Polymerization of Styrene, Methyl Methacrylate and Acrylonitrile onto Wool by Gamma Irradiation

(Preliminary Report)

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Styrene, methyl methacrylate and acrylonitrile were polymerized onto wool by irradiating it in the solution of each of these monomers by the gamma rays. The radiation doses applied ranged from $2\cdot10^5$ to $4\cdot10^6$ roentgens. A considerable amount of polymer was fixed onto wool after thorough extraction, which was defined as the amount of grafting. The stress-strain curves of fibers grafted moderately by the monomers are modified with the result that the initial modulus, stress at yield point and tensile strength in dry and wet state are increased, while the large extensibility characteristic to wool is well retained. Extremely highly grafted fibers lose the original character of wool and become brittle. Supercontraction is reduced by grafting the wool moderately by the monomers, but, when the amount of grafting is too large, the character of wool is overcome by that of synthetic polymer. Microscopic examination revealed that the scales of fibers grafted highly by styrene are splitted hither and thither giving spaces to the grafting polymer. Association of synthetic polymer with wool cannot be simply attributed to grafting.

INTRODUCTION

Preparation of graft copolymer by reacting a monomer with a natural polymer such as cellulose has drawn an intense interest in recent years from a scientific and practical point of view. In this paper the preliminary study on the grafting of some monomers onto wool using gamma irradiation is reported.

The material used in this study is the same as that described in the previous report.[1]

200–250 mg of air dried fibers were immersed in 20 ml of monomer solution in a test-tube, which was sealed by fusing the upper part leaving an air space upon the liquid. The tube was placed in the center of irradiation chamber of the gamma ray installation, of which a description was given in the previous paper[1].

The composition of each monomer solution is as follows:

For styrene,	Styrene : Aceton = 1 : 1 (in volume).
For methyl methacrylate,	MMA : Aceton = 1 : 1 (in volume).
For acrylonitrile,	8 vol. % solution of acrylonitrile in water.

Aceton had not been dehydrated beforehand, and it contained a small amount of water. Wool also was used in air-dried state. Therefore, there would exist an amount of water in the mixture enough to catalyze the polymerization reaction.

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After being irradiated, the fibers were separated and extracted with a solvent pertinent to remove the homopolymer. The solvent used was, benzene for polystyrene, aceton for polymethyl methacrylate, and dimethylformamide for polyacrylonitrile. Extraction lasted for one week, the solvent being replaced every day by a fresh one. The substrate was dried carefully, and the increase in weight was determined, which, according to the definition, arbitrary as it is, denotes the amount of grafting.

1. AMOUNT OF GRAFTING AND STRESS-STRAIN CURVES

The percentage of grafting is shown in Table 1 as a function of irradiation dose. The radiation doses applied are those, which, according to the result of the previous report, do not bring about any apparent changes in tensile strength and elongation, when the fibers are irradiated in the absense of monomer.

Table 1.

A. Grafting of styrene onto wool		
Time of irradiation, hr.	Radiation dose, roentgen	Amount of grafting*, %
1	$2 \cdot 10^5$	0.0
5	10^6	30.8
10	$2 \cdot 10^6$	81.9
20	$4 \cdot 10^6$	194.0
B. Grafting of methyl methacrylate onto wool		
1	$2 \cdot 10^5$	0.1
2	$4 \cdot 10^5$	40.1
5	10^6	87.1
C. Grafting of acrylonitrile onto wool		
1	$2 \cdot 10^5$	53.4

* Expressed by the increase in weight in %.

It is interesting to see that a considerable amount of monomer polymerizes onto wool by gamma irradiation with doses from 10^5 to 10^6 roentgens. Practical interest is drawn to the facts relative to the mechanical properties of grafted wool. In this regard it would be interesting to investigate the stress-strain curves of grafted wool. Each individual curve was obtained by taking an average of thirty load-elongation curves of fibers of the same sort. Since the fineness of individual fibers is not the same, the value of load was converted into the value of stress by dividing it with the original cross-sectional area. In this case it was assumed that the cross-section is circular.

Fig. 1 shows the stress-strain curves in dry and wet state of the original fibers and the fibers grafted by polystyrene. It is interesting to note that the stress-strain curve is modified by grafting styrene onto wool. At the amount of grafting up to 81.9% of the original weight of wool, the original character of stress-strain curve of wool is well preserved, but the stress at the yield point is increased both in dry and wet state and therefore, the initial modulus is increased, especially noticeably in the case of wet state. Tensile strength is not reduced, rather has a tendency to increase, while the elongation at break retains the original large value characteristic to wool. However, at the extremely great amount of grafting such as 140% of the original weight of wool, the fibers lose the original wool character, as can be seen from the fundamentally modified stress-strain curve shown in Fig. 1. The elongation at break is strikingly decreased, and the fibers become brittle. These experiments suggest that there would exist a possibility to modify or, it is to be hoped, to improve the practical behavior of wool without losing its virtue by grafting an appropriate amount of a synthetic monomer onto wool.

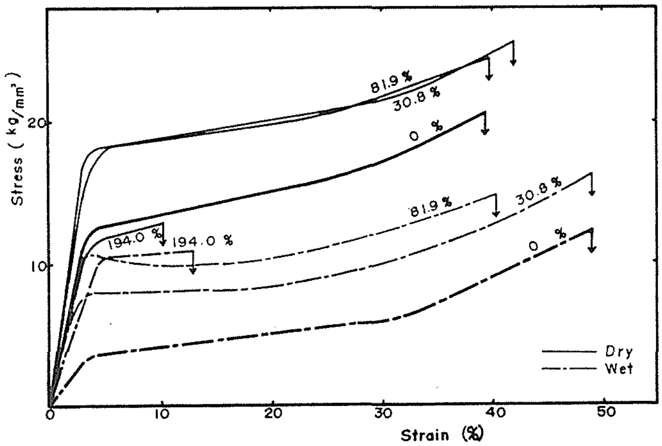


Fig. 1. Stress-strain curves of wool fibers grafted by styrene in comparison with those of the original fibers. The figures noted on the curves denote the amount of grafting in percent.

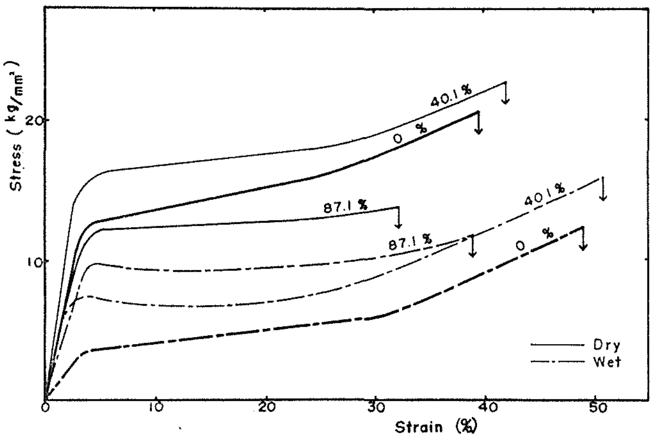


Fig. 2. Stress-strain curves of wool fibers grafted by methyl methacrylate in comparison with those of the original fibers. The figures noted on the curves denote the amount of grafting in percent.

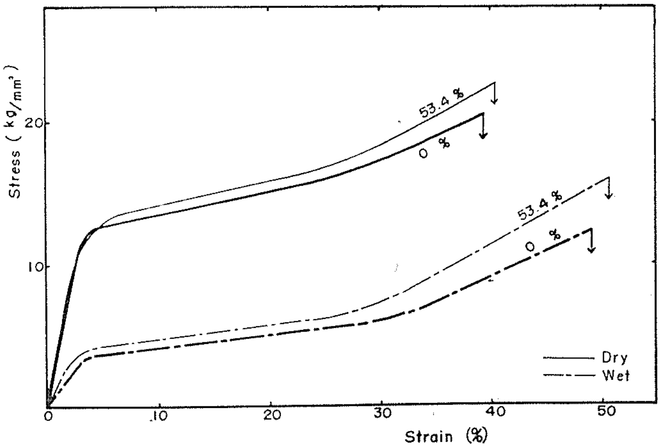


Fig. 3. Stress-strain curves of wool fibers grafted by acrylonitrile in comparison with those of the original fibers. The figures noted on the curves denote the amount of grafting in percent.

Similar effect can be seen also in the case of grafting by methyl methacrylate, as shown in Fig. 2. At an amount of grafting of 40.1%, the tensile strength and the initial modulus in dry and wet state are increased, while a high elongation of wool is well retained. At a greater amount of grafting, say at 87.1%, the elongation is decreased, and the fibers become brittle and harsh.

So far as this study is concerned, the effect of grafting by acrylonitrile is smaller than those of styrene and methyl methacrylate, as can be deduced from Fig. 3.

2. SUPERCONTRACTION

Supercontraction is also a subject of practical interest. An apparatus similar to that proposed recently by Whiteley[2] was used, and the contraction of fibers in 20% phenol solution in water at 97–98°C was measured. Plotting of supercontraction against time for the fibers grafted by styrene to various degrees is shown in Fig. 4. With increasing time of irradiation, that is — with increasing amount of grafting, the supercontraction decreases. However, in the case of more highly grafted fibers, the nature of substrate polymer is overcome by that of the grafted polymer, since the fibers elongate instead of contracting immediately after immersion in the medium.

Similar effect can be seen with the fibers grafted by methyl methacrylate, as shown in Fig. 5.

Grafting by acrylonitrile has a smaller effect upon supercontraction, similar to the effect upon stress-strain curves, as shown in Fig. 6.

3. MICROSCOPIC OBSERVATION

As mentioned before, the definition of amount of grafting is very arbitrary, since the amount of polymer which is fixed onto fibers and is proof against

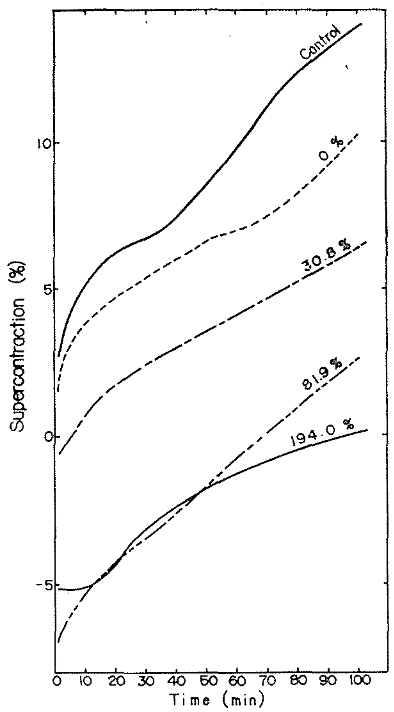


Fig. 4. Plots of supercontraction in 20% phenol solution vs. time for the fibers grafted by styrene. The figures noted on the curves denote the amount of grafting in percent.

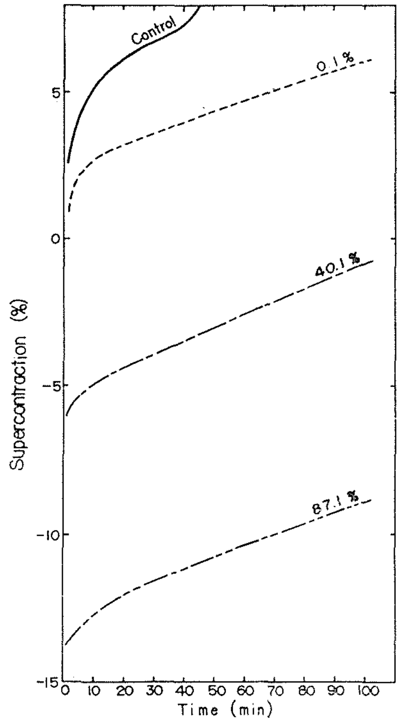


Fig. 5. Plots of supercontraction in 20% phenol solution vs. time for the fibers grafted by methyl methacrylate. The figures noted on the curves denote the amount of grafting in percent.

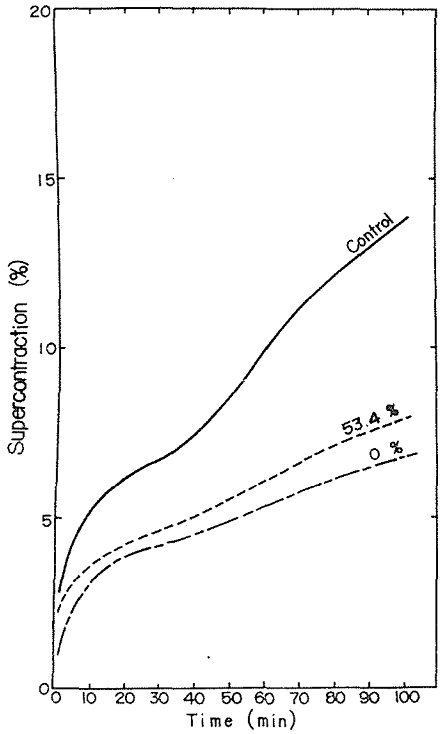


Fig. 6. Plots of supercontraction in 20% phenol solution vs. time for the fibers grafted by acrylonitrile. The figures noted on the curves denote the amount of grafting in percent.

extraction decreases considerably when the fibers are disintegrated, as we have confirmed in a number of cases of grafting onto cellulose. Furthermore, the structure of surface of wool fibers is very complicated compared to any other natural and synthetic fibers and therefore, it would be more difficult to remove completely the homopolymer penetrated deep into very fine interspaces. The photomicrographs of cross-sections of highly grafted wool by styrene by gamma irradiation show that the scales covering the surface of wool are torn hither and thither and furnish the grafting polymer with spaces to come into contact with

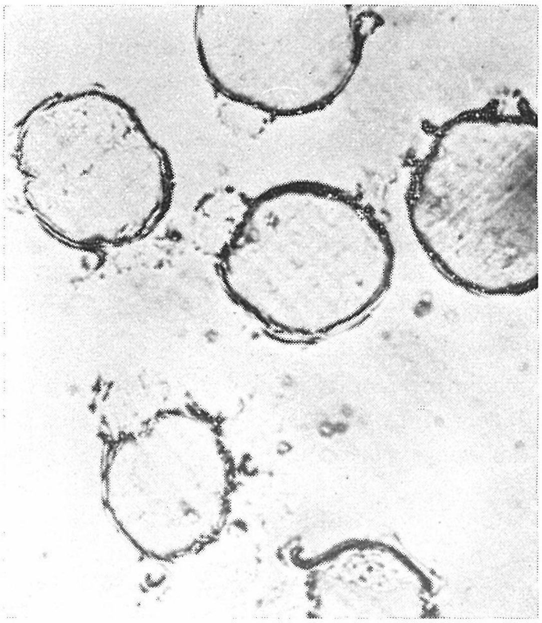
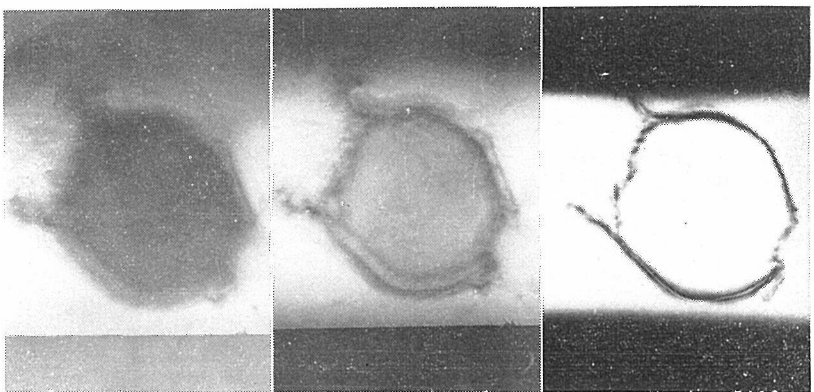


Fig. 7. Photomicrograph of cross-sections of wool fibers grafted by styrene by gamma irradiation. Amount of grafting is 194%. Scales are torn partially. So far as this experiment is concerned scales are broken only on the side of B-cortex (ortho-cortex).



Wavelength 2537 Å 2800 Å 4360 Å

Fig. 8. Ultraviolet photomicrographs of cross-sections of wool grafted by styrene by gamma irradiation.

cortex, as indicated in Fig. 7. Ultraviolet photomicrograph, Fig. 8, also shows this. It must be noticed here that both keratin and styrene have each a characteristic ultraviolet absorption. It is interesting to note that the cross-sections of fibers which were irradiated without a monomer with a dose of 10^7 roentgens did not show the splitting of surface, as is described in the previous paper.* Therefore, it must be assumed that the presence of a monomer in a solvent gave rise to the splitting of scales.

The experiments show that the amount of polymer fixed onto fiber under the condition as described here cannot be attributed simply to the grafting and therefore, the effect of polymerization upon the properties of fibers would be considerably influenced by the distribution of polymer on and within the fibers and by the manner, in which the polymer associates with wool.

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REFERENCE

(1) M. Horio, K. Ōgami, T. Kondo and K. Sekimoto, *This Bulletin*, 41, 1 (1963).
(2) K. J. Whiteley, *Textile Res. J.*, 32, 123 (1962).

* See Fig. 8 (b) of the preceding paper entitled "*Effect of Gamma Irradiation upon Wool Fibers*", p. 7 of this issue.