Investigation of Impact Damage in Thin-Ply CFRP Laminates with Biomimetic Layup Design and Resin Properties Control

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Abstract

To improve the brittle characteristics of CFRPs and suppress matrix-dominated damage, it is essential to optimize the layup pattern of CFRP laminated structures and control the resin properties of CFRP materials. In this study, we investigated this issue from two perspectives: laminate technology and resin design technology. We proposed a CFRP laminated structure that partially adopted a novel biomimetic laminate pattern (Bouligand structure) and verified its effect on improving the damage resistance of Thin-Ply CFRP laminates under impact load. We also verified the effect of modifying the matrix resin by changing the main compound ratio of the matrix epoxy resin in thermosetting CFRP laminates to improve the brittle properties of the resin.

1. Introduction

To further improve the performance of carbon fiber reinforced plastics (CFRPs) for the weight reduction of transportation systems in aerospace and automotive applications, ply thinning technologies have been researched to reduce the thickness of each ply of the CFRP laminated structure by thinning the intermediate prepreg materials. Thin-Ply CFRP prepregs not only greatly increase the design freedom of CFRP laminated structures but are also effective in suppressing intralaminar matrix cracking and delamination, which are issues of initial damage in brittle CFRP composites. However, even if Thin-Ply CFRPs are used, there are also cases where the brittle characteristics of CFRPs are clearly evident, such as brittle fracture in open-hole test specimens and large delamination in the middle plane when subjected to impact loading. Thus, there are still challenges in controlling the damage pattern in CFRP laminates.

While CFRP Thin-Ply technology contributes to weight reduction and increased design flexibility, controlling impact damage remains a major challenge. There are many examples of laminated structures in nature, such as biological structures with hard shells or exoskeletons that exhibit high impact resistance through the microscale arrangement of laminate structures. Inspired by the biomimetic concept, the Bouligand structure has recently attracted attention [1, 2]. A Bouligand structure is a type of structure found in biological tissues, where protein fibers stack in layers, gradually changing their angle to form a helical pattern. When this microstructure is reproduced in CFRP, cracks are difficult to propagate in a straight path and must follow complicated paths, thus effectively inhibiting crack propagation and resulting in high toughness and impact resistance [3, 4]. With improved design flexibility owing to Thin-Ply technology and advancements in automated layup technology, employing the Bouligand structure in CFRP laminates is becoming a realistic solution, and its application is expected in fields requiring high-performance composite materials.

To improve the brittle characteristics of CFRPs and suppress matrix-dominated damage, it is essential to optimize the layup pattern of CFRP laminated structures and control the resin properties of CFRP materials. In this study, we investigated this issue from two perspectives: laminate technology and resin design technology. We proposed a CFRP laminated structure that partially adopted a novel biomimetic laminate pattern (Bouligand structure) and verified its effect on improving the damage resistance of Thin-Ply CFRPs under an impact load. We also verified the effect of modifying the matrix resin by changing the main compound ratio of the matrix epoxy resin in thermosetting CFRPs to improve the brittle properties of the resin.

2. Experimental Method

2.1. Materials

Our research group, in collaboration with the Industrial Technology Center of Fukui Prefecture, which possesses Thin-Ply CFRP manufacturing technology, has been fabricating and evaluating Thin-Ply CFRP laminates using a thermosetting epoxy system with the difunctional bisphenol A main component, Diglycidyl Ether Bisphenol A (DGEBA), and the curing agent, dicyandiamide (DICY). In the previous literature, a similar system was investigated using epoxy resin alone, as described by Kishi et al. [5]. In systems with a broad molecular weight distribution of the main component, variations in the crosslink density at the sub-micron scale or nanoscale are likely to occur. However, the resin in this study corresponds to a system with a narrow molecular weight distribution of the main component, as described in the study by Kishi et al. The carbon fiber used in the prepreg was TR50S 15 L (Mitsubishi Chemical), the nominal thickness of the prepreg was 0.04 mm, and the nominal fiber volume content was approximately 55%.

2.2. Biomimetic Layup Design

To improve the impact damage resistance, we investigated a new laminate configuration of CFRP Thin-Ply laminated plates. For this purpose, we fabricated CFRP Thin-Ply laminates with a partially Bouligand structure in the intermediate layers. We then performed drop-weight impact tests and CAI (Compression After Impact) tests and evaluated the delamination damage progression behavior and strength reduction after damage. Our study aims to provide new design guidelines for Thin-Ply CFRP by examining the contribution of the Bouligand structure to impact energy absorption and crack propagation compared with conventional quasi-isotropic laminates. Thin-Ply CFRP prepregs used to produce the test laminates employed a main component consisting of jER828 and jER1001 (Mitsubishi Chemical) in a mass ratio of 4:6 as the resin compound. Using this prepreg, we fabricated a Thin-Ply CFRP laminate employing a Bouligand structure with 5° angle variations in the intermediate layers of the plate thickness. The laminate sequence was [(45/0/-45/90)3/(45/40/35/30/25/20/15/10/5/0/-5/-10/-15/-20/-25/-30/-35/-40/-45/-50/-55/-60/-65/-70/-75/-80/-85/-90(=90)/85/80/75/70/65/60/55/50/45)]$_s$. The layup process was performed by hand lay-up, followed by molding in an autoclave (130 °C, 0.5 MPa, and 120 min).

2.3. Resin Properties Control

In prepreg production and subsequent CFRP production processes, both excessively low and excessively high resin viscosities cause manufacturing issues. Therefore, in our previous studies, the main epoxy components consisting of jER828 and jER1001 (Mitsubishi Chemical) in a mass ratio of 4:6, along with the hardener DICY15 (Mitsubishi Chemical), have been used. On the other hand, a challenge with Thin-Ply prepregs is their low flowability during the molding of laminated composite plates using prepregs. Therefore, in the present study, we used the main epoxy components in mass ratios of (A) 6:4, (B) 5:5, and (C) 4:6, and determined in advance the amount of curing agent DICY15 required to crosslink the epoxy groups without excess or deficiency based on the epoxy equivalent weight. We then mixed them to produce resins and CFRP prepregs using these resins. Resin sheet and CFRP specimens were prepared from these raw materials. Regarding the CFRP specimens, CFRP quai-isotropic laminates were fabricated, and the autoclave molding conditions for the CFRP laminates were 130°C, 0.5 MPa, and 120 min.

2.4. Test Methods

First, as evaluation tests for mechanical properties of resins, we conducted bending tests of the resin sheet specimens (ASTM D790, specimen: length 100 mm, width 10 mm, thickness 4 mm, support distance 72 mm, stroke control with speed 1 mm/min.). Furthermore, to investigate the differences in mechanical properties, thermal analysis was performed on cured CFRP prepregs which were cured under the same heating conditions as the molding conditions (135°C, 120 min.). The T_g of the cured resin was measured using a Differential Scanning Calorimetry (DSC) instrument (Rigaku Thermo plus EVO2 DSCvesta) in a nitrogen environment. Chemical analysis using a Fourier-transform infrared (FT-IR) spectrometer (Thermo Fisher Scientific, FT-IR iS10) was performed on the cured resin based on the Attenuated Total Reflection (ATR) method.

Impact and CAI tests were performed on the CFRP specimens. Impact tests were conducted using a drop-weight testing machine IM1C-15 (IMATEK) based on ASTM D7136M, with test specimens of length 150 mm and width 100 mm (the longitudinal direction was the 0° direction). The impact energy was 3 J/mm, the impactor had a hemispherical tip with a diameter of 16 mm, and the impactor weight was 5 kg. The impact energy was applied to the center of the test specimen, and a double-impact prevention mechanism was used to ensure that the impactor and test specimen made contact only once. The specimen support plate had a 125 mm × 75 mm cutout to allow for out-of-plane deformation of the specimen during impact. The load during the impact test was measured using a load cell connected to an impactor. The displacement and velocity of the impactor were measured using an optical sensor. The impact energy was determined based on the measured impact velocity, and the absorbed energy was calculated from the measured load-displacement curve. For the test specimens after the impact test, the depth of the dents that occurred at the center of the surface was measured using a depth gauge (DMD-210S (Teclock)). We then observed interlaminar delamination inside the tested specimens using an ultrasonic C-scan device (Flex Scan System (Insight)). Finally, we conducted CAI tests on the specimens, based on ASTM D7137M. Compression tests were conducted under 1 mm/min. displacement control using a testing machine AGX-300kN (Shimadzu).

3. Experimental Results

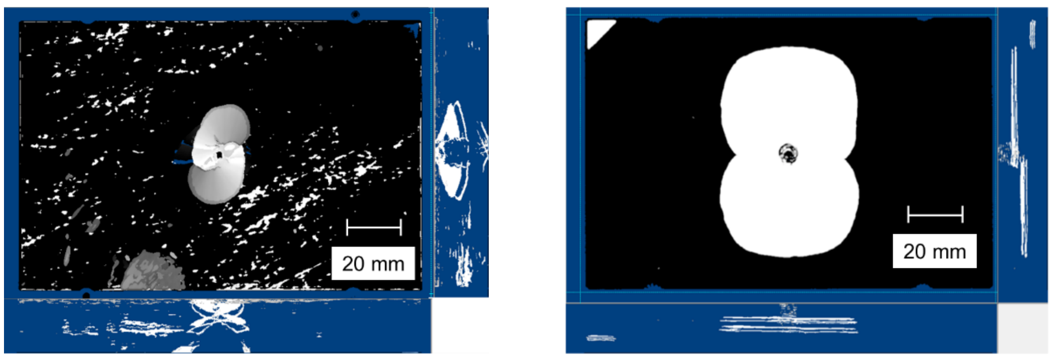
3.1. Improvement of Impact Damage Resistance Using Biomimetic Layup Design

Figure 1 and Table 1 show the results of the impact (impact energy: 3 J/mm) and CAI tests for the CFRP specimens to demonstrate the effect of our Bouligand layup design. The results obtained from the test specimens with the Bouligand layup configuration fabricated in this study were compared with those of quasi-isotropic laminates fabricated using the same CFRP Thin-Ply prepregs from previous experiments in our research group [6]. The laminate sequence of the reference quasi-isotropic CFRP laminates was $[(45/90/-45/0)_{16}]_s$. Table 1 lists the specimen thickness, maximum impact load, absorbed energy, projected area of delamination, dent depth, and CAI strength for each test specimen. Figure 1 shows the interlaminar delamination images obtained using the ultrasonic C-scan technique. In the image, the black rectangular area represents an ultrasound image projected from the surface of a 150 mm × 100 mm test specimen, and the white area indicates the damaged area. The right and bottom of the images show two-dimensional images projected from the longitudinal and width directions, respectively, of the test specimen, with the damaged areas indicated in white.

As shown in Fig. 1 (b), in the Thin-Ply quasi-isotropic laminates from our previous study, the crack suppression effect owing to the adjacent plies is significant, and transverse cracks are suppressed by ply thinning. However, delamination occurs only in a limited area near the center of the plate thickness, and the projected area of delamination from the top surface is large. In contrast, as shown in Fig. 1 (a), the test specimens in this study, which employed a Bouligand structure in the intermediate layers, showed delamination mainly from the center of the plate thickness to the top surface, with a small projected area and in a double helicoidal shape. These results are considered to be in good agreement with the existing literature by Mencattelli et al. [3], who reported that, compared to laminates with large fiber orientation angle changes of 45° in the interlaminar interface, such as quasi-isotropic laminates, when the interlaminar fiber orientation angle change is small at 5°, the crack suppression effect within the ply becomes limited, and the effect of double helicoidal delamination due to the Bouligand structure becomes more pronounced. These results suggest that even if the surface layers consist of quasi-isotropic layup configurations, the Bouligand structure of the intermediate layers effectively absorbs the impact energy, thereby suppressing the delamination area. On the other hand, delamination also progressed in the surface layers, and the ply thinning effect on the surface layer was limited. This may have led to a decrease in CAI strength, which will be discussed later.

As shown in Table 1, compared with the quasi-isotropic (QI) laminates, the specimens in this study with the Bouligand structure showed increased dent depth and decreased CAI strength. The dent depth was significantly larger in the Bouligand structure, suggesting that the energy that could not be absorbed by delamination was absorbed by internal fiber fracture or plastic deformation of the resin. Regarding the decrease in CAI strength, the effect of ply thinning in the surface layers on suppressing interlaminar delamination was limited, and delamination propagated towards the upper surface in the thickness direction. This delamination, along with the dents that occurred on the upper surface, initiated compressive failure, which is one of the main causes of CAI strength reduction.

These results confirmed that by employing the Bouligand structure, the damage area could be suppressed compared with conventional quasi-isotropic laminates. Thus, our layup design with a Bouligand structure in the intermediate layers is an effective method for controlling impact damage. However, because the CAI strength decreased, it was suggested that other methods for effectively absorbing impact energy should be considered.



(a) Hybrid Bouligand laminates (b) Quasi-isotropic (QI) laminates

Figure 1. Impact-induced damage in CFRP laminates with hybrid Bouligand layup and conventional quasi-isotropic layup

Table 1. Impact and CAI test results for CFRP laminates with different layup configurations.

Specimen	Bouligand	QI
Thickness [mm]	3.69	4.87
Peak force [kN]	5.18	7.96
Absorbed energy [J/mm]	1.45	1.5
Projected damage area [mm^2]	734	3483
Dent depth [mm]	0.15	0.06
CAI strength [MPa]	255	301

3.2. Effect of Resin Properties Control

Figure 2 and Table 2 show the results of the bending tests on the epoxy resin sheet specimens. Resins with a higher proportion of low-molecular-weight components exhibited improved bending modulus and bending failure strain. This method significantly improved the ductility of the resin compared to that of conventionally formulated resins.

Table 2 also shows the results of evaluating the glass transition temperature (T_g) of the CFRP-cured products from the thermal analysis using DSC. Resins with a high proportion of low-molecular-weight components showed an improved T_g, suggesting that a high crosslinking density was achieved.

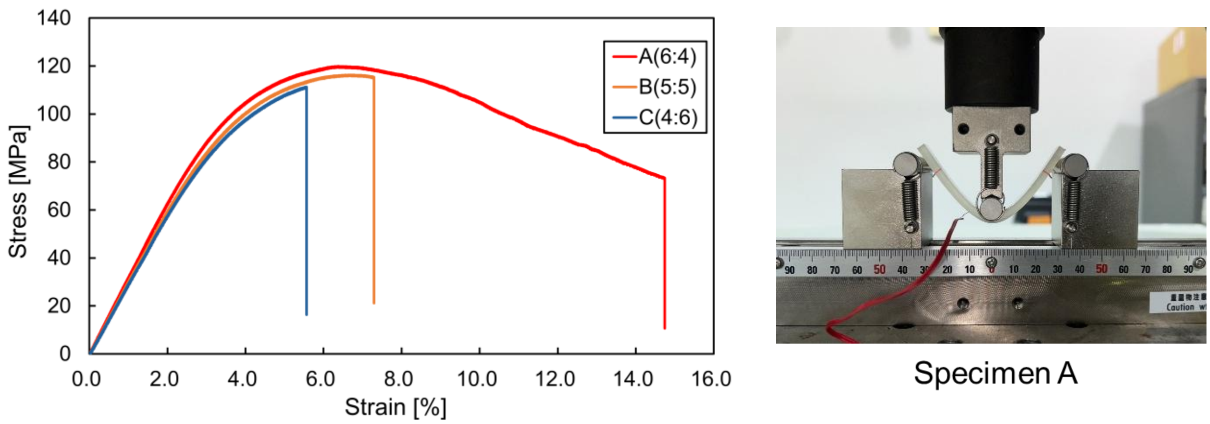


Figure 2. Comparison of bending stress-strain curves of resin sheet specimens with different main component formulations.

Table 2. Bending test results of the epoxy resin sheet specimens.

Specimen	A	B	C
jER828 : jER1001	6 : 4	5 : 5	4 : 6
Thickness [mm]	3.85	4.14	4.08
Flexural strength [MPa]	120	116	111
Flexural modulus [GPa]	3.28	2.95	2.81
Strain at maximum stress [%]	6.37	6.7	5.56
Fracture strain [%]	14.7	7.29	5.57
Glass transition temperature [℃]	119.5	113.2	110.5

Next, Figure 3 and Table 3 present the results of the impact test (3 J/mm) and CAI test of the CFRP with epoxy resin with the different formulation. Since the prepreg with the 6:4 mixing ratio had issues with mold release, the present paper only included a new experimental result for CFRP

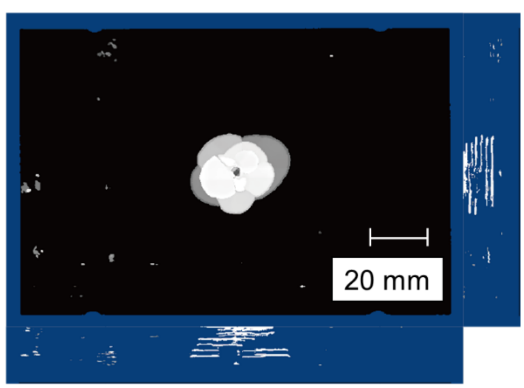


Figure 3. Impact-induced delamination in CFRP laminates with enhanced resin ductility (5:5 ratio).

Table 3. Impact and CAI test results for CFRP laminates with different resin formulations (5:5 vs. 4:6).

Specimen	B (5:5)	C (4:6)
Thickness [mm]	3.78	4.87
Peak force [kN]	6.45	7.96
Absorbed energy [J/mm]	1.65	1.5
Projected damage area [mm^2]	761	3483
Dent depth [mm]	0.14	0.06
CAI strength [MPa]	289	301

laminates with a resin of a 5:5 mixing ratio. The result of CFRP with a 4:6 mixing ratio is the previous experimental result in our research group [6], and it is noted that the laminate configuration and total thickness of the laminates were different. The laminate configuration of CFRP laminates with a 5:5 mixing ratio was $[(45/0/-45/90)_{12}]_s$, while that with a 4:6 mixing ratio was $[(45/90/-45/0)_{16}]_s$.

As shown in Figure 3, which displays C-scan ultrasonic flaw detection images after impact loading, the highly ductile resin (5:5 mixing ratio) appeared to have little effect in the bending tests, but interlayer delamination due to impact loading was significantly suppressed. Furthermore, as shown in Table 3, this formulation resulted in a deeper dent and greater plastic deformation. Although the CAI strength decreased slightly, this was thought to be due to the increased dent depth. However, our additional verification using specimens with further enhanced resin ductility (6:4 mixing ratio) showed a small suppression effect on impact-induced delamination, indicating that the effect of resin ductility needs to be further investigated. This additional result indicates that resin ductility is not the only factor affecting impact-induced damage.

Finally, the reason for the ductility of the resin was investigated by analyzing its chemical structure after curing using FT-IR. Figure 4 shows the results of a quantitative analysis of the differences in chemical structure due to differences in the mixing ratios, using FT-IR chemical structure analysis

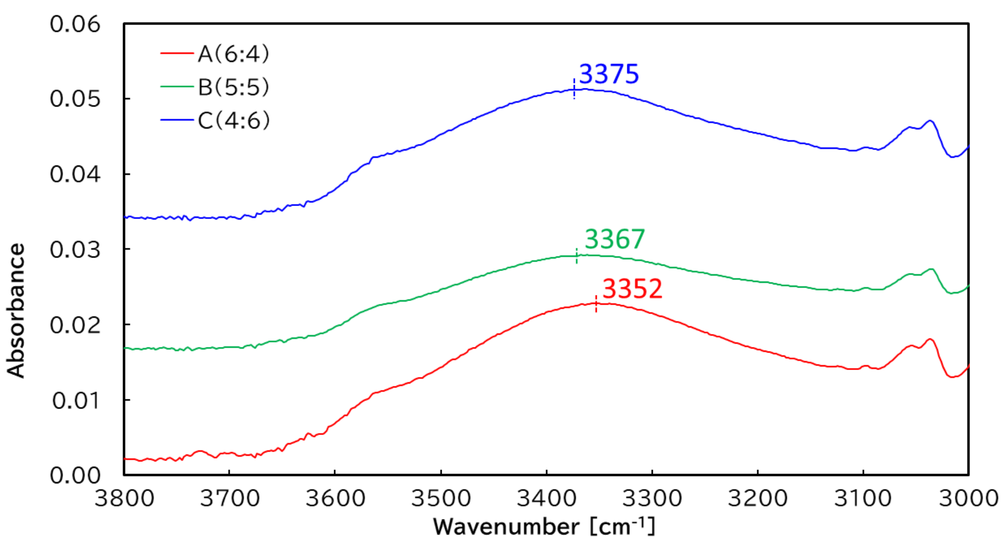


Figure 4. Comparison of FT-IR spectra.

of the cured resin. When we compared the results focusing on hydroxyl groups (-OH groups), it was found that as the amount of low-molecular-weight components increased, the peak top shifted significantly to the lower wavenumber side. In other words, this indicates that the hydroxyl group is constrained in the molecular structure after curing. This result suggests that the formation of a hydrogen-bond network is a factor in the increased ductility.

4. Conclusions

The present study focused on CFRP Thin-Ply technology and investigated two aspects, laminated structure and modification of the base resin, with the aim of achieving both impact damage suppression and enhancement of CAI strength.

First, from the perspective of the laminated structure, we fabricated Thin-Ply CFRP laminates with a partial Bouligand structure in the intermediate layers to suppress interlaminar delamination, which is a typical impact-induced damage in Thin-Ply CFRP laminates. We conducted drop-weight impact and CAI tests and compared the results with those of quasi-isotropic laminates obtained in our previous experiments. The results confirmed that the damaged area could be suppressed, suggesting that the Bouligand structure is an effective concept for controlling impact damage. On the other hand, because the CAI strength decreased, it was suggested that other methods should be considered for effectively absorbing impact energy.

Additionally, to improve the ductility of CFRP laminates, we attempted to improve the resin properties by designing an epoxy resin used as the base material. Specifically, we investigated how the properties of the cured resin changed by varying the mixing ratio of the main components with different molecular weights using three-point bending tests and thermal analysis by DSC. Consequently, increasing the proportion of the main component with a low molecular weight increased the glass transition temperature (T_g), indicating a denser crosslinked structure. Simultaneously, an improved bending modulus and failure strain were obtained. This suggests the existence of a complicated molecular structure after curing, which cannot be fully explained by the conventional knowledge that a high crosslink density decreases ductility, although it contributes to an improved elastic modulus and T_g. Further investigation using FT-IR revealed that the peak position and shape of the FT-IR spectrum related to the hydroxyl groups changed depending on the proportion of the main component, suggesting a change in the constrained state of the hydroxyl groups after curing of the resin.

Next, to evaluate the effect of the improved resin properties obtained by changing the resin composition on the impact damage of Thin-Ply CFRP laminates, test specimens were prepared using the modified epoxy resin, and their impact damage behavior and CAI strength were compared with those of test specimens using the conventional formulation of resin. In the impact tests, specimens with enhanced resin ductility showed a reduction in the damaged area, whereas the dents tended to become deeper. This indicates that delamination was suppressed because the impact energy was absorbed by the plastic deformation of the ductile resin. Although the CAI strength decreased slightly, the reduction in the damaged area suggests that it may still provide sufficiently useful design guidelines for future applications. However, additional verification using specimens with further enhanced resin ductility showed a small suppression effect, indicating that the effect of resin ductility requires further investigation.

Our study demonstrated that differences in the mixing ratio of the main components of epoxy resins used as CFRP may contribute to the increased ductility of the resin and improved damage resistance of the CFRP. Even in material systems where chemical crosslinks are expected to occur relatively uniformly, changes in the mixing ratio may lead to increased physical bonding, such as hydrogen bonding, which increases the ductility of the resin. Our study suggests that further resin and laminate design techniques can enhance the potential for damage control in CFRP laminates; however, we believe that these effects have not yet been fully optimized. This matter remains a subject for future study.

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