Polymer(Korea). Published by the Polymer Society of Korea
Vol. 13, No. 6, 1989

고무에 의한 에폭시수지의 변성에 관한 연구
2. 탄소섬유 복합재료에의 응용

최 철 림 · 오 창 록
한국과학기술원 고분자공정연구실
(1989년 2월 22일 접수)

Rubber Modified Epoxies; 2. Study on the Application to the Carbon Fiber Composites

Chul Rim Choe and Chang Rok Oh
Polymer Processing lab., KAIST, P. O. Box 131 Cheongyang, Seoul 130-650, Korea
(Received February 22, 1989)

요 약 : 복합재료의 물성을 향상시키기 위하여 반응성 액체고무 CTBN으로 변성한 에폭시와 표면을 CTBN 혹은 변성에폭시의 희석용액으로 코팅한 탄소섬유를 조합하여 복합재료를 제조하였으며 에폭시의 변성과 섬유표면의 코팅조건에 따른 복합재료 특성의 변화를 고찰하였다. 에폭시의 변성은 복합재료의 특성향상에 실제적인 기여를 하지 못하는 것으로 밝혀졌다. 즉 인장강도는 다소 증가되나 모듀라스와 충격특성은 거의 영향을 받지 않았다. 탄소섬유의 표면에 코팅된 고무상의 박막은 최적의 코팅조건 즉 코팅액의 농도가 1% 내지 5% 범위 내에서도 복합재료 특성을 크게 향상시키는 역할을 하지 못하는 것으로 관찰되었다.

Abstract : Combination of toughened epoxy matrix and surface-modified carbon fiber was executed to get improved mechanical properties of composite systems. Epoxy was toughened by incorporating reactive rubber, CTBN(carboxyl-terminated acrylonitrile butadiene copolymer), and carbon fiber was treated with dilute MEK(methyl ethyl ketone) solution of CTBN or modified epoxy resin. Rubber-toughening of epoxy resins does not contribute substantially to the improvement of the mechanical properties of composite systems : tensile strength gains appreciably, but modulus and impact strength remain almost unchanged. Elastomeric thin layer coated on the carbon fibers can give increased tensile properties, but influence only slightly on the toughness of composite systems.

INTRODUCTION

Rubber modification has been one of the generally accepted tools to improve fracture toughness of epoxy systems.[1~6] Surface-modified reinforcements in combination with toughened epoxy systems might result in the considerable improvement of mechanical properties in composite systems, since nature of interface between matrix resins and reinforcements is the key factor to fix the composite properties along with the inherent properties of reinforcing fibers and matrix resins.[7~11] Factors associated with the interface are chemistry of surface, adhesion between phases and the nature of interlayer, which are mainly affected by the chemical nature and the thickness of interlayer.[12~15] The purpose of this study was to get the improved mechanical properties of composite systems by utilizing rubber-toughened epoxy matrices and controlling the thickness of interlayer between matrix resins and reinforcing fibers.

EXPERIMENTAL

Materials

For rubber-toughned epoxy systems tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) was used as base resin and CTBN with acrylonitrile content of 26% as rubber modifier. 4,4'-Diaminodi phenyl sulfone (DDS) was employed as hardener. Bisphenol A was also used to control the size and distribution of rubber domains. Carbon fibers, Torayca T-300 (tensile strength=3.04 GPa, tensile modulus=226 GPa) was applied as reinforcing fiber.

Specimen Preparation and Measurements

Modified epoxy systems with rubber content of 12.5 phr, which were formulated in the same manner as introduced in the previous paper,[16] were combined to surface treated carbon fibers. Rubbery interlayer in carbon fiber surface can be made by utilizing a simple dipping procedure as shown in Fig. 1. Carbon fibers had been surface-modified by dipping them into dilute MEK solutions of CTBN and then drying at 80℃ for 8min. in air circulating oven. Also, the coating of rubber-modified epoxy resin solution was performed by the same method. Prepregs were cured in blanket press with the cure cycle shown schematically in Fig. 2 to get unidirectional specimens suitable for the test of mechanical properties.[4]

Tensile modulus and strength are measured by the method of ASTM D3039-76. And the measurement of Izod impact strength followed the method A of ASTM D256 with 0°plies. Scanning electron microscope (Hitachi S-510) was also used to observe morphologies.

RESULTS AND DISCUSSION

Chemical nature of interlayer is one of the key factors which affect composite properties. To compare the effect of CTBN interlayer with that of epoxy interlayer, tensile properties and

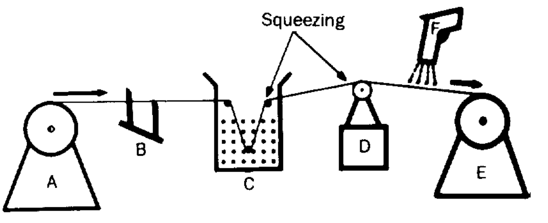


Fig. 1. Coating process of carbon fiber ; A)Carbon fiber bundle, B)Filament supporter, C)Dipping bath of coating sol., D)Traverse machine, E)Nylon cylinder wrapped with release paper, F)Heat gun.

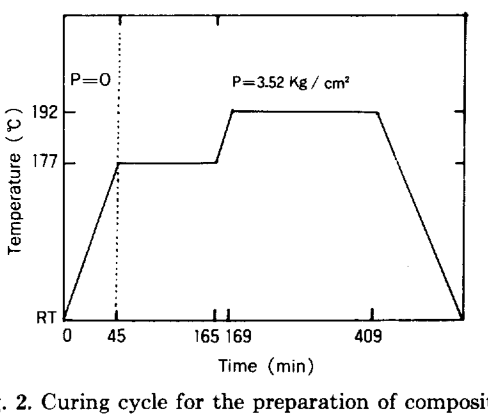


Fig. 2. Curing cycle for the preparation of composite specimen.

impact strengths were preliminarily measured for two composite systems : CTBN-modified epoxy resin / surface treated carbon fibers with 5% MEK solution of CTBN and CTBN-modified epoxy resin / surface-treated carbon fibers with 5% MEK solution of the same epoxy systems as in matrix. As can be seen in Figs. 3,4 and 5, CTBN interlayer is more effective than epoxy interlayer. CTBN interlayer enhances appreciably the mechanical properties of composite systems. However, that is not the case with modulus and impact strength for epoxy interlayer. Consequently CTBN coating system was chosen to study the effect of the thickness of interfacial region on composite properties. The thickness of interlayer coated on the surface of carbon fiber depends on the concentration of coating solution. Quantitative calculation of the coated thickness may be executed by burning off the coated organic layer under the assumption that its evenness be perfect. Table 1 shows the thickness change of coated layer with the concentration of coating solutions. The thickness of coated layer varies in the range of 700Å and 1600Å with the concentration change of coating solutions from 1% to 10%.

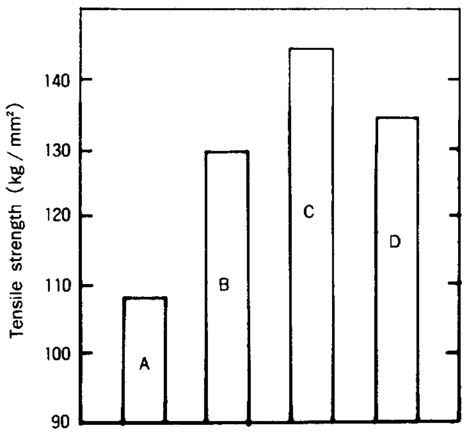


Fig. 3. Tensile strength of various composite systems in variation of matrix and reinforcement ; A)neat epoxy+untreated C. F., B)CTBN-modified epoxy +untreated C. F., C)CTBN-modified epoxy+CTBN treated C. F., D)CTBN-modified epoxy+epoxy treated C. F.

Figs. 6,7 and 8 show tensile strength, modulus and impact strength of composite systems with the change of the concentration in coating solution. Dotted lines represent the property level of control specimen, unmodified epoxy / untreated carbon fiber. As seen in Figs. 6 and 7, tensile strength can be considerably improved by rubber modification of matrix and / or surface treatment of reinforcement,

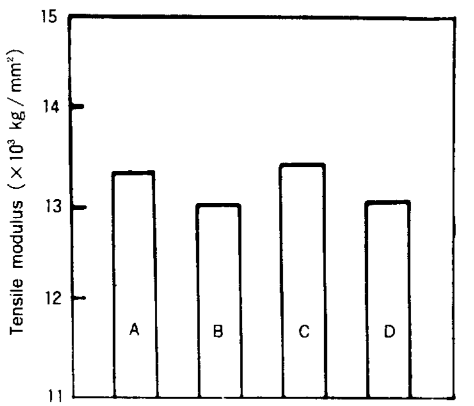


Fig. 4. Tensile modulus of various composite systems in variation of matrix and reinforcement ; A)neat epoxy+untreated C. F., B)CTBN-modified epoxy + untreated C. F., C)CTBN-modified epoxy+CTBN treated C. F., D)CTBN-modified epoxy+epoxy treated C. F.

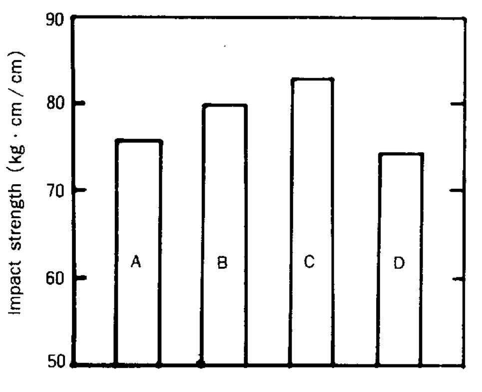


Fig. 5. Impact strength of various composite systems in variation of matrix and reinforcement ; A)neat epoxy+untreated C. F., B)CTBN-modified epoxy + untreated C. F., C)CTBN-modified epoxy+CTBN treatedC. F., D)CTBN-modified epoxy+epoxy treated C. F.

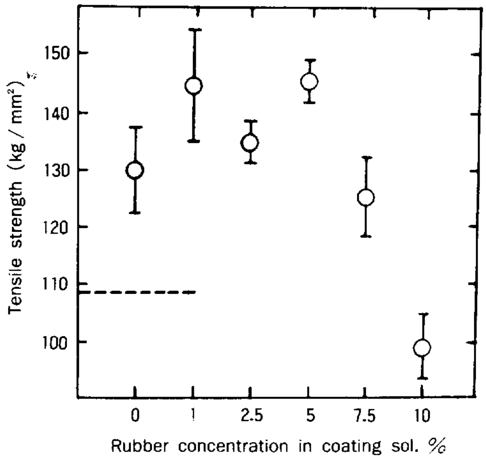


Fig. 6. Tensile strength of modified epoxy / surface treated C. F. systems with the rubber conc. in coating solution.

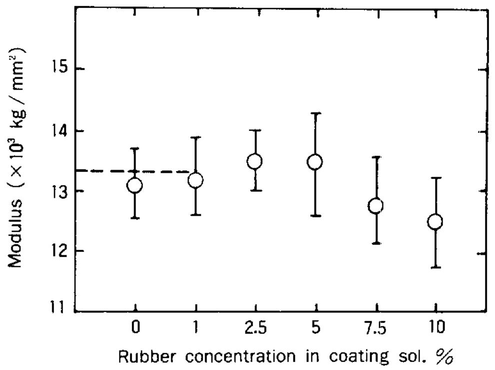


Fig. 7. Modulus of modified epoxy / surface treated C. F. systems with the rubber conc. in coating sol.

while modulus remains almost constant in the concentration range up to 5% of coating solution. It is noted that tensile strength is affected more or less by the matrix properties and the nature of interface in composite systems. On the other hand the modulus of reinforcing fibers is a dominant factor to determine the stiffness of composite systems.

A thicker coated interlayer can deteriorate the properties of composite systems. Over the thickness of 1000Å (equivalent to around 5 % of coating solution, see table 1) coated CTBN layer can not take a positive role to enhance

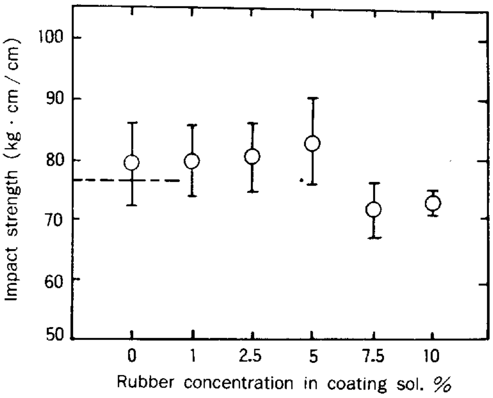
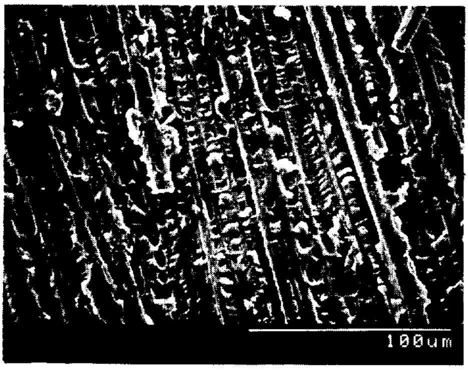


Fig. 8. Impact strength of modified epoxy / surface treated C. F. systems with the rubber conc. in coating sol.

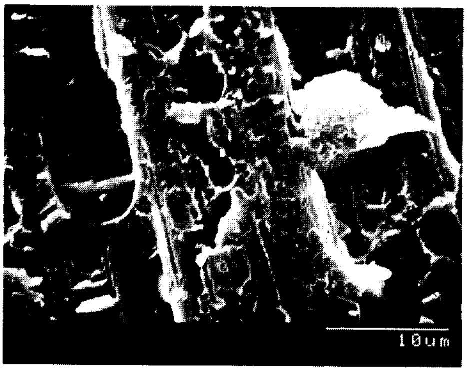
Table 1. Rubber Thickness Coated on C. F. Surface in Variation of the Rubber Conc. in Coating Solution

CTBN conc.	Thickness(Å)
1 %	708
2.5 %	856
5 %	962
7.5 %	1210
10 %	1570

the tensile properties. It is generally recognized that rubber modification of epoxy resins is a powerful way to improve pronouncedly the impact properties of the system itself. By combining rubber modified epoxy resin with carbon fibers, the effect of rubber modification on impact properties can not be obtained as expected. As seen in Fig. 8, The impact strength of composite systems seems to be hardly influenced by the rubber modification of matrix resins and the surface treatment of reinforcing fibers. This result may be attributed to the different nature of rubber particels formed in composite systems due to the existence of reinforcing fibers, which might hinder the radial growth of rubber particles. As seen in Fig. 9, which shows scanning electron micrographs for the interply surface of a composite systems, it is recognized that rubber particles are formed ellipsoidally and nonuniformly between



(a) 500X



(b) 3000X

Fig. 9. Scanning electron micrographs for interply surface of the carbon fiber composites (a)500X, (b)3000X.

reinforcing fibers.

CONCLUSION

It is observed that rubber-toughening of epoxy resins does not contribute substantially to the improvement of the mechanical properties of composite systems. It is also noted that elastomeric thin layer coated on the carbon fibers can give increased tensile properties, but influences only slightly on the toughness of composite systems. It is confirmed, however, that the optimal thickness of interlayer between epoxy matrices and carbon fibers lies in the range of 700A and 1000A(up to 5% of rubber concentration in coating solution).

REFERENCE

1. L. T. Manzione and J. K. Gillham., *J. Appl. Polym. Sci.*, **26**, 889(1981).
2. L. T. Manzione and J. K. Gillham, *J. Appl. Polym. Sci.*, **26**, 907(1981).
3. C. B. Bucknall, "Toughened Plastics", Applied Science Publishers, London, pp36-37, 1977.
4. W. J. Gilwee and Z. Nir, "Rubber-modified Thermoset Resins", American Chemical Society, Washington, D. C., p321, 1984.
5. W. D. Bascom, R. Y. Ting, R. J. Moulton, and C. K. Riew, *J. Material Sci.*, **16**, 2657 (1981).
6. W. D. Bascom, R. L. Cottington, R. L. Jones, and P. Peyser, *J. Appl. Polym. Sci.*, **19**, 2545 (1975).
7. D. G. Peiffer and L. E. Nielsen, *J. Appl. polym. Sci.*, **23**, 2253(1979).
8. L. E. Nielsen, "Mechanical Properties of Polymers and Composites Vol. 2", Marcell Dekker, New York, 1974.
9. J. L. Kardos, F. S. Chang, and T. L. Tolbert, *Polym. Eng. Sci.*, **13**, 445(1974).
10. M. Xanthos and R. T. Woodhams, *J. Appl. Polym. Sci.*, **16**, 381(1972).
11. G. A. Pogany, *Polymer*, **11**, 66(1970).
12. A. S. Kenyon and H. J. Duffy, *Polym. Eng. Sci.*, **7**, 189(1967).
13. L. Broutman and B. D. Agarwal, *Polym. Eng. Sci.*, **14**, 581(1974).
14. J. P. Bell, J. Chang, H. W. Rhee and R. Joseph, *Polym. Composites*, **8**, 46(1987).
15. W. M. Speri and C. F. Jenkins, *Polym. Eng. Sci.*, **13**, 445(1973).
16. C. R. Choe, C. R. Oh, *Polymer(Korea)*, **12**, 627(1988).