

압력이 가해진 고온 습윤 조건하에서의 Carbon / Epoxy 적층판의 굴곡특성 변화

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Change of Flexural Properties of the Carbon/Epoxy Laminates in Pressurized Hot-Wet Environment

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요 약 : 자체적으로 제작된 TGDDM, DDS, BF₃ · MEA를 포함하는 에폭시 매트릭스를 가지는 carbon/epoxy 프리프레그를 사용하여 적층판을 만들었다. 수분흡수에 대한 내부구조의 영향을 살펴보기 위하여 (0°)₈, (0°/90°)₂₈, (±45°)₂₈의 구조를 가지는 적층판을 사용하였다. 적층판내로의 빠르고 효과적인 수분침투를 위하여 5기압, 150°C, 상대습도 95%의 가혹한 조건하에서 pressure-cooker tester를 사용하였다. 용기내에서의 실험조건하에서의 체재시간은 0, 1, 2, 4, 8, 16시간이었다. 시편의 내부구조와 수분흡수 및 체재시간과의 관계를 구하기 위하여 굴곡시험이 채택되었다. 실험결과 위의 상태에서 수분흡수량보다 체재시간과 내부구조가 물성변화에 더 큰 영향을 줄을 알 수 있었다.

Abstract : Self-made carbon/epoxy prepregs with the exactly known matrix system(TGDDM/ DDS/BF₃ · MEA) were used to make the carbon/epoxy laminates. To know the structural effect on the moisture absorption three kinds of structures(0°)₈, (0°/90°)₂₈ and (±45°)₂₈ were used. The pressure cooker test, 5atm, 150°C with relative humidity (R.H) of 95%, was done to give the dynamic diffusion condition of the moisture into the laminates. The residence times were 0, 1, 2, 4, 8, and 16 hours. The flexural test was chosen to correlate the internal structural effect with the moisture absorption and the residence time effect. The results show that the residence time and the internal structures of the laminates give more important effect on the variation of the flexural properties than the quantity of the absorbed moisture.

INTRODUCTION

The environmental exposure at the hot-wet conditions may cause the degradation of the mechanical properties of carbon/epoxy composites. This degradation was assumed due to the absorbed moisture. Many works have been done on the moisture absorption rates related to the temperatures and on the degradation of the mechanical properties related to the quantity of the absorbed moisture. These works were generally done by using the available commercial prepregs.¹⁻³⁶ In these cases the testing temperatures were generally lower than 100°C. Water molecules were reported to act as plasticizers or crazing agents for the epoxy.³⁷⁻⁴¹ But the effect of the absorbed moisture in the matrix of the carbon/epoxy composites was not exactly determined.

Some works for the moisture absorption were based on the Fickian diffusion model of the moisture at the moderate temperatures.^{2-5, 12-15, 17, 19, 20} But other works have demonstrated that there are some deviations in the moisture take-up from the Fickian diffusion of the moisture at the even moderate temperatures.^{4, 6-9, 16, 18, 42} In these cases the effect of the internal structures and the exact constituents of the matrix were generally ignored.

The results at the temperatures higher than 100°C are very rare.⁴³ But the results at the extreme service conditions are necessary for the more generalized application of the carbon/epoxy composites. The pressurized hot-wet conditions can accelerate the environmental degradation of the carbon/epoxy composites. But there are few results for these testing

conditions. To avoid inconvenience in using the commercial prepregs the self made prepregs with the known matrix system(TGDDM/DDS/BF₃·MEA) were used. Three kinds of laminates, (0°)₈, (0°/90°)_{2s} and (±45°)_{2s} were used to know the structural effects. The pressure cooker test was selected to give an extremely severe condition, 5 atm, 150°C with R. H. of 95%. This kind of test was chosen to permit the dynamic diffusion of the moisture into the carbon/epoxy laminates. The environmental degradation of the mechanical properties of the laminates were checked by the flexural test, which was chosen to correlate the moisture absorption with the residence time and the structural effect on the variation of the mechanical response in the pressurized hot-wet environment.

EXPERIMENTAL

Materials

The carbon fibers T300 from Toray Co. were used as the reinforcing fibers. The specifications of T300 was illustrated at Table 1.

The carbon fibers were impregnated by the epoxy resin matrix system. This matrix system will be called as KRC-2. The formulation of KRC-2 was presented at Table 2.

To ensure better impregnation of the carbon fibers in prepreg fabrication, the epoxy resin matrix system dissolved in the methyl-ethyl-ketone(MEK) was used. In this case the solid content was 50% by weight. The prepregs were made by the drum winding machine with the speed control units. The fresh prepregs were stored at the ventilation cabinet to control the

Table 1. Specifications of the Carbon Fiber used in this Experiment

Filament Diameter (μ)	Carbon Content (%)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Ultimate Elongation (%)	Density (g/cm ³)
7	95	3,430	230	1.4	1.77

Table 2. Formulation of KRC-2

Constituents	Parts
MY 720 (TGDDM)	100
DDS	27
BF ₃ · MEA	1

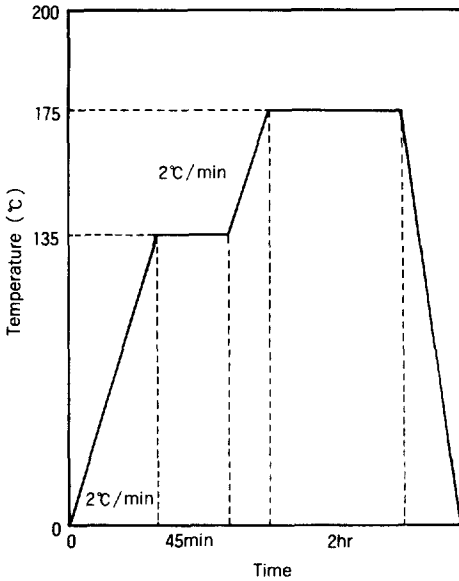


Fig. 1. Curing schedule of T300/KRC-2 in autoclave.

residual solvent content and the tackiness. The prepreps were then designed and cut. In this case the residual solvent content was about 2 % by weight. The designed prepreps were cured in autoclave, the curing schedule was shown in Fig. 1. From the starting point to the end of the dwell period at 135°C, vacuum was applied to eliminate the residual solvent. The applied maximum pressure was 4 atm. The fiber volume fraction was about 0.65 for (0°)₈ and about 0.63 for (0°/90°)₂₈. The microscopic observation was done to detect the void in the specimens. The obvious void was not observed.

Specimens and Test

Two kinds of panels were prepared. Their structures were (0°)₈ and (0°/90°)₂₈. The panels of (0°/90°)₂₈ were cut to prepare the

specimens of (0°/90°)₂₈ and (±45°)₂₈ by controlling the cutting angles. The dimension of (0°)₈ and (0°/90°)₂₈ was 80×20×1 mm³. The dimension of (±45°)₂₈ was 80×25×1 mm³, the width of (±45°)₂₈ was chosen as 25mm to minimize the free edge effect on the mechanical properties. After cutting the specimens were stored in the conditioning chamber for 3 days at the temperature of 23°C with the R. H. of 65%.

The pressurized hot-wet environment was given by the Pressure Cooker Tester (PCT) which had been made by Yashima Works Ltd in Japan. The testing temperature was 150°C. The R. H. was 95%. The applied pressure was 5 atm. The residence time in the PCT was 0, 1, 2, 4 8 and 16 hours, the moisture gain was calculated by the weight difference of specimens, before and after the test. The degradation of the mechanical properties of the conditioned specimens was measured by the three points flexural test. The measurement was done by using servo hydraulic machine (Instron 1125). The cross head speed was 1 mm/min and the ration of the loading span to the thickness of the specimen was 40:1. 5 specimens were used for each condition.

RESULTS AND DISCUSSION

There are few studies reported at the pressurized hot-wet conditions. The results at the pressurized extreme service conditions of the carbon/epoxy composites would enhance the replacement of the metals at the turbine blade in the electrical power plant. Because of the constraints at the experiment, the pressure of 5 atm, the temperature of 150°C, and the R. H. of 95% were chosen. The moisture absorption curve of the laminates prepared by T300/KRC-2 in the above testing condition was shown in Fig. 2. Three kinds of structures were considered to know the effect of internal structures for the moisture absorption. To reduce

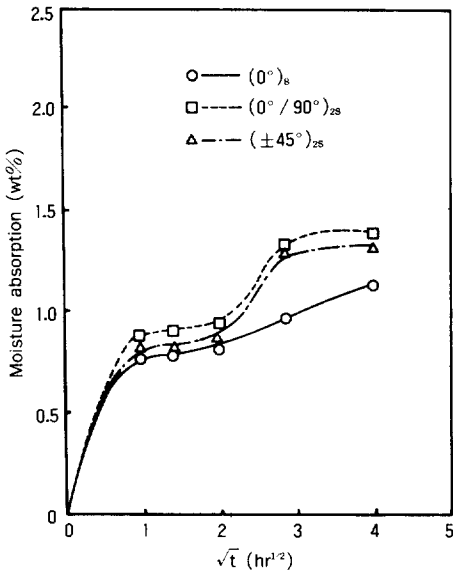


Fig. 2. Moisture absorption of the three kinds of laminates due to the residence time in the pressurized hot-wet condition.

the edge effect the thickness of the laminates was chosen as 1 mm. In this case the ratio of the edge surface to the total surface was less than 6%. And then the moisture absorption could be assumed as the one dimensional problem. This fact was presented schematically in Fig. 3.

The moisture absorption curves showed differences with the different structures as shown in Fig. 2. Three kinds of laminates absorbed moisture very fastly for the initial 1hr of residence time. And then the moisture absorption was slowed down for the subsequent 3 hr. After this period the moisture absorption curve of the laminates of (0°)₈ became different from those of the laminates (0°/90°)_{2S} and (±45°)_{2S}. These results and the structural considerations^{44,45} could lead us to the following assumptions. The initial fast moisture absorption can be attributed to the fast moisture absorption at the matrix of the outer plies. The diffusion of moisture into the internal plies can be altered by the presence of the fiber and the

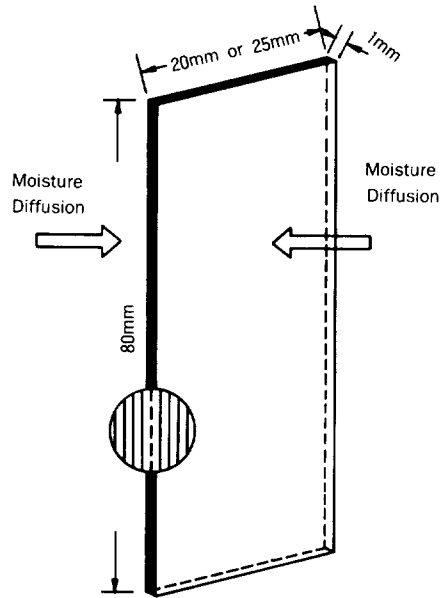


Fig. 3. Dimension of the specimen and the main direction of the moisture diffusion.

swelling of the matrix. This fact induces the slowdown of the moisture absorption. The small increase of the moisture absorption is due to the moisture diffusion to the interface between the fiber and the matrix. This moisture absorption at the interface between the fiber and the matrix may cause the hygrothermal damage at this interface. The hygrothermal damage at the interface between the fiber and the matrix accelerates the moisture diffusion into the internal plies and the interface between the fiber and matrix. This fact can also occurs in the laminates of (0°/90°)_{2S} and (±45°)_{2S}. The sudden increase of the moisture absorption between the residence time of 4 hr and 8 hr can be attributed to the moisture absorption in the resin rich area between the 0° ply and the central, (90°)₂ ply.^{46,47} The moisture absorption was nearly saturated after the sudden increase of the moisture absorption. This fact suggests that there is no cracking at the 90° plies and the negligible crazing of the epoxy matrix at these testing conditions. The edge

of the specimens of the laminates, $(0^\circ/90^\circ)_{2S}$ and $(\pm 45^\circ)_{2S}$, were microscopically observed. There was no evidence of the transversal cracks and the crazing of the matrix. The moisture absorption of the $(0^\circ/90^\circ)_{2S}$ was slightly greater than that of $(\pm 45^\circ)_{2S}$. It comes from the difference in the fiber angles to the main direction of the moisture diffusion.⁴²

The absorbed moisture was generally known as the controlling factor for the degradation of the mechanical properties. The relations between the moisture absorption and the variations of the flexural modulus were shown in Fig. 4. The moisture absorption could not be directly related to the variation of the flexural modulus of the laminates, $(0^\circ)_8$, $(0^\circ/90^\circ)_{2S}$ and $(\pm 45^\circ)_{2S}$. Particularly the laminates of $(\pm 45^\circ)_{2S}$ showed some change of the flexural modulus at the same moisture absorption and no change for the additional moisture absorption. The relations between the moisture absorption and the variations of the flexural strength were shown in Fig. 5. As shown in

Fig. 4 the moisture absorption could not be directly related to the variation of the flexural strength of the laminates, $(0^\circ)_8$, $(0^\circ/90^\circ)_{2S}$ and $(\pm 45^\circ)_{2S}$. In Fig. 5 there are little change of the flexural strength for the great change of the moisture absorption for the laminates of $(0^\circ/90^\circ)_{2S}$ and there is much change of the flexural strength for some additional moisture absorption for the laminates of $(\pm 45^\circ)_{2S}$.

The above results demonstrated that the mechanical degradation of the carbon/epoxy laminates should be considered in terms of the residence time and the absorbed moisture, correlated in considering the internal structures. The relations between the residence time and the variation of the flexural modulus were shown in Fig. 6. The laminates of $(0^\circ)_8$ showed slight decrease of the flexural modulus to the residence time of 4 hr. The additional residence time increased the flexural modulus of the laminates of $(0^\circ)_8$. The laminates of $(0^\circ/90^\circ)_{2S}$ showed little decrease of the flexural modulus to the residence time of 4 hr. The additional

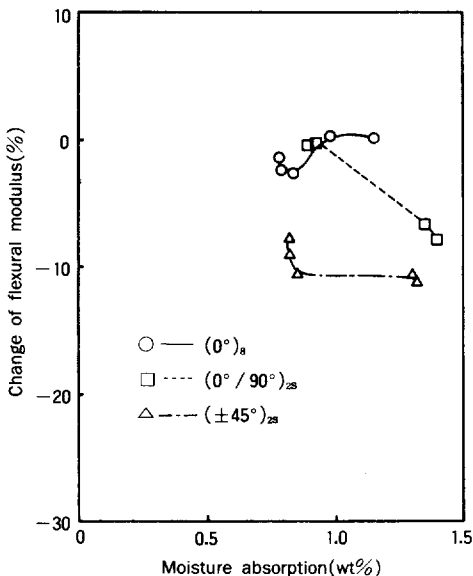


Fig. 4. Change of the flexural modulus due to the absorbed moisture in the pressurized hot-wet condition.

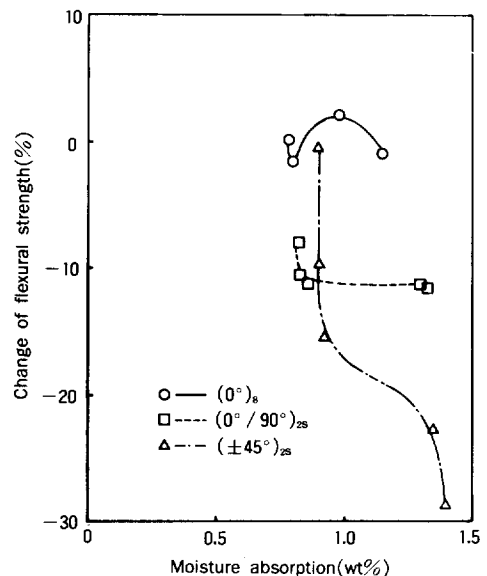


Fig. 5. Change of the flexural strength due to the absorbed moisture in the pressurized hot-wet condition.

residence time reduced the flexural modulus of the laminates of $(0^\circ/90^\circ)_{2S}$. Comparing the results in Fig. 6 to the results in Fig. 4, one could see that the variation of the flexural modulus with the residence time showed more continuous tendency than that with the moisture absorption. The variation of the residence time was greater than that of the absorbed moisture. The residence time showed the possibility as a absorbed moisture.

The precedent assumptions and the results in Figs 2, 4-7 lead us to the following mechanisms in the variation of the flexural properties. The absorbed moisture plasticized the matrix at the initial stage of the moisture absorption. This plasticization of the matrix induced the slight decrease of the flexural modulus of the laminates of $(0^\circ)_8$ to the residence time of 4 hr and the fast decrease of the flexural modulus of the laminates of $(\pm 45^\circ)_{2S}$ to the residence time of 1 hr. In the laminates of $(0^\circ/90^\circ)_{2S}$ this absorbed moisture relaxed the residual thermal stress between the 0° ply and 90° ply.⁴⁴ This relaxation resulted

in the little decrease of the flexural modulus to the residence time of 4 hr. The additional moisture absorption at the interface between the fiber and the matrix relaxed the residual thermal stress at this interface. This fact enhances the increase in the flexural modulus of the laminates of $(0^\circ)_8$, and the slow decrease in the flexural modulus of the laminates of $(\pm 45^\circ)_{2S}$, some decrease of the flexural modulus of the laminates $(0^\circ/90^\circ)_{2S}$, for the residence time from 4 hr to 8 hr could attributed to the enough relaxation of the residual thermal stress.

The relations between the residence time and the flexural strength decrease were shown in Fig. 7. The laminates of $(0^\circ)_8$ showed slight decrease of the flexural strength for the residence time of 2 hr and 16 hr and the slight increase of the flexural strength for the residence time of 8 hr. The laminates of $(0^\circ/90^\circ)_{2S}$ showed the sharp decrease of the flexural strength for the residence time of 1 hr. And then the additional residence time induced the slight decrease of the flexural strength of the laminates of $(0^\circ/90^\circ)_{2S}$. The laminates of

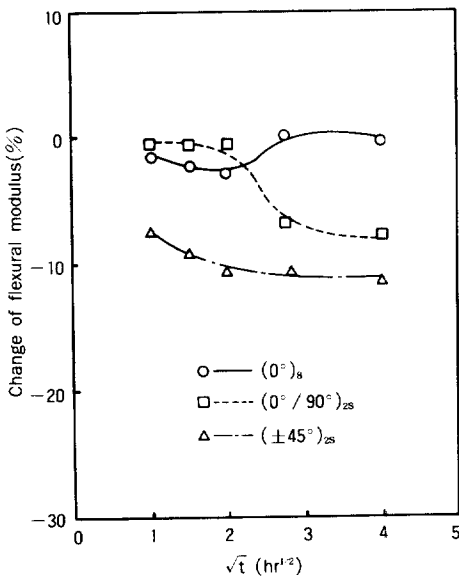


Fig. 6. Change of the flexural modulus due to the residence time in the pressurized hot-wet condition.

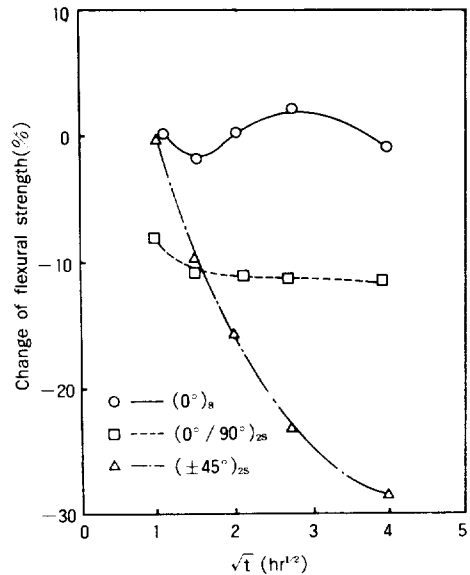


Fig. 7. Change of the flexural strength due to the residence time in the pressurized hot-wet condition.

$(\pm 45^\circ)_{2s}$ showed little decrease of the flexural strength for the residence time of 1 hr. The additional residence time decreases fastly the flexural strength of the laminates of $(\pm 45^\circ)_{2s}$. As shown in Fig. 6 the residence time was also revealed as an important factor for the flexural strength change in this pressurized hot-wet condition. The above observations demonstrated that the changes of the flexural properties in this pressurized hot-wet condition should be considered in terms of the residence time, and the moisture absorption in considering the internal structures and the variation of the residual thermal stress between the 0° plies and 90° plies.

The absorbed moisture in the laminates of $(0^\circ)_8$ induced slight decrease of the flexural strength at the residence time of 2 hr by the plasticization of the matrix. The additional absorbed moisture in the laminates of $(0^\circ)_8$ induced slight increase of the flexural strength at the residence time of 8 hr due to the relaxation of the residual thermal stress at the interface between the fiber and the matrix.⁴⁴ The final decrease of the flexural strength of the laminates of $(0^\circ)_8$ could be attributed to the hygrothermal damage at the interface between the fiber and the matrix.

The absorbed moisture in the laminates of $(0^\circ/90^\circ)_{2s}$ induced the relaxation of the thermal residual stress between the 0° plies and the 90° plies. This fact reduced the constraining stress at the 90° plies^{48,49} and resulted in the sharp decrease of the flexural strength for the residence time of 1 hr. The additional decrease of the flexural strength could be attributed to the plasticization of the matrix and the resin rich area.

The moisture absorption of the laminates of $(\pm 45^\circ)_{2s}$ at the matrix in the outer plies showed little decrease of the flexural strength. The decrease of the flexural strength of the laminates of $(\pm 45^\circ)_{2s}$ would come from the plasticization at the matrix in the internal plies and

the resin rich area. The more pronounced decrease of the flexural strength of the laminates of $(\pm 45^\circ)_{2s}$ came from the development of the hygroscopic interlaminar normal stress⁵⁰. The interactions among the above reasons induced the severe decrease of the flexural strength of the laminates, $(\pm 45^\circ)_{2s}$.

CONCLUSIONS

In the pressurized hot-wet condition of 150 °C, 5 atm and R. H. of 95 %, the degradation of the flexural properties should be considered in terms of the residence time and the absorbed moisture correlated with the internal structures. The moisture absorption firstly occurs at the matrix of the outer plies and then it occurs at the interface between the fiber and the matrix. The moisture diffusion into the inner plies needs some residence time. The residence time is the more important factor than the quantity of the absorbed moisture. The presence of the residual thermal stress, its change due to the absorbed moisture, the internal structures and the presence of the hygroscopic stress are the very important factors and the presence of the hygroscopic stress are the very important factors for the variation of the flexural properties in the pressurized hot-wet condition.

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REFERENCES

1. C. H. Shen and G. S. Springer, *J. of Comp. Mat.* **11**, 2(1977).
2. A. S. D. Wang and P. K. Liu, *J. of Aircraft*, **14**, 383(1977).
3. C. E. Browning, G. E. Husman, and J. M. Whitney, "Moisture Effects in Epoxy Matrix Composites", ASTM STP 617, p.481 (1977).
4. G. S. Springer, *J. of Comp. Mat.*, **11**, 107 (1977).

5. C. H. Shen and G. S. Springer, *J. of Comp. Mat.*, **11**, 250(1977).
6. C. Y. Ludemo and S. E. Thor, *J. of Comp. Mat.*, **11**, 276(1977).
7. D. F. Adams and A. K. Miller, *J. of Comp. Mat.*, **11**, 285(1977).
8. A. C. Loos and G. S. Springer, *J. of Comp. Mat.*, **13**, 131(1979).
9. M. Blikstad, O. W. Sjobom, and T. R. Johannesson, *J. of Comp. Mat.*, **18**, 32 (1984).
10. D. Shyprykevich and W. Wolter, "Effects of Extreme Aircraft Storage and Flight Environments on Graphite / Epoxy", ASTM STP 768, 118(1982).
11. H. T. Sumsion and D. P. Williams, "Effects of Environment on the Fatigue of Graphite-Epoxy Composites", ASTM STP 569, 226 (1975).
12. G. S. Springer, "Environmental Effects on Epoxy Matrix Composites", ASTM STP 674, 291(1979).
13. C. E. Shirrell and J. Halpin, "Moisture Absorption and Desorption in Epoxy Composite Laminates", ASTM STP 617, 514 (1977).
14. H. T. Hahn, *J. of Comp. Mat.*, **10**, 266 (1976).
15. J. M. Tang and G. S. Springer, *J. of Rein. Plast. and Comp.*, **7**, 120(1988).
16. H. T. Hahn, *J. of Eng. Mat. and Tech.*, **109**, 3(1987).
17. M Blikstad, *J. of Rein. Plast. and Comp.*, **5**, 9(1986).
18. D. A. Souglass and Y. Weitsman, "Stresses due to Environmental Conditioning of Cross-Ply Graphite / Epoxy Laminates", ICCM 3, Paris, 1981.
19. R. Belasi and J. B. Whiteside, "Effect of Moisture on Epoxy Resins and Composites", ASTM STP 658, 2(1978).
20. S. S. Wang and I. Choi, *J. of Comp. Mat.*, **16**, 244(1982).
21. F. W. Crossman, R. E. Mauri, and W. J. Warren, "Moisture-Altered Viscolastic Response of Graphite / Epoxy Composites", ASTM STP 658, 205(1978).
22. H. Ohta, O. I. Byon, M. Uemura, M. Hirata and A. Kudo, *Rein. Plast. (Japan)*, **32**, 145 (1986).
23. T. A. Collings and D. E. W. Stone, *Composites*, **16**, 305(1985).
24. E. Demuts and D. Shyprykevich, *Composites*, **15**, 25(1984).
25. H. T. Hahn and R. Y. Kim, "Swelling of Composite Laminates", ASTM STP 658, 98(1978).
26. R. Boulay, B. Drouin, R. Gagnon, P. A. Belanger, and P. Cielo, *Polym. Comm.*, **26**, 69(1985).
27. E. S. W. Kong, M. Adamson, and L. Mueller, *Comp. Tech. Rev.*, **6**, 170(1984).
28. D. Lawing, R. E. Fornes, R. D. Gilbert, and J. D. Memory, *J. Appl. Phys.*, **52**, 5906 (1981).
29. P. D. Anstice and P. W. R. Beaumont, *J. Mater. Sci.*, **18**, 3404(1983).
30. J. P. Sargent, and K. H. G. Ashbee, *Polym. Comm.*, **23**, 327(1982).
31. E. S. W. Kong and M. J. Adamson, *Polym. Comm.*, **24**, 171(1983).
32. A. N. Netavelli, R. E. Fornes, R. D. Gilbert, and J. D. Memory, *J. Appl. Poly. Sci.*, **30**, 1573, (1985).
33. E. B. Stark, A. M. Ibrahim T. E. Munns, and J. C. Seferis, *J. Appl. Sci.*, **30**, 1717, (1985).
34. G. A. Luoma and R. P. Rowland, *J. Appl. Poly. Sci.*, **32**, 5777 (1986).
35. J. Mijovic and K. L. Lin, *J. Appl. Poly. Sci.*, **30**, 2527 (1985).
36. A. Apicella and L. Nicolais, "Epoxy Resins and Composites", ed. by. K. Dusek, Vol 1., p.69, Springer-Verlag, Berlin, 1986.
37. C. E. Browning, *Poly. Eng. Sci.*, **18**, 16 (1978).
38. R. J. Morgan, E. T. Mones, and W. J. Steele, *J. Polymer* **20**, 315(1982).

39. R. J. Morgan, J. O'Meal, *J. Mater. Sci.*, **12**, 1966 (1977).
40. G. A. Pogany, *Polymer*, **17**, 690 (1976).
41. A. Apicella, L. Nicolais, G. Astarita and E. Drioli, *Polymer*, **20**, 9(1979).
42. M. A. Zaidi, "Etude du comportement viscoelastique de stratifiés carbone epoxy", thesis of Doc. Ing. 1982, Univ. of Tech. of Compiègne.
43. P. Shyprykevich and W. Wolter, ASTM STP 768, 118(1982).
44. S. W. Tsai and H. T. Hahn, "Introduction to Composite Materials", Technomic Co., (1980).
45. M. Blikstad, *J. of Rein. Plast and Comp.* **5**, 9(1986).
46. R. D. Jamison, "On the interrelationship between fiber fracture and ply cracking in graphite / epoxy laminates", ASTM Symposium, Dallas Oct. 24-25, 1984.
47. K. Schultz, "Development of microdamage in composite laminates during fatigue loading", Int. Conf. on testing, eval. and quality control of comp., Guilford, Sept. 13-14, 1983.
48. J. Aveston and A. Kelly, *J. of Mat. Sci.*, **8**, 352(1973).
49. M. D. Kistner, J. M. Whitney and C. E. Browning, "First ply failure of graphite / epoxy laminates", U. S. -Japan Conf. on Composite Materials, Hampton, June 6-8, 1983.
50. S. S. Wange and I. Choi, *J. Comp. Mat.* **16**, 244(1982).