

# Plasma-Graft Polymerization of a Monomer with Double Bonds onto the Surface of Carbon Fiber and Its Adhesion to a Vinyl Ester Resin

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**ABSTRACT:** Double bonds reactive with active radical species were introduced onto the surface of carbon yarn by the plasma-graft polymerization of adipic acid divinyl ester and ethylene glycol dimethacrylate monomers to increase the adhesive strength in the interface between the carbon yarn and a vinyl ester resin. The degree of grafting increased with increasing polymerization time and polymerization temperature. The degree of grafting depended on both the solvent and the monomer species used in the polymerization, and a high degree was obtained with ethylene glycol dimethacrylate as the conjugated monomer and in a mixture

of methyl isobutyrate and water. The grafted yarn, whose surface layer contained double bonds, was reacted with a vinyl ester resin containing benzoyl peroxide and *N,N*-dimethylaniline. The pull-out force of the yarn embedded in the resin increased with increasing degree of grafting. The failure in pulling out the yarn was cohesive. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2415–2419, 2003

**Key words:** adhesion; cold plasma; composites; fibers; surfaces

## INTRODUCTION

The mechanical properties of fiber-reinforced composites depend on the state of the interface between the fiber and the matrix. To improve fiber–matrix adhesion, the surfaces of fibers have been treated by plasma techniques.<sup>1–5</sup> The surface treatment of carbon fibers was investigated with selected monomers via plasma polymerization, and it was found that the monomers used during the plasma polymerization process at selected plasma conditions led to significant improvements in both the interlaminar shear strength and flexural strength values of carbon fiber/epoxy composites.<sup>1</sup> Kevlar 49 fibers were surface modified by ammonia plasma treatment to find the optimum conditions for adhesion to aromatic bismaleimides, and an obvious improvement in the interfacial shear strength of the fiber/bismaleimide composites was realized by the introduction of amino groups onto the fiber surface.<sup>2</sup> Aramid cords and fibers and polyester tire cords were treated in a continuous or pulsed direct-current plasma containing organic monomers such as pyrrole or acetylene, and the plasma polymer coating significantly increased pull-out forces, when the rubber adhesion was measured in a standard pull-out test.<sup>3</sup> Plasma-graft polymerization method is an

effective technique for the surface modification of polymers with plasma<sup>4,5</sup> because the functional groups desired are able to be definitely introduced on the surface. In a previous work,<sup>6,7</sup> functional groups reactive with epoxy or amino group were introduced onto the surfaces of Kevlar 49 yarn and carbon yarn by means of plasma-graft polymerization and were then reacted with an epoxy resin/curing agent mixture as a matrix resin to form covalent bonds, which gave strong adhesion between the yarn and the matrix resin.

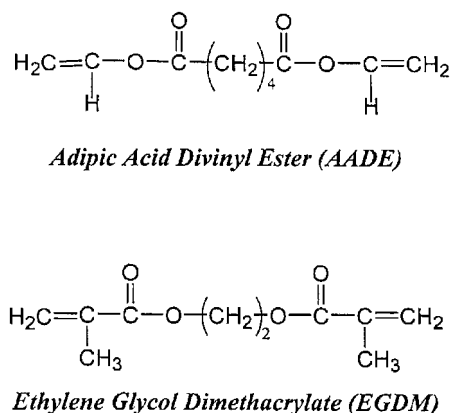
In this study, we obtained strong adhesion between a carbon yarn and a vinyl ester resin through the formation of covalent bonds. Double bonds reactive with radical species were introduced onto the surface of the yarn by means of plasma-graft polymerization and were then reacted with the vinyl ester resin to form covalent bonds. The adhesive property between the grafted yarn and the vinyl ester resin was assessed by the evaluation of the pull-out force of the yarn embedded in the resin.

## EXPERIMENTAL

### Plasma-graft polymerization

The polyacrylonitrile-based carbon yarn used in this work was Besfight TA-12K (Toho Rayon Co., Shizuoka, Japan) in the form of a 7350-denier, 12,000-filament yarn without any surface treatments. To form active radical species on the surface of the yarn, the

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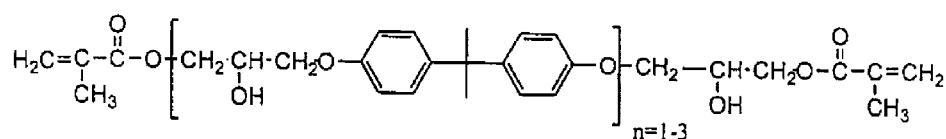


**Figure 1** Chemical structures of AADE and EGDM, which were used as monomers for the plasma-graft polymerization.

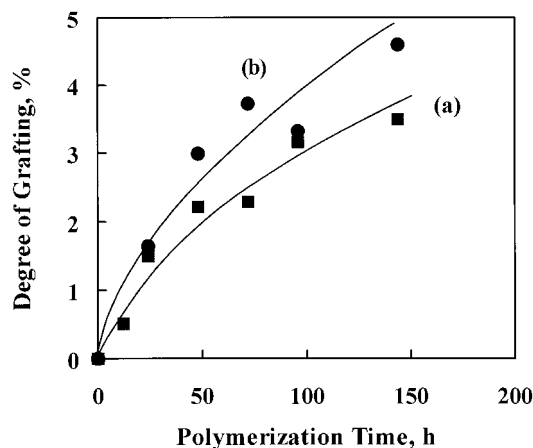
yarn suspended in the apparatus for plasma-graft polymerization<sup>4,5</sup> was irradiated for 60 s with a plasma that was generated at discharge power of 50 W in an atmosphere of 13 Pa of argon by a radio frequency generator operating at 13.56 MHz. Then, the plasma-irradiated yarn without exposure to air was left for 24–144 h at 298–323 K in monomer solution. Figure 1 shows the chemical structures of adipic acid divinyl ester (AADE) and ethylene glycol dimethacrylate (EGDM), which were used as the monomers of the plasma-graft polymerization, and the monomer solvents used were methanol, a methanol–water mixture, methyl isobutyrate, and a methyl isobutyrate–water mixture. The content of water was 2 vol % in both the methanol–water mixture and the methyl isobutyrate–water mixture. The concentration of the monomer was 2 mol/L. The monomer solution was freeze-vaporized to remove dissolved oxygen gas before the yarn was graft-polymerized.

### Surface analyses of the plasma-grafted yarn

An IR spectrum was measured with a Magna 550 Fourier transform infrared spectroscope (Nicolet Analytical Instruments, Madison, 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 with a Nihondenshi JSM-6301FZ scanning electron microscope (Nihondenshi Co., Ltd., Tokyo, Japan).



**Figure 2** Chemical structure of the vinyl ester resin used in this work.



**Figure 3** Degree of grafting as a function of polymerization time in (a) AADE and (b) EGDM. The solvent of the monomers was a methanol–water mixture; the polymerization temperature was 297 K.

### Evaluation of adhesion between the yarn and the vinyl ester resin

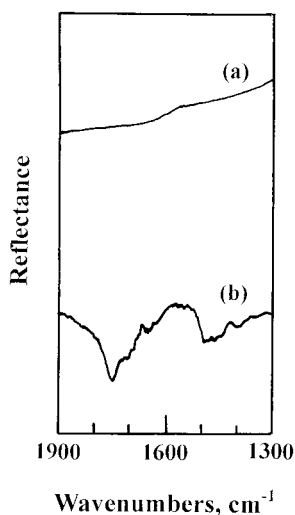
The vinyl ester resin, benzoyl peroxide, and *N,N*-dimethylaniline were used as the matrix resin, initiator, and promoter for the decomposition of benzoyl peroxide, respectively. Figure 2 shows the chemical structure of the vinyl ester resin. The yarn was embedded in the vinyl ester resin/benzoyl peroxide/*N,N*-dimethylaniline mixture to form a fiber-reinforced plastic, and then, the mixture was cured at 298 K over 48 h. The weight ratio of vinyl ester resin/benzoyl peroxide/*N,N*-dimethylaniline was 98:1.5:0.5. The width of the yarn embedded in the mixture was 2 mm so it could be pulled out with a Tensilon UTM-III tensile tester (Toyo Baldwin Co., Ltd., Tokyo, Japan). The pull-out speed was 2 mm/min, and the gauge length was 15 mm. We evaluated the pull-out force by dividing the pull-out load by the embedded width of the yarn.

## RESULTS AND DISCUSSION

### Plasma-graft polymerization

#### Effect of monomer species

Figure 3 shows the degree of grafting of the yarn as a function of polymerization time in AADE and EGDM. The methanol–water mixture was used as a solvent for



**Figure 4** IR spectra of the surface of carbon yarn (a) before and (b) after plasma-grafting in AADE. The degree of grafting was 3.5%.

the monomers, and the polymerization temperature was 297 K. The degree of grafting ( $G$ ) was evaluated as follows:

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

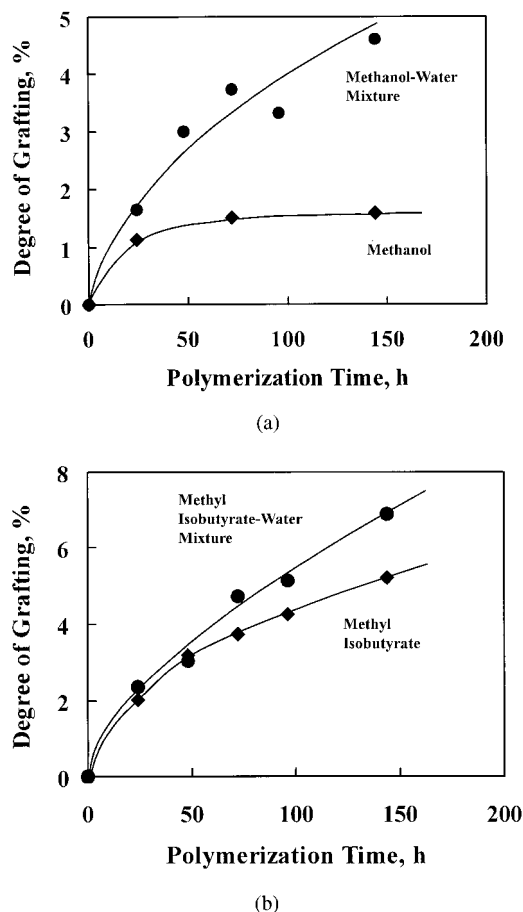
where  $W_0$  and  $W$  are the weights of the yarn before and after plasma grafting, respectively. The degree of grafting increased with increasing polymerization time. The rate of polymerization in EGDM was higher than that in AADE. We assumed that the initiation reaction was the rate-determining stage in the plasma-graft polymerization of the carbon yarn because EGDM and AADE are conjugated and nonconjugated monomers, respectively, and the reactivity of EGDM and the radical species formed on the surface of the yarn was generally higher than that of AADE and the species, whereas the propagation reaction in EGDM was more depressed than that in AADE.

We recognized from scanning electromicrographs of the yarn before and after the plasma-grafting of AADE and EGDM that aggregations of the graft polymers were formed on the surface of the yarn. Figure 4 shows the IR spectra of the surface of the carbon yarn before and after plasma-grafting in AADE. The absorption peaks at  $1650$  and  $1760\text{ cm}^{-1}$ , which are attributable to a  $\text{C}=\text{C}$  stretching vibration and a  $\text{C}=\text{O}$  stretching vibration, respectively, were recognized in the IR spectrum of the surface of the yarn after plasma-grafting. Therefore, it was apparent that the vinyl group of AADE remained as the end group of the side chain in the polymers formed by plasma-grafting with AADE. The absorption peaks attributable to these stretching vibrations were also recognized at  $1645$  and  $1750\text{ cm}^{-1}$  in the plasma-grafting of EGDM. The vinylidene group of EGDM also remained as the end

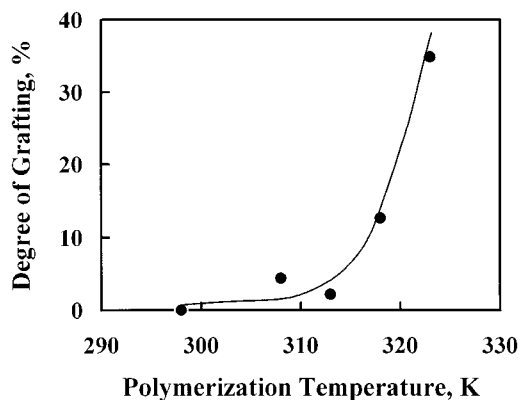
group of the side chain in the polymers formed by plasma-grafting with EGDM.

### Effect of the solvent species

Figure 5(a,b) shows the degree of grafting as a function of the polymerization time of EGDM in methanol, the methanol-water mixture, methyl isobutyrate, and the methyl isobutyrate-water mixture. The polymerization temperature was 297 K. The degree of grafting depended on the solvent species, and a higher degree of grafting was obtained in methyl isobutyrate, compared with methanol. This result means that solubility of the graft chains of EGDM in methyl isobutyrate was higher than that in methanol, and the high solubility resulted in continuance of the polymerization. The degree of grafting increased when 2 vol % water was contained in the solvent. However, water was a non-solvent of EGDM. It was, therefore, assumed that the initiation reaction, by which the rate of the graft polymerization was governed, was accelerated by water, but termination and transfer reactions were depressed



**Figure 5** Degree of grafting as a function of polymerization time in EGDM: (a) methanol and the methanol-water mixture and (b) methyl isobutyrate and the methyl isobutyrate-water mixture. The polymerization temperature was 297 K.



**Figure 6** Degree of grafting as a function of polymerization temperature at a polymerization time of 150 min in EGDM. The solvent of the monomer was the methyl isobutyrate–water mixture.

because propagation chain radicals were stabilized by interaction with water molecules having a lone pair of electrons.

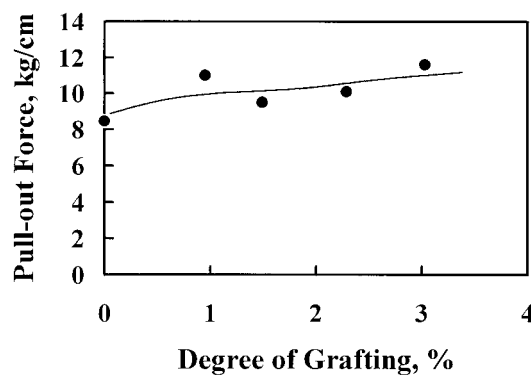
#### Effect of polymerization temperature

Figure 6 shows the degree of grafting as a function of polymerization temperature at a polymerization time of 150 min in EGDM. The solvent of EGDM was the methyl isobutyrate–water mixture. The degree of grafting largely increased with increasing polymerization temperature. As long as the polymerization temperatures in this study were much lower than the ceiling temperature of EGDM, the propagation rate in the graft polymerization increased with increasing polymerization temperature in the region of temperatures higher than 297 K. Because the increase in the rate of the degree of grafting decreased at the lower polymerization temperature of 313 K, as shown in Figure 6, the propagation reaction was depressed. Therefore, we assumed that the propagation chain radicals were occluded with the growing graft chains, and the transport of the monomers to the chain radicals was prevented. However, the propagation reaction became predominant in the higher temperature region above 313 K because the gel effect in graft chains region on the fiber took place. According to the gel effect, the termination reaction would be largely depressed, whereas the transport of the monomers to the chain radicals would not be prevented.

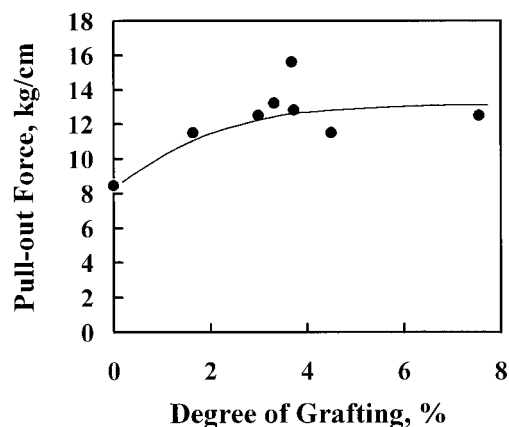
#### Adhesion between the carbon yarn and the vinyl ester resin

Figure 7 (a,b) shows the pull-out force of the yarns, which were grafted by poly(adipic acid divinyl ester) chains and poly(ethylene glycol dimethacrylate) chains and were then embedded in the cured vinyl ester resin/benzoyl peroxide/*N,N*-dimethylaniline

mixture, as a function of the degree of grafting. The solvents of AADE and EGDM were the methanol–water and methyl isobutyrate–water mixtures, respectively, and the polymerization temperature was 297 K. The pull-out force increased with increasing degree of grafting. The degree of grafting was proportional to the number of graft chains formed on the surface of the yarn because the average molecular weight of the graft chains did not depend on the degree of grafting. Figure 8(a,b) shows the IR spectra of the surface of carbon yarn after pulling out in AADE and EGDM. The degrees of grafting for AADE and EGDM were 3.0 and 3.7%, respectively. The absorption peak, which was attributable to the in-plane skeletal vibration of benzene ring, appeared at  $1510\text{ cm}^{-1}$  in both of the pulled-out yarns. Therefore, it was apparent that the component of the matrix resin composed of the cured vinyl ester resin/benzoyl peroxide/*N,N*-dimethylaniline mixture remained on the surface of the yarn, and the failure in the pulling out the grafted yarn was cohesive. As shown in Figure 8(a,b), the absorption peaks attributable to the C=C stretching vibration did

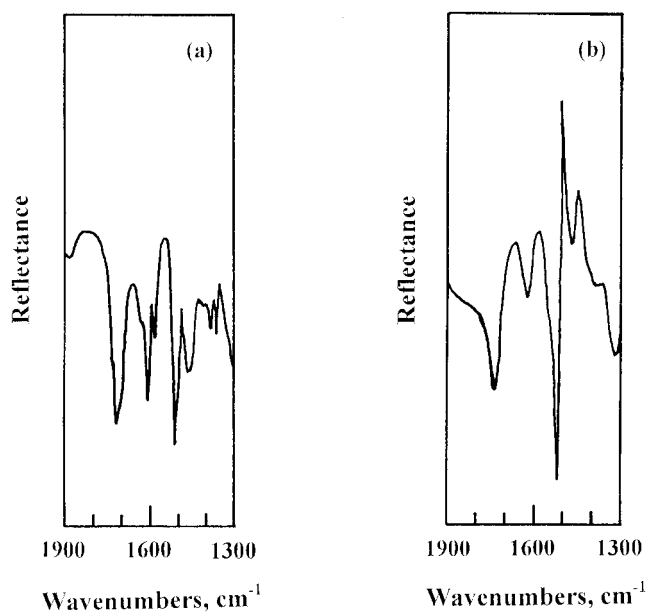


(a)



(b)

**Figure 7** Pull-out force of the grafted carbon yarn as a function of the degree of grafting in (a) AADE and (b) EGDM. The solvent of AADE was the methanol–water mixture. The solvent of EGDM was the methyl isobutyrate–water mixture. The polymerization temperature was 297 K.



**Figure 8** IR spectra of the surface of the carbon yarn after pulling out in (a) AADE and (b) EGDM. The degree of grafting for adipic acid vinyl ester was 3.0%, and that for EGDM was 3.7%.

not appear. It was, therefore, presumed that the double bonds of the graft chains, that is, poly(adipic acid divinyl ester) and poly(ethylene glycol dimethacrylate), reacted with the radical species generated from the vinyl ester resin to form covalent bonds between the graft polymers and the resin. The cohesive failure in the pulling out originated from the formation of the covalent bonds.

### CONCLUSIONS

Double bonds reactive with the vinyl ester resin were introduced onto the surface of carbon yarn by the

plasma-grafting of AADE and EGDM. The degree of grafting increased with increasing polymerization time and polymerization temperature. The degree of grafting depended on both the conjugation state of the monomer and solvent species, and a higher degree was obtained in EGDM as the conjugated monomer and in methyl isobutyrate–water mixture.

The pull-out force of the carbon yarn embedded in the vinyl ester resin increased with increasing degree of grafting. The plasma-graft polymerization of AADE and EGDM was effective on an increment of the adhesion between the carbon yarn and the resin. The increment of the adhesion was realized by the formation of covalent bonds between the grafted polymer and the resin. The failure in the pulling out of the yarn was cohesive.

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