Grafting of Polymers onto Carbon Fiber Surface by Ligand Exchange Reaction of Poly(vinylferrocene-*co*-methyl methacrylate) with Polycondensed Aromatic Ring of the Surface

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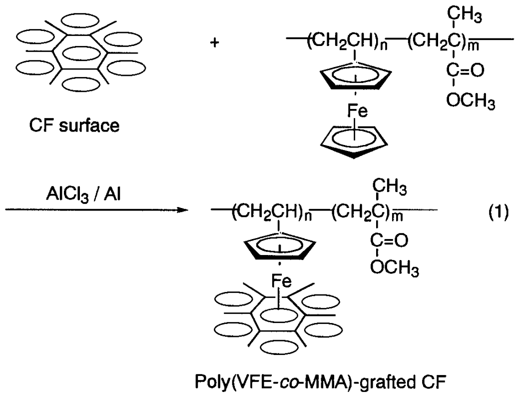
The grafting reaction of poly(vinylferrocene-*co*-methyl methacrylate) onto carbon fiber (CF) surface was successfully achieved by ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of CF in the presence of $AlCl_3$ and aluminum powder. The percentage of grafting onto CF surface reached to 46.1%.

The properties of fiber-reinforced composite materials are known to depend on the mechanical properties of matrix polymer, the load bearing ability of fiber, and the strength of interfacial regions between polymer matrix and fiber.[1] Therefore, various techniques of surface modification of high strength fibers have been reported.[1–3] We have reported the surface grafting of polymers onto CF surface by the polymerization initiated by initiating groups introduced onto the surface.[4–7] The percentage of grafting, however, was less than 10% because CF has a few functional groups for the grafting site.

On the other hand, Nesmeyanov et al. reported that the η^6-benzene-η^5-cyclopentadienyliron cation could be readily prepared by ligand exchange reaction of ferrocene with benzene in the presence of $AlCl_3$ and Al powder.[8–13] Furthermore, Miyake et al. reported that the ligand exchange reaction is successfully applied for the introduction of functional groups to polycondensed aromatic ring, hexagonal-plane, of various carbon materials.[14] In the present paper, the grafting reaction of poly(vinylferrocene-*co*-methyl methacrylate) [poly(VFE-*co*-MMA)] onto CF surface by ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of CF was examined (eq 1).



CF was obtained from Toray Company Ltd. The CF was cut into about 5 mm in length, and washed with pure water, and dried in vacuo at 120 °C before use. Methyl methacrylate (MMA) and vinylferrocene (VFE) obtained from Aldrich Chemical Co., Inc. were purified by the ordinary methods. $AlCl_3$ and Al powder (particle size: 53–150 μm) were used without further purification. Poly(VFE-*co*-MMA) was prepared by radical copolymerization of VFE with MMA.[15,16]

The grafting of poly(VFE-*co*-MMA) onto CF surface was carried out as follows. Into a flask, 0.10 g of CF, 0.10 g of the copolymer, 0.65 mmol of $AlCl_3$, 0.17 mmol of Al powder, and 20.0 mL of dioxane were charged and the mixture was refluxed for definite time with stirring. After the reaction, to separate the polymer-grafted CF from the reaction mixture containing ungrafted polymer and Al powder, the product was dispersed in dioxane by ultrasonication. Then, the dispersion of polymer-grafted CF was allowed to stand at room temperature and the Al powder precipitated was removed by decantation. The dispersion of polymer-grafted CF was centrifuged at 5.0×10^3 rpm and the precipitated polymer-grafted CF was dispersed again in dioxane. The procedures were repeated several times to remove most of ungrafted polymer and Al powder. Then, to remove ungrafted copolymer completely, CF was allowed to extract with THF using a Soxhlet apparatus until no more polymers could be extracted in the solvent. To remove Al compounds on the polymer-grafted CF surface, the polymer-grafted CF was washed with 1.0 mol/L HCl aqueous solution under stirring with a magnetic stirrer for 30 min. The percentage of grafting was calculated by eq 2.

$$\text{Grafting (\%)} = (A/B) \times 100 \qquad (2)$$

where A is copolymer grafted (g) and B is CF used (g). The amount of copolymer grafted onto the surface was determined by weight loss when the polymer-grafted CF was heated at 500 °C by use of a thermal analyzer: it was confirmed that by heating at 500 °C, the copolymer decomposed completely in leaving about 10% ash. Therefore, the amount of grafted polymer was corrected considering of remaining ash after decomposition of grafted copolymer.

Table 1 shows the results of grafting reaction of poly(VFE-*co*-MMA) ($M_n = 2.1 \times 10^4$; VFE content = 11 mol%) with CF surface under various conditions. As shown in Table 1, even if CF was heated with poly(VFE-*co*-MMA) in dioxane in the absence of $AlCl_3$, no grafting of the copolymer onto CF surface was observed (Run 1). In addition, the grafting of the copolymer onto the CF surface was hardly observed in the presence of Al powder alone (Run 2). On the contrary, the grafting reaction considerably proceeded in the presence of $AlCl_3$ (Run 3). In the coexistence of $AlCl_3$ and Al powder, poly(VFE-*co*-MMA) was successfully grafted onto the CF surface and the percentage of grafting reached to 27.6%. The value was much higher than that obtained from the radical graft polymerization initiated by azo groups on the surface[7] or by the system consisting of CF having trichlroacetyl groups and $Mo(CO)_6$.[17]

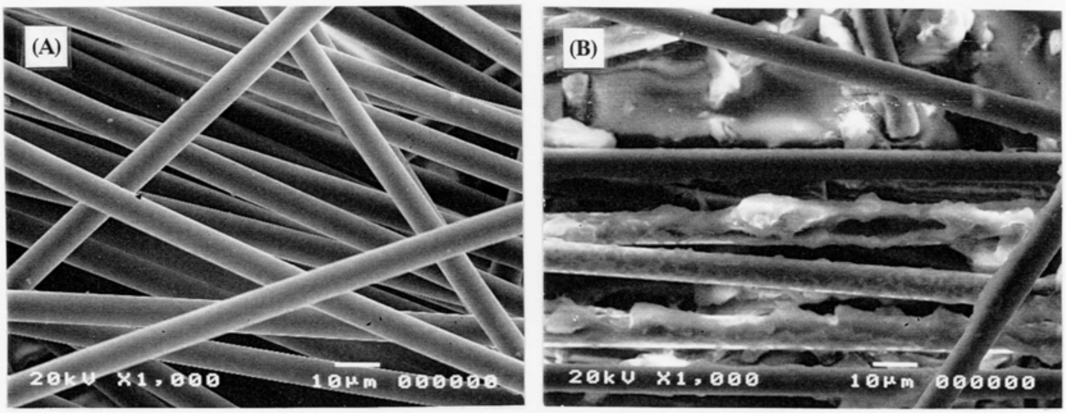


Figure 2. SEM aspects of (A) untreated and (B) poly(VFE-co-MMA)-grafted CF

Table 1. Grafting of poly(VFE-*co*-MMA) onto CF by ligand exchange reaction under various conditions[a]

Run	$AlCl_3$ / mmol	Al / mmol	Grafting / %
1	-	-	trace
2	-	0.17	trace
3	0.65	-	4.4
4	0.65	0.17	27.6

[a] CF, 0.10 g; poly(VFE-*co*-MMA) (Mn=2.1x10^4), 0.10 g; 1,4-dioxane, 20 mL; 80 °C; 24 h.

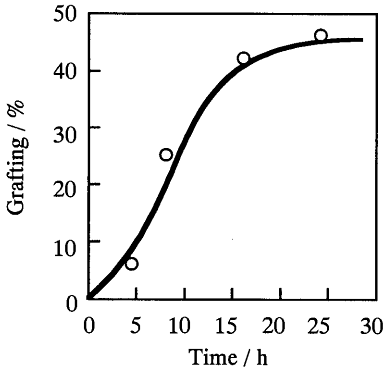


Figure 1. Grafting of poly(VFE-*co*-MMA) onto CF surface by ligand exchange reaction.
CF, 0.10 g; poly(VFE-*co*-MMA) (Mn=2.1x10^3), 0.10 g; $AlCl_3$, 2.20 mmol; Al, 0.56 mmol; 1,4-dioxane, 20 mL; 80 °C.

Figure 1 shows the time–percentage of grafting curve in the grafting reaction of poly(VFE-*co*-MMA) onto CF surface. The percentage of grafting increased with progress of the reaction, and no longer increased after 24 h. This may be due to the fact that CF surface was blocked by the grafted polymer chains.

It was found that the optimum mole ratio between ferrocene moieties, $AlCl_3$, and Al powder is 1 vs 20 vs 5. The percentage of poly(VFE-*co*-MMA) grafting onto CF surface increased with increasing temperature and reached to 46.1% at 80 °C.

Based on the above results, it is concluded that the grafting of poly(VFE-*co*-MMA) onto CF surface proceed by ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of CF as shown in eq 1.

The SEM aspects of poly(VFE-*co*-MMA)-grafted CF (grafting = 46.1%) and untreated CF are shown in Figure 2. It was found that CF surface was covered with poly(VFE-*co*-MMA).

In summary, the grafting of poly(VFE-*co*-MMA) onto CF surface was successfully achieved by ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of CF. The confirmation of formation of cyclopentadine during the reaction and XPS study on the poly(VFE-*co*-MMA)-grafted CF are now under investigation.

The surface grafting by ligand exchange reaction between ferrocene moieties of the copolymer and polycondensed aromatic rings of CF is very effective to obtain carbon fiber with higher percentage of grafting.

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References and Notes

1 P. Ehrburger and J. B. Donnet, "High Technology Fibers," Marcel Dekker, New York (1989), Vol. 3, Part A, p. 169.
2 D. W. McKee and V. J. Mimeaullt, "Chemistry and Physics of Carbon," Marcel Dekker, New York (1973), Vol. 8, p. 151.
3 J. B. Donnet, *Carbon* , **20**, 267 (1982).
4 N. Tsubokawa, H. Hamada, and Y. Sone, *Polym. Plast. Technol. Eng.*, **28**, 201 (1989).
5 N. Tsubokawa, H. Maruyama, and Y. Sone, *Polym. Bull.*, **15**, 209 (1986).
6 N. Tsubokawa, H. Maruyama, and Y. Sone, *J. Macromol. Sci. Chem.*, **A25**, 171 (1988).
7 K. Fujiki K, N. Motoji, and A. Yoshida, *Composite Interfaces*, **3**, 371 (1996).
8 A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk. SSSR*, **149**, 615 (1963).
9 A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Tetrahedoron Lett.*, **1963**, 1725.
10 A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk. SSSR*, **160**, 1327 (1965).
11 A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk. SSSR*, **166**, 607 (1966).
12 A. N. Nesmeyanov, N. A. Vol'kenau, E. I. Sirotkina, and V. V. Deryabin , *Dokl. Akad. Nauk SSSR*, **177**, 1110 (1967).
13 W. H. Morrison, Jr., E. Y. Ho, and D. N. Heudrickson, *J. Am. Chem. Soc.*, **96**, 3603 (1974).
14 M. Miyake, K. Yasuda, T. Kashihara, and T. Teranishi, *Chem. Lett.*, **1999**, 1037.
15 M. G. Baldwin and K. Johnson, *J. Polym. Sci. Part. A-1*, **5**, 2091 (1967).
16 J. C. Lai, T. Rounsfell, and C. U. Pittman, *J. Polym. Sci., Part A-1*, **9**, 651 (1971).
17 N. Abe N, Y. Seida, N. Tsubokawa, K. Fujiki, and M. Sakamoto, *Polym. Preprints Jpn.*, **48**, 1177 (1999).