Materials Science Research International, Vol.4, No.4 pp.287-293 (1998)

General paper

THE EFFECT OF WATER-ABSORPTION AND CRYOGENIC TEMPERATURE ON THE STRENGTH OF ArFRP

Sohei SHIROSHITA*, Keiji OKAMOTO** and Kenjiro KOMAI***

**The Kyoto University Museum, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

***Komatsu Ltd., Ueno, Hirakata 573-1011, Japan*

****Department of Mechanical Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

Abstract: Aramid fiber reinforced plastics (ArFRP) is being applied in severe service conditions, such as aeronautical or space environments. Therefore, it is necessary to elucidate their strength in various environments. In the present study, static tensile and fatigue tests of dry and wet specimens of ArFRP were carried out at room temperature and at cryogenic temperature, 77K. Two types of aramid fibers, du Pont's Kevlar49® and Teijin's Technora® were used for the reinforcement. The fractured specimens were inspected under a Scanning Electron Microscope (SEM) after the tests and the fracture mechanisms were analyzed. The tensile strength of individual aramid fibers was also measured at the same temperatures. The effects of cryogenic temperature and water absorption on the strength of ArFRP and aramid fibers were made clear.

Key words: *ArFRP, Static strength, Fatigue strength, Cryogenic temperature, Water absorption, SEM, Fractogragphy*

1. INTRODUCTION

ArFRR (aramid fiber reinforced plastics), an advanced composite, is applied in various fields whereby the operating conditions have become more severe. For example, it is applied in cryogenic environments such as in vessels for transportation, storage of liquefied gases, and in aeronautic and space applications. Therefore, it is necessary to elucidate the fracture mechanisms when ArFRP is used in such severe conditions.

The authors have made clear the environmental strength characteristics of advanced composites and elucidated the fracture mechanisms of the composites in various environments by fractographical methods such as SEM (Scanning Electron Microscope) and SAM (Scanning Acoustic Microscope) to study the interior damage of the fractured material [1-10]. In this study, we carried out static tensile and fatigue tests on dry and water-absorbed specimens of ArFRP at cryogenic temperature and discovered similar strength characteristics. Simultaneously, we elucidated the fracture mechanisms of the dry and water-absorbed specimens at cryogenic temperature. We also did tensile tests of aramid fibers themselves at room temperature and at cryogenic temperatures.

2. EXPERIMENTAL PROCEDURE

2.1. Material

Two types of aramid fibers, Teijin's Technora® (i.e. HM50) and du Pont's Kevlar49® were tested in this experiment. Three gauge lengths of 20mm, 25mm and 30mm were used to obtain the elastic modulus of the fibers, and 10 fibers were tested in each length.

Two types of composites reinforced by HM50 and Kevlar49 fibers were tested. One was unidirectionally reinforced composites, $(0°)_{14}$, and another was cross-ply composites, $(\pm 45°)_{3S}$. Fiber volume fractions of the laminates were 67 - 72% in 0° unidirectionally reinforced, and approximately 70% in ±45° cross-ply laminates. The matrix was standard epoxy-resin, Epikote828 with Epicure Z(100/20) from Shell. The curing cycle was recommended at 150°C for 20 minutes, then 160°C for 2h. The specimens were rectangular in shape with dimensions of 10mm wide, 200mm long and about 2mm thick. The gauge lengths were 90mm for the tensile tests and 72mm for the fatigue tests.

"Dry" specimens were kept in dry air, and "Wet" specimens were immersed in distilled water for around 3 weeks for fibers, and around 3 months for composites. The temperature of the distilled water was 80°C to absorb into the material rapidly. These specimens were used in the tensile and fatigue tests.

2.2. Test Method

Tensile tests of the fibers were carried out using an electro-hydraulic servo-controlled fatigue tester (Shimadzu EHF-01, the loading capacity: 980N), and a load-cell (the capacity: 1.96N) was installed to measure the load. The test piece was made by sticking the fibers on mounting-paper following ASTM D3379 and JIS R7601. The tests were done under displacement controlled conditions at a cross-head speed of 2.5×10^{-2}mm/s.

Static tensile tests of the composites were carried out using a computer-controlled universal tester

Received December 3, 1997

Original paper in Japanese was published in Journal of the Society of Materials Science, Japan Vol. 46, No. 2 (1997) pp. 157-162.

(Shimadzu AG-10TD type Autograph, the loading capacity: 98kN), with the cross-head speed set at 2 mm/min under the controlled displacement. An electro-hydraulic servo-controlled horizontal type fatigue tester (Shimadzu, loading capacity: 49kN) was used in the fatigue tests. The stress ratio R was 0.1 and the wave shape was a sinusoidal wave at f = 1Hz. Dry and wet specimens were tested at room temperature (RT) (Dry-RT, and Wet-RT) and at cryogenic temperature (Dry-77K, and Wet-77K) with fibers and composites. Specimens tested at cryogenic temperature were immersed in a nitrogen-cell, which was fitted around the full gauge length of the specimen. Liquid nitrogen filled the cell thirty minutes prior to the test, enabling the specimen to adequately cool. In the case of fatigue tests, the cell was always filled with liquid nitrogen using an automatic liquid nitrogen supplier. The fracture surfaces were observed using a scanning electron microscope (SEM, JEOL JSM5400-LV).

3. EXPERIMENTAL RESULTS AND CONSIDERATION

3.1. Tensile Tests of Fibers

The mechanical properties of the fibers are shown in Table 1. The elastic moduli ($E_{0.3}$) were calculated from the initial 30 - 40% section of the fracture load in the load - elongation diagram. Comparing the tensile strength (σ_B) at RT to 77K, the strength of dry and wet specimens increased by around 5 - 10% in HM50 fibers, but there was little change in Kevlar49 fibers. The elastic modulus of dry and wet fibers increased significantly at 77K by about 30 - 50% and 50 - 60%, respectively. Comparing the dry fibers with the wet ones, there was little difference between either the strength or elastic modulus of the HM50 fibers. Both the strength and the elastic modulus of the wet specimens of Kevlar49 fibers were significantly lower than the dry ones. The water-absorption had a greater effect on the mechanical properties of the Kevlar49 fibers than those of the HM50 fibers.

3.2. Tensile and Fatigue Tests of 0° Unidirectionally Reinforced Composites

3.2.1 Tensile tests

The mechanical properties of 0° unidirectionally reinforced composites are shown in Table 2. E_i is the initial Young's modulus (initial 5 - 10% section of the tensile strength), E_f is the final elastic modulus (final 80 - 90% section of the tensile strength) and ε_f is the fracture strain. In both of HM50 and Kevlar49 composites, the tensile strength at 77K decreased by 8 - 13% from those at RT, but the modulus increased. The tensile strength of the wet composites decreased by 1 - 6% compared to the dry ones, at the same temperature. The effect of water-absorption on the tensile strength at the same temperatures was comparatively small.

Though the strength and modulus of the resin at 77K increased from RT, the fracture strain decreased because of embrittlement of the resin [11]. Therefore, the large deformation of a specimen causes an initial fracture of the resin, leading to an uneven transmission of load to the fibers through the resin, local stress concentration in the fibers, and a decrease in the tensile strength. Assuming the load is transmitted uniformly to the fibers in the composites and using the rule of mixture, we calculated the load to be transmitted to the fibers upon the fracture of the composites. However, the data obtained from our tensile tests showed that the load was too small to break the fibers and that the fracture probability of fibers was about 2%, even at the highest value. Therefore, it is thought that the stress is concentrated locally in the fibers.

Because both the modulus and the strength of the fibers are far larger than those of the resin, the properties of the 0° unidirectionally reinforced composites were affected significantly by those of the fibers. Therefore, the modulus of the composites increased and the strength of wet composites was lower than dry ones at 77K. Furthermore there is other evidence to suggest that water-absorption makes the resin ductile, relaxes the stress concentrations and increases the tensile strength [12]. This leads us to the inconclusive result that water-absorption decreases the tensile strength. While the tensile strength of wet HM50 fibers increases compared to dry ones at 77K, the strength of wet composites decreases more than dry ones.

3.2.2 Fatigue tests

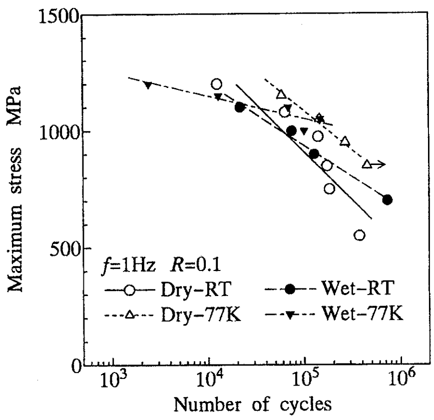
The S - N diagrams are shown in Figs.1(a) and (b). The inclinations of 77K were smaller than those of RT

Table 1. Mechanical properties of fibers.

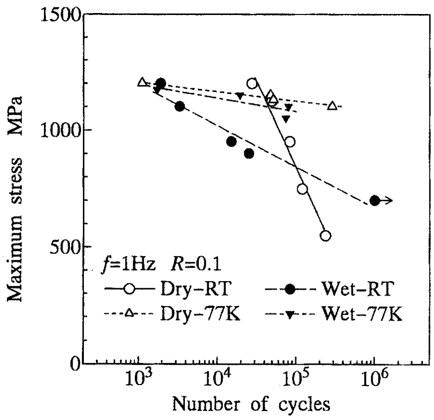
			σ_B(MPa)	$E_{0.3}$(GPa)
HM50	Dry	RT	3100	67
		77K	3250	100
	Wet	RT	2980	69
		77K	3300	112
Kev.49	Dry	RT	3060	125
		77K	3070	161
	Wet	RT	2640	101
		77K	2660	154

Table 2. Mechanical properties of 0° unidirectional composites.

			σ_B, MPa	E_i, GPa	E_f, GPa	ε_f, %
HM50	Dry	RT	1470	58	52	3.0
		77K	1330	79	109	1.4
	Wet	RT	1400	58	52	2.8
		77K	1260	77	108	1.4
Kev.49	Dry	RT	1530	63	69	2.7
		77K	1330	84	119	1.3
	Wet	RT	1440	64	74	2.1
		77K	1320	91	119	1.3



(a) HM50 composite



(b) Kevlar49 composite

Fig.1 $S-N$ diagrams of 0° unidirectional composites.

in every circumstance, and the fatigue life at 77K was apparently larger than that at RT in low stress area (relatively low stress area on the S - N diagram). This is contrary to the case of the tensile strength.

Under cyclic low stress at a cryogenic temperature of 77K, the strain of a specimen decreases due to an increase in the modulus of the composites, and the cooling embrittles the resin. In addition, the cooling further increases the axial residual stress at the interfaces between the fiber and resin generated when laminating, in accordance with the difference between the axial coefficients of thermal expansion of the fiber and of the resin. The cooling further lowers the radial bond strength at the interfaces between fiber and resin. This is caused by the difference between the radial coefficients of thermal expansion of the fiber and of the resin; the fibers contract more than the resin. As a result, the strength of the interfaces decreases. It is thought that a lot of microcracks generate gradually in the resin and interfaces between fiber and resin. This absorbs energy, relaxes the stress concentration and prevents the crack propagations from breaking. This coincides with the reports that brittle resin has better fatigue properties than ductile in the case of CFRP [13], and that the fatigue strength of resin is higher at low temperature rather than at RT [14].

While the fatigue lives at RT of both dry Kevlar49 and dry HM50 composites are higher than wet ones in the high stress area (relatively high stress area on the S - N diagram), those of wet ones are lower than dry ones in the low stress area. At 77K, the same tendency is observed in HM50 composites, but there is no clear difference between the fatigue lives of dry and wet Kevlar49 composites.

In the low stress area the fatigue properties of the composites are determined by the resin because the fiber has enough strength to the stress in contrast with the resin. In wet-RT, the ductilization of the resin prevents the initiation of cracks and the large deformability due to the decrease in the modulus of the resin relaxes the local stress concentrations in the fibers. As a result, there is an inclination for the fatigue strength in Wet-RT to be higher than that in Dry-RT in low stress area.

3.2.3 SEM inspection of fracture surfaces

Figures 2 - 5 show SEM photographs of fracture surfaces. Hackles are observed at the resin parts in Dry-RT of both composites (Fig.2). The hackles in Dry-77K are comparatively fine, and cracks are found (Fig.3). It is thought that the decrease in the ductility of the resin at 77K leads to the generation of cracks and fine hackles.

While there are some hackles in Wet-RT (Fig.4), some basements of hackles whose upper parts seem to have disappeared and some cutting sections of the resin are observed in Fig.5, which shows that the resin embrittles more in Wet-77K.

3.3. Tensile and Fatigue Tests of ±45° Cross-Ply Laminates

3.3.1 Tensile tests

Mechanical properties of ±45° cross-ply composites are shown in Table 3. The moduli were calculated from the approximate straight lines, which seemed to coincide with the initial linear sections (5 - 20% of the fracture stress) of load - elongation diagrams.

In both composites, the tensile strength of the dry ones at 77K decreases from those at RT and the percentage of the decreases in Kevlar49 composites is higher than that in HM50 composites. Residual shear stress at the interfaces between fiber and resin occurs when the composites are laminated, and the stress increases at 77K. Furthermore, the bond strength of the interface decreases, as fibers contract more than resin. Consequently, the shear strength of the interfaces decreases. In addition, the residual interlaminar shear stress increases at 77K and the shear strength decreases as the direction of the fibers in each layer are at right angles to each other. Supposedly, the decrease of the shear strength at the interfaces between fiber

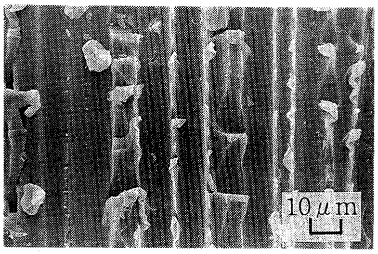


Fig.2. Fracture surface of 0° unidirectional composites (Kevlar49 composite. Dry-RT).

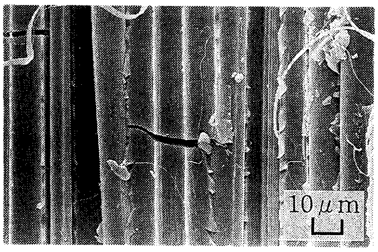


Fig.3. Fracture surface of 0° unidirectional composites (Kevlar49 composite. Dry-77K).

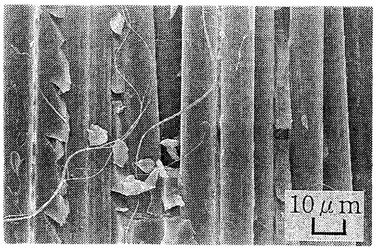


Fig.4. Fracture surface of 0° unidirectional composites (Kevlar49 composite. Wet-RT).

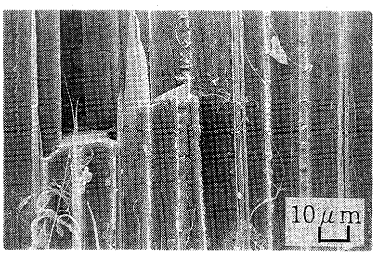


Fig.5. Fracture surface of 0° unidirectional composites (HM50 composite. Wet-77K).

Table 3. Mechanical properties of ±45° cross-ply composites.

			σ_B, MPa	E, GPa	ε_f, %
HM50	Dry	RT	100.1	5.6	4.1
		77K	81.5	10.0	1.3
	Wet	RT	77.0	4.5	12.1
		77K	85.0	9.8	2.0
Kev.49	Dry	RT	125.4	6.4	6.2
		77K	89.0	11.9	1.6
	Wet	RT	87.9	5.3	5.4
		77K	95.1	10.8	2.3

and resin and the interlaminae decreases the tensile and fatigue strength (Section 3.3.2) of dry composites at 77K.

Conversely, the reasons why the tensile strength of wet specimens at 77K was larger than those at RT, are based on the following reasons. The cooling process recovered the shear strength of resin and the transverse strength of fibers, and the increase of residual stress which causes a decrease of the shear strength of the laminates was not large, because the water-absorption had reduced the residual shear stress between laminae.

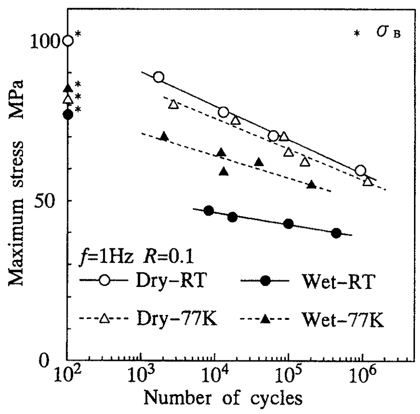
The water-absorption has two opposing effects; it decreases and increases the tensile strength of the composites. The decrease is due to the decreases in the shear strength of the resin, the transverse strength of the fibers [15], and the strength of the interfaces between fiber and resin. These decreases brought on a reduction of the tensile strength of the composites. The increase effect resulted from the decrease in residual shear stress of the interlaminae due to ductilization of the resin [12], therefore increasing the tensile strength of the composites. The former effects exceeded the latter ones justifying why the tensile strength at RT of wet composites decreased largely from those of dry ones.

The elastic moduli at 77K of both HM50 and Kevlar49 composites rose from those at RT. The moduli of wet specimens were lower than dry ones at the same temperature, because the modulus of the resin and the transverse modulus of the fibers increase at 77K [16]. Also, it is believed that the water-absorption decreases the modulus of the resin [17], which decreased the modulus of the wet composites.

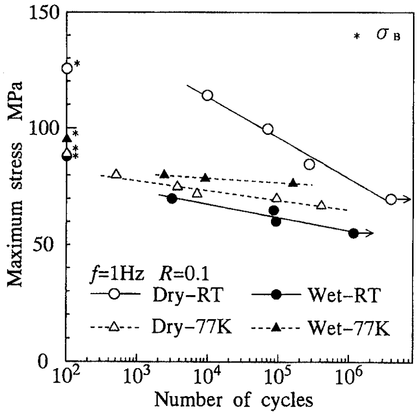
3.3.2 Fatigue tests

Figure 6(a) and (b) show the S - N diagrams, and the tensile strengths are indicated by asterisk marks on the axis of ordinate ($N = 10^2$). The order of the fatigue strength of Kevlar49 composites in each condition coincides with the tensile strength in a range of this study, which shows the cause of the increase and decrease in the fatigue strength to be the same as the tensile strength. Furthermore, in HM50 composites, the tensile strength in Dry-77K decreased from Dry-RT on a large scale, but the decrease in the fatigue strength at 77K from RT was minor. This is due to many fiber-splittings generated in HM50 composites (Section 3.3.3), preventing the interface fractures.

The decrease in fatigue strength in Wet-RT of HM50 composites was considerably larger than that of the tensile strength. Water-absorption increases the strength of interlaminae because the resin becomes ductile and reduces the residual shear stress between layers. Conversely, the water-absorption decreases the adhesive strength of the interfaces between fiber and resin which decreases not only the interlaminar but also intralaminar strength [12]. While water-absorption promotes generation of fiber-splittings [15] due to weakening of the bond strength in the transverse direction of the fiber, the shear strength of the



(a) HM50 composite



(b) Kevlar49 composite

Fig.6 $S-N$ diagrams of ±45° cross-ply composites.

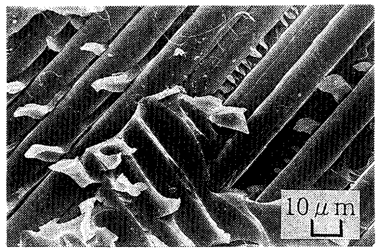


Fig.7. Fracture surface of ±45° cross-ply composites (Kevlar49 composite. Dry-RT).

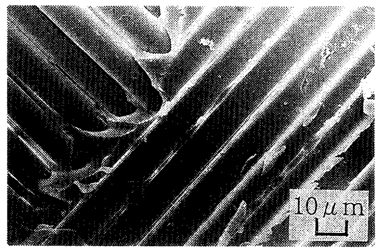


Fig.8. Fracture surface of ±45° cross-ply composites (Kevlar49 composite. Dry-77K).

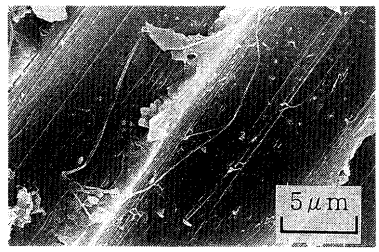


Fig.9. Fracture surface of ±45° cross-ply composites (HM50 composite. Dry-RT).

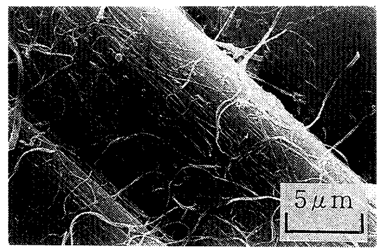


Fig.10. Fracture surface of ±45° cross-ply composites (HM50 composite. Dry-77K).

interfaces between fiber and resin drops significantly under cyclic loading in Wet-RT. Consequently, bridging effects resulting from fiber-splittings were neutralized (Section 3.3.3) and the fatigue strength decreased sharply.

3.3.3 SEM inspection of fracture surfaces

Figures 7 - 14 show SEM photographs of fracture surfaces after the fatigue tests. While the resin fractured with a large plastic deformation in Dry-RT (Fig.7), the plastic deformation was small in Dry-77K (Fig.8).

No major difference was found between the fracture of the Kevlar49 fiber surfaces at RT and 77K. More fiber-splittings were generated at 77K (Fig.10) than at Dry-RT (Fig.9) in HM50 composites. One reason is that the decrease in transverse strength of the fibers led to easier fiber-splittings, because cooling made fibers brittle [18]. Another reason is that the friction between fiber and resin was large because the surface of a HM50 fiber was comparatively rough. These fiber-splittings are the major attributing factor to the decrease in the fatigue strength in Dry-77K from Dry-RT of HM50 composites was less than that of Kevlar49 composites. The damage of Kevlar49 composites propagates faster due to the interface's ease of fracture under cyclic loading.

In Wet specimens, the resin fracture was ductile (Fig.11), and many vestiges like tunnels were observed (Fig.12) where fibers were dislodged. Usually, water-absorption weakens the transverse bond strength of a fiber which leads to fiber-splittings. However, there was minimal damage on the surface of HM50 fibers in Wet-77K (Fig.13), compared to severe damage in

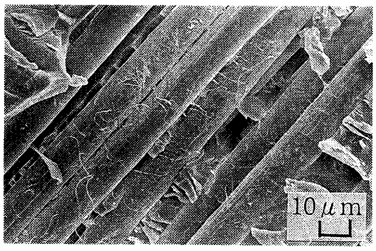


Fig.11. Fracture surface of ±45° cross-ply composites (HM50 composite. Wet-RT).

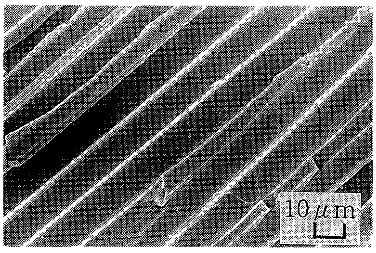


Fig.12. Fracture surface of ±45° cross-ply composites (Kevlar49 composite. Wet-RT).

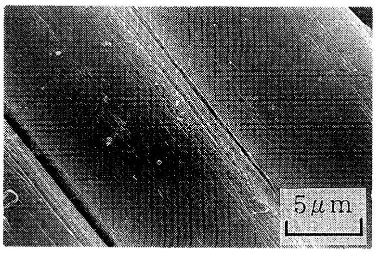


Fig.13. Fracture surface of ±45° cross-ply composites (HM50 composite. Wet-77K).

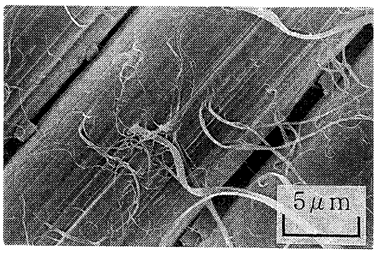


Fig.14. Fracture surface of ±45° cross-ply composites (Kevlar49 composite. Wet-77K).

Dry-77K (Fig.10). The water-absorption markedly decreased the shear strength of the interfaces between fiber and resin of HM50 composites. Therefore, fiber-splittings caused by the friction between fiber and resin appeared to decrease considerably.

Most of the fractures in Wet-RT of Kevlar49 composites occurred at the interface between fiber and resin unlike Dry-RT. The fiber-splittings were scarce (Fig.12), which shows that the water-absorption decreased the shear strength of the interfaces between fiber and resin, and that the interface fractures occurred preferentially. A lot of vestiges were observed in Wet-77K similar to in Wet-RT. But fiber-splittings were more noticeable in Wet-77K (Fig.14) than in Wet-RT. It is thought that the fiber-splittings occurred at the same time as the resin fracture in Wet-77K because of the decrease in the resin ductility. More energy was consumed in the deformation of the resin than in the generation of fiber-splittings in Wet-RT because of the high ductility of the resin. This suggests that wet specimens fractured mainly at the interfaces between fiber and resin, the resin deformed in the same direction with the fiber's dislodgement without shear fracture, and the specimens finally fractured. Two reasons can be made as to why the fatigue strengths in Wet-77K specimens were higher than those in Dry-77K ones. Firstly, the water-absorption relaxed the interlaminar residual stress which occurred during the laminating process. Secondly, the resin became slightly less sensitive to crack initiations after the water-absorption.

4. CONCLUSION

The effects of cryogenic temperature and water-absorption on the static tensile and fatigue strength of aramid fiber reinforced composites were examined. The fracture mechanisms were investigated fundamentally by observation of the fracture surfaces using SEM. The following conclusions can be drawn:

(1) The tensile strength of HM50 fibers increased at cryogenic temperature (77K), but there was little change to Kevlar49 fibers. The elastic modulus of both aramid fibers at cryogenic temperature increased considerably from at RT.

Water-absorption decreased the tensile strength and modulus of Kevlar49 fibers significantly. Also, the change in the strength and modulus of HM50 fibers was small, thus the water-absorption affected Kevlar49 more than HM50 fibers.

(2) The tensile strength of 0° unidirectionally reinforced composites of both HM50 and Kevlar49 decreased by about 8 - 13% at cryogenic temperature, while the modulus increased. The reason for the decrease in the tensile strength is that, apparently, it became difficult for the load to be dispersed adequately into the resin due to increased brittleness of the resin. It is apparent that the increase in the modulus is a result of increased fiber modulus.

(3) On the fatigue strength of 0° unidirectionally reinforced composites, there was little difference between cryogenic temperature and RT in the high stress range. But in the low stress range, the fatigue strength at cryogenic temperature was much greater than at RT, in contrast to the tensile tests. It is thought that the cyclic strain of a specimen was small, due to the increase in modulus of the composites. The cryogenic temperature changed the resin to become brittle, and weakened the strength of the interfaces between fiber and resin. This condition generated many

micro cracks in the resin and interfaces. The cracks relaxed the stress concentrations, and prevented the crack propagations to lead to the fracture.

The fatigue lives of wet composites at RT were longer than those of dry ones in the low stress range. The reasons include; the decrease in crack initiations due to the ductilization of the resin at RT, and the decrease in local stress concentrations to fibers due to the decrease in modulus of the resin.

(4) In the case of $\pm 45°$ cross-ply composites, the tensile strength of dry specimens decreased at cryogenic temperature. This is apparently due to the decrease of shear strength at the interfaces between fiber and resin and at the interlaminae. Conversely, the tensile strength of water-absorbed composites decreased at RT, but recovered a little at cryogenic temperature.

In the example of Wet-77K, the cooling effect increases the shear strength of the resin and the transverse strength of the fiber. It is also assumed that the increase in residual shear stress at the interlaminae in Wet-77K was less than in Dry-77K because water-absorption relaxes the residual shear stress at the interlaminae. As a result the tensile strength in Wet-77K was higher than in Wet-RT.

The elastic modulus increase at cryogenic temperature, was caused by both the increase in the modulus of the resin and the transverse modulus of the fibers.

(5) The order of the fatigue strength of $\pm 45°$ cross-ply Kevlar49 composites in each condition were coincidental with that of the overall tensile strength in a range of this study. In the case of dry HM50 composites, the rate of decrease in the fatigue strength at cryogenic temperature from RT was less than that for the tensile strength. The cooling made the fiber brittle with many fiber-splittings being generated during the fatigue. Consequently, the splittings created a bridging effect. The rate of decrease in fatigue strength of Wet-RT HM50 composites was high. It is assumed that the decrease in shear strength at the interfaces between fiber and resin lessened the generation of fiber-splittings because of water-absorption.

Acknowledgment – Authors are grateful to Dr. Michiel V. Bruschke (Unilever com., Netherlands) for his apropos suggestion.

REFERENCES

1. K. Komai, S. Shiroshita and M. V. Bruschke, J. Soc. Mater. Sci., Japan, **36** (1987) 1395 (in Japanese).
2. K. Komai, S. Shiroshita and S. Kinoshita, J. Soc. Mater. Sci., Japan, **40** (1991) 341(in Japanese).
3. K. Komai and S. Shiroshita, J. Soc. Mater. Sci., Japan, **41** (1992) 1427 (in Japanese).
4. K. Komai and S. Shiroshita, J. Soc. Mater. Sci., Japan, **41** (1992) 1539 (in Japanese).
5. K. Komai, K. Minoshima and T. Miki, Trans. Japan Soc. Mech. Eng., **A58** (1992) 830 (in Japanese).
6. K. Komai, S. Shiroshita, S. Kinoshita and J. Grenestedt, J. Soc. Mater. Sci., Japan, **38** (1989) 1329 (in Japanese).
7. K. Komai, K. Minoshima, S. Kinoshita, H. Ogawa and A. Kuroda, J. Soc. Mater. Sci., Japan, **39** (1990) 271 (in Japanese).
8. K. Komai, K. Minoshima and T. Shibutani, Trans. Japan Soc. Mech. Eng., **A56** (1990) 1021 (in Japanese).
9. K. Komai, K. Minoshima, S. Kinoshita, M. Nakano and Y. Uematsu, Trans. Japan Soc. Mech. Eng., **A58** (1992) 206 (in Japanese).
10. K. Komai, S. Shiroshita and G. Kilidjian, Mater. Sci. Res. Int., **1** (1995) 226.
11. T. Takaai, K. Sano and E. Fukushima, J. Soc. Mater. Sci., Japan, **38** (1989) 673 (in Japanese).
12. S. Shiroshita, Dr. Dissertation, Kyoto Univ., (1992) 56 (in Japanese).
13. K. Pannkoke and H. Wagner, Cryogenics, **31** (1991) 248.
14. G. Hartwig and S. Knaak, Cryogenics, **31** (1991) 231.
15. R. Allred and D. Roylance, J. Mater. Sci., **18** (1983) 652.
16. G. Hartwig and S. Knaak, Cryogenics, **24** (1984) 639.
17. T. Honjo and Y. Nakanishi, J. Soc. Mater. Sci., Japan, **40** (1991) 464 (in Japanese).
18. R. P. Reed and M. Golda, Cryogenics, **34** (1994) 909.