated samples by using Eq. (2):

\[
\text{Repair Efficiency (\%)} = \frac{F_{\text{rep}} - F_{\text{delam}}}{F_{\text{pristine}} - F_{\text{delam}}} \times 100
\]

where \( F_{\text{rep}} \), \( F_{\text{delam}} \), and \( F_{\text{pristine}} \) are the peak loads for the repaired, delaminated, and pristine specimens, respectively. The average failure stress from CAI testing from pristine, delaminated and repaired panels are plotted in Fig. 9. Although, the pristine sample failed via edge crushing at the test grips (i.e. undesired failure mode), the repaired specimens failed in a similar manner indicating a high degree of repair efficiency up to the limits of the ASTM test method. The repaired samples showed an average 53\% increase in compression strength compared to the delaminated specimens. The observed high repair efficiency may be attributed to effective resin infiltration into the delamination zone and strong adhesive strength with the BMI-cf composite, which is consistent with the results observed previously from the bending stiffness measurements.

Fig. 9: CAI compression strength of 32 ply pristine, delaminated, and repaired specimens.

### 4. Conclusion

A laboratory-scale injection repair setup was developed to repair delaminations in bismaleimide carbon fiber panels that are commonly used as structural composites for high temperature applications. Bisphenol E cyanate ester resin was used as the injection resin because its low viscosity allowed for infiltration into the delamination damage. Rheological tests of the resin determined an optimum injection temperature necessary for high resin infiltration into the delaminations. Injection repairs were performed on specimens of different thickness that were initially delaminated by both static loading and drop tower impact. For specimens delaminated by static loading, the through thickness repair efficiency calculated from the surface stiffness restored after repair exceeded 100\%, rendering their repair superior to specimens delaminated by drop tower impact. This result may be attributed to the well-connected delaminations in the static loaded samples. The 24-ply specimens showed higher repair efficiencies than the thicker 32-ply specimens because of the higher density of delaminations in thicker panels. Successful resin infiltration into the damage zone was confirmed by ultrasonic C-scans and flash thermography.
Cross-section analysis showed that the majority of delaminations were filled with resin during the injection repair process, confirming that the newly developed repair setup with bisphenol E cyanate ester resin for bismaleimide carbon fiber panels provided high repair efficiency.

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