

Radiation-Grafting of Acrylic Acid onto Ultrahigh Molecular, High-Strength Polyethylene Fibers

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SYNOPSIS

Radiation-induced grafting of acrylic acid onto ultrahigh molecular weight (UHMW) high-strength polyethylene fibers to impart heat resistance and dyeability was undertaken. A preirradiation method was employed for grafting in an aqueous solution of acrylic acid containing a small amount of Mohr's salt as inhibitor. The grafting rate for UHMW high-strength polyethylene fibers is one-tenth of that for high-density polyethylene fibers currently in use, and one-hundredth, for high-density polyethylene film. It has become clear that the preirradiation dose should be as low as 1 Mrad to keep the high strength of the starting fibers. The starting UHMW high-strength polyethylene fiber begins to shrink remarkably at around 145°C, showing a maximum shrinkage of 90%, and then breaks at 154°C. When a 24% acrylic acid graft is converted to calcium salt, the grafted fiber retains the fiber form even at 300°C and gives only a maximum shrinkage of 11%. The less than 1% acrylic acid graft UHMW high-strength polyethylene fibers and their calcium salt can be dyed to a deep shade with cationic dyes, whereas the starting fibers cannot be dyed with usual dyes including the cationic dye. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Ultrahigh molecular weight, high-strength polyethylene fibers, which have recently appeared on the market, are expected to be used in the field of industry as a high-performance material by itself or in a form of composite material. This material has high strength and high modulus properties in addition to the excellent properties of polyethylene, but has disadvantages in that it is thermally unstable and is of poor dyeability due to its extreme hydrophobic nature.

In this paper, to improve these disadvantages of this material, studies have been carried out on grafting of acrylic acid onto ultrahigh molecular weight, high-strength polyethylene fibers as a series of our previous studies of the modification of fiber materials such as polyester, poly(vinyl chloride),

poly(vinylidene chloride), or high-density polyethylene by radiation grafting.^{1,2}

EXPERIMENTAL

Materials

Ultrahigh molecular weight (UHMW), high-strength polyethylene fibers used in the present study were Tekmilon (10d) provided by Mitsui Petrochemical Industries. Conventional high-density polyethylene fibers for reference purposes were Hizex (337d), which were supplied by Mitsui Toatsu Chemicals. High-density polyethylene films were Sholex S5008 obtained from Showa Denko K. K. These materials were used after washing with methanol.

Acrylic acid was obtained from Nakarai Chemicals and used after purification using an activated alumina gel column. Mohr's salt and calcium acetate were of reagent grade purchased from Nakarai Chemicals.

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Graft Copolymerization

Grafting was carried out using a preirradiation technique throughout the present study. UHMW high-strength polyethylene fibers (ca. 0.1 g) were wound on a glass reel to prevent the fibers from shrinking during reaction. The fibers wound on the glass reel were put into a polyethylene film bag, air in the bag was replaced with nitrogen, and then the bag was sealed off. The fibers were irradiated with an electron beam from a Van de Graaff (dose rate: 0.092 Mrad/s). After irradiation, fibers were taken out from the bag and transferred to a glass ampule, into which 6 mL of 50% acrylic acid aqueous solution containing Mohr's salt as the inhibitor of homopolymerization was poured. Nitrogen gas stream was passed through the solution to remove air and then the ampule was sealed off. The ampule was put into a water bath at desired temperatures to effect grafting reactions at different times. After the reaction, fibers were taken out and washed with water at room temperature and then immersed in a water bath at 50°C to remove the homopolymer. The fibers were dried in air at room temperature and then in a vacuum oven at 50°C. The dried fibers were weighed to determine graft percent. Grafting was also carried out for high-density polyethylene fibers and films (8 × 40 mm) using exactly the same procedure.

Measurement of Tensile Property

Tensile strength, elongation, and Young's modulus were measured with a monofilament on an Instron tensile tester at a crosshead speed of 100%/min at 22°C and 65% RH.

Thermal Stability

Heat shrinkage was measured to determine the thermal stability of the fibers. A monofilament loaded with 0.01 g/d was heated at a heating rate of 2°C/min from room temperature to 300°C, and the change of the filament length was measured using a cathetometer to obtain the degree of shrinkage.

DSC Analysis

The DSC curve was obtained on a Perkin-Elmer DSC-2C analyzer in a nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 250°C. The temperature scale was calibrated using the melting point of high-purity indium. The melting point of the filament was determined from a peak of the DSC curve.

Dyeability

Dyeability was tested using 0.04% cationic dye solution (Sevron Brilliant Red B) at 50°C and for 30 min. The weight ratio of the filament and dye solution was 1 : 50.

RESULTS AND DISCUSSION

Comparison of Grafting Behavior of the Three Kinds of High-Density Polyethylenes

The grafting behavior of UHMW high-strength polyethylene fibers was compared with that of conventional high-density polyethylene fibers and high-density polyethylene film in Figures 1–3, where graft percent was plotted as a function of grafting time for preirradiation doses of 1, 5, and 10 Mrad, respectively. In any case, the monomer solution contained 4×10^{-3} mol/L Mohr's salt as the inhibitor of homopolymerization and grafting temperature was 50°C. When a monomer of a high polymerization rate such as acrylic acid or methacrylic acid is used for grafting, a large amount of homopolymer is formed in the monomer solution, which decreases graft efficiency and also makes grafting handling difficult. Our past studies^{2,3} that examined the efficiency of various inhibitors for the aqueous solution of acrylic acid revealed that conventional inhibitors such as hydroquinone do not inhibit polymerization, but ferrous, cuprous, or cupric ion effectively inhibits polymerization. Further, it was also revealed that among these ions Mohr's salt containing ferrous ion is most suitably used for the grafting of acrylic acid onto polyester in view of the high inhibition effect of homopolymerization and the high degree of grafting.

As shown in Figures 1–3, the graft percent increases with increasing grafting time, but it levels off as the grafting time increases. This leveling-off phenomenon of graft percent was also observed for preirradiation grafting of acrylic acid onto low-density polyethylene foam.⁴ One would conclude that consumption of the radical in the polymer is responsible for this leveling-off, but the presence of inhibitor in the grafting reaction system is related to this phenomenon, because similar leveling-off phenomenon is observed for simultaneous grafting of acrylic acid onto high-density polyethylene films⁵ or simultaneous grafting of methacrylic acid onto polyester fibers⁶ where radicals are continuously supplied to the grafting systems. It is considered that the inhibitor suppresses homopolymerization in the monomer solution outside the fibers or films, but

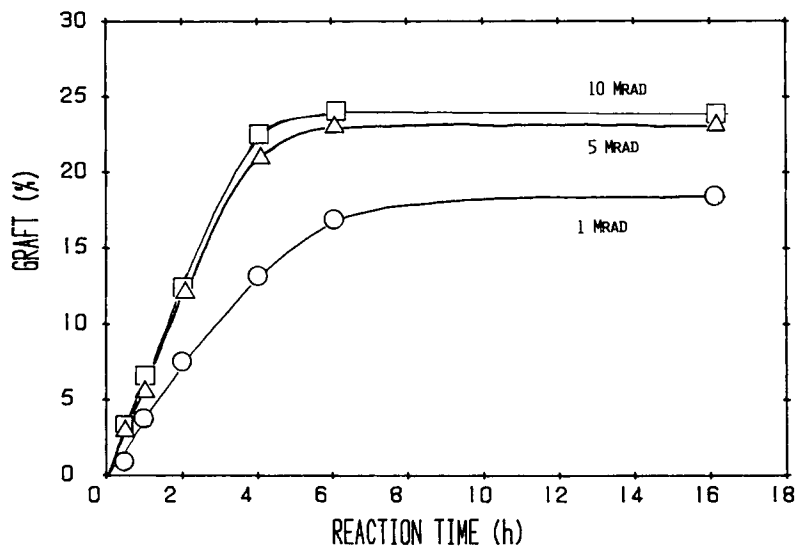


Figure 1 Effect of preirradiation dose on the grafting of acrylic acid onto UHMW high-strength polyethylene fibers at 50°C; concentration of Mohr's salt: 4×10^{-3} mol/L.

that the inhibitor diffuses into the fibers or films to inhibit the grafting reaction as the grafting time increases.

To confirm this point, the grafting reaction by the preirradiation method with or without the presence of Mohr's salt was carried out, and the result is shown in Figure 4 where graft percent is plotted as a function of grafting time. In this experiment, films had to be used instead of fibers, because severe

gluing of fibers occurred during grafting of fibers without Mohr's salt and, therefore, accurate graft percent could not be obtained in this condition. As shown in Figure 4, graft percent leveled off to 40% after 1 h grafting when Mohr's salt was present, whereas without Mohr's salt, graft percent was higher by one order of magnitude compared with that obtained with Mohr's salt and no leveling-off was observed in this case.

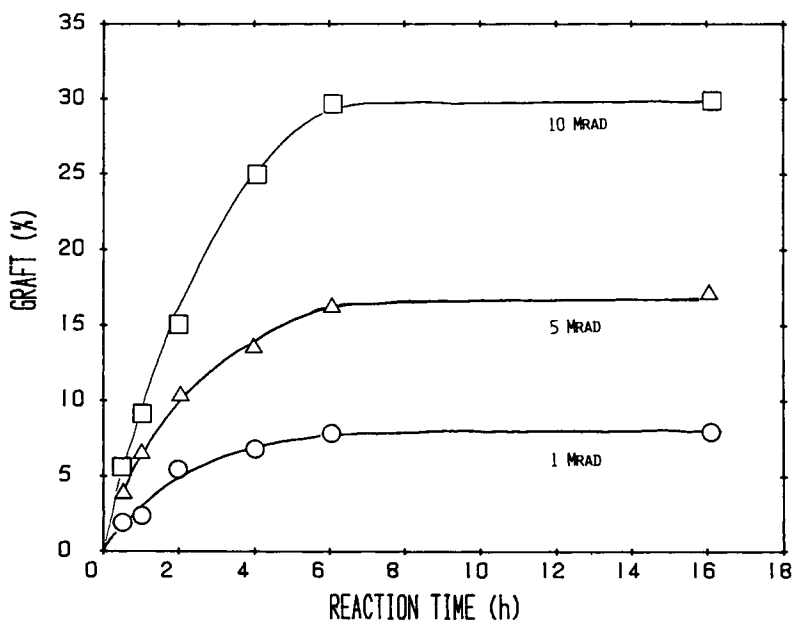


Figure 2 Effect of preirradiation dose on the grafting of acrylic acid onto conventional high-density polyethylene fibers at 50°C; concentration of Mohr's salt: 4×10^{-3} mol/L.

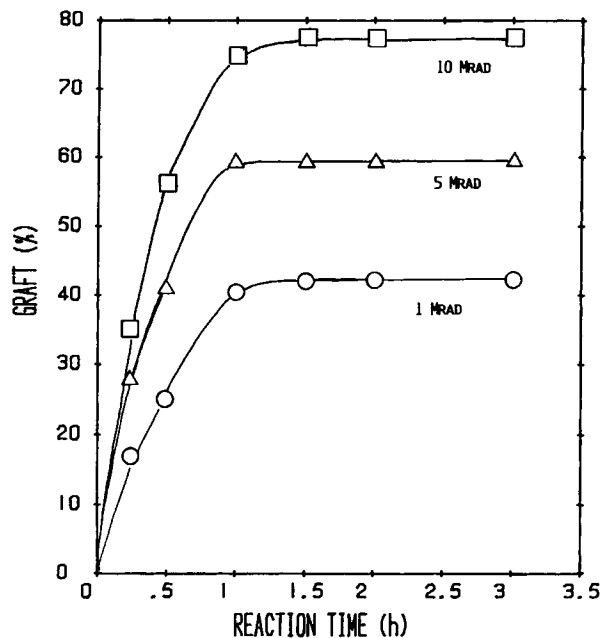


Figure 3 Effect of preirradiation dose on the grafting of acrylic acid onto high-density polyethylene film at 50°C; concentration of Mohr's salt: 4×10^{-3} mol/L.

Initial rates of grafting for the fibers of different preirradiation doses were obtained from the initial slope of the graft percent–time curves in Figures 1–3, and the results are compared in Table I, where apparent rates of grafting and normalized rates of grafting are listed. The latter rate was calculated

from the apparent rate of grafting divided by the surface area of the sample, and the value obtained for UHMW high-strength polyethylene at the corresponding preirradiation dose was taken as unity. The reason that the apparent rate of grafting is normalized to the unit surface area, which is already known from our previous studies,^{7,8} is that grafting proceeds gradually from the surface toward the inner part of the sample, because high-density polyethylene does not swell in the aqueous solution of acrylic acid, and, thus, the rate of grafting depends on the surface area of the samples. It is evident from the table that the normalized rate of grafting obtained for UHMW high-strength polyethylene is one-tenth of that obtained for high-density polyethylene and one-hundredth of that obtained for high-density polyethylene film. The degree of crystallinity of UHMW high-strength polyethylene is different from those of the other two, but the values obtained from a density method for the latter two are almost the same as for each other. Therefore, the difference found for the grafting rates of the three polyethylenes is considered to be due to the difference in orientation of the amorphous part⁹ where the grafting takes place. In the preirradiation grafting of acrylic acid onto the UHMW high-strength polyethylene as in those of the other two polyethylenes, graft percent increased with grafting time and then leveled off when the grafting time increased further. The rate of grafting was considerably lower than that of the other two.

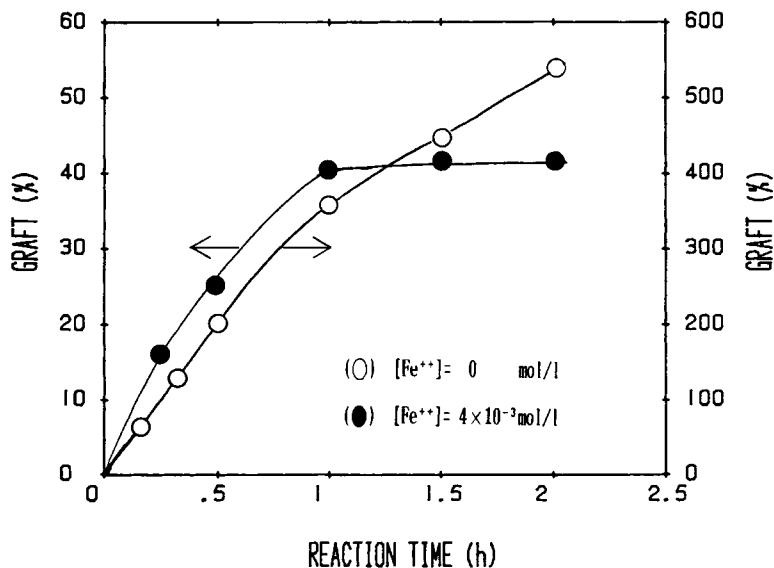


Figure 4 Effect of Mohr's salt on the grafting of acrylic acid onto UHMW high-strength polyethylene film at 50°C; concentration of Mohr's salt: (○) 0 mol/L; (●) 4×10^{-3} mol/L.

Table I Grafting Rates for Various Types of High-Density Polyethylene; Concentration of Mohr's Salt: 4×10^{-3} mol/L; Reaction Temperature: 50°C

Sample	Density ^a (g/cm ³)	Preirradiation Dose (Mrad)	Apparent Grafting Rate (%/h)	Normalized Grafting Rate (arb. unit)
UHMW high-strength polyethylene fibers (40 μm ϕ)	0.985	1	4.6	1
		5	6.0	1
		10	6.6	1
High-density polyethylene fibers (220 μm ϕ)	0.946	1	4.1	6
		5	7.8	8
		10	11.6	11
High-density polyethylene film (100 μm thick)	0.945	1	66	85
		5	104	93
		10	140	113

^a Determined by flotation method.

Effect of Preirradiation Dose

As shown in Figure 1, the initial rate of grafting and the graft percent after leveling-off (hereafter, referred as final graft percent) increased a little with increasing preirradiation dose, but above 5 Mrad, these values hardly changed with increasing preirradiation dose. However, the final graft percent and initial rate of grafting increased with increasing preirradiation dose as seen in Figure 5, where graft percent is plotted as a function of grafting time under

the same conditions as in Figure 1 except that the concentration of Mohr's salt was decreased to 8×10^{-5} mol/L.

These relations are more clearly shown in Figure 6 where the initial rate of grafting and the final graft percent, which were obtained from the curves in Figures 1 and 5, are plotted as a function of preirradiation dose. As evident from the figure, the initial rate of grafting depends not only on the preirradiation dose, but also on other reaction conditions. This means that many factors affect the inhomogeneous

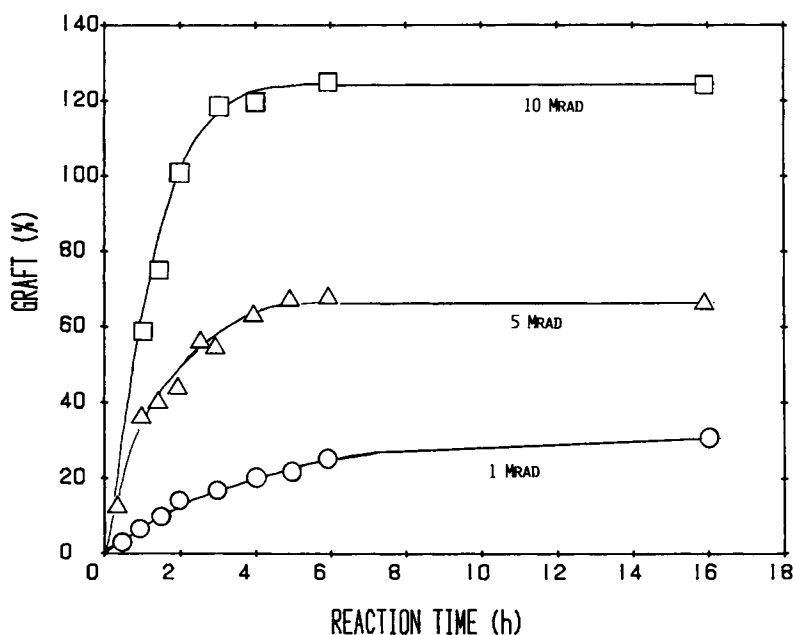


Figure 5 Effect of preirradiation dose on the grafting of acrylic acid onto UHMW high-strength polyethylene film at 50°C ; concentration of Mohr's salt: 8×10^{-3} mol/L.

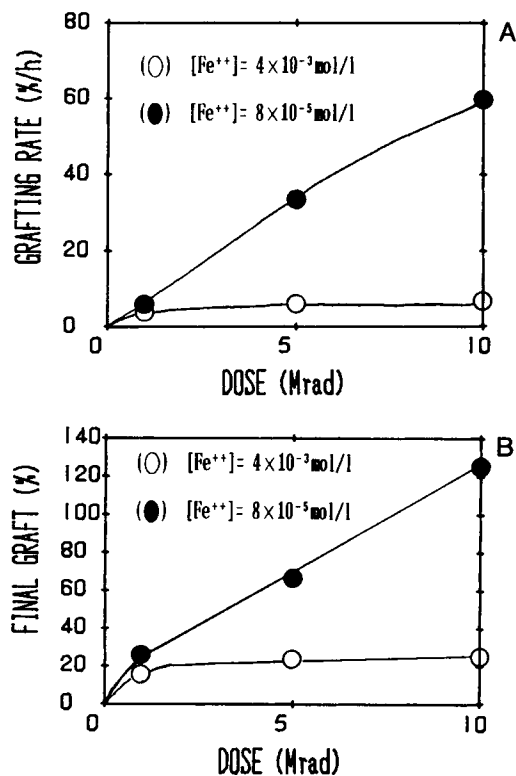


Figure 6 Effect of preirradiation dose on the rate of grafting of acrylic acid (A) and final graft percent (B) onto UHMW high-strength polyethylene fibers; reaction temperature: 50°C ; concentration of Mohr's salt: (A) 4×10^{-3} mol/L; (B) 8×10^{-3} mol/L.

grafting reaction; these factors are (1) number of initiators (usually, radicals), (2) concentration of monomer, and (3) concentration of inhibitor in the amorphous part where grafting takes place, when one considers a system in which one monomer is to be grafted onto one polymer of a unit surface area. In relation to (1), the following two factors are to be considered: (a) number of radicals existing in the crystalline part; the radicals move to the amorphous part to initiate the grafting reaction, and (b) migration rate of the radicals. The former is governed by the irradiation dose and irradiation temperature, etc., and the latter, by irradiation temperature and reaction temperature, etc. Factor (2) may be determined by (c) the monomer concentration in the monomer solution and (d) the diffusion rate of the monomer in the polymer. Factor (3) is determined by (e) the concentration of the inhibitor in the monomer solution and (f) the diffusion rate of the inhibitor into the polymer. Factors (d) and (f) depend on temperature. Therefore, reaction conditions should be changed widely to find the optimum condition for grafting.

Effect of Concentration of Mohr's Salt

In Figures 7 and 8, the initial rate of grafting and final graft percent are plotted as a function of the concentration of Mohr's salt, preirradiation dose

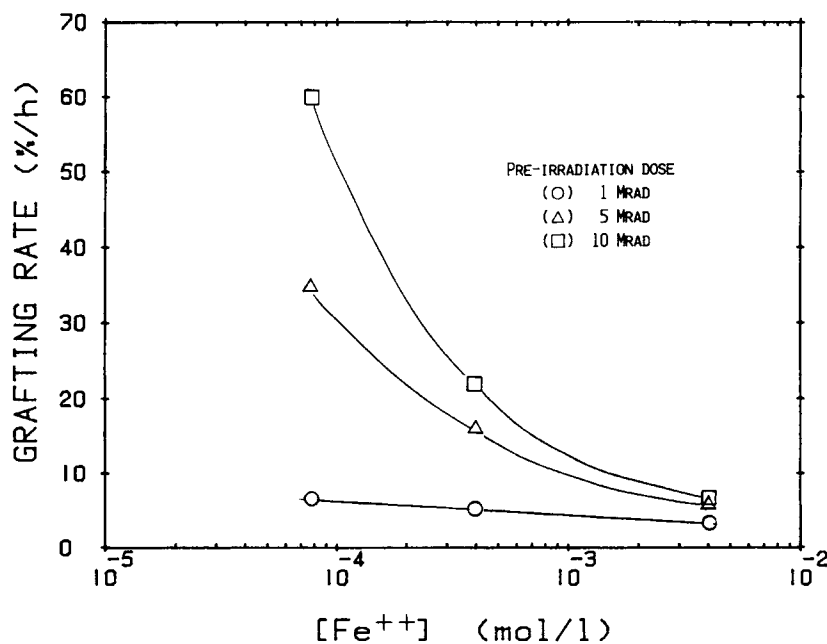


Figure 7 Effect of concentration of Mohr's salt on the grafting rate; preirradiation dose: (○) 1; (△) 5; (□) 10 Mrad.

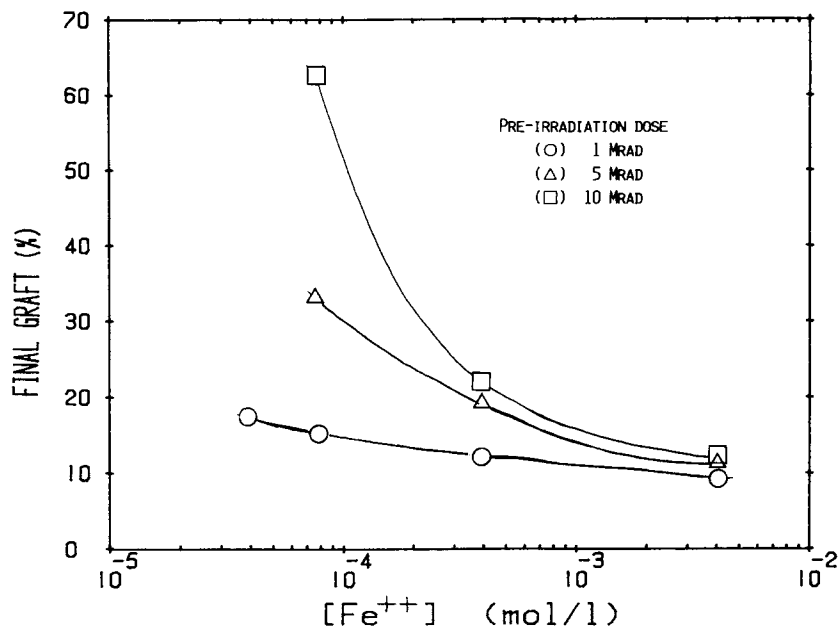


Figure 8 Effect of concentration of Mohr's salt on the final graft percent; preirradiation dose: (○) 1; (△) 5; (□) 10 Mrad.

being taken as a parameter. As shown in Figures 7 and 8, the larger effect of the inhibitor on these values is observed when the preirradiation dose is larger. In this system, Mohr's salt concerns the termination reaction.^{10,11} The reason why the initial rate of grafting and the final graft percent do not become higher with increasing preirradiation dose in the case of a high concentration of Mohr's salt is

considered to be as follows: As the number of radicals as the initiator increases with increasing preirradiation dose, the chance of termination by the ferrous ion also increases and radicals are not utilized effectively.

Grafting of as high as 126% was obtained after a reaction time of 16 h without a large increase of viscosity of the monomer solution containing Mohr's

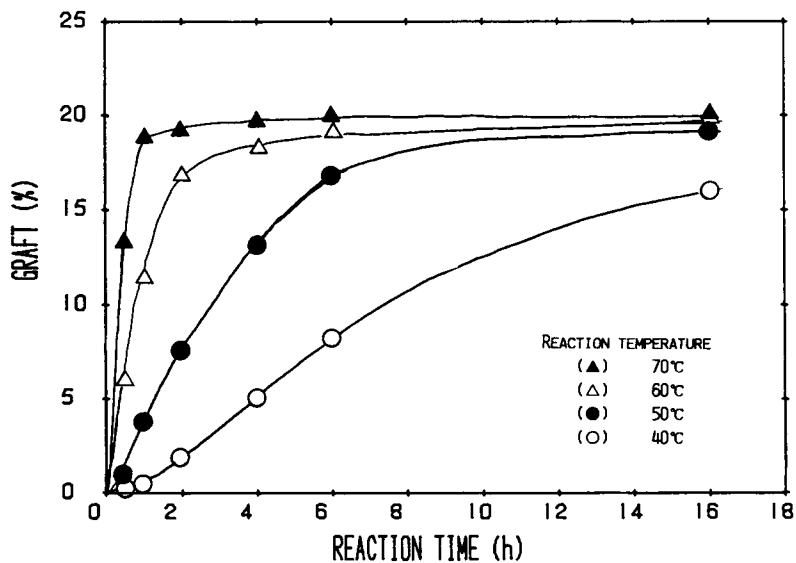


Figure 9 Effect of reaction temperature on the grafting of acrylic acid onto UHMW high-strength polyethylene fibers; preirradiation dose: 1 Mrad; concentration of Mohr's salt: 4×10^{-3} mol/L.

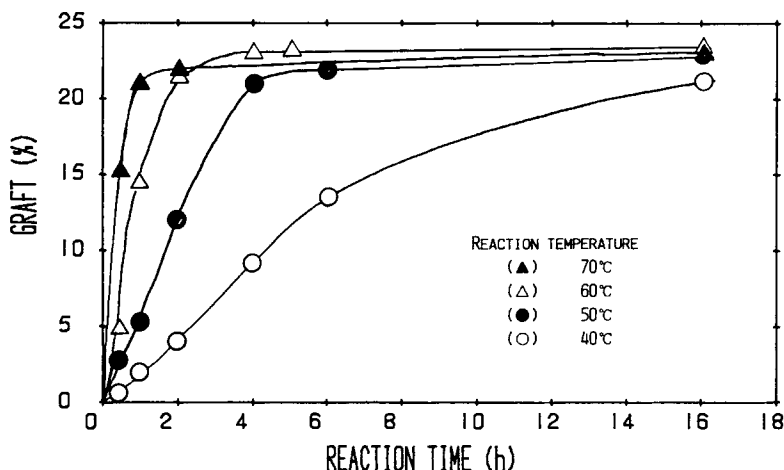


Figure 10 Effect of reaction temperature on the grafting of acrylic acid onto UHMW high-strength polyethylene fibers; preirradiation dose: 5 Mrad; concentration of Mohr's salt: 4×10^{-3} mol/L.

salt of 8×10^{-5} mol/L for the samples of the preirradiation dose of 10 Mrad. The result proved that even UHMW high-strength polyethylene fibers can be successfully grafted to a high degree by selecting proper grafting conditions, though the crystallinity is very high, i.e., the fraction of the amorphous part is only about 10%, and, furthermore, the mobility of molecules in the amorphous part is very limited.

Effect of Reaction Temperature

In Figures 9 and 10, graft percent is plotted as a function of reaction time for samples preirradiated

by 1 and 5 Mrad, respectively, where the reaction temperatures were 40, 50, 60, and 70°C and the concentration of Mohr's salt was 4×10^{-3} mol/L. For both preirradiation doses, the initial rate of grafting increases and the time required to reach the final graft percent becomes shorter as the reaction temperature increases. Arrhenius plots of initial grafting rates obtained from Figures 9 and 10 are shown in Figure 11, and the apparent activation energy determined from the slopes is 20.7 kcal/mol for both cases. Such a high apparent activation energy seems to be due to the diffusion of the monomer in the polymer.

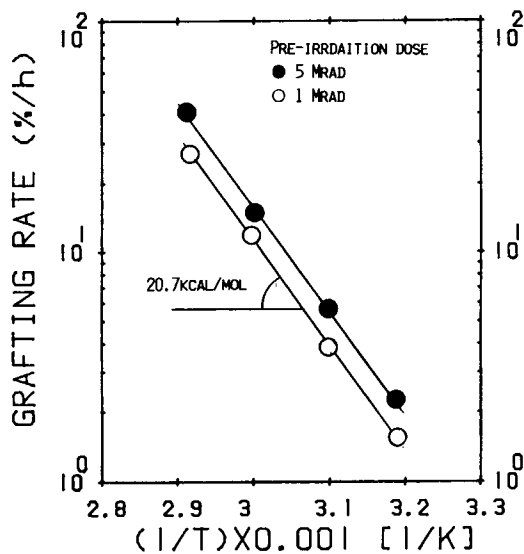


Figure 11 Arrhenius plots for the grafting rate of acrylic acid onto UHMW high-strength polyethylene fibers; concentration of Mohr's salt: 4×10^{-3} mol/L.

Properties of Acrylic Acid-Grafted UHMW High-Strength Polyethylene Fibers

Strength, elongation, and initial Young's modulus of the UHMW high-strength polyethylene fibers are

Table II Effect of Irradiation of Electron Beams on Tensile Properties of UHMW High-Strength Fibers

Dose ^a (Mrad)	Strength (g)	Elongation (%)	Young's Modulus (g/d)
0	324.4	5.2	1006
1	324.5	5.5	1040
2	314.6	5.2	1020
5	283.8	4.8	1111
10	249.0	3.6	1032
20	205.5	2.9	968

^a Irradiation was carried out in nitrogen atmosphere. Dose rate: 9.2×10^4 rad/s.

Table III Tensile Properties of Acrylic Acid-Grafted UHMW High-Strength Fibers and Their Calcium Salts

Preirradiation Dose (Mrad)	Graft (%)	Acid Form		Ca Salt	
		Strength (g)	Elongation (%)	Strength (g)	Elongation (%)
0	0	324.4	5.2	324.4	5.2
1	9.3	308.6	4.7	315.0	4.9
1	10.9	321.7	5.4	—	—
1	23.9	312.0	4.7	343.8	5.2
1	30.0	326.5	4.7	353.0	5.8
5	23.1	239.5	—	254.9	—
10	22.8	—	—	217.3	—

shown in Table II as a function of dose during irradiation in nitrogen atmosphere. Strength decreases gradually with a dose above 1 Mrad and reaches values of 87 and 77% of the original value at 5 and 10 Mrad, respectively. The decrease of the

strength was prevented when the irradiated samples were heated at 70°C for 1 h without exposing them to air. Elongation also decreases with increasing dose, indicating that scission of the molecular chain was caused by irradiation. However, decrease of the

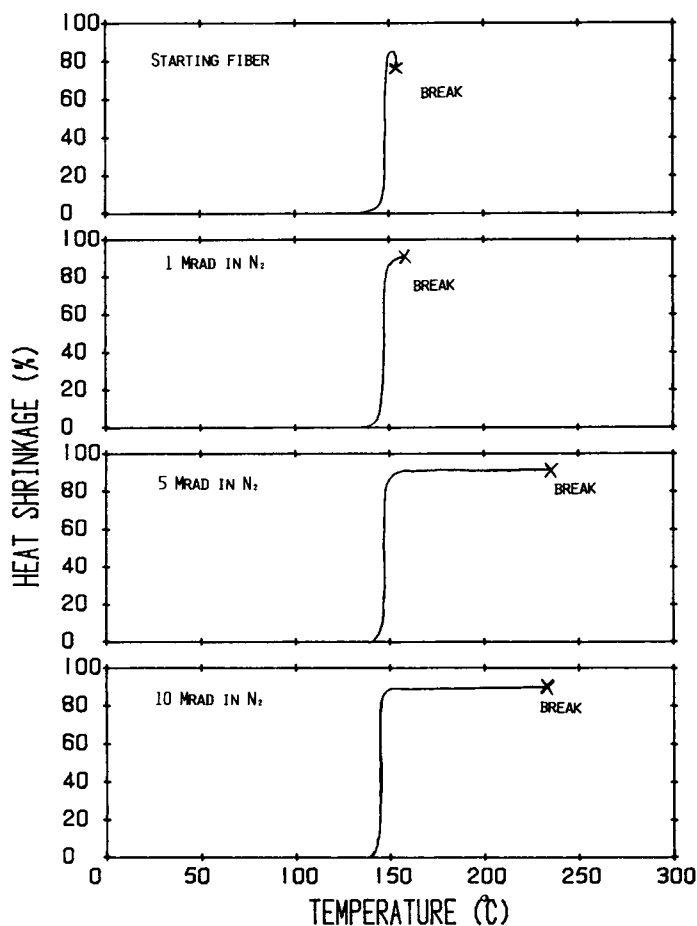


Figure 12 Effect of irradiation on the heat shrinkage of UHMW high-strength polyethylene fibers.

initial Young's modulus during the irradiation was not observed below 10 Mrad and a small decrease was observed above 20 Mrad.

Table III shows the strength and elongation of grafted fibers obtained by 1 Mrad preirradiation dose and those of grafted fibers in which carboxyl groups were converted to calcium salt. The data of strength observed for fibers obtained by a 5 or 10 Mrad preirradiation dose are also included in the table for reference. For grafted fibers obtained by a 1 Mrad preirradiation dose, strength and elongation do not decrease by the grafting of acrylic acid and the strength of the calcium salt of grafted fibers is rather higher than that of the starting fibers.

From comparison of the data in Tables II and III, it is noted that for 5 or 10 Mrad preirradiated fibers the strength and elongation decrease with preirradiation and further decrease with the grafting procedure, but slightly increase by converting carboxyl group to calcium salt. Thus, these data lead us to conclusion that the preirradiation dose should not exceed 5 Mrad.

Thermal Stability

The thermal stability of the grafted fibers was studied from the heat-shrinkage test. In Figure 12, heat shrinkage of the starting and the irradiated fibers

is shown as a function of temperature. The starting fibers begin to shrink at 130°C, and the heat shrinkage rate becomes maximum at 145°C. However, the fibers start to elongate at 150°C and break down at 154°C. A similar thermal change of fiber length is observed for the fibers irradiated by 1 and 5 Mrad, except that the breaking temperature increases to 230°C for the latter. Even for the sample irradiated by 10 Mrad, decrease of heat shrinkage is hardly seen. Thus, as for conventional high-density polyethylene fibers, improvement of the heat stability of UHMW high-strength polyethylene fibers was impossible only by irradiation.

In Figure 13, heat shrinkage of the starting and the grafted fibers is shown as a function of temperature. Again, no improvement of the heat-shrinkage property is obtained by 20% grafting.

Figure 14 shows the heat-shrinkage property of the starting fibers and the grafted fibers in which carboxyl groups were converted to calcium salt. Some improvement in thermal stability is already recognized at 9.6 graft %. For 24.3% grafted fibers, the heat shrinkage is only 11%, and they did not break down even at 300°C while retaining the fiber form.

This technique of grafting of acrylic acid onto polyethylene fibers and converting to calcium salt could be successfully applied for conventional high-

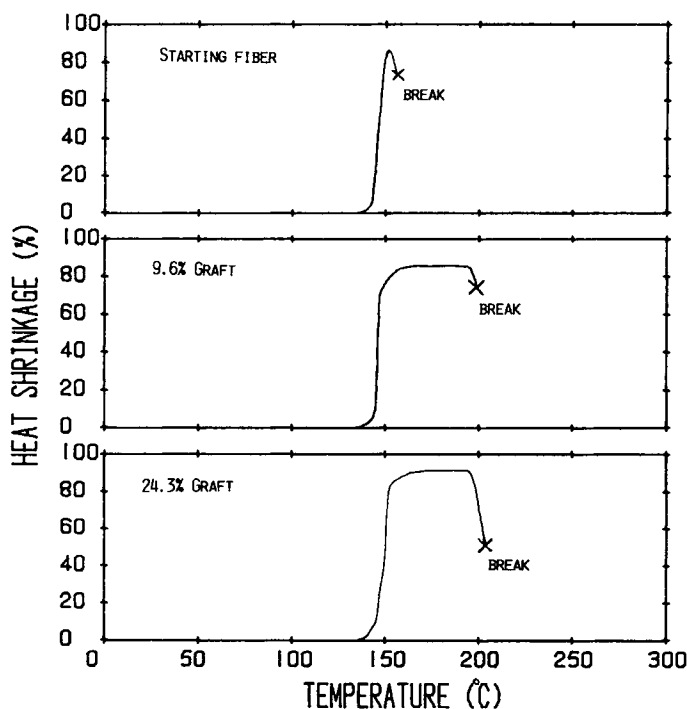


Figure 13 Heat shrinkage of acrylic acid-grafted UHMW high-strength polyethylene fibers prepared by preirradiation dose of 1 Mrad.

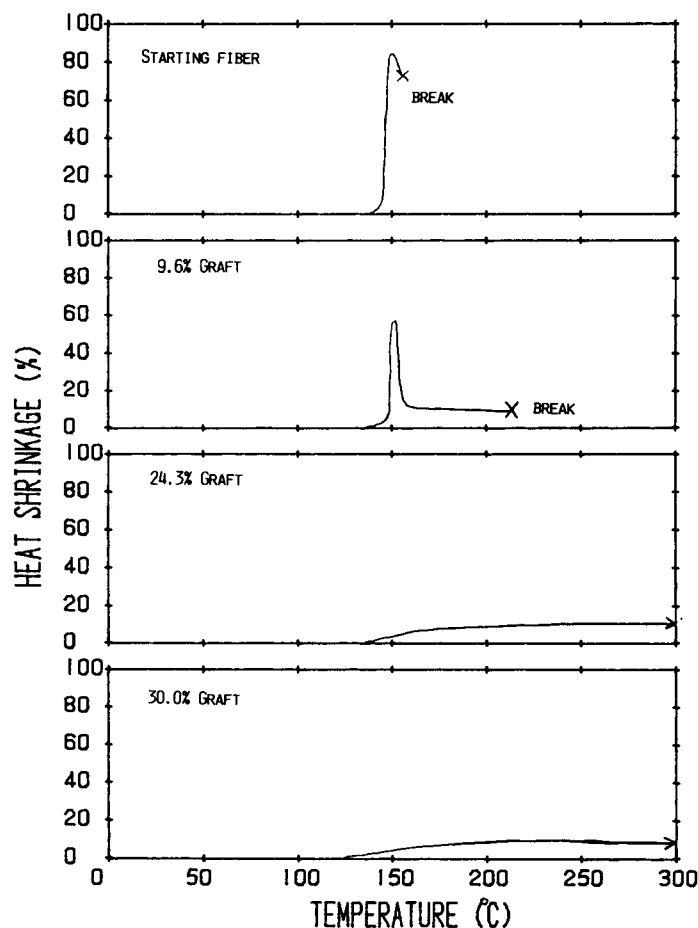


Figure 14 Heat shrinkage of calcium salt of acrylic acid-grafted UHMW high-strength polyethylene fibers prepared by preirradiation dose of 1 Mrad.

density polyethylene fibers,¹² but higher graft percent of more than 30% was necessary to obtain a similar result.

To answer the question of whether the remarkable increase of breaking temperature and reduction

of heat shrinkage would mean an increase of the melting point of the crystalline part, DSC analysis was carried out on (1) starting fibers, (2) fibers irradiated with 1 Mrad, (3) fibers grafted with 24.3%, and (4) grafted fibers (24.3%) converted to calcium salt. One endothermic peak appeared in all these DSC curves except that minor shoulders were observed at the higher-temperature side for (1) and (2). The melting points obtained from these peaks are listed in Table IV. The melting point of the starting fibers does not change by 1 Mrad irradiation. It increases when the fibers were grafted and further increases by converting to calcium salt, but the increment is only 9°C and is not high enough to explain the observed high breaking temperature (300°C) and low heat shrinkage. Therefore, their cause is not due to higher melting points. The X-ray diffraction patterns of the grafted and calcium salt-converted fibers show that a considerable amount of molecular orientation is still kept even after the crystalline parts are melted. This means

Table IV Melting Point of Grafted UHMW High-Strength Fibers Determined from DSC Heating Curve

Sample	Graft (%)	Melting Point (°C)
(1) Starting fibers	0	141.8
(2) Irradiated fibers ^a	0	141.7
(3) AA-grafted fibers ^b	24.3	144.3
(4) Ca salt of grafted fibers ^b	24.3 ^c	150.4

^a Dose: 1 Mrad.

^b Preirradiation dose: 1 Mrad.

^c Graft percent as AA form.

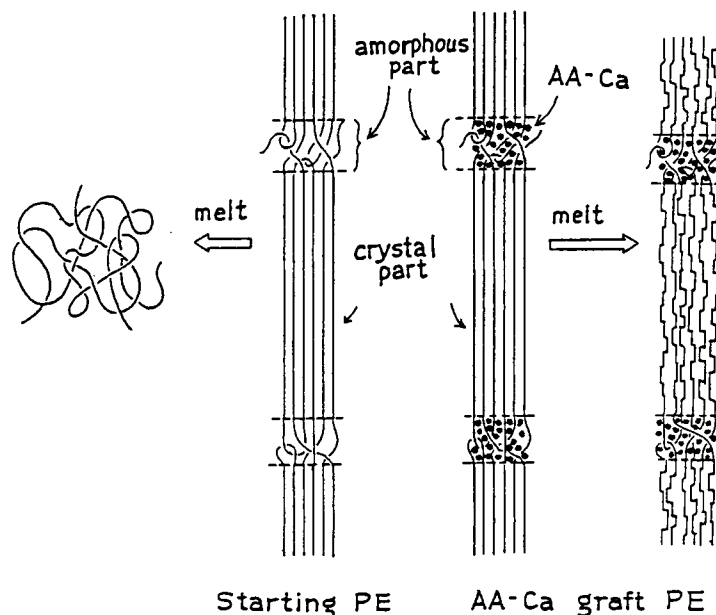


Figure 15 Schematic diagram indicating the difference in melting mechanism between starting polyethylene fibers and calcium salt of acrylic acid-grafted polyethylene fibers. Dots in the amorphous domains denote calcium salt of the grafted acrylic acid as the cross-linking point.

that the grafting and, thereafter, converting to the salt fix the amorphous domains as weak and strong cross-linking points, respectively. The strong cross-linking points increase breaking-down temperature and prevent melted segments of the crystalline parts from assuming random orientation to reduce the heat shrinkage, as shown in Figure 15. Further, a small increase of melting point caused by the introduction of calcium ions is explained by the decrease of the entropy change under melting.

Dyeability

The starting UHMW high-strength polyethylene fibers are hydrophobic and cannot be dyed with cationic dye. Since grafting of acrylic acid onto polyethylene fibers or films was successful to give dyeability to these hydrophobic materials,^{6,7,12} it is expected that grafting of acrylic acid will give dyeability to UHMW high-strength polyethylene fibers. It was found that the grafting of 0.1% makes it possible to dye homogeneously in a pale color and, by the grafting of 0.6%, the material can be dyed homogeneously in a deep color. Similar dyeability was obtained for the calcium salt of the grafted fibers.

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