Plasma-Graft Polymerization of Vinyl Monomer with an Acid Amide Group Onto a Surface of Carbon Fiber and Its Adhesion to Epoxy Resin

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ABSTRACT: The mechanical properties of a fiber-reinforced plastic are influenced by the adhesion between a reinforced fiber and a matrix resin. In this work it is shown how to obtain strong adhesion between a carbon yarn and an epoxy resin through the formation of covalent bonds. Acid amide groups reactive with epoxy groups were introduced onto a surface of the yarn by means of plasma-graft polymerization of acrylamide. The density of active radicals formed on a surface of the yarn by the plasma irradiation was first increased with increasing discharge power and plasma irradiation time, and then the rates of the increase were largely decreased. The degree of grafting was linearly increased with increasing the surface density of active radicals. The yarn embedded in diglycidyl ether of bisphenol-A/triethylenetetramine mixture was pulled out to obtain pull-out force after curing. Pull-out force was increased with increasing degree of grafting and the failure in pulling out of the yarn was cohesive. The covalent bonds formed in the graft layer will result in an increment of pull-out force. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 284–290, 2000

Key words: plasma-graft polymerization; carbon fiber; acrylamide; epoxy resin; adhesion

INTRODUCTION

The mechanical properties of a fiber-reinforced plastic are influenced by the adhesion between a reinforced fiber and a matrix resin. A carbon fiber is chemically less reactive and therefore adhesion with a matrix is poor.[1] The surface of the carbon fiber was oxidized to improve the adhesion. For instance, carbon fiber was heated in 60 or 70% HNO_3 by boiling,[2] or in air at 723 K.[1] In electrolytic oxidation, an electric current was conducted through a carbon-fiber anode in an electrolyte such as an aqueous solution of sulfuric acid, ammonium bicarbonate, or sodium hydroxide.[3] The surface oxygen content was increased by CO_2 plasma treatment on a carbon fiber and the interface in an epoxy matrix composite system was modified.[4] In previous work[5,6] reactive groups were introduced onto a surface of Kevlar 49 yarn by means of plasma-graft polymerization and then reacted with an epoxy resin/curing agent mixture as a matrix resin to form covalent bonds, which will give strong adhesion between the yarn and the matrix resin.

In this work it is shown how to obtain strong adhesion between a carbon yarn and an epoxy resin through the formation of covalent bonds. Acid amide groups are introduced onto the sur-

face of the yarn by means of plasma-graft polymerization and then are reacted with the epoxy resin containing curing agent to form covalent bonds. The adhesive property between the grafted yarn and the epoxy resin is assessed by evaluating pull-out force of the yarn embedded in the epoxy resin.

EXPERIMENTAL

Evaluation of Surface Density of Active Radicals

The polyacrylnitrile-based carbon yarn used in this work was Besfight TA-12K, which was supplied by Toho Rayon Co. in the form of a 7350-denier, 12000-filament yarn, without any surface treatments. To form radical species on the surface of the yarn, the yarn suspended in the apparatus for plasma-graft polymerization[5,6] was irradiated for 3–100 s with a plasma that was generated at discharge powers of 20–80 W in an atmosphere of 13 Pa argon by an RF generator operating at 13.56 MHz. Then the yarn was left for 24 h at 300 K in dried air to form peroxy groups on the surface. The peroxy groups are formed from active radicals that are reacted with oxygen molecules in dried air.

The plasma-irradiated yarn 200 mm long was immersed into 60 mL of benzene solution of 0.1 mM 1,1-diphenyl-2-picrylhydrazyl (hereafter abbreviated DPPH) and then the solution was freeze vaporized to remove dissolved oxygen gas. The yarn was reacted with DPPH in the solution at 343 K for 24 h. The reaction amount of DPPH was evaluated from a difference in absorbance at 520 nm that was measured before and after the reaction with a Shimadzu UV-160 UV-visible spectrophotometer (Shimadzu Co., Ltd., Kyoto, Japan). The surface density of active species formed by plasma irradiation was evaluated from the reaction amount.

Plasma-Graft Polymerization

The yarn was irradiated for 3–100 s with a plasma that was generated at 13.56 MHz at 20–80 W in an atmosphere of 13 Pa argon, and then immersed for 6–24 h in 2M acrylamide solution. Acrylamide was reagent grade and was used without further purification. The plasma-grafted yarn was washed successively with pure water and methanol under ultrasonic irradiation and then dried in vacuum at 300 K.

Surface Analyses of Plasma-Grafted Yarn

X-ray photoelectron spectroscopy measurement was carried out with a Shimadzu ESCA750 X-ray photoelectron spectroscope (Shimadzu Co., Ltd., Kyoto, Japan) to identify the species of atoms constituting the graft layer. An infrared spectrum was measured with a Magna 550 Fourier transform infrared spectroscope (Nicolet Analytical Instruments, WI) equipped with a Barnes analytical diffuse reflectance accessory to identify the chemical structure of the graft layer. The surface morphology of the yarn was observed by using a Nihondenshi JSM-6301FZ scanning electron microscope (Nihondenshi Co., Ltd., Tokyo, Japan).

Evaluation of Adhesion Between Yarn and Epoxy Resin

Diglycidyl ether of bisphenol-A[6] and triethylenetetramine (hereafter abbreviated TETA) were used as the epoxy resin and the curing agent, respectively. The average molecular weight of digrycidyl ether of bisphenol-A was about 330. The yarn was embedded in the epoxy resin/TETA mixture to form a fiber-reinforced plastic and then the mixture was cured at 300 K over 120 h. The weight ratio of the epoxy resin/TETA was 5 : 1. The width of the yarn embedded in the mixture was 2 mm to be able to pull out the yarn without yarn breakage. The yarn was pulled out with a Tensilon UTM-III tensile tester (Toyo Baldwin Co., Ltd., Tokyo, Japan). Pull-out speed was 2 mm/min and gauge length was 15 mm. Pull-out force was evaluated by dividing pull-out load by the embedded width of the yarn.

RESULTS AND DISCUSSION

Activating the Surface of Carbon Yarn by Plasma Irradiation

Table I shows absorbances at 520 nm in ultraviolet-visible absorption spectra of DPPH solutions before and after immersing the plasma-irradiated carbon yarns. The absorbance was decreased after immersing the yarn, since the peroxides formed on the surface of the yarns will be decomposed at 343 K and reacted with DPPH, similar to the peroxides formed on the surface of argon plasma-treated polyethylene film.[7] Absorbance difference between the solutions before and after immersing the yarn was used to evaluate the surface density of active radicals formed by plasma irradiating, as follows: On the basis on the

Table I   Absorbances at 520 nm in Ultraviolet-Visible Spectra of 1,1-Diphenyl-2-Picrylhydrazyl Solution Before and After Immersing the Plasma-Irradiated Carbon Yarns for Various Conditions of Plasma Irradiation

Conditions of Plasma Irradiation		Absorbance at 520 nm		
Discharge Power of Plasma (W)	Plasma-Irradiation Time (s)	Before Immersing Plasma-Irradiated Yarn	After Immersing Plasma-Irradiated Yarn	Surface Density of Active Species (nm^{-2})
20	30		1.100	0.41
30	30		1.029	4.80
40	30		1.024	5.10
50	30		1.016	5.64
60	30		1.014	5.72
80	30	1.107	1.013	5.81
30	10		1.044	3.91
30	20		1.037	4.33
30	30		1.030	4.76
30	60		1.018	5.48
30	80		1.014	5.72
30	100		1.017	5.55

assumptions in which a peroxy group is formed by reacting two active radicals with an oxygen molecule and is reacted with two DPPH molecules at 343 K, the number of active radicals formed on the surface of the yarn is able to be evaluated from the absorbance difference corresponding to DPPH consumption. Furthermore, it is tentatively assumed in evaluating the surface area of the yarn that a surface of the fiber is completely smooth and the cross section is circle of 7 μm diameter. The surface density of active radicals is obtained as the number of active radicals divided by surface area of the yarn.

Figures 1(a) and 1(b) show density of the active species formed on the surface of the yarn as functions of discharge power of the plasma and plasma-irradiation time, respectively. The density was increased with increasing the discharge power and then the rate of increase was largely decreased in the range of higher discharge power above 30 W. The density was also increased with increasing the plasma-irradiation time and then the rate of increase was largely decreased in the range of longer time above 10 s.

It is confirmed that the abrasion of the yarn was little generated by plasma irradiating in the ranges of the discharge power of 20–50 W and the plasma-irradiation time of 10–60 s, since decrease in the weight of the yarn was less than 0.5% after plasma irradiating. The abrasion became remarkable at discharge powers above 50 W and at plasma-irradiation times above 60 s.

Plasma-Graft Polymerization

Table II shows weights of the yarn before and after plasma-grafting and the degrees of grafting for various conditions of plasma-irradiation and polymerization times. The degree of grafting G was evaluated as follows:

$$G = (W - W_0)/W_0 \times 100 \ (\%)$$

in which W_0 and W are weights of the yarn before and after plasma grafting, respectively. Figure 2 shows the degree of grafting of the yarn as a function of polymerization time, using data of Table II. The degree of grafting was increased with increasing polymerization time at discharge powers of 20 and 30 W. The rate of polymerization at 30 W was higher than that at 20 W. This result means that the rate of polymerization depends on the surface density of the active radicals, which was increased with increasing the discharge power as shown in Figure 1(a).

Figure 3 shows X-ray photoelectron spectra of the yarn before and after plasma grafting. Since the O_{1s} peak is recognized in the yarn before plasma grafting, the surface of the fiber contains oxygen at fairly high level. When the fiber is heated at carbonization temperature on the manufacturing process, the fiber will generate free radicals that react with oxygen to form the oxygen-rich layer containing peroxy groups if fiber is taken out into the air.[8,9] The peroxy groups will
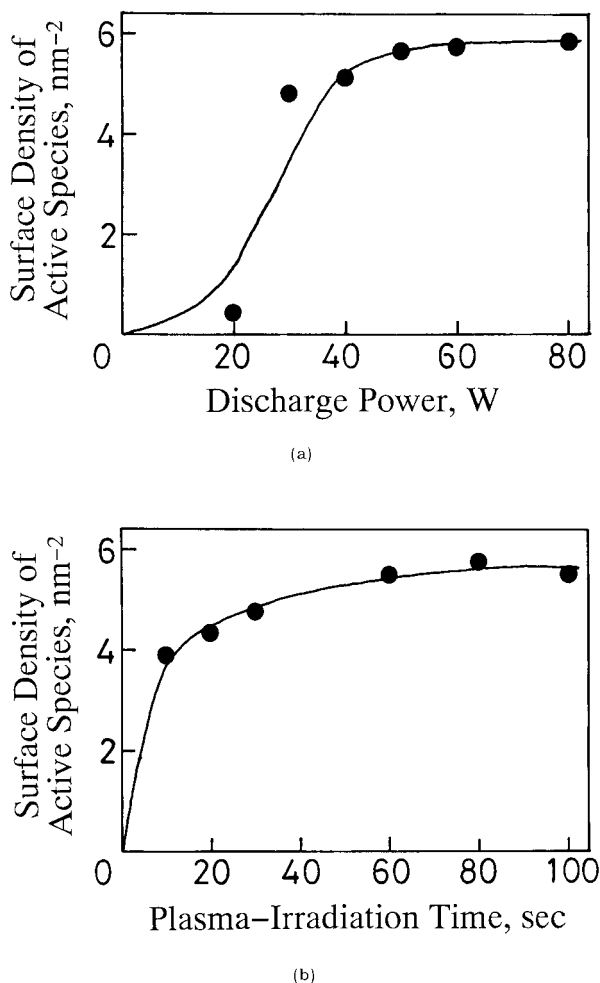
(a)

(b)

Figure 1 Density of active species formed on a surface of the carbon yarn as functions of (a) discharge power at plasma-irradiation time of 30 s and (b) plasma-irradiation time at discharge power of 30 W.
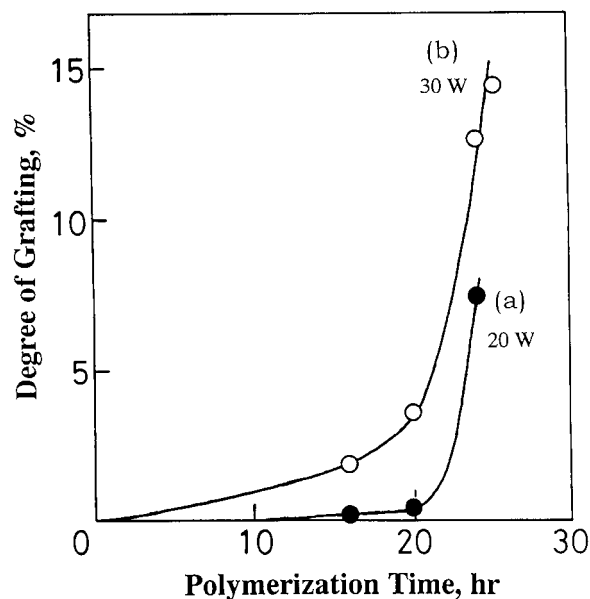

Figure 2 Degree of grafting as a function of polymerization time at (a) 20 W and (b) 30 W.

be removed or/and reacted by argon plasma irradiation, which is applied on the surface of the fiber before plasma-graft polymerization and free radicals will be freshly formed on the surface of the fiber. Therefore it is reasonable that the value of surface density of active species shown in Figure 1 depends only on plasma-irradiation condition. N_{1s} peak, which originates from nitrogen atom as the constituent atom of poly(acrylamide), is recognized after plasma-grafting, as shown in Figure 3.

Table II Weights of Carbon Fibers Before and After Plasma Grafting and Degrees of Grafting for Various Conditions of Plasma Irradiation and Polymerization Times

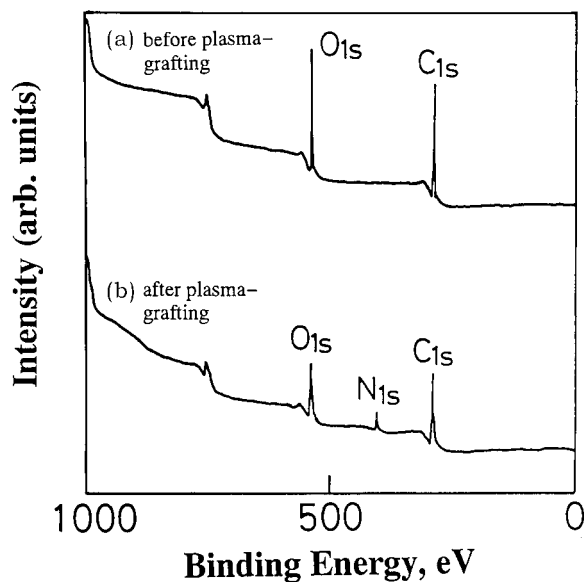| Conditions of Plasma Irradiation			Weight of Carbon Yarn (mg)		
Discharge Power of Plasma (W)	Plasma-Irradiation Time (s)	Polymerization Time (h)	Before Plasma Grafting	After Plasma Grafting	Degree of Grafting (%)
20	30	16	161.6	161.9	0.2
	30	20		162.4	0.5
	30	24		173.7	7.5
30	3	24		163.1	0.9
	10	24		177.2	9.7
	30	16		164.5	1.8
	30	20		167.6	3.7
	30	24		182.4	12.9
	30	25		184.8	14.4
	60	24		189.2	17.1
	100	24		182.1	12.7
50	30	24		186.7	15.5

Figure 3 X-ray photoelectron spectra of the carbon yarn (a) before and (b) after plasma grafting (degree of grafting was 3.7%).

Figure 4 shows infrared spectra of a surface of carbon yarn before and after plasma grafting. The absorption peaks at 1700 and 3380 cm^{-1}, which are attributable to C=O stretching vibration and NH stretching vibration, respectively, were recognized in the infrared spectrum of a surface of the yarn after plasma grafting. Figure 5 shows scanning electromicrographs of the fiber before and after plasma grafting. Well-defined streaks parallel to the fiber axis were observed before plasma grafting and the surface of the fiber was uneven. The streaks became unclear after plasma grafting. It becomes apparent from the results of Figure 3–5 that poly(acrylamide) chains are plasma grafted onto a surface of the yarn.
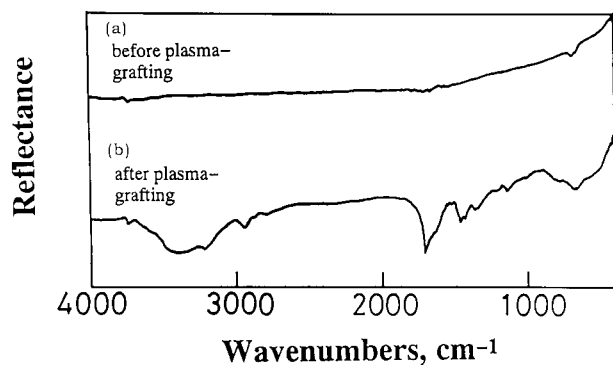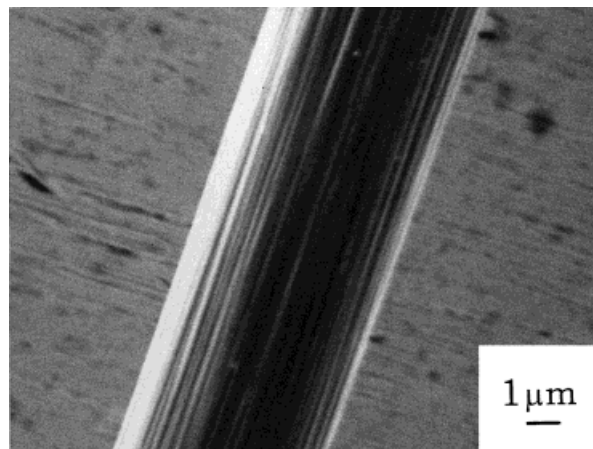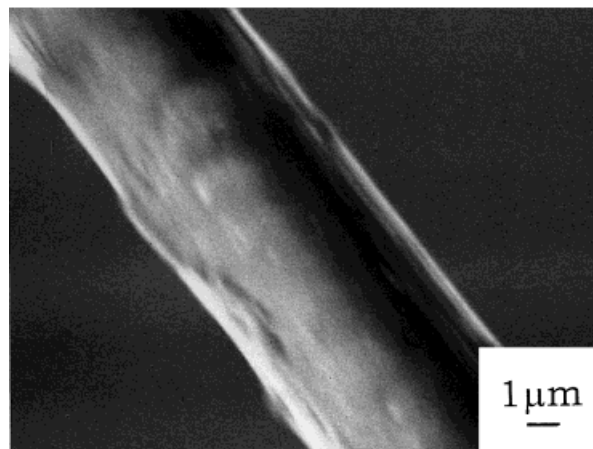

Figure 4 Infrared spectra of a surface of the carbon yarn (a) before and (b) after plasma grafting (degree of grafting was 3.7%).

(a)

(b)

Figure 5 Scanning electromicrographs of the carbon fiber (a) before and (b) after plasma grafting (degree of grafting was 3.7%).

Figure 6(a) shows the degree of grafting of the yarn as a function of discharge power at plasma-irradiation time of 30 s at polymerization time of 24 h. The degree of grafting was increased with increasing discharge power and then the rate of increase was largely decreased above 30 W. Figure 6(b) shows the degree of grafting of the yarn as a function of plasma-irradiation time at discharge power of 30 W at a polymerization time of 24 h. The degree of grafting was increased with increasing plasma-irradiation time and then the rate of increase was largely decreased above 10 sec. Figure 7 shows the degree of grafting as a
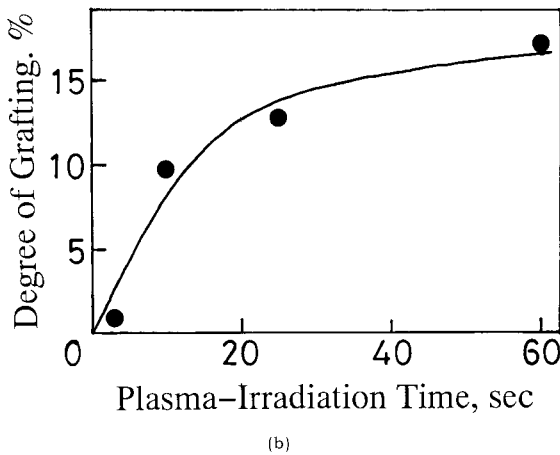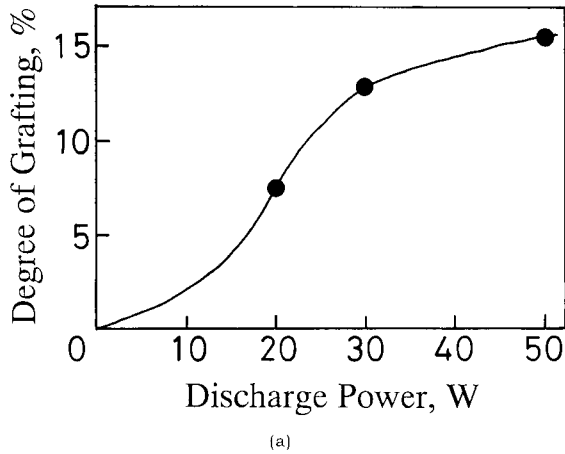
(a)

(b)

Figure 6 (a) Degree of grafting as a function of discharge power at plasma-irradiation time of 30 s at polymerization time of 24 h. (b) Degree of grafting as a function of plasma-irradiation time at discharge power of 30 W at polymerization time of 24 h.

function of the density of active species formed on a surface of the yarn, using the results of Tables I and II. The degree of grafting increased almost linearly with increasing surface density of active species and it is therefore confirmed that graft polymerization of acrylamide can be initiated by the active radicals. The number of graft chains per unit surface area of the carbon fiber will be increased with increasing the surface density of the active radicals.

Adhesion Between Carbon Yarn and Epoxy Resin

Figure 8 shows the pull-out force of the yarns that were grafted by poly(acrylamide) chains and then embedded in the epoxy resin/TETA mixture cured, as a function of the degree of grafting.
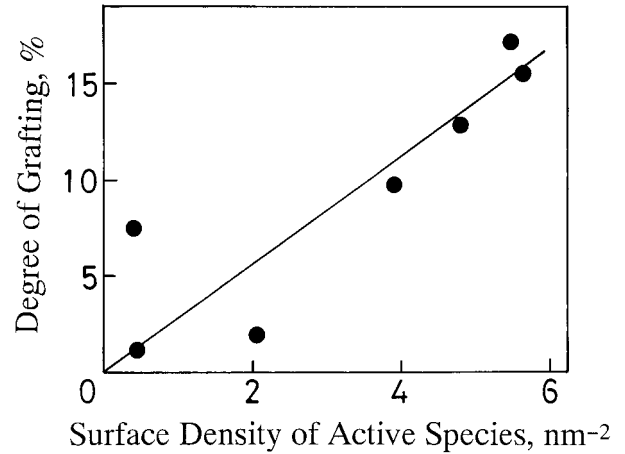

Figure 7 Degree of grafting as a function of surface density of active species.

Pull-out force was increased with increasing the degree of grafting, which will be proportional to the number of graft chains. Figure 9 shows the infrared spectrum of a surface of the grafted yarn after pulling out. The absorption peaks, which are attributable to the in-plane skeletal vibration of the benzene ring and CH stretching vibration of methyl group, appeared at 1600 and 2950 cm^{-1}, respectively. Figure 10 shows scanning electromicrograph of the yarn after pulling out. The fracture surface of the matrix resin is observed. Therefore it becomes apparent from Figures 9 and
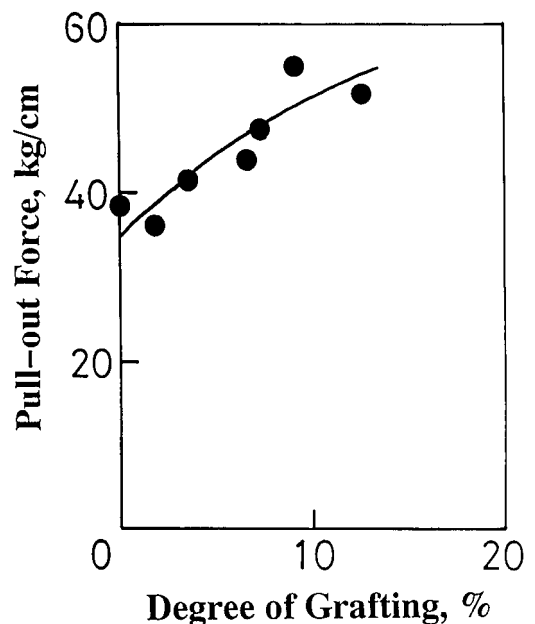

Figure 8 Pull-out force of the carbon yarn grafted by poly(acrylamide) as a function of degree of grafting.

10 that the component of the matrix resin composed of the epoxy resin/TETA mixture cured is remained on the surface of the yarn and the failure in pulling out of the grafted yarn is cohesive.

The absorption peak appeared at 1650 cm^{-1} in Figure 9 would originate from the C=O stretching vibration of the amide group, which will be formed by reacting acid amide group of acrylamide with epoxy group of the epoxy resin. The reactivity of acid amide group and epoxy group was investigated by reacting acrylamide with diglycidyl ether of bisphenol-A at 298 K for 24 h. The molar ratio of acrylamide to diglycidyl ether of bisphenol-A was 1 : 1. The reactivity was confirmed from ^{1}H-NMR spectra of diglycidyl ether of bisphenol-A and the reactant, in which the proportion of the peak areas of the methylene proton of epoxy group to benzene proton decreased after the reaction. The covalent bonds formed between the graft polymer and the matrix resin will result in an increment of pull-out force and therefore cohesive failure will occur in pulling out of the grafted yarn. The plasma-graft polymerization of acrylamide onto a surface of the yarn is effective on an increment of the adhesion between the yarn and the epoxy resin.

CONCLUSION

Active radicals are formed on a surface of the carbon yarn by irradiating argon plasma and result in plasma-graft polymerization of acrylamide. The surface density of the active radicals
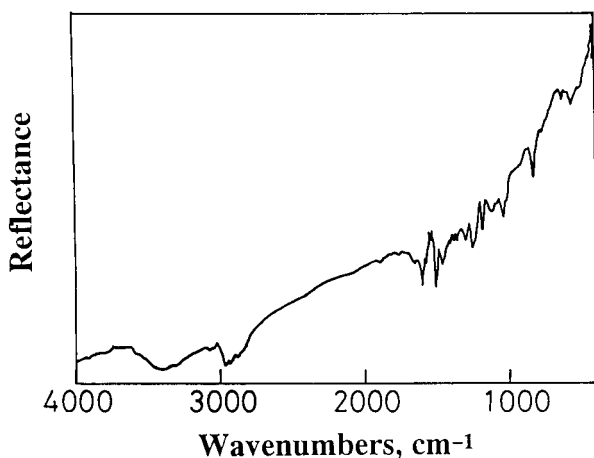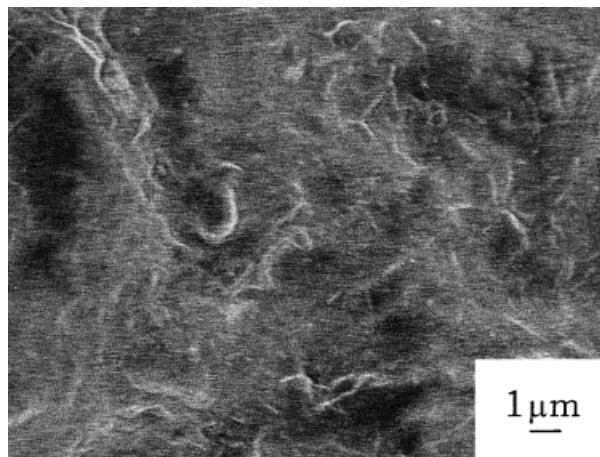

Figure 10   Scanning electromicrograph of the carbon fiber of which degree of grafting was 9.7%, after pulling out.

was increased with increasing the discharge power and the plasma-irradiation time and the rate of increase was decreased in the ranges of higher power and longer time.

Pull-out force of the carbon yarn embedded in the epoxy resin/curing agent mixture cured was increased with increasing the degree of grafting. The plasma-graft polymerization of acrylamide onto a surface of the carbon yarn is effective on an increment of the adhesion between the carbon yarn and the epoxy resin. The increment of the adhesion will be realized by forming covalent bonds between grafted poly(acrylamide) and the epoxy resin.

Figure 9   Infrared spectrum of a surface of the carbon yarn of which degree of grafting was 9.7%, after pulling out.

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