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The effect of long-term exposure to high temperature atmosphere on weight change and damage progress in carbon fiber-reinforced polycyanate ester composites

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Composites degradation in thermo-oxidative environment was investigated by measuring weight change and characterized using quantitative methods. Isothermal aging experiment was conducted on carbon fiber/polycyanate (T700SC/FSD-M-08178) unidirectional, angle-ply and quasi-isotropic (QI) laminate at 180 °C in air up to 1500 h. Two empirically based weight change models were used to predict weight change of unidirectional, angle-ply, and QI laminates. Microscopic observation was also conducted on exposed surfaces to investigate damage progress due to thermo-oxidative-degradation induced matrix crack.

Keywords: weight change; composites; thermo-oxidative; polycyanate

1. Introduction

High-performance polymeric composites have been employed in the aerospace industry due to their high-specific strength and high-specific stiffness.[1,2] Some kinds of heat-resistant polymer matrix-based composites (PMCs) (e.g. bismaleimide or polyimide resin systems) are currently being used on structures for both military and commercial aircraft. For development of next generation supersonic transporter (SST), heat-resistant PMCs must be applied to primary structure for airframe of SST in order to satisfy economic viability and service conditions. In accordance with requirements of velocity and altitude of a supersonic aircraft, it is estimated that the surface of airframe is heated to 180 °C or more by aerodynamic heating. In addition, like a structure of a fighter aircraft which carries the engine in a fuselage, the airframe is exposed to high temperature by radiation and heat transfer from the engine. Because of being subjected to a static heat loading for several thousand hours or more during operation, thermo-oxidative stability for PMCs must be evaluated. We chose polycyanate ester-based PMCs as a heat-resistant material. In general, polycyanate resin has better heat resistance than conventional epoxy resin. The processability of the polycyanate is similar to an epoxy resin. Furthermore, polycyanate resin shows lower water absorption characteristic under hygroscopic environment. Thus, the strength reduction due to moisture absorption in a high temperature environment might be small as expected. However, few study [3–5] investigated the effect of thermo-oxidative aging for polycyanate. Thus, the evaluation of long-term thermal stability for the polycyanate laminate is necessary for the usage of the resin to actual structure.

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The effect of long-term exposure to high-temperature environment on physical properties of heat-resistant PMCs has been a great deal of interest since before. Hence, many researchers have conducted investigation,[4–18] such as isothermal test, to clarify thermal stability of PMCs in high temperature thermo-oxidative environment. Because it is easier than conducting strength test, weight measurements have been well conducted to evaluate thermal stability of PMCs under the thermo-oxidative environment for a long term. At first, the anisotropic behavior of thermo-oxidative degradation in PMCs was reported by Nelson.[7] He observed that oxidation process was sensitive to the surface area. He found that the dominant degradation mechanism for the graphite/polyimide was oxidation of the matrix at the laminate edge. Additionally, the laminates degraded preferentially at the surface perpendicular to the fiber and the rate of degradation was accelerated by micro crack openings on the surface of 90° plies which provided increasing exposed surface area.

The first quantitative prediction for the weight change at a high temperature exposure environment considering surface geometry was investigated by Bowles.[8] After that, various models to predict weight change have been proposed in other researches.[15–17] In those studies, the weight change predictions for PMCs under long-term exposure to thermo-oxidative environment have been investigated for unidirectional composites and cross-ply laminates with epoxy,[17] bismaleimide [15], and PMR-15 [16] systems. However these weight prediction methods were not analyzed with polycyanate laminate. In addition, those specimen sizes were limited. Moreover quasi-isotropic (QI) and off-angle laminates which are important for aircraft structural design have not been investigated with these weight change prediction method. In this study, we aimed to validate weight prediction method and to predict weight change for general laminate configuration, such as both angle-ply and QI laminates with polycyanate-based CFRP.

2. Experimental setup

2.1. *Preparation of sample*

The material used for this study was a carbon fiber/polycyanate T700SC/FSD-M-08178 composites fabricated using unidirectional prepreg system. The CFRP laminates were cured by Fuji Heavy Industries Ltd (FHI) in Japan. The number of plies for both unidirectional and off-angle laminates was 8. On the other hand, the number of plies for QI laminate was 24, as shown in Table 1. All panels were cured according to manufacturer's recommended cure cycle. The temperature of cure for laminates was 180 °C and post-curing temperature was 230 °C. These panels were cut using a diamond blade into

Table 1. Sample geometries, stacking sequence, and identification.

No.	ID	Stacking sequence	Dimension (mm)			Initial weight (g)
			Width	Length	Thickness	
1	0T	$[0]_8$	14.83	249.88	1.15	6.5463
2	0C	$[0]_8$	10.23	139.90	1.13	2.4888
3	90T	$[90]_8$	24.76	175.52	1.15	7.6867
4	90C	$[90]_8$	25.28	139.89	1.15	6.2157
5	45T	$[\pm45]_{2S}$	25.37	199.87	1.10	8.7394
6	QI	$[+45/0/-45/90]_{3S}$	25.19	140.22	3.48	18.5973

a dimension as shown in Table 1 for subsequent mechanical tests. Then each section for all samples without top and bottom (or tool) surfaces were polished with SiC grinding paper (#400–#2000) and alumina powder (0.3 μm) because of observation for degradation process. The specimens were then placed in a vacuum oven at 110 °C under 0.5 atm for 48 h to remove moisture and volatile elements within the samples. After drying, the weight of all samples was measured to define initial weight for each sample. The number of specimens to measure weight for each laminate was from 5–20.

2.2. Isothermal aging and microscopic observation

The future high-speed commercial transporter will withstand long-term exposure at elevated temperatures between 177 and 232 °C.[18] Because the glass transition temperature (T_g) of this polycyanate CFRP was approximately 235 °C when measured by thermo-mechanical analysis, the temperature of 180 °C was expected as the temperature in-service and was selected as the aging temperature. The specimens were placed in natural convection oven for exposure tests. At specified time intervals, specimens were removed from the oven and were cooled to room temperature. When cooled, these specimens were set on aluminum plate for approximately five min. After cooled, specimens were weighed immediately to reduce the effect of moisture absorption from atmosphere. Those specimens were aged up to 1500 h. In order to investigate thermo-oxidative degradation-induced damage during isothermal aging, laser microscopy apparatus was employed to investigate the damage progress in the exposed edge section for each sample.

3. Results and discussion

3.1. Weight changes

Figure 1 shows composites weight change for each unidirectional sample with aging hours. Up to 197 h, the weight of the polycyanate composites increased with aging time. Then, the weight decreased with aging time. In the previous study, it was reported that the weight of bismaleimide composites increased at the beginning under thermo-oxidative environment due to oxygen incorporation in macromolecules.[19] This would be caused by autoxidation scheme. The weight increase is associated with

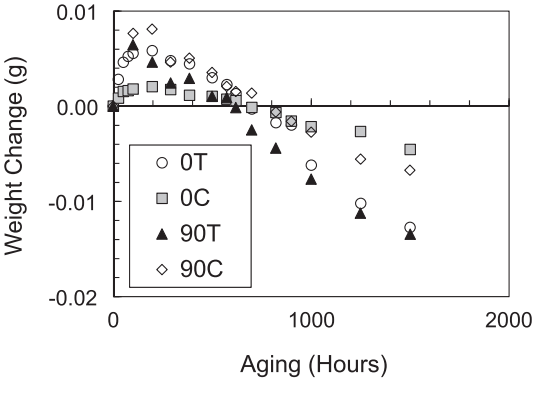


Figure 1. Weight change for each unidirectional sample with aging hours.

oxygen uptake within the propagation reaction. Figure 2 shows percentage weight change divided by initial weight (W_i) as a function of aging time. The percentage weight change was calculated with Equation (1).

$$\text{Weight change}(\%) = \frac{W - W_i}{W_i} \times 100 \tag{1}$$

where, W was the measured weight at each hours. The percentage weight which increase and decrease at 180 °C were lower (only 0.13 to −0.19%) than epoxy-based [17] and other heat-resistant PMCs.[20] Thus, the effect of thermo-oxidative environment at 180 °C on the amount of weight change was a little for the present aging period.

3.2. *Weight change models for unidirectional laminates*

As a simple consideration, the weight change of PMC laminates does not have anisotropic behavior in the weight change. In such case, the total weight change Q for each sample is proportional to the average weight flux q that was obtained from the weight change data for any unidirectional laminates and total surface area A_{total} for each sample. This assumption leads to the following Equation (2) between the total weight change Q, and the total surface area A_{total} and the weight flux q.

$$Q = A_{\text{total}}\, q \tag{2}$$

Figure 3 shows the weight flux q of 0C sample with aging hours. The q increased with first aging period and then decreased with further aging hours. This tendency was similar to percentage weight change result of unidirectional laminate.

On the other hand, previous study [8,15–17] reported that sample geometry affects the weight change behavior of PMCs. That is, unidirectional composites would preferentially oxidize along the fiber direction or ξ axis in Figure 4. The oxidation in the transverse direction or η and ζ axes in Figure 4 is suppressed due to less presence of continuous fiber/matrix interface. In this study, it was assumed that the degradation of PMC laminates proceeded in each surface independently, and total weight change was the summation of the weight outflux from each surface.

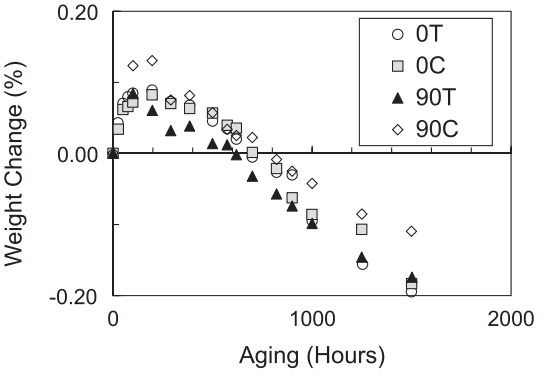


Figure 2. Weight change (%) for each unidirectional sample with aging hours.

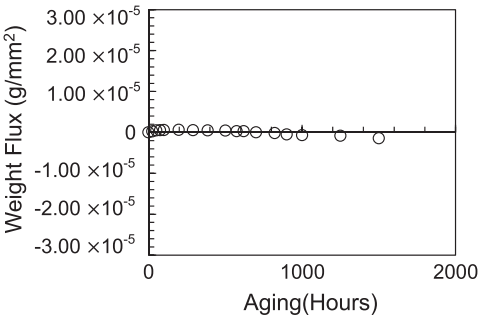


Figure 3. Weight flux q of 0C sample with aging hours.

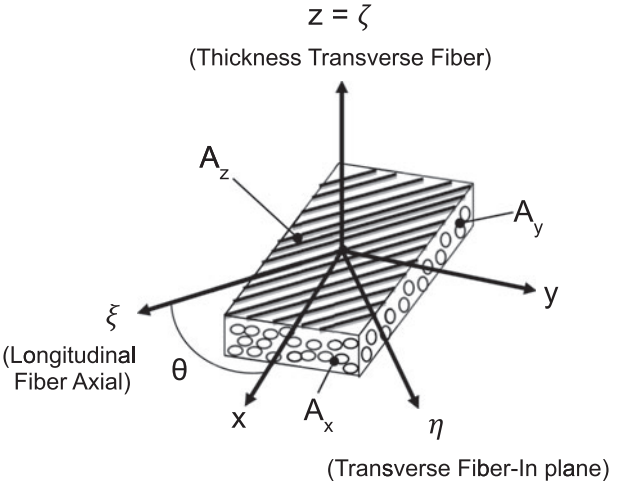


Figure 4. Sample geometry and axes definition.

To predict a weight change of a sample from the weight change data for specific specimens considering the geometry, some models were proposed previously.[8,15–17] Using the similar nomenclature to Nam et al. [15], the schematics in Figure 4 show the nomenclature used. The x, y, and z directions were fixed to represent the directions in the length, width, and through thickness of samples. The ξ, η, and ζ are denoted as longitudinal fiber (axial), transverse fiber (in-plane), and transverse through thickness (out-of-plane) directions. The fiber orientation angle is defined as an angle between x and ξ. Three different types of composite surface area were defined for unidirectional composite specimens as A_ξ = area of surfaces that is cut perpendicular to fibers, A_η = area of surfaces that is cut parallel to fibers, and A_ζ = area of surfaces that is top and bottom surfaces. Considering that the weight change is the result of mass loss from the surfaces of a specimen, the total weight change Q can be defined as a summation of the weight change per unit surface area q_i (g/mm^2). Thus, the amount of total weight change is shown in Equation (3).[17]

$$Q = A_\xi q_\xi + A_\eta q_\eta + A_\zeta q_\zeta \tag{3}$$

where q_i is weight flux per unit surface area. Using Equation (3), the weight flux per unit areas q_ξ, q_η, and q_ζ can be determined using three specimens with different surface area A_ξ, A_η, and A_ζ by solving the resultant set of three linear equations. In the present study, using the weight change data and each surface area for three specimens (0T, 0C and 90T), the parameter q_ξ, q_η, and q_ζ were calculated for aging times up to 1500 h. Table 2 shows each surface area A_ξ, A_η, and A_ζ for each unidirectional laminates. Figure 5 shows the weight flux for each surface area in three principal directions as a function of aging hours. Actually, we had not measured weight for all specimens, thus the result was calculated with interpolation weight data. For first aging period which was up to 385 h, q_ξ and q_η were negative. On the other hand, q_ζ had positive value. This results indicated that the surfaces perpendicular and parallel to fiber lost weight is due to thermo-oxidation before exposure, even though the total weight for all unidirectional samples increased with aging time for first aging period. The value of q_ξ was larger than that of q_η. This result was corresponding to previous study.[8,15,16,21] In contrast, the top and bottom surfaces gained weight at beginning. The top and bottom surfaces on the sample had resin-rich layers. This report does not treat the data for neat resin of this polycyanate, but the neat resin might gain the weight at first aging period at 180 °C in air. Thus, the top and bottom surfaces gained weight at the beginning due to the weight gain of resin-rich surfaces. Therefore, total weight increased at the beginning as a result of summation of the weight decreased in the surfaces perpendicular and parallel to fiber and weight increased in the top and bottom surfaces. After 385-h aging, the q_ξ increased with aging time. As mentioned in Section 3.5, some cracks onset along fiber direction. If cracks occurred in the surface perpendicular to the fiber, the cracks would propagate along the fiber direction and reach the unreacted core layer.[15] Then, the cracks became new paths to supply oxygen to the unreacted core and oxygen reacted with non-reacted resin. As a result, the surface perpendicular to fiber gained weight with aging period. In contrast, q_ζ decreases slightly with aging

Table 2. Surface areas for each unidirectional laminates.

		Surface area (mm^2)			
No.	ID	A_ξ	A_η	A_ζ	A_{total}
1	0T	34.14	575.22	7410.94	8020.30
2	0C	23.05	315.33	2861.23	3199.62
3	90T	404.75	27.11	8693.15	9155.01
4	90C	322.87	58.36	7073.96	7455.18

Table 3. Surface areas for each ply of angle-ply and QI laminates.

		Surface area (mm^2)			
ID	Angle	A_x	A_y	A_z	Number of each ply
45T	45	13.9	109.7	10143.0	4
	−45			–	
QI	45	14.6	81.2	7064.5	6
	0			–	
	−45			–	
	90			–	

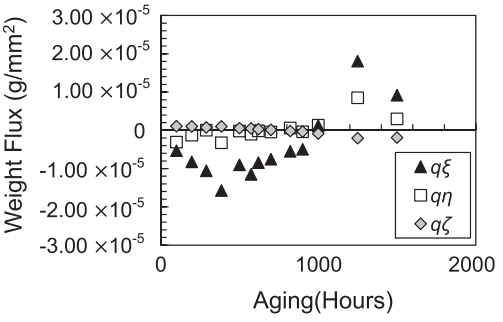


Figure 5. Weight flux for each surface area in three principal directions as a function of aging hours.

time. Thus, no crack would appear on the top and bottom surfaces at 180 °C in this aging period. In this study, specimen shapes were determined to carry out the strength test. Hence, the areas A_ξ and A_η were small percentage with respect to total surface area. Thus, small error for weight measurement caused large q_ξ and q_η error in Figure 5. In order to validate this method more accurately, thick specimen might be employed in isothermal aging.

Comparing Figure 3 with Figure 5, weight flux q was one order smaller when compared with weight flux q_ξ and q_η. This result suggests that the usage of weight flux for each surface might be effective for qualification of anisotropy in thermo-oxidative degradation.

3.3. *Weight change prediction for unidirectional laminates*

In this section, weight change would be calculated. The weight change prediction using q that was obtained from 0C sample was model 1. The weight change prediction using q_ξ, q_η, and q_ζ was model 2. Figures 6–8 show the results of weight change predictions calculated with models 1 and 2 for 0T, 90T, and 90C samples, respectively. In Figures 6–8, same tendencies were observed between experimental results and predictions calculated using model 1 and model 2 and both models could depict the weight change

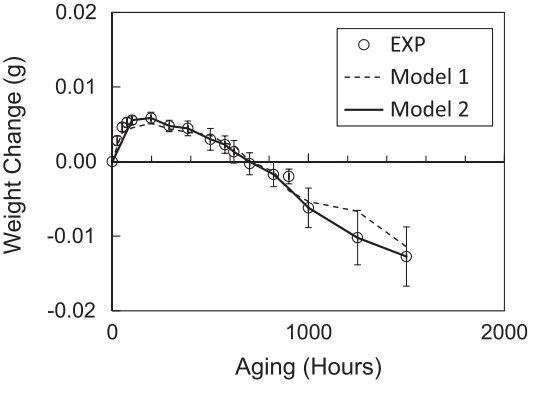


Figure 6. Results of weight change predictions for 0T calculated with models 1 and 2 as a function of aging hours.

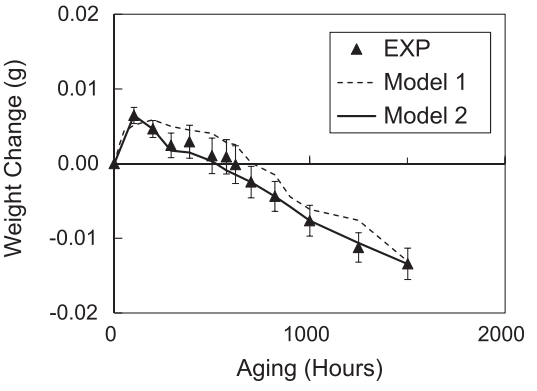


Figure 7. Result of weight change predictions for 90T sample calculated with model 1 and model 2 as a function of aging hours.

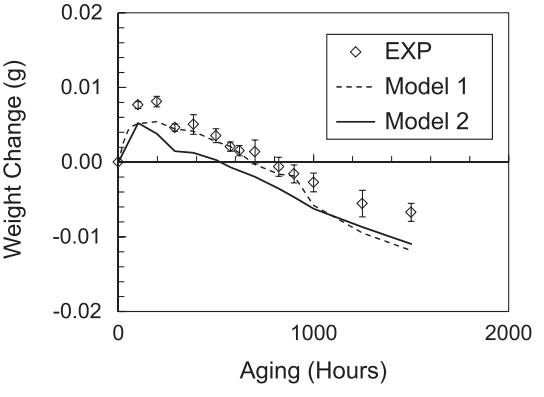


Figure 8. Result of weight change predictions for 90C sample and calculated with model 1 and model 2 as a function of aging hours.

up to 1500 h aging time. The reason was that the percentages of surface area for unidirectional laminate samples that was perpendicular to fiber to total surface area were approximately from 0.4–4.4%. Thus, the effect of weight change of surface perpendicular to fiber, which is oxidized significantly, was not so large when compared to the other surface area. These sample shapes were determined as the subsequent mechanical test. Therefore, to estimate the weight flux accurately, the sample that has larger percentage area in surface perpendicular to fiber to total surface area would be better. However, as shown in Figure 5, anisotropic behavior on weight due to thermo-oxidative environment could be evaluated for current sample shape with Equation (3). Thus, the weight change resulting from each area could be an important result to estimate the thermo-oxidative degradation mechanism for each surface area.

3.4. Weight change models and prediction for angle-ply and QI laminates

To account for the direction dependency of the weight change of samples, the following transformations can be used to express the angle dependency of the weight flux for unidirectional samples that have a fiber angle with respect to the cut surface.[15,17]

$$q_x = q_\xi \cos^2\theta + q_\eta \sin^2\theta \tag{4}$$

$$q_y = q_\xi \sin^2\theta + q_\eta \cos^2\theta \tag{5}$$

$$q_z = q_\zeta \tag{6}$$

where θ is defined as the angle between the sample axis and the fiber axis. For a practical usage, more complicated laminate configuration, such as $[\pm 45]_{2S}$ and $[45/0/-45/90]_{3S}$, were characterized experimentally and analytically. When the layers that have different orientations were exposed on a cut surface, the total weight change Q_{Total} can be obtained from

$$Q_j = \sum_i A_i q_i \text{ in } j\text{th ply} \tag{7}$$

$$Q_{\text{Total}} = \sum_j Q_j \tag{8}$$

where i indicate arbitrary x, y, and z directions and j is defined as ply number. The weight change q_i was a function of the fiber orientation angle θ and obtained from Equations (4)–(6). For most outer layers of specimen, the A_z is top or bottom surface areas, and the other layers, the A_z is actually zero. Q_j is calculated for each ply, and then they were summated to obtain the total weight change for the sample. Figures 9 and 10 show the weight change results and predictions for 45T and QI samples, respectively. To predict the weight change with model 1, the weight flux q which was obtained from the 0C weight change data was used. To predict the weight change with model 2, the weight flux q_ξ, q_η, and q_ζ which were obtained by the weight change data from the 0T, 0C, and 90T unidirectional laminates were used. Figure 9 shows that the 45T samples gained weight for the first 100 aging period. Then the weight decreased slowly when compared to the predicted value that was calculated from the model 1 and model 2. Thus, the degradation mechanism in the 45T would be different when compared with the unidirectional samples. Figure 10 shows that the weight of the sample QI decreased for first 25 h. It might cause by insufficient moisture dissipation at

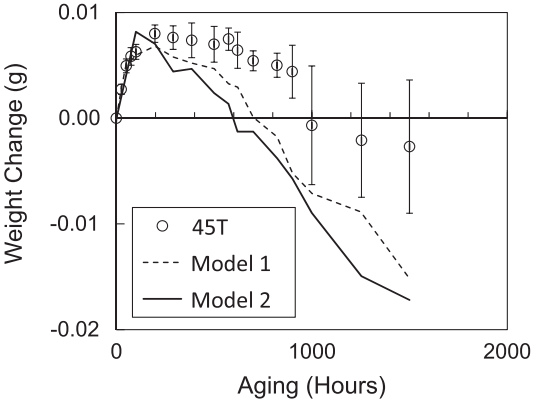


Figure 9. Weight change results compared with model 1 and model 2 predictions for $[\pm 45]_{2S}$ (45T) sample with aging hours.

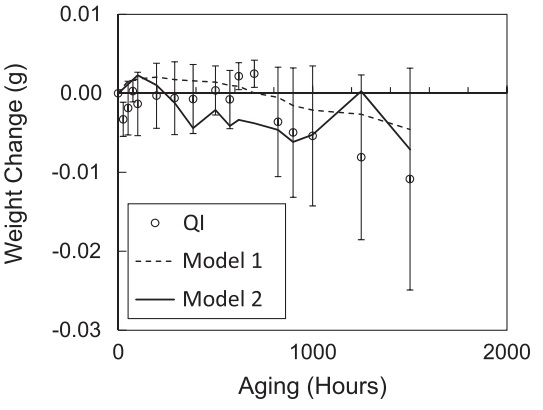
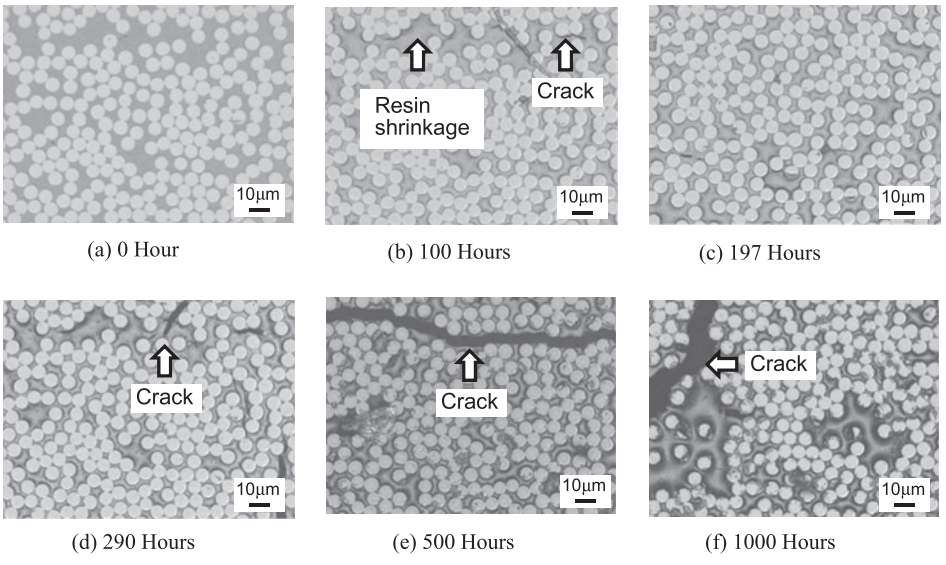


Figure 10. Weight change results compared with model 1 and model 2 predictions for QI sample with aging hours.

110 °C under 0.5 atm for 48hours in air for thicker specimens. After 25 h, the weight increase up to 200 h because of moisture of the sample sufficiently disappeared and uptake oxygen for resin. After 290 h, the weight decreased. In both figures, models 1 and 2 denoted predicted values in Equations (7) and (8), and Equation (2), respectively. In comparison with the experimental and analytical results, for the weight prediction in the 45T, both the model 1 and model 2 were good agreement for the first 197 h aging period. However, after 197 h, the difference between experimental and both models value became gradually larger with aging hours. Thus, the mechanism of weight change of the 45T would be different when compared with unidirectional laminates. On the contrary, in Figure 10, the difference between experimental and both models value were similar with aging. Hence, the mechanism of weight change in the QI would be same when compared with unidirectional laminates.

3.5. *Microscopic morphology for thermo-oxidative degradation*

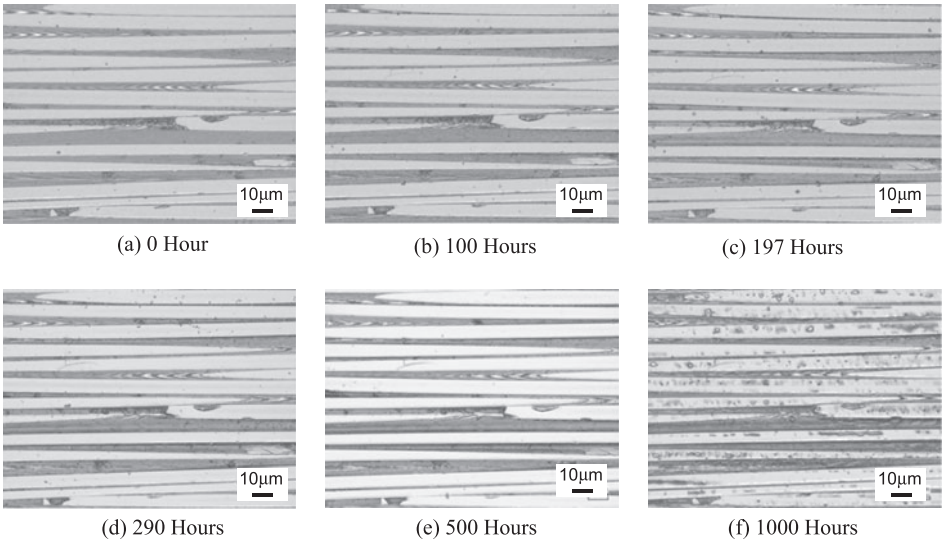
Figure 11 shows the surface perpendicular to fiber in the 90C unidirectional sample. In Figure 11(b), for 100 h, the resin shrank due to thermo-oxidative degradation, and some micro cracks were observed near the fiber. These damages proceeded up to 195 h aging shown in Figure 11(c). After 290 h aging shown in Figure 11(d), the number of micro cracks increased and the micro cracks propagated in the lamina. There was no regularity in the propagation direction of crack. After 1000 h exposure, the crack opening displacement of the micro crack became larger and the resin shrinkage became deeper. On the contrary, on the surface along the fiber direction in the 0C sample as shown in Figure 12, the matrix between fibers shrank and no matrix crack was observed with increasing exposure time. On the surface of the inner layer in thickness for the 45T sample as shown in Figure 13, resin shrinkage was observed and no crack appeared up to 1000 h. Figure 14 shows the inter-laminar region between + 45° and −45° plies in the 45T sample. Through Figure 14(a)–(c), no crack was observed. However, after 385 h aging, the matrix cracks appeared in the inter-laminar region between the + 45°and −45° ply as shown in Figure 14(d), and the matrix cracks increased with aging time (Figure 14(e) and (f)). The matrix cracks deflected against the sample thickness direction. These cracks appeared surfaces in parallel to each other. Thus, it would be



(a) 0 Hour (b) 100 Hours (c) 197 Hours

(d) 290 Hours (e) 500 Hours (f) 1000 Hours

Figure 11. Exposed surface perpendicular to fiber in 90C sample with aging hours.



(a) 0 Hour (b) 100 Hours (c) 197 Hours

(d) 290 Hours (e) 500 Hours (f) 1000 Hours

Figure 12. Exposed surface parallel to fiber in 0C sample with aging hours.

caused by shear stress due to the cross-elasticity effect of thermal stress. Since the matrix in inter-laminar region was easily oxidized, the 45T sample gained weight due to autoxidation reaction. Therefore, the weight change in the 45T sample would be larger than that of model 1 and model 2. Figure 15 shows side view of the QI sample with aging hours and Figure 16 shows enlarged image of exposed surface in 90° ply adjacent to 45° ply of the QI sample with aging hours. The micro cracks were observed inside of the 90° layers and around the interface between 90° and adjacent + 45° or

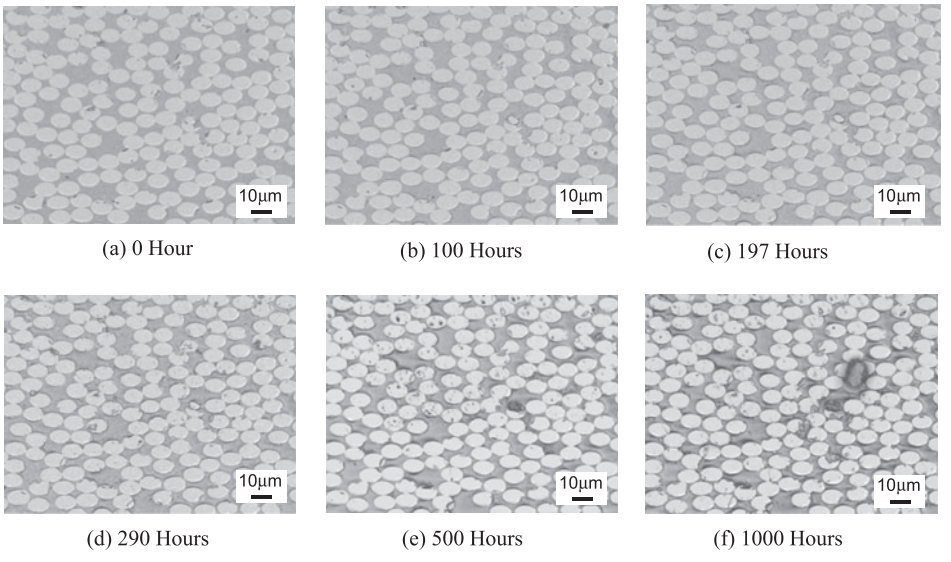


Figure 13. Exposed surface with 45° fiber angle between fiber and normal of exposed surface in in-plane shear (45T) sample with aging hours.

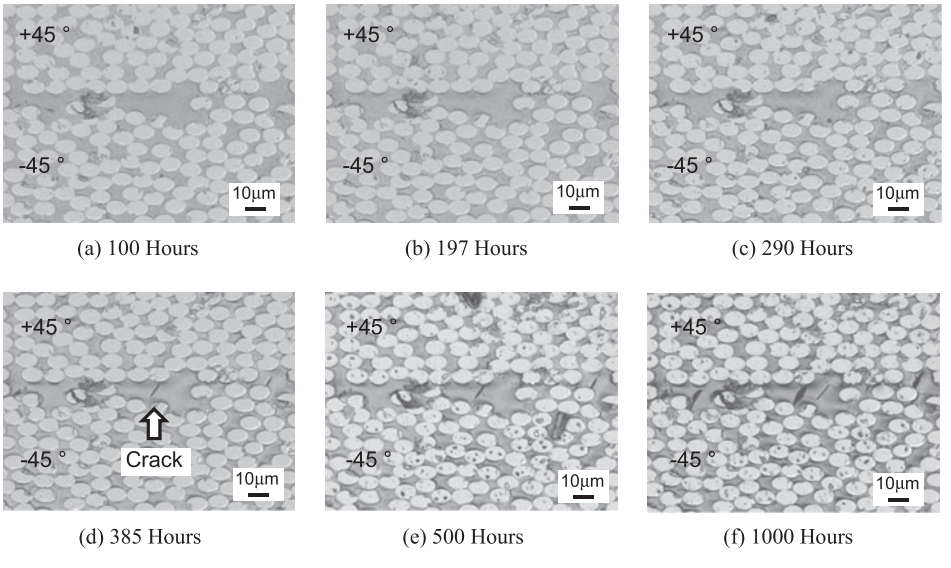


Figure 14. Exposed surface with 45° fiber angle between fiber and normal of exposed surface adjacent to other 45° in in-plane shear (45T) sample with aging hours.

−45° layers after 100 h aging (Figures 15(b) and 16(b)). After 290 h aging, the micro cracks in 90° layer propagated along the specimen thickness and transverse cracks were arrested at the interface between layers (Figures 15(c) and 16(c)). After 500 h as shown in Figures 15(d) and 16(d), the transverse cracks that reached interface between layers did not grow in the adjacent layers, even though the matrix crack that appeared in

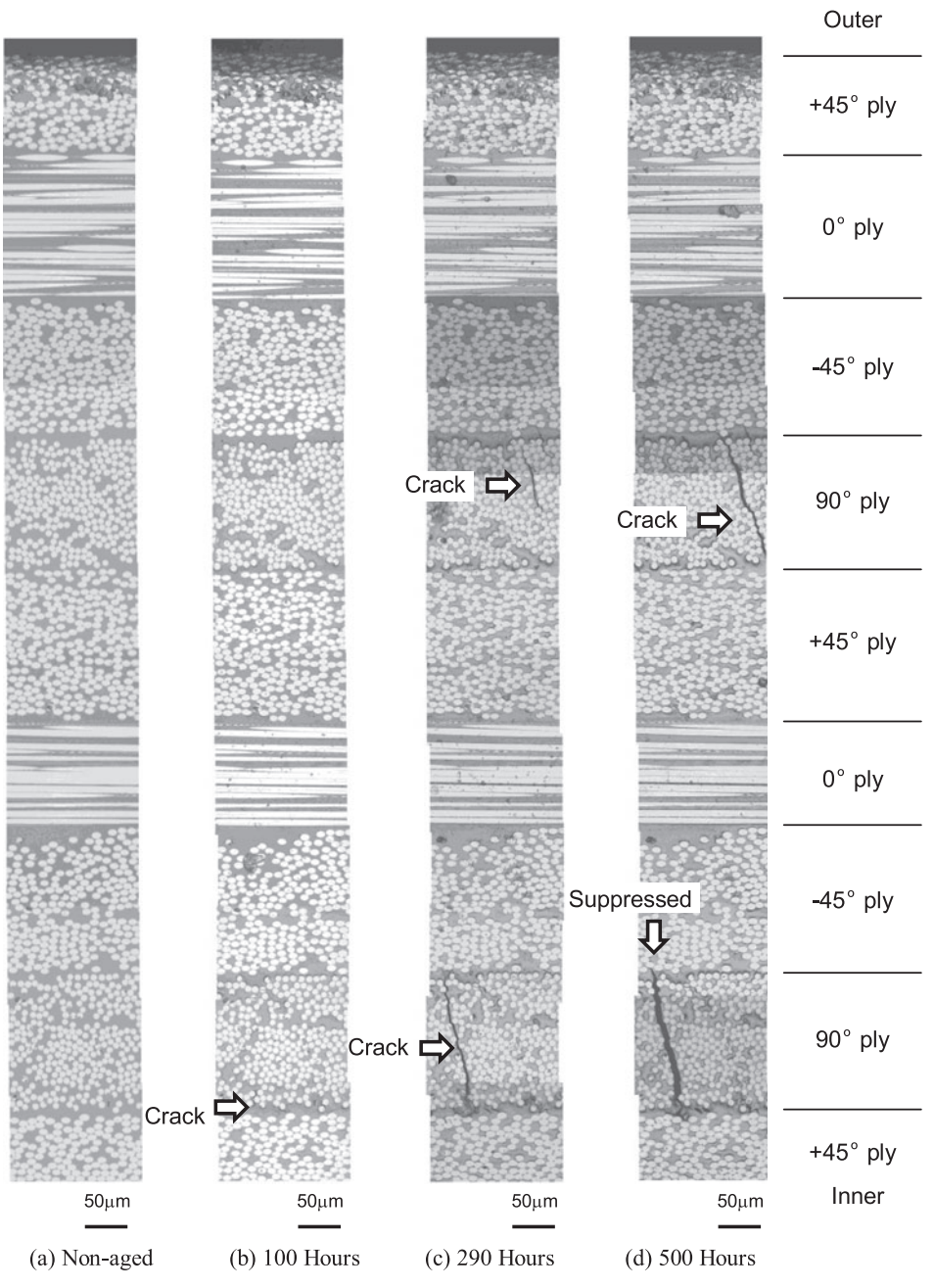


Figure 15. Exposed surface of QI sample with aging hours.

intra-lamina of 90° was propagated along to the thickness direction. The temperatures both curing and isothermal aging were at 180 °C. Thus, thermal stress is ideally zero. However, the matrix shrunk [22,23] along to fiber direction near the fibers during isothermal aging which result in induction of local tension stress. Furthermore, 90° layers could shrink easily along to longitudinal direction of specimen, and the shrink

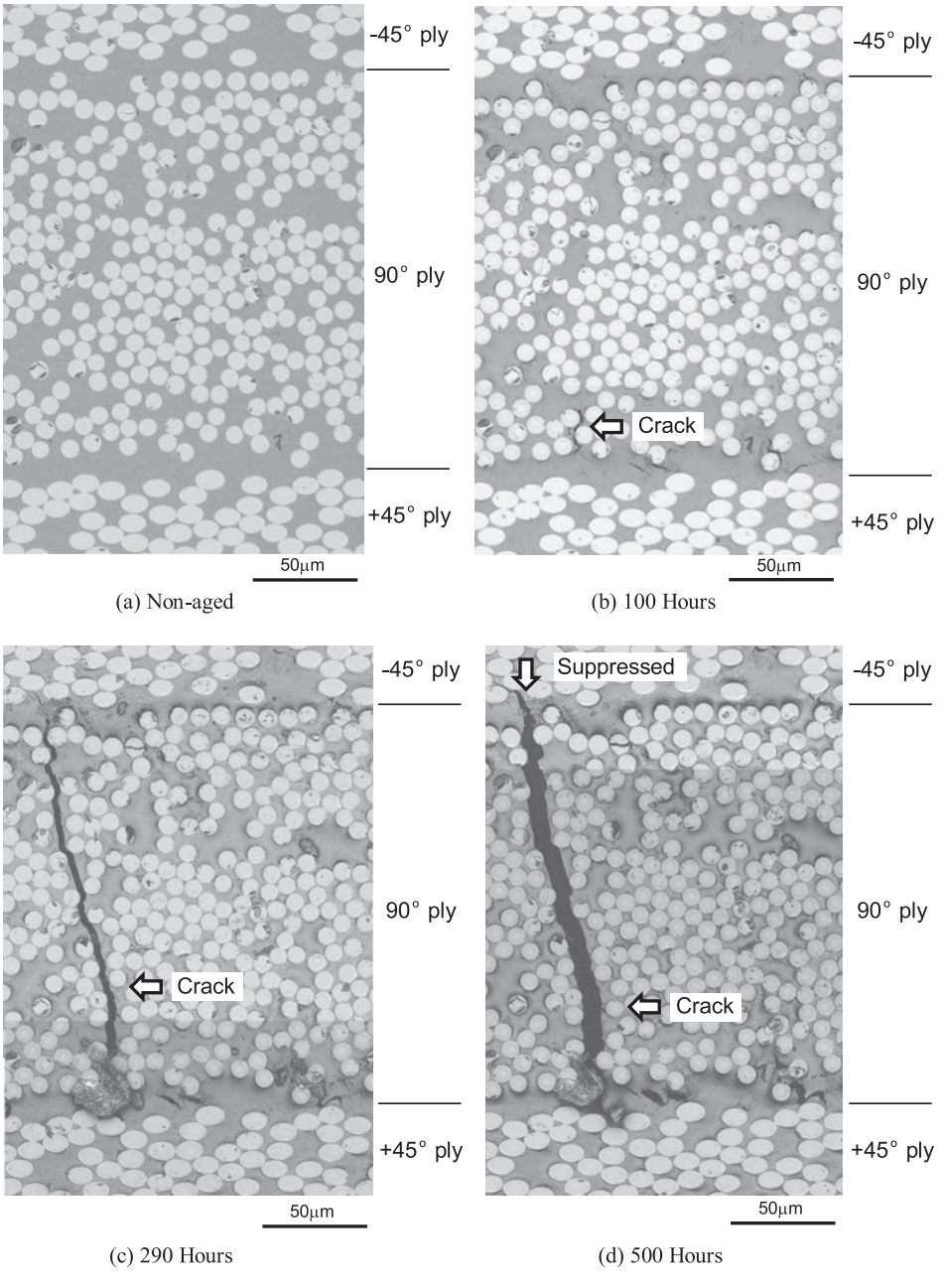


Figure 16. Exposed surface in 90° ply adjacent to 45° ply of QI sample with aging hours.

deformation in 90° layers could be restrained by adjacent ± 45° layers. Tension stress along to longitudinal direction of specimen could be generated in 90° layers. In addition, isothermal aging embrittled the matrix so that the transverse cracks appeared. Comparing Figure 15 with Figure 11, these matrix and transverse cracks appeared after almost same aging hours for both the 90C unidirectional sample and the 90° layer in

the QI sample. Thus, the degradation mechanism caused by matrix crack and transverse crack that affect to weight change was almost same and the weight change difference between experiment and prediction was smaller in the QI sample than that in the 45T sample. The matrix and transverse crack damages that appeared in each ply or between plies due to thermo-oxidative degradation affect the weight change. Therefore, in case of evaluation of thermal stability for PMCs, it is necessary to clarify the damage behavior caused by thermo-oxidative environment.

4. Conclusions

In this study, in order to investigate thermal stability of polycyanate-based CFRP to a long-term exposure, the weight change of the samples and the initiation and progress of damages resulting from isothermal aging on unidirectional, angle-ply and QI laminates were investigated. Samples were aged at 180 °C in air up to 1500 h. It was found that the weight for all samples increased at the beginning of the aging. Then, the weight decreased with aging hours. The weight change for all polycyanate laminate was small at 180 °C in air up to 1500 h. Therefore, polycyanate-based PMCs had thermal stability on the weight change. Anisotropic thermo-oxidative behavior for unidirectional laminates was investigated to evaluate the weight change mechanism and damage extension. Unidirectional laminates with different geometries were employed to confirm the effectiveness of the weight change models. The weight flux q_ξ and q_η show that the area perpendicular and parallel to fiber decreased even though weight flux from the top and bottom surface increased in the first 385 h. After 385 h aging, the weight flux q_ξ increase with aging. It would be caused by oxygen uptake into the matrix due to matrix cracks onset. The weight change models could depict the weight increase and decrease tendency with the results of weight change for a specific sample shapes. On the other hand, the model considering anisotropic behavior was better to understand anisotropic behavior in the thermo-oxidative environment. Only for angle-ply specimen, the both weight change predictions were different from experimental results. From the surface observation results, the crack extension in the angle-ply specimen was quite different when compared with other laminates. Therefore, for the characterization of thermal stability of PMCs, the cross-section area both perpendicular and parallel to fiber must be observed carefully to understand damage initiation and progress.

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