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COMPRESSIVE STRENGTH/DEGRADATION RELATIONSHIP OF CARBON/BMI COMPOSITES AFTER THERMAL CYCLING AND AGING FOR THE SECOND GENERATION SST STRUCTURES

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SUMMARY : The paper investigates the effects of long-term thermal cycling and isothermal aging on the residual compressive strength of carbon fiber/BMI matrix composite laminates. Two kinds of composites from the same family were tested by static compression load and examined by microscopy after subjecting to various aging conditions. The compression tests were carried out on unnotched and open-hole specimens. Damage was separately assessed by weight loss and observed by electron and light microscopes on aged open-hole coupons. Over the glassy range of the composites, it appears that the residual compressive strength is not only depending on both weight loss and cracking. The chemical structure of the matrix is the major parameter and it is necessary to take into account damage of the entire volume of aged test specimens to predict the long-term behavior. During thermal aging, consolidation and degradation of the chemical network, cracking in the outer or inner plies and phase separation in the matrix are combined parameters to modify the thermo-mechanical properties. In prospect, it appears necessary to develop a model for each parameter and include them in a more complex mechanical model.

KEYWORDS : Organic matrix composites, Compressive strength, Degradation, Cracking, Thermal cycling and aging

INTRODUCTION

Carbon fiber/organic matrix composite laminates have high potentialities as light structural materials for the second generation supersonic transport but they must undergo rigorous testing to be qualified. The qualification of composite materials requires a significant number of physical and mechanical tests. Particularly, the long-term behavior is a major barrier to expand their use in such aircraft structures. The problems associated with aging, durability and predicting life of organic matrix composites have been highlighted by all aerospace companies. To predict the response of new generation of composite materials, it is therefore proposed to establish a relationship between mechanical characterization and damage achieved after aging through experimental proofs. Delamination or cracking can severely degrade the performance of composite materials. As a result, structural design using organic matrix composites is based on very conservative design allowables. There is a strong need to develop composite materials which are more tolerant of damage. Toughened resins have been developed in order to improve the performance of composites (Smith and Dow [1]). Particularly, certain bismaleimide resins have been modified by mixed thermoplastic polymers to increase toughness. These new resins have the potential to offer substantial structural performances and to day are commercially available as prepregs. Thus, carbon/BMI

composite systems have been developed recently and have shown some good mechanical properties even at elevated temperatures. However, fundamental understanding of mechanical characteristics associated with damage must be emphasized to predict the response of the material systems to long-term exposure in service environments. Since compression testing has been proven to be meaningful and relevant for behavior analysis of material structures, an understanding can be established by residual compressive strength of the laminates previously subjected to oxidizing and high thermal environments. Thus, this paper examines the effect of thermal cycling and isothermal aging conditions (temperatures and times) on the mechanical properties and attempts to explain the role of the overall aging process.

MATERIALS AND EXPERIMENTAL PROCEDURE

Two kinds of composite materials from the same family were used to investigate the effects of thermal cycling and isothermal aging on compressive strength. One sort of materials was prepared by NAL (National Aerospace Laboratory of Japan) and consisted of Cytec Fiberite prepregs made of G40-800 carbon fibers and 5260 BMI resin. The other sort was prepared by ONERA (National Aerospace Research Agency of France) and consisted of Hexcel prepregs made of T800H carbon fibers and F655-2 resin. The two kinds of materials were 32-ply laminates with a stacking sequence of $[+45/0/-45/90]_{4s}$ and cut into the geometry appropriate to the thermal cycling and isothermal aging in ovens. For each laminate, a series of panels were unnotched and another panels with a center hole of 6.35 mm in diameter. In addition, small square coupons from the same laminates were machined (40 mm × 40 mm), polished and used for examining of cracks during thermal cycling and isothermal aging.

First, panels and coupons were thermal-cycled up to 1,000 cycles in an oven with an increasing and decreasing temperature rate of $10°C.min^{-1}$ and a holding of 5 minutes at the lowest and highest temperatures. A first series was conducted between –50 and +120°C, a second series between –50 and +150°C and another between –50 and +180°C. Then, these three series were isothermally aged at 120, 150 and 180°C respectively. For each temperature, three isothermal aging times were 1,000, 3,000 and 6,000 hours. After thermal cycling and isothermal aging, the coupons were removed and examined by a light microscope for counting cracks initiated on free edges. Likewise, the unnotched and open-hole panels were removed and machined into the specimens for compression tests. Hence, damaged free edges from panels were taken away. Only damaged areas from surfaces and holes were preserved within the test specimens (Shimokawa et al [2]).

Compression tests were carried out at room temperature and three respective isothermal aging temperatures mentioned above. Each test temperature was measured by two thermocouples installed in the oven near the surface of the specimen. Unnotched and open-hole specimens were mounted in grips that were separated to give a gage length of 30 mm. The grips were positioned in an anti-buckling fixture to provide stability during tests. The test fixture was not heated before clamping a specimen. After the test fixture was placed between compression platens in the oven, the latter was raised up to the test temperature followed by a dwell time of 15 min to balance heating between fixture, apparatus and specimens. Compression tests were conducted by means of a hydraulic testing machine. Static compression load was applied at the rate of $0.5\ mm.min^{-1}$. Load versus deflection plots were recorded for all tests and obtained results were linked to damage from the respective examined and aged coupons. Isothermal aging and compression tests were carried out on the French specimens by NAL and inversely. The compression test method used by NAL is described in ref. [2] and that used by ONERA is the Airbus Industrie method (AITM [3]).

TEST RESULTS

For all specimens from two kinds of composite laminates, damage and compression data were analyzed and numerous significant observations gained from the experimental

works were discussed. To clarify the future discussion, first we present below all the results separately by sections on compressive strength then degradation assessment.

Compression data

The sets of all mechanical test results are given in Tables 1 and 2. Each result is an average value obtained from two test specimens. For the two laminates and all the test configurations, either before or after aging, compressive strength decreases slightly with temperature. Standard deviation is often narrow for open-hole specimens whereas it is rather large for unnotched specimens. Even, as a general rule, whatever test temperature and undergone aging are, compressive failure is always catastrophic. The sequence of events that leads to the final failure seems the same for all aging times and test temperatures. For unnotched specimens, failure is frequently initiated in the vicinity of the grip ends, although subsequent failure is spread over the entire gage length. Examination of failed specimens shows that compressive failure of the quasi-isotropic laminate seems bring about the kinking of fibers in the 0° plies then damage propagates around. This is followed by delamination of the laminate. For open-hole specimens, failure is quite sudden and triggered in the section comprising the hole. The initial failure starts at the hole boundary and propagates towards the specimen edges. The values in Tables 1 and 2 will be discussed in the data analysis after examination of coupons aged without any loading test.

			FAILURE STRESS (MPa)			
			Initial condition	**Thermal cycling + isothermal aging**		
	σr (MPa) at 20°C	**Test Temp. (°C)**	**0 h**	**1000 h**	**3000 h**	**6000 h**
Non-hole specimen	513	120	452	540	560	606
		150	439	503	566	564
		180	437	494	474	515
Open-hole specimen	338	120	306	304	327	310
		150	291	297	292	289
		180	277	286	276	266
Neat section open-hole specimen	430	120	388	395	415	394
		150	370	377	370	367
		180	351	363	351	338
Hole coeff.		20	0.84			
		120	0.86	0.73	0.74	0.65
		150	0.84	0.74	0.65	0.65
		180	0.80	0.73	0.74	0.66

Table 1 Compressive strength of the quasi-isotropic G40-800 carbon fiber/5260 BMI resin composite before and after thermal aging

			FAILURE STRESS (MPa)			
			Initial condition	Thermal cycling + isothermal aging		
	σr (MPa) at 20°C	Test Temp. (°C)	0 h	1000 h	3000 h	6000 h
Non-hole specimen	723	120	636	595	556	560
		150	630	562	540	480
		180	535	564	444	387
Open-hole specimen	303	120	300	304	300	296
		150	293	280	279	261
		180	283	255	233	208
Neat section open-hole specimen	364	120	360	365	360	355
		150	352	334	334	313
		180	341	305	280	249
Hole coeff.		20	0.52			
		120	0.57	0.61	0.65	0.63
		150	0.56	0.59	0.62	0.65
		180	0.64	0.54	0.63	0.64

Table 2 Compressive strength of the quasi-isotropic T 800 H carbon fiber/F 655-2 BMI resin composite before and after thermal aging

Degradation assessment

First, weight losses have been collected during thermal cycling and isothermal aging on the small open-hole square coupons. To determine the weight of coupons, first, they were removed from the oven and cooled for 5 min at room temperature then weighed accurately. Data show that there is not very much or not at all in the development of weight losses for 1,000 cycles because dwell times are very short (5 min). Cumulated hours at the maximum temperature were only 80 hours. Moreover, for each thermal cycling, there were continuously remove and recovery about humidity and therefore weight losses are not significant on the degradation of composite laminates. During the isothermal aging, only 180°C is a temperature capable possibly to degrade the BMI structure. It is true that the BMI resin is recommended for use temperatures at least equivalent otherwise higher than the test temperatures. Particularly, oxidation at 180°C is more effective than at lower temperatures and gives rise a removal of various volatile products (Salin and Seferis [4]). However, as indicated in Fig. 2, even at 180°C weight loss decreases very slightly.

Cracking of the two composite laminates has been observed on the square coupons after thermal cycling and during isothermal aging. Starting at a corner of the specimen, one previously polished section was slowly transversed with the light microscope. After completely viewing the section, the number of cracks was counted on every ply. Cracks are visible as thin lines, lightly tilted in each +45, -45 or 0° ply. After thermal cycling, the material composites are slightly cracked and cracking states are almost similar whatever the temperature might be. Usually, cracks initiate first in the outer plies and few in inner plies. During isothermal aging, the situation is more complicated. Damage consists of transverse and longitudinal cracks. Figure 3 shows a photomicrograph of the G40-800/5260 composite aged at 180°C for 6,000 hours.

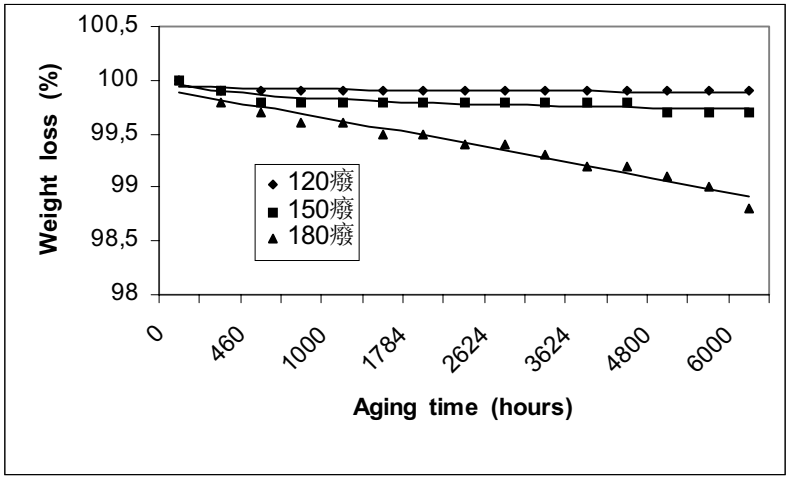


Fig. 2 Weight loss versus aging time at three temperatures of G 40-800/5260 composites

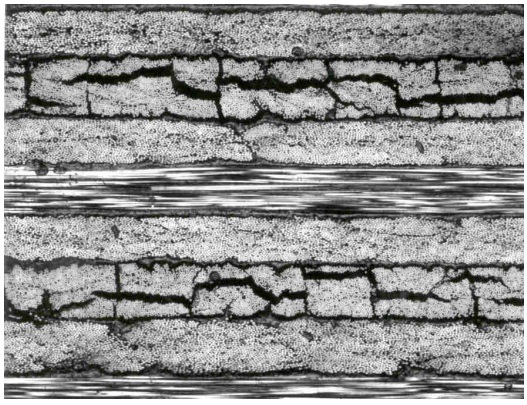


Fig. 3 Cracking after thermal cycling and isothermal aging at 180°C/6000 h of the quasi-isotropic G40-800 carbon fiber/5260 BMI resin composite.

In all cases, crack distribution is homogeneous in the eight 0° plies. If one consider only transverse cracking, Figure 4 shows a straightforward representation of transverse crack densities as a function of aging time for all coupons and at the three temperatures.

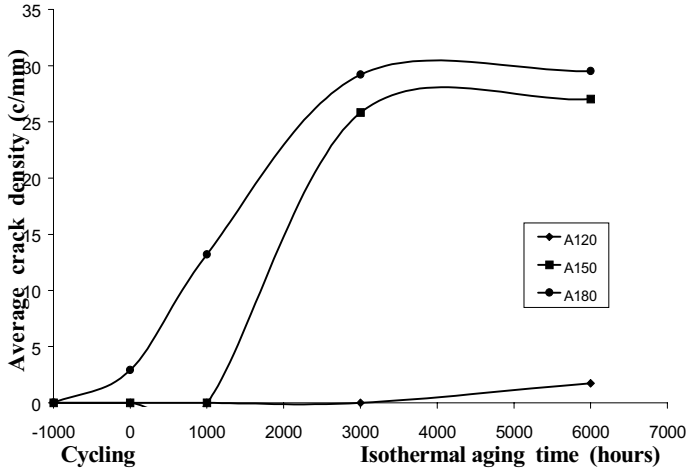
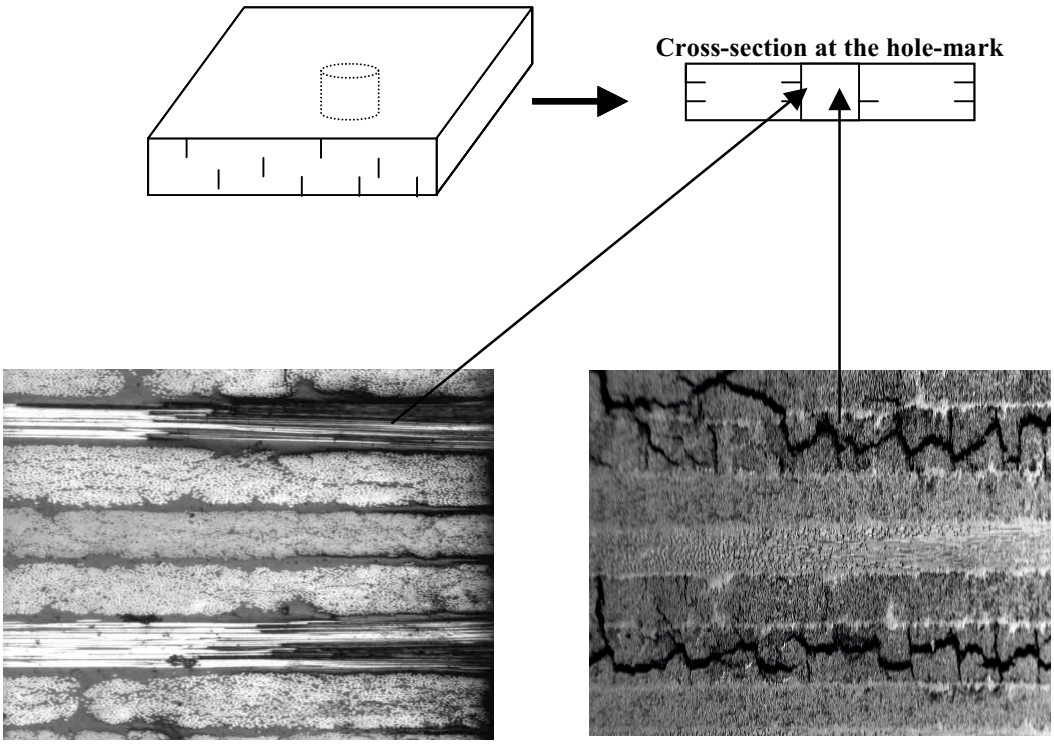


Fig. 4 Transverse crack densities of the quasi-isotropic G40-800 carbon fiber/5260 BMI resin composite.

Crack density is the average number of transverse cracks crossing entirely a layer and determined per one millimeter long. This figure illustrates clearly the existence of two diagnostic points in transverse cracking. The first point is the onset of cracking only insured by thermal cycling at 180°C for G40-800/5260 whereas a small number of cracks were already observed for T800H/F655-2 at 120°C and 150°C. For thermal cycling at 120°C and 150°C, the onset is superimposed on the time axis for G40-800/5260. This point is followed by a transition region in which cracks develop very rapidly at 150°C and 180°C. The second diagnostic point marks the end of the development at which a crack saturation is reached and maintained. This type of plot also shows the effect of temperature on the crack density versus time. On the other hand, to examine the internal part in the bulk of the laminate, all the coupons were machined as indicated in Fig. 5.



Photomicrograph *a* Photomicrograph *b*

Fig. 5 Different side views of longitudinal cracks in polished cross-section (photo *a*) and non-polished hole surface (photo *b*).

On the cross-section, far from the hole, all of the coupons present transverse cracks without additional longitudinal cracks in the first or the two first outer plies. Now, next to the hole, there are short longitudinal cracks in the 90° plies (0° observed since the hole edge). Photomicrograph *a* in Fig. 5 shows an example of longitudinal cracks in two 90° plies. Photomicrograph *b* taken by a scanning electron microscope shows longitudinal cracks in 0° plies on the hole surface and indicates a connection of longitudinal cracks on the polished cross-section (on the left) and the non-polished hole surface (on the right). Depth of longitudinal cracks depends on aging time. For the least damaged holes, depth is about 0.1 mm (150°C/3000 h) and for the most damaged holes, depth is 0.5 mm (180°C/6000 h) as shown in the case of the photomicrograph *a*. On the hole surface, it must be pointed that there are transverse cracks in the same 0° plies and that the crack saturation is identical at that observed on the free edges of the coupons.

DISCUSSION

A discussion about degradation tendencies can be made from compression data regarding damages as functions of aging time. On the one hand, we have an evolution of the compressive strength and the other hand, a development of damage consisting of weight loss and cracking. Figures 6 and 7 show the failure strength at the three temperatures on unnotched and open-hole specimens from the two quasi-isotropic (QI) carbon/BMI composites.

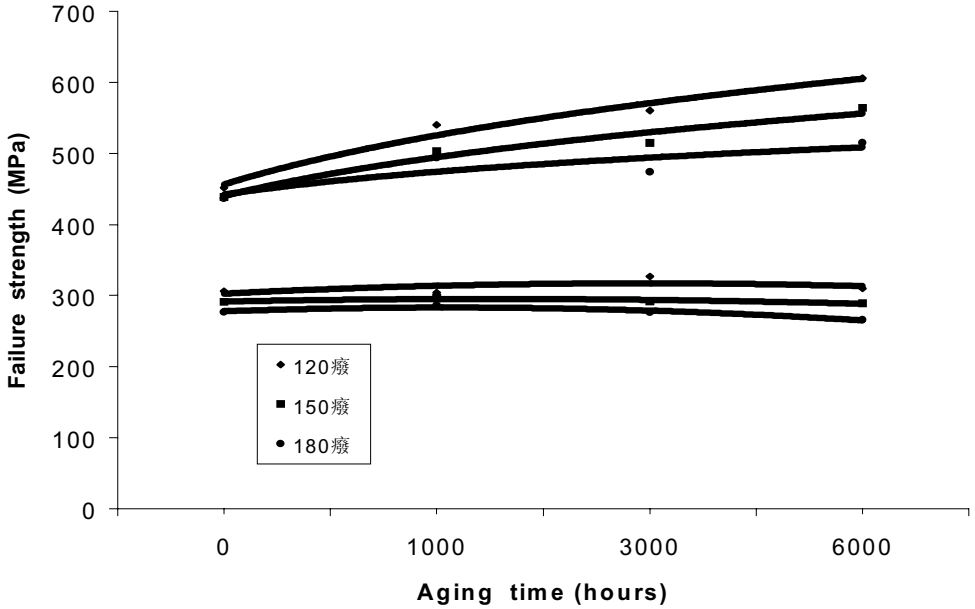


Fig. 6 Compressive strength versus aging time of unnotched (upper curves) and open-hole (lower curves) specimens from QI G40-800 carbon fiber/5260 BMI resin composite.

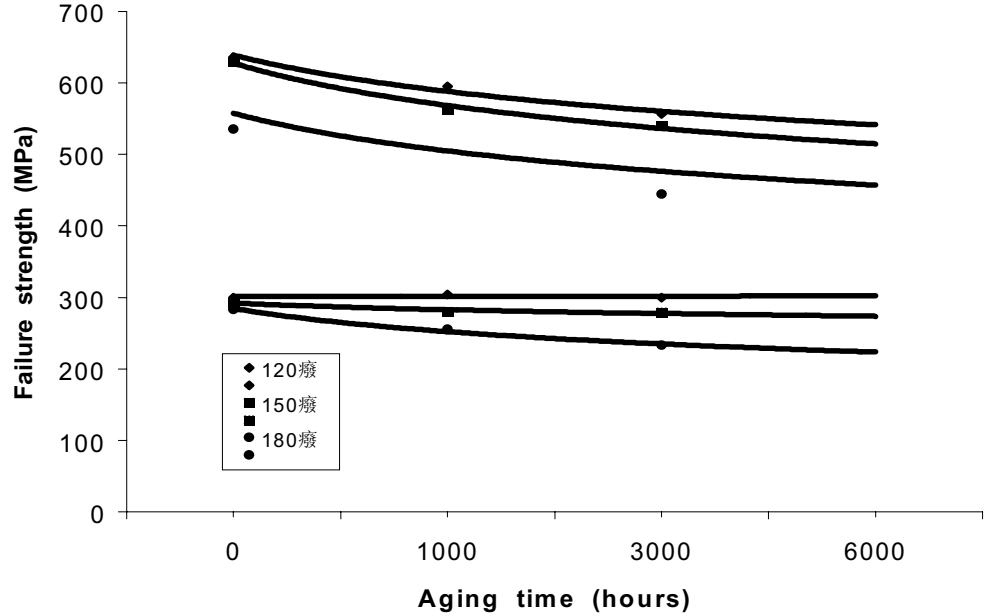


Fig. 7 Compressive strength versus aging time of unnotched (upper curves) and open-hole (lower curves) specimens from QI T 800H carbon fiber/F 655-2 BMI resin composite.

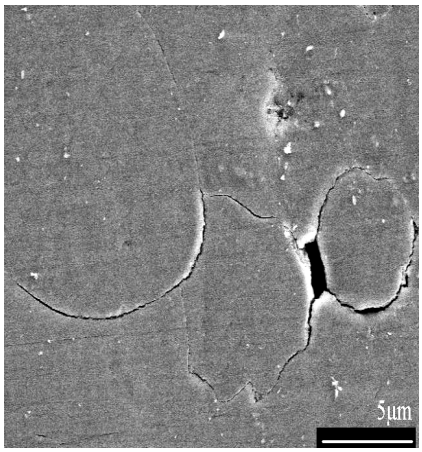
It appears clearly significant results and fundamental differences between the two materials. Though compressive strength measurements of two composites are in the same order of magnitude, the evolution of curves is significantly different. For the T800H/F 655-2 composite, all the failure strengths of unnotched specimens decrease monotonously due to the damage which develops for thermal aging. The decrease of the failure strength of open-hole specimens is slighter at 180°C even slighter still for the two other temperatures than those respectively from unnotched specimens. On the contrary, the shape of curves of the G40-800/5260 are reversed though very slightly for the open-hole specimens. This evolution was already noted on other composites (Plunkett et al [5]).

Regarding to the G40-800/5260, it is assumed that this increase is due partly to a post-cure effect. Actually, these composites laminates were post-cured at 215°C for 4 hours so that these conditions possibly are not high enough for keeping its chemical structure for thermal aging. In compensation, this post-cure recommended by the supplier seems ideal for crack resistance and can be quite suitable for some various applications. Therefore, this reversed evolution appears be as a result from a combination between post-cure effect and damaging. This post-cure effect is well highlighted on the unnotched specimens for isothermal aging at 120°C whereas damage prevails for aging at 180°C. For the open-hole specimens, cracking is more voluminous because there is a free edge representing the hole surface. Crack density must be similar to that determined on the polished free edges from sides of coupons. On all the compression test specimens, the damaged free edges do not exist since they have been removed in machining aged panels into specimens. Hence, for the unnotched specimens, there are cracks only in the outer plies. Consequently, damage is more efficient in the open-hole than the unnotched specimens. Particularly for 180°C, strength decreases monotonously and very slightly for all aging times because the damage in the outer plies and around the hole is more effective on failure strength than the post-cure effect. At 180°C, there is damage around the hole represented mainly by deep longitudinal and transverse cracks. Consequently, there is a reduction in evolution of compression data. On the other hand, the hole coefficient versus aging time renders roughly the damage effect around the hole (Table 1).

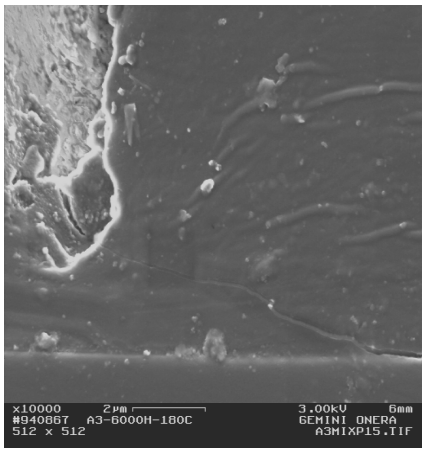
Regarding to the T800H/F 655-2 postcured under higher temperature conditions, compressive strength appears only depending on the damage development. Actually, for thermal aging, also there is a consolidation of the chemical structure of the matrix and subsequently the plotted curves represents a combination between degradation and consolidation but with a dominant degradation. In Fig. 7, the decreasing content from curves of open-hole specimens seems less pronounced than that from curves of unnotched specimens. In fact, the declines of upper and lower curves are proportional to the initial value of failure strength. Besides, the hole coefficient is almost constant at every temperature. That means that damage around the hole has not very much effect upon compressive strength.

In summary, we are dealing with two composite materials from the same family but with different matrix nature and behavior. In all cases, compressive strength is depending on the chemical structure of the matrix. Indeed, it is assumed that if manufacture of these composite laminates is quite suitable (fiber volume fraction, porosity, fiber alignment, balanced moisture) then compressive strength only depends on load transfer from fiber to fiber (Favre et al [6]). The load transfer is directly linked to the health of the matrix. This one consolidates and degrades constantly during thermal aging. Degradation causes very many breaks of chains which lead to a radicalar decomposition of the structure following a precise mechanistic scheme. In the same time, new combinations and forms from radicalar polymers are realized giving rise structure changes (Colin et al [7]). Weight loss is a consequence of the departure of volatile products from the thermo-oxidative reaction. Now, damage leading to a decrease of the compressive strength is not only represented by weight loss and cracking in the outer plies and hole surface but also by chemical structure changes and movements in the matrix. For example, Fig. 8 shows morphologies of the BMI structure in the bulk of coupons investigated by SEM. For thermal aging, there exists a decomposition process leading to phase separations since the two BMI matrices are consisted of thermoset and thermoplastic phases. These ones also take part in the decline of mechanical properties. In addition, there

should be thermolysis reactions (Struik [8]), fiber/resin interface effects (Tsotsis and Lee [9]), thermal stress states (Bowles et al [10]), size effects (Bowles et al [11]) and so on.



F655-2 BMI resin
after 6,000 h at 150°C



5260 BMI resin
after 6,000 h at 180°C

Figure 8 Photomicrographs showing phase separations in BMI matrix after thermal aging.

CONCLUSION

To day, there exist mathematical models developed to predict the long-term behavior of organic matrix composite materials from accelerated aging tests. Sometimes, these models include damage represented weight losses and crack densities. About composites investigated herein, made of BMI matrices having a high glass transition temperature, it was reasonable to think establishing a relationship between damage obtained from accelerated aging tests over the glassy range and compressive strength. The results of this study show quite obviously that damage is a matter very complex with a lot of parameters. It is clear that there is not equivalence between the behavior obtained from accelerated aging tests and that obtained on a long time under usual use conditions and therefore an extrapolation, for example by an Arrhenius law, on a long time would not reliable. To predict long-term behavior, it would be necessary to develop a model for each parameter and include them in a more complex mechanical model. Examination of surfaces and free edges of damaged composites is not sufficient to depict the decrease of compressive strength. It is necessary to take into account the entire volume damage of the material. Also, the compressive strength is not only depending on the weight loss. Postcure effect and damage obtained from phase separations in the bulk of the matrix must be considered and probably thermolysis effect, adhesion to the fibers and so on. The resin nature is the dominant factor in the evolution of thermomechanical properties. The investigated BMI matrices are not thermostable resins and it is assumed that their chemical structure modified in thermal aging changes load transfer capability from fiber to fiber and therefore the compressive behavior.

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