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The Graft Copolymerization of a Vinyl Monomer Containing a Glucose Residue onto Polypropylene Fiber

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The graft copolymerization of 3-*O*-methacryloyl 1,2; 5,6-diisopropylidene-α-D-glucofuranose (MDG) onto polypropylene fibers was carried out by the γ-ray pre-irradiation technique in the presence of oxygen. The isopropylidene groups of the glucose residue grafted on the copolymer were removed by hydrolysis in aqueous formic acid, and the hydroxyl and hemiacetal groups were regenerated. The deacetonated fibers exhibited a considerable affinity for water vapor and could be dyed with a reactive dye.

In our laboratory, several polymers containing sugar residues were synthesized and their graft copolymerizations onto polymers were studied in a series of studies of the reactive polymer,[1,2] because the polymers containing sugar residues was expected to have a high affinity for water vapor and chemical reactivities through the hydroxyl and hemiacetal groups of the sugar residue. Polypropylene is known to have no affinity for water vapor because it has no hygroscopic groups and little chemical reactivities through the lack of an active center such as hydroxyl groups except hydrogen atoms on the tertiary carbons in the main chain. If hydroxyl groups are introduced into polypropylene by grafting a vinyl monomer with a sugar residue, the physical and chemical character of the grafted polypropylene is modified.

In the present study, 3-*O*-methacryloyl 1,2;5,6-diisopropylidene-α-D-glucofuranose (MDG), prepared from 1,2;5,6-diisopropylidene-α-glucose (DG) and methacryloyl chloride as a vinyl monomer, was used to modify polypropylene. Graft copolymerization was carried out by means of a pre-irradiation process in air. It is well known that when a polymer is irradiated in air, hydroperoxides and peroxides are generally formed on the polymer chain. Therefore, the pre-irradiated polypropylene fiber was heated in MDG to give a MDG-grafted polypropylene fiber. The polypropylene fiber grafted with MDG was hydrolyzed by acid at the acetal linkages of its sugar residue in order to generate the hydroxyl group. The behavior of the hydrolyzed grafted fiber in reaction to water vapor and its dyeability were examined. The hydrolyzed grafted fiber could be dyed with a reactive dye through chemical bonding.

Experimental

Preparation of 3-*O*-Methacryloyl-1,2;5,6-diisopropylidene-α-D-glucofuranose (MDG). MDG was prepared by the method described in the literature,[3,4] and was recrystallized from *n*-hexane at 0°C. Mp 40.5—41.5°C, $[\alpha]_D = -28.96°$ in benzene. ($[\alpha]_D = -28.8°$ in benzene[4]).

Graft Copolymerization. Unstretched polypropylene fiber, a product of the Chisso Co., was extracted with acetone for 5 hr in a Soxhlet apparatus and then irradiated by ^{60}Co in air at room temperature. An ampoule containing the irradiated fiber and the MDG-benzene solution was sealed, after having degassed by the freeze-and-thaw method under 10^{-4} mmHg. Graft copolymerization was carried out by heating the ampoule at a definite temperature. After the reaction, the resulting viscous solution was poured into a large amount of methanol, and the homopolymer thus precipitated was collected by filtration. The grafted fiber was extracted with benzene in a Soxhlet apparatus.

The percentage of grafting (G) and the grafting efficiency (F) were given by:

$$G = \frac{100(W_g - W_0)}{W_0}$$

$$F = \frac{100(W_g - W_0)}{(W_g - W_0) + \mathrm{H}}$$

where W_0 is the initial weight of the polypropylene fiber, W_g is the weight of the grafted fiber, and H is the weight of the homopolymer produced during the graft copolymerization.

Hydrolysis.[5] The isopropylidene groups were removed from the MDG units of the grafted fiber by heating the fiber in aqueous formic acid (70 wt%) at

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[1] Y. Iwakura, Y. Imai and K. Yagi, *J. Polym. Sci.*, **A6**, 801 (1968).

[2] Y. Iwakura, Y. Imai and K. Yagi, *ibid.*, **A6**, 1625 (1968).

[3] A. Chapiro, M. Magat and J. Sebban, French PV 690659, and PV 692736.

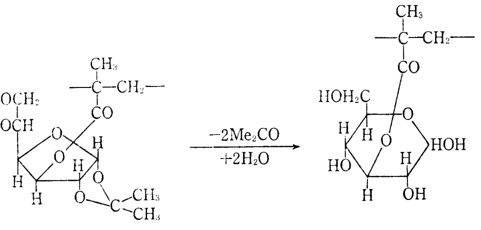
[4] S. Kimura, K. Hirai and M. Imoto, *Kogyo Kagaku Zasshi*, **65**, 688 (1962).

[5] T. P. Bird, W. A. P. Black, J. A. Colquhorn, E. T. Dewar and D. Rutherford, *J. Chem. Soc.*, **1966**, 1913.

65°C for 6 hr. After the reaction, the fiber was washed with water and acetone, and then dried *in vacuo* at 60°C. Through hydrolysis, two moles of acetone can be eliminated from the MDG (molecular wt 328) unit by the addition of two moles of water. Thus, the extent of deacetonation (D) can be calculated by the following equation:

$$D=\frac{W_g-W_d}{\frac{80}{328}(W_g-W_0)}$$

were W_d is the weight of the polypropylene fiber after hydrolysis.



Dyeing. Mikacion Brilliant Red, a product of Mitsubishi Chemical Industries, Ltd., was used as the reactive dye. A solution of 0.3 g of the reactive dye, 1 g of sodium sulfate, 0.3 g of sodium carbonate, 2 m*l* of toluene, 1 m*l* of pyridine, a small amount of an emulsifier (Scourol 400), and 40 m*l* of water was prepared as the dyeing solution. Dyeing was carried out by dipping 0.1 g of the fiber into 3 m*l* of the above solution at room temperature. After standing overnight, the fiber was extracted with water in a Soxhlet apparatus.

Results and Discussion

In general, the variables which seemed to be important in a graft copolymerization carried out by the pre-irradiation method are the dose rate of irradiation, the total dose delivered to a polymer, the monomer concentration, the reaction temperature, the crystallinity of a polymer, and the time interval between irradiation and grafting. The effects of some of these variables on the pre-irradiation of the grafting of MDG to polypropylene were examined. The percentage of grafting and the grafting efficiency are plotted against the total doses in Fig. 1. It is well known that the characteristics of some polymers, such as polyethylene and polypropylene are changed by irradiation with γ-rays because of the formation of cross linkings.[6] It has also been reported that the monomer diffusion into the irradiated polymer is, in some cases, the rate-determining step in graft copolymerization by means of the pre-irradiated method.[7]

In this study, the fiber which was irradiated with a total dose of 3 Mrad was hard and brittle and was, further, not soluble in any solvent. This change in property was considered to be caused by cross-linking. As is shown in Fig. 1, the percentage of grafting increased with an increase in the total dose, whereas the grafting efficiency decreased.

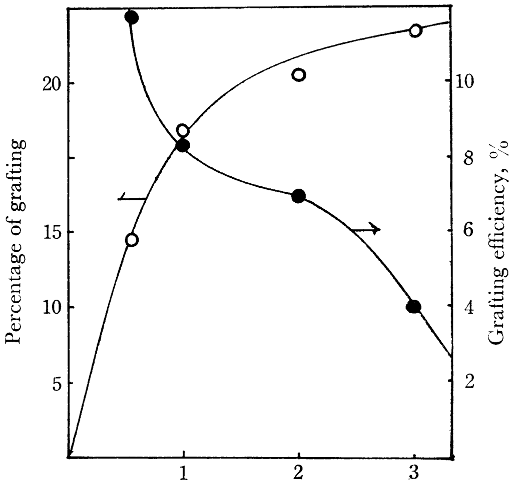


Fig. 1. Influence of irradiation total dose.
Dose rate: 2×10^5 r/hr; monomer concentration: 40 wt%; grafting temperature: 85°C; reaction time: 4 hr

The results obtained may be interpreted as follows. The cross-linked region of the fiber increased with an increased in the total dose, while the rate of the diffusion of the bulky monomer into the fiber decrease with an increase in the cross-linked region. On the other hand, the rate of the diffusion of the hydroxyl radical produced by the decomposition of hydroperoxide into the solution from cross-linked fiber is not much affected; as a result, a depression in grafting efficiency is observed.

Both the percentage of grafting and the grafting efficiency increased with an increase in the monomer concentration, as is shown in Fig. 2.

This fact can also be interpreted in terms of the diffusion of the monomer as follows. When the monomer concentration in the solution is high, the monomer concentration in the solid fiber will be high and the diffusion of the monomer from the solution into the fiber will also be high. This increases the propagation rate and results in the increase in the percentage of grafting. When the diffusion rate of the monomer from the solution into the fiber increases, the amount of homopolymer in the fiber which is polymerized by hydroxyl radical still in the fiber may be considered to increase also, because the diffusion rate of the hydroxide ion produced in the fiber into the solution is influenced by the monomer concentration in the solution. As the diffusion of the homopolymer produced in the fiber into the solution is usually very difficult, the result here obtained, the increase in the grafting

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6) A. Chapiro, *J. Chim. Phys.*, **52**, 246 (1955).

7) A. Hoffman, E. R. Gillil, E. W. Merrill and W. H. Stockmayer, *J. Polym. Sci.*, **34**, 461 (1959).

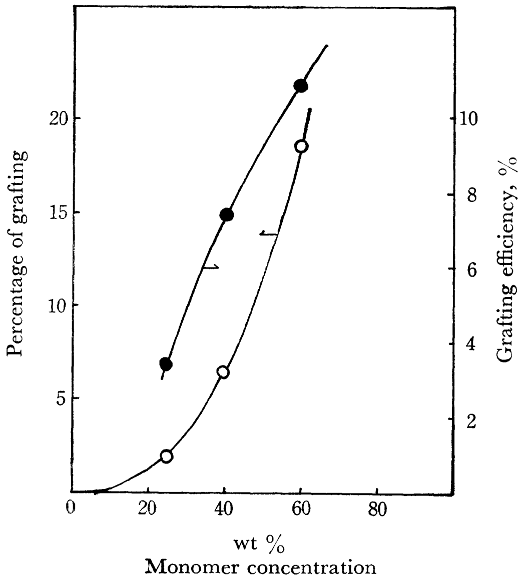


Fig. 2. Influence of monomer concentration.
Irradiation total dose: 2.0 Mrad; reaction condition: 85°C, 50 min
○ percentage of grafting
● grafting efficiency

efficiency, may be interpreted in the above terms.

The temperature dependency on the percentage of grafting is shown in Fig. 3.

The percentage of grafting increased with an increase in the temperature, whereas the grafting efficiency showed little change. These phenomena may indicate that the grafting is controlled by the diffusion of the monomer into the solid fiber. The diffusion rate of the monomer into the fiber from the solution, as well as that of the hydroxyl radical produced in the fiber, into the solution was accelerated by the increase in the reaction temperature. This results in an increase in the percentage of grafting for the reason described above, but it has almost no influence on the efficiency of the grafting.

The grafted fiber and the deacetonated fiber were

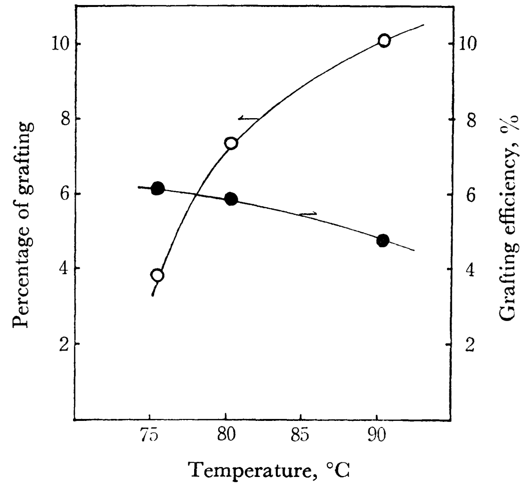
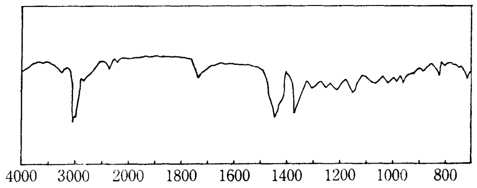
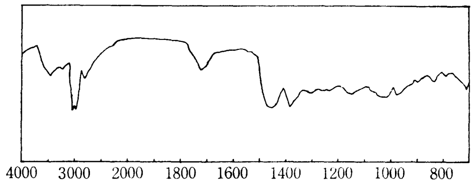


Fig. 3. Influence of reaction temperature.
Irradiation total dose: 2.0 Mrad; monomer concentration: 25 wt%; reaction time: 5 hr



MDG-grafted polypropylene, percentage of grafting 13.



Deacetonated polypropylene, percentage of grafting 43.

Fig. 4. Infrared absorption spectra of MDG-grafted polypropylene.

TABLE 1. RESULT OF DEACETONATION

Grafting reaction					Deacetonation
Total irradiation Mrad	Monomer concentration wt %	Temperature °C	Time hr	Percentage of grafting %	Extent of deacetonation %
0.55	40	85	4	11.7	34
1.0	40	85	4	17.4	47
2.0	40	85	4	20.3	89
2.0	40	85	5/6	6.5	53
2.0	60	85	5/6	18.6	93
2.0	25	75	5	3.8	101
2.0	25	80	5	7.3	92
2.0	25	90	5	10.0	84

smashed to powder in liquid nitrogen and then analyzed by means of the infrared absorption spectra. The grafted polypropylene showed an absorption characteristic of the carbonyl group at 1730 cm^{-1} and a new absorption of the hydroxyl group at 3400 cm^{-1} after hydrolysis, as is shown in Fig. 4.

This indicates that the isopropylidene groups were removed. The results of the hydrolysis are summarized in Table 1.

The extent of deacetonation was calculated from the weight loss of the fiber.

The introduction of MDG units onto the polymer changed the physical properties of the fiber. A fiber grafted over 200% with MDG was obtained when the grafting reaction was carried out at 85°C for 9.5 hr. The fiber thus obtained was very brittle and was easily torn to pieces. The water-vapor adsorption aspect of the deacetonated homopolymer was also examined. The deacetonated homopolymer, when placed in air saturated with water vapor, adsorbed the water vapor in time and gradually became a viscous mass. The water adsorbed by a deacetonated grafted fiber placed in air saturated with water vapor increased with an increase in the percentage of grafting, as is shown in Fig. 5.

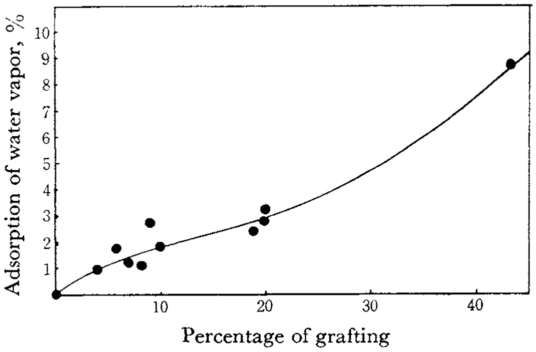


Fig. 5. Water vapor adsorption by the deacetonated grafted fiber at saturated vapor pressure

The amount of water adsorbed by the MDG units of the deacetonated grafted fiber is plotted against the percentage of grafting in Fig. 6.

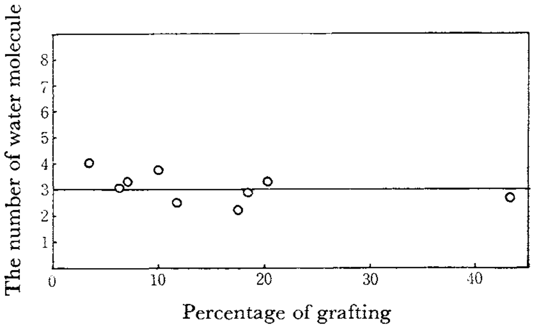


Fig. 6. The number of water molecule adsorbed by each MDG unit of deacetonated grafted fiber

Though no clear conclusion can be deduced from this figure, it can be pointed out that one MDG monomer unit adsorbs about three water molecules on the average.

Reactive dyes generally react with compounds containing hydroxyl groups, such as cellulose, by making covalent bond. The dyeability of the deacetonated fibers was examined with Mikacion Brilliant Red (MBR) as the reactive dye; this was the same kind of dye as Procion M. The shade of the colored fiber was responsible for the percentage of grafting. The observation of the cross-section of the dyed fiber by means of a microscope showed that the dyeing reaction occurred evenly in the fiber.