Damage behaviors in cross-ply cloth CFRP laminates cured at different temperatures

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1. Introduction

Carbon Fiber Reinforced Plastic (CFRP) laminates are excellent structural materials in aeronautical structures because of their stiff and strong yet light-weighted properties. The application of composite materials in aircraft structures are increasingly being used especially for commercial and military industries as it produces high-performance aircrafts that are environmentally compatible, cost-effective, etc. The fibers and matrix materials can be obtained commercially in a variety of forms, both individually and as laminae. Fibers are available individually or as roving, which is a continuous, bundled but not twisted group of fibers. The common fibers used are usually unidirectional or interwoven. Fibers used in the aeronautical industry are mostly saturated with resin which is subsequently used as a matrix material where this form of pre-impregnated fibers are called “prepregs” and often manufactured in tape form (Jones, 1975). However, the application of CFRP laminates are not limited to industries related to aircrafts but their outstanding features are also well-known in construction and automotive industries which mostly use the fibers in the cloth or woven form. Cloth and woven structures are often used in these industries instead of prepregs as they are more excellent in the aspect of drapeability. It allows complex shapes to be formed, reduces manufacturing costs and increases resistance to impact damage as it improves the compressive strengths after impact following from a reduction in the area of impact damage (Gao, 1999).

Any types of CFRP laminates are susceptible to the accumulation of microscopic damages such as matrix cracks and delamination, which confines the application of CFRP to the manufacturing structures within the limited strain levels. Many researchers have studied the damage mechanisms in CFRP laminates such as Ogihara et al. (1998) and Kobayashi...
et al. (2000a, 2000b) who observed and explained the behavior of transverse cracks in several types of CFRP laminates in parallel with some analytical studies. There are also some studies conducted to investigate the matrix cracks behavior in interlaminar-toughened composite laminates like had been done by Ogihara et al. (1998) where the stress and displacement fields in interlaminar-toughened composite laminates with transverse cracks was analyzed. Recently, Fikry et al. (2018) experimentally conducted a study on the effects of matrix cracks on the mechanical properties of cross-ply and angle-ply laminates manufactured by prepreg-type fibers which provides validation to the variational analysis results in Vinogradov (2019). They then developed their study about the matrix cracks by experimentally measuring the strain distributions of the cracked laminates using Digital Image Correlation (DIC) and found that secondary mode damages such as oblique and curved cracks have also occurred in the laminates, especially cross-ply laminates with a thick 90-degree ply (Fikry et al., 2019).

For fabric CFRP laminates, despite having a more complicated damage behavior, many kinds of research can be found in both experimental and analytical form on account of its drapeability properties. For instance, Gao et al. (1999) observed the damage development in composite laminates reinforced with several layers of the carbon-fiber-reinforced polyimide satin-weave fabric as a function of applied strain. Besides explaining the initiation and progressive behavior of the damages e.g. transverse matrix cracking, delamination and longitudinal splitting, they also investigated the effective mechanical properties of the laminates such as the Young’s modulus, Poisson’s ratio and residual strain when these damages emerged. Ajaja and Barthelat (2016) on the other hand, characterized the microcracking behavior of the fabric carbon fiber reinforced cyanate ester composites a cyanate ester composite, focusing on the conditions under which microcracking initiates.

In order to deeply characterize the damages behavior in fabric laminates, and as resin properties is one of the most important aspects in contributing to the damages, there are some studies related to the resin properties conducted such as Kobayashi et al. (2012a, 2012b) who experimentally and analytically investigated the resin impregnation behavior in laminates. In addition to that, Yokozeki et al. (2015) proposed a property control method in vacuum-assisted resin transfer molding (VaRTM) using porous mold process (PMP) to fabricate carbon fiber-reinforced plastics (CFRP) composites where they demonstrated that volume fraction of carbon fibers and the resultant mechanical properties of CFRP can be controlled by the infusion process control. Kobayashi et al. (2017) on the other hand, investigated the effects of yarn thickness, fabric laminating and sizing content on resin impregnation behavior in carbon fiber reinforced polyamide 6 composites. They showed that the composites with dense fabrics inhibited fiber yarn flattening and restricted the influence of fabric lamination.

Carbon fibers that have exceptional tensile strength and stiffness have the primary role to carry the load imposed on the composite laminate while matrix transfers load between the fibers. The matrix can be brittle with poor strength and toughness depending on the curing conditions as it changes the interfacial strength of the fiber and matrix (Davis et al., 2010). There are some studies on the effects of curing conditions on the mechanical properties and damage behaviors in woven laminates such as Sales et al. (2017) who studied the interlaminar fracture behaviors of VaRTM molded carbon composite laminates subjected to Modes I and II at two different temperatures which are 25ºC and 80ºC. The results showed the significant influence of the temperature on the interlaminar fracture toughness of composites. In addition to this, Jiang et al. (2018) studied the effects of curing conditions on volume fraction, spatial distribution, geometrical shape and size of voids of the carbon fiber fabric-reinforced polycarbonate composites fabricated by thermoforming process. They revealed that at elevated temperature, the stiffness, energy-based damage degree and delaminated area were decreased where it is associated with the enhancement of matrix ductility, which was characterized by the plasticity of matrix and the formation of kink band. Besides that, Benedetti et al. (2016) on the other hand, investigated the influence of temperature on the curing process of the epoxy resin where the results showed that increasing the curing temperature significantly accelerated both the curing process of the epoxy adhesive and the evolution of bond performance. They also showed that, in terms of failures modes, the failure mode was cohesive in the adhesive due to the low mechanical properties of the adhesive at the beginning of the curing, and after certain curing degree the failure mode changed from cohesive shear failure in epoxy to debonding at CFRP–epoxy interface.

Cure-induced shrinkage leads to residual stresses when deformation is restrained, as it occurs in fiber-reinforced composite materials. The problem of predicting residual cure stresses in composite laminates has been studied extensively. Early work by Hahn and Pagano (1975) considered the effect of cooling on the curing stresses by incremental linear elasticity. Bogetti et al. (1992) considered the combined effect of chemical and thermal shrinkage on residual stress development in unidirectional continuous fiber-reinforced composites. Kravchenko et al. (2016) on the other hand,
measured the in-situ development of chemical and thermal shrinkage deformation during a specified thermal cycle an unbalanced cross-ply laminate. However, most of these studies were about the damage behaviors in laminates manufactured by prepregs and woven cloth laminates although some applications such as in the construction industry, on the contrary, are using the non-woven unidirectional cloth laminates which gives lesser focus on their mechanical properties and damage behavior. Although there are several studies such as by Sakai et al. (2013) who did the observation on damage accumulation behavior in non-crimp fabric laminates, they used only the laminate with complex configuration such as quasi-isotropic laminates. Therefore, in order to deeply understand the basic damage behavior of this material, a simpler cross-ply cloth CFRP laminates with the configuration of [0/90\text{4}]_{S} made from the unidirectional cloth fibers which cured at two different curing conditions (room temperature and high temperature, 80°C; post-curing temperature) was scrutinized in this study.

2. Materials and methods

2.1 Materials and manufacturing of laminates

The materials used is the unidirectional high-strength cloth carbon fiber (Torayca UT70-20G, 0.111mm/sheet) and the epoxy resin (DENATITE XNR 6815, XNH 6815). This type of resin is decent for transfer moulding (RTM) and infusions for wind energy, marine, and other applications. The key features of this resin are the ambient temperature curing and low viscosity; therefore, it is suitable for curing at an air temperature of an environment including room temperature. The carbon fiber cloth used is a common unidirectional fiber used in construction and aeronautical industries with transversely woven glass fiber weft (Fig. 1) and glass fiber roving yarn for resin transfer identification. Also, as a marker for distinction purpose to differentiate materials during the manufacturing process in the industry, some parts of the laminates were equipped with red-colored glass fibers with a larger diameter of carbon fiber (Torayca HP). In this study, we included all originally existing internal structures in the manufacturing process of the laminates.

<table>
<thead>
<tr>
<th>Type of resin/ curing agent</th>
<th>Mixing weight ratio</th>
<th>Curing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>XNR6815/XNH6815</td>
<td>1</td>
<td>A: Room temperature, 25°C *</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>B (Post-curing condition): 25°C \text{/}24h + 80°C /2h</td>
</tr>
</tbody>
</table>

*Laminate cured at room temperature was left as it is in VaRTM apparatus setting for at least 24 hours before being cut into specimens following the curing condition given by the resin’s supplier (Nagase Chemtex HP).

![Unidirectional carbon fiber fabric structure](image)

Laminates with configuration of [0/90\text{4}]_{S}, and [0]_{16} were manufactured by the Vacuum-assisted Resin Transfer Molding (VaRTM) method with the setting of the apparatus shown in Fig. 2. Table 1 shows the curing conditions used in this study.
2.2 Tensile test, DCB test and damage observation

The [0/90_4] coupons were monotonically and cyclically (loading-unloading tensile test) loaded using a tensile test machine (TENSILON RTF-1350, A&D) to obtain the mechanical properties and to observe the damage behaviors respectively. For tensile tests, laminates were cut into the coupon measurement as shown in Fig. 3. The cross-head speed for both of the tensile tests was 1.0 mm/min. Damages such as matrix cracks and delamination occurring at the edge of the coupon were observed by an optical microscope, KEYENCE VHX-2000 while damages inside the coupon were observed by using X-ray radiography, SOFTEX M-100S. Residual properties which are Young’s modulus and residual strain, together with damage accumulation, have been recorded as a function of applied stress. Both residual properties were determined from the stress-strain curves resulting from tensile tests. Residual strains are the nonrecoverable strain values in the laminates as the strain does not return to 0% even after being unloaded back to 0 MPa.

DCB tests were also conducted for the fractured surface observation to further study the damage mechanism in the laminates. DCB test was conducted following the JIS K7086 standard (JIS Japanese Industrial Standard, 1993). The unidirectional [0]_{10} laminates were used where the initial crosshead speed for the crack length of 0 mm - 20 mm was 0.5 mm/min while it was increased to 1.0 mm/min after the crack length exceeds 20 mm. The crack opening displacement was measured until the crack length reached 70 mm where the crack propagation was monitored using an optical microscope, D2XZ-KSH.

3. Results and discussion

3.1 Material properties

Table 2 shows the mechanical properties of the unidirectional laminates that were obtained by the tensile test and to be used in the analysis to predict the mechanical properties degradation due to matrix cracks for validation purposes. Table 3 and Fig. 4 shows the mechanical properties and stress-strain curves obtained from monotonic tensile tests of the cross-ply laminates respectively. The results shown in Table 2 and 3 are the average values when at least three specimens are used in the testing. The \( \nu_{23} \) value is quoted from Okabe and Yashiro (2009) while \( G_{23} \) was a calculated value using the values of \( E_2 \) and \( \nu_{23} \).

As shown in both mechanical properties of unidirectional and cross-ply laminates, laminates cured with curing condition A are stiffer and stronger than the laminates cured with curing condition B as Young’s modulus in longitudinal
Direction and tensile strength are higher in these laminates. This shows that curing at higher temperature reduced the mechanical properties of the laminates. However, in contrast to this statement, the UD laminate post-cured by curing condition B showed a higher transverse modulus, $E_2$ value compared to laminate cured by curing condition A as shown in Table 2. As the value of $E_2$ is particularly affected by the resin properties, this phenomenon can be mainly attributed to a higher cross-link density formation of the epoxy resin cured at higher temperatures which cause the stiffness of the matrix itself to become higher than the resin cured at RT. This is when typically, higher temperatures produce a more complete reaction with a greater degree of cross-linking than lower temperatures, providing enough kinetic energy to quickly initiate chemical reactions (Sancaktar et al., 1983, Benedetti et al., 2016).

<table>
<thead>
<tr>
<th>Material properties</th>
<th>Curing condition</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus in longitudinal direction, $E_1$ [GPa]</td>
<td>104 (4.08)</td>
<td>83.4 (1.04)</td>
<td></td>
</tr>
<tr>
<td>Young’s modulus in transverse direction, $E_2$ [GPa]</td>
<td>5.98 (0.23)</td>
<td>6.20 (0.11)</td>
<td></td>
</tr>
<tr>
<td>Poisson’s ratio in longitudinal direction, $\nu_{12}$ [-]</td>
<td>0.29 (0.03)</td>
<td>0.32 (0.02)</td>
<td></td>
</tr>
<tr>
<td>Poisson’s ratio in transverse direction, $\nu_{23}$ [-]</td>
<td>0.49\textsuperscript{a}</td>
<td>0.49\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>Shear modulus in longitudinal direction, $G_{12}$ [GPa]</td>
<td>3.01 (0.20)</td>
<td>2.53 (0.04)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} $\nu_{23}$ value is quoted from Okabe and Yashiro (2009) ( ) showing the standard deviation

<table>
<thead>
<tr>
<th>Curing condition</th>
<th>Young’s modulus [GPa]</th>
<th>Poisson’s ratio [-]</th>
<th>Tensile strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25.8 (1.13)</td>
<td>0.032 (0.006)</td>
<td>378 (6.36)</td>
</tr>
<tr>
<td>B</td>
<td>22.0 (0.76)</td>
<td>0.055 (0.003)</td>
<td>306 (18.0)</td>
</tr>
</tbody>
</table>

( ) showing the standard deviation

Fig. 4 Stress-strain curves for monotonic tensile test.

The loss of strength in laminate post-cured by curing condition B on the other hand might occur due to the weakened fiber-matrix interfacial strength after being post-cured which causing the damages to take place earlier thus cause fracture at the lower stress level. This is proved by the curing condition B’s lower slope of the stress-strain curve at a very small strain range in Fig. 4 where there is a possibility that some tiny fiber-matrix debonding became easily occurred when the laminate undergoes the post-curing procedure. As another evidence, we also conducted the fractured surface observation.
which is being discussed in the next sections. This weak fiber-matrix debonding might happen due to a large-scale deformation involving a substantial portion of the polymer chains when the resin is cured at the higher temperature (Raju et al., 2014). Additionally, this lower slope of the stress-strain curve caused by the occurrence of the fiber-matrix debonding also yielded a lower Young’s modulus value for laminate cured by curing condition B in comparison to laminate cured by curing condition A.

The initial damage can be identified by observing the first non-linearity on the curve wherein this case, the first matrix crack occurred at about 230 MPa for curing condition A while 320 MPa for curing condition B (Fig. 4) (Fikry et al., 2018, 2019). The non-linearity properties shown by the stress-strain curves of the monotonic and loading-unloading tensile tests in this study are similar to the properties observed in the cross-ply laminates made from prepregs tape in Fikry et al. (2018). This also showed that damages such as matrix cracks occurred earlier in laminates cured at higher temperatures which eventually lowered the stiffness and strength of the laminates.

3.1.1 Condition A

Figure 5 shows the stress-strain curves obtained from the loading-unloading tensile test of a laminate cured with curing condition A. The first load applied was 320 MPa where there was no significant non-linearity due to damage seen in the curve but when unloaded to 0 MPa, the strain value became non-zero due to the existence of residual strains. The residual strain might exist due to the viscoelastic behavior and some insignificant microcracks occurring in the laminates (Fikry et al., 2018). Further loading of the laminates to a higher stress level of 350 MPa showed no significant changes to the curve.

3.1.2 Condition B

Compared to laminates cured with curing condition A, stress-strain curves obtained from the loading-unloading tensile test of laminates cured with curing condition B showed a clearer non-linearity starting from the first load until fracture. This showed that damages increased gradually with the increase of loads that eventually caused the gradient of each curve (which represents the stiffness) to decrease and caused the residual strains to exist (Fig. 6) (Fikry et al., 2018).

The stiffness reduction and crack density at each stress level for a laminate were recorded and represented as a damage parameter shown in Fig. 7. We present only a representative result of a specimen as we found that there were almost no variations compared to the other two specimens. The experimental results were compared to the variational analysis results based on the analysis by Vinogradov (2019). In this relationship, crack density is the average number of cracks in a specified measuring area on the laminates while stiffness reduction is the stiffness’s reduced rate of perturbed laminates compared to the virgin laminates. As shown in the figure, the experimental results agreed excellently with the analysis. The artificial crack technique might be used to increase the crack density range as was suggested in Fikry et al. (2018).
3.2 Damage behaviors

3.2.1 Condition A

Figure 8 shows the edge’s optical microscopy of a laminate cured with curing condition A. There were no cracks observed at the edges in the main structure of the laminates, but some small matrix cracks can be observed occurring around the red-colored glass fiber (which was used for material distinction purpose during the manufacturing process). These matrix cracks however propagated incompletely in the thickness direction between the two 0-90-degree-ply interfaces.
On the other hand, X-ray radiograph in Fig. 9 showed no cracks propagated in the width direction of the laminates. The black lines appearing at/around the area labeled glass fiber I and II in the figure are not crack lines but the glass fiber that initially existed in the laminates. Glass fiber I is the glass fiber roving yarn for resin transfer identification while glass fiber II represents the glass fiber for material distinction function. It is difficult to show that there were cracks in glass fiber I and II area by the X-ray radiograph as the cracks may be overlapped by the GF lines as cracks are easier to occur in GFRP laminates compared to CFRP laminates (Fikry et al., 2018) and the final fracture occurred at these areas.

Fig. 9  X-ray radiograph of coupon with curing condition A (Glass fiber I: Glass fiber roving yarn for resin transfer identification, Glass fiber II: Red-colored glass fiber for material distinction function).

3.2.2 Condition B

Similar to laminates cured with curing condition A, matrix cracks in laminates cured with curing condition B initially occurred at the edges around the area with glass fiber wefts, roving yarns, and red-colored glass fibers. Figure 10 shows the edge’s optical microscopy of a laminate cured with curing condition B where (a) shows a void induced matrix crack, (b) shows a matrix crack that grew at the fiber-matrix interface, (c) shows a matrix crack that passed through the 0-degree wefts in 90-degree ply while (d) shows a matrix crack that may initiate at 90-degree weft in 0-degree ply and propagated through the 0-degree wefts in 90-degree ply.

Fig. 10 Edge’s optical microscopy of a laminate cured with curing condition B; (a) Void induced matrix crack, (b) Matrix crack at the glass fiber roving yarn, (c) (d) Glass fiber weft induced matrix crack.
Most of these matrix cracks propagated completely through the thickness direction of the laminates. As the loading stress increased, the number of matrix cracks propagating in the thickness direction at the edges and into the width direction increased. This is shown by the X-ray radiographs in Fig. 11 (a), (b), (c), (d) and (e) taken after loading to 230, 250, 270, 290, 310 MPa respectively. The matrix cracks onset from both edges grew into the width direction, combined and formed the transversely propagated cracks in the middle of the laminates. At lower loading stress, matrix cracks formed earlier at the glass fiber roving yarn and red-colored glass fiber areas where the number of cracks in those areas showed no significant increases although being loaded to higher loads.

SEM observation was done on the edges of the fractured laminates to investigate the fiber-matrix interfacial bonding behavior where the fractured stress of laminates cured with curing conditions A and B was 382 and 305 MPa respectively. As shown in Fig. 12 (b), laminates cured with curing condition B showed more fiber-matrix interfacial debonding compared to laminates with curing condition A (Fig. 12 (a)) which explains that high-temperature curing of resin loosens the fiber-matrix interfacial bonding strength in the laminates. As the stress increases, the fiber-matrix interfacial debonding will eventually causes the matrix cracks such in Fig. 13 to occur thus lower the strength of the laminates. In this curing condition, we believe that as the degree of curing progresses, the resin shrinks which inevitably results in the development of residual stresses at the fiber/matrix interface (Zhao et al., 2006). This explains the mechanism of the fiber-matrix interfacial debonding occurred when post-curing is done in the laminates.

![X-ray radiographs showing transverse matrix cracks for laminates cured by curing condition B; (a) At 230 MPa, (b) 250 MPa, (c) 270 MPa (d) 290 MPa (e) 310 MPa.](image1)

![SEM observation of fractured laminates; (a) Laminates cured with curing condition A, (b) Laminates cured with curing condition B.](image2)
3.3 SEM fracture surface observation

DCB tests have been conducted for matrix fractography purpose where the scanning electron microscope (SEM) was used in this study. Figure 14 and 15 shows the SEM matrix fractography of a DCB fractured laminate cured with curing conditions A and B respectively. As expected, without considering the resin’s curing temperature, both laminates showed some common mode I plastic deformation failure such as river marks and scarps. For example, Fig. 14 (a): “A” and Fig. 15 (a): “A” shows one of the fracture characteristics which is the brittle-looking and distinct river patterns called river marks that occurred as a result of cracks deflection and subsequent propagation on two slightly different fracture planes (Liu et al., 2005). On the other hand, with increasing planar separation of the crack fronts, the greater deviation of each plane necessary for convergence produces a scarp (Purslow, 1986, Kusy and Turner, 1977). The formation of scarps can be clearly observed in Fig. 14 (b): “A” and Fig. 15 (b): “B”. However, for laminates with curing condition A, it is possible to observe that the fiber is mostly coated with resin (Fig. 14 (a): “B”) while for laminates cured with curing condition B, as shown in Fig. 15 (a): “B”, the fiber emerged from the resin without having resin attached to the fiber. Besides that, the fiber imprints as in Fig. 15 (b): “A”, were also present in laminates cured with curing condition B which significantly showed that the fiber-matrix interfacial bonding strength became weaker when the laminates were cured at a higher temperature compared to curing at room temperature. The results thus also explained that the damages such as matrix cracks and delamination easily occur in laminates cured at higher temperatures as the debonding between fiber and matrix gives a larger contribution to the formation of cracks besides encouraging a faster fiber breakage that eventually causes an earlier final fracture.

In addition, some small and dense cusps between the fibers can also be found in laminates cured with curing condition A (Fig. 14(b): “B”) which is not visible in laminates cured with curing condition B. These cusps may be caused by the
complex stress distribution in the laminates due to the fiber-matrix bonding properties (Purslow, 1986, Gilchrist and Svensson, 1995). Cusps that occurred between the fibers are also reported to occur due to the impulses of applied loading in the fiber surface during the sample opening process, disposing the transversal interlaminar shear on the interface fiber/matrix (Sales et al., 2017). Observing the accumulation of resin on the fractured surface, laminates cured with curing condition B (Fig. 15 (c)) exhibited a smooth and featureless surface representing brittle failure of the laminates compared to laminates cured with curing condition A (Fig. 14 (c)) that showed more complex resin accumulation representing remarkable ductility of the laminates (Hojo et al., 1994). Observing from a larger observation area as in Fig. 14 (c) also showed that the fiber-matrix interfaces remains bonded where there is no significant fiber-matrix interfacial debonding in the form of fiber imprint were observed in laminates cured with curing condition A, indicating a strong interfacial bonding between fiber and matrix when the laminates are cured at room temperature.

![Image](image.png)

Fig. 15 SEM observation of a DCB fractured laminate cured with curing condition B; (a) Image showing resin-coated fiber and river marks (b) Image showing fiber imprints and scarp (c) Resin accumulation image.

4. Conclusion

Damage behaviors in cross-ply, [0/90]s, cloth Carbon Fiber Reinforced Plastic (CFRP) laminates with different curing conditions have been observed as a function of applied stress. Significant differences can be observed in the mechanical properties, damage initiation, and progression in the laminates when the post-curing procedure is implemented. The mechanical properties degradation after the post-curing procedure in this study might occurred due to the weakened fiber-matrix interfacial strength after being post-cured. For laminates cured at room temperatures, small matrix cracks formed only at the edges around the glass fiber roving yarn and red-colored glass fiber areas without propagating into the thickness nor width direction of the laminates, whereas for posts-cured laminates, most of the matrix cracks propagated completely in both directions. Matrix fractography results shows that laminates cured at room temperature exhibit more plastic deformation which showed fewer brittle properties compared to post-cured laminates as the matrix behaved in a more brittle fashion, which enhanced the tensile microcracking such as matrix cracks and delamination.

References


Fikry, M.J., Ogihara, S., Vinogradov, V., The effect of matrix cracking on mechanical properties in FRP laminates,


