Properties of Graft Copolymerized Cellulose Fiber. (I)

Styrene Grafted Cotton

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Received January 22, 1964

Styrene was graft copolymerized onto cotton by high energy radiation and some properties of the grafted cotton were studied.

It was found that excellent thermoplasticity, dimensional stability and water repellency were given to cotton by this graft copolymerization without appreciable decreasing of the mechanical properties.

INTRODUCTION

Recently a considerable number of researches on the graft copolymerization onto cellulose has been reported, but very little was known on the property of the grafted fiber in detail.

The main object of this work is to improve the dimensional stability, thermoplasticity (heat settability) and elasticity, etc. of cotton fiber.

It has been found by Sakurada[1,2] that styrene or methyl methacrylate could be very easily graft copolymerized onto cellulose or polyvinyl alcohol, if the graft reaction were carried out in the presence of water or methanol. In the present work these results were applied to cotton and various properties of styrene graft copolymerized cotton were studied.

EXPERIMENTAL AND DISCUSSION

1. Tensile Properties

The cotton cloth used in this work is scoured and bleached 30's calico (not mercerized; furnished by the Toyo Spinning Co.).

Table 1. Tensile properties of styrene grafted cotton (mutual irradiation grafting by Co^{60} γ-ray).

% Grafting (%)	Single Fiber		Warp Yarn			
	Tenacity (g)	Elongation (%)	Tenacity (g)		Elongation (%)	
			Ordinary	Knot	Ordinary	Knot
0	4.65	5.55	254	270	10.84	13.34
50	4.44	6.36	233	208	11.79	19.41
77	4.43	6.87	183	193	13.08	17.79
91	6.50	11.37	189	189	20.70	23.59

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The cotton cloth containing 20% of water was put into the glass tube, and after adding of styrene (ST) monomer the mixture was irradiated by Co^{60} γ-ray at room temperature, the total dose of which was 2.5×10^6 r (mutual or direct irradiation grafting).

The tensile properties of ST grafted fiber and yarn taken out from the grafted cotton cloth are shown in Table 1.

As shown in Table 1, the tensile strength and knot strength are lowered only slightly at least at a % grafting of 40-50%, at which the satisfactory thermoplasticity (heat settability) is gained as described afterwards. The ultimate elongation is increased by grafting.

Next, St was graft copolymerized onto the same cotton cloth by pre-irradiation grafting method. The cotton cloth was pre-irradiated in air with Van de Graaff accelerator (1.5 Mev., 100 μA, mean dose rate 2×10^4 r/sec) in Osaka Laboratories of Japanese Association for Radiation Research on Polymers, and then polymerization was carried out in water-methanol solution of St (water : St : methanol is 1 : 6.6 : 17.6 in volume) at 50°C for various durations under vacuum lower than 10^{-4} mmHg. The homopolymer was removed by benzene extraction.

The properties of cotton thus grafted are shown in Table 2.

Table 2. Tensile properties of styrene grafted cotton (Pre-irradiation grafting by Van de Graaff accelerator, total dose 1.4×10^6 r).

Time of Polymerization (hr)	% Grafting (%)	Cloth Shrinkage (%)		Warp Yarn	
		Warp	Filling	Tenacity (g)	Elongation (%)
Untreated	0	—	—	331	12.4
Irradiation only	0	—	—	305	16.0
1	1.8	0	0	—	—
2	8.9	2	0	—	—
4	41.2	18	12	—	—
5	44.2	22	14	266	14.4
7	83.1	22	14	202	12.9

Similarly to the results shown in Table 1, the tensile strength of grafted cotton yarn is not much lowered until a % grafting of 40-50% is reached. The cloth shrinks to some extent during grafting.

Other properties of these St grafted cotton are shown in the following.

2. Crease Resistance

The crease resistance of St grafted cotton cloth was measured.

The test sample of cloth (1×4 cm ; the larger dimension in warp direction) was folded at the center of its long direction and a definite weight was put on it for 5 min., then the weight was removed and after a defininite time the crease angle was measured.

The results obtained for some St grafted cotton clothes are shown in Table 3.

Table 3. Crease revovery (%) of styrene grafted cotton cloth.

% Grafting (%)	500 g Weight for 5 min.		50 g Weight for 5 min.	
	2 min. after[c]	30 min. after[c]	2 min. after[c]	30 min. after[c]
0 (Untreated)	37.2	40.0	46.7	55.6
41.2[a]	37.2	43.1	56.4	61.4
46.2[b]	37.3	43.1	58.1	64.7

[a] Preirradiation grafting method.
[b] Mutual irradiation grafting method.
[c] Time after the removing of the weight.

It is shown that when the weight of 500 g was used the crease recovery did not vary by the St grafting, but in the case of lower weight some increase was observed. The effect of the stiffness of the grafted cloth on the crease recovery will be discussed afterwards.

Next, a similar experiment was carried out to study the effect of % grafting on the crease resistance using other grafted samples prepared by preirradiation method.

The method of preparation is shown in Table 4.

The results obtained using these samples are shown in Table 5.

Table 4. Styrene crafting onto cotton cloth by the preirradiation with the electron beam of Van de Graaff accelerator.
(Total dose of pre-irradiation 1×10^6 r ; composition of the solution used for polymerization, styrene 30 : methanol 70 ; polymerized under vacuum at 50°C ; homopolymer was extracted with benzene).

Time of polymerization (hr)	% Grafting (%)
—	7.8
3	18.0
5	49.0
7	72.3
8	60.7

Table 5. Crease recovery of styrene grafted cotton clothes of various % grafting.

% Grafting (%)	Crease recovery (%)[b]	
	500 g Weight[b]	50 g Weight[b]
0	43.5	48.3
7.8	47.5	54.9
18.0	46.7	59.1
49.0	46.9	58.2
60.7	33.4	46.7
72.3	38.0	47.5

[a] Crease recovery at 2 min. after the removing of the weight.
[b] Time of weighting is 5 min.

It is found from the results shown in Table 5 that in the case of 500 g weight the crease recovery of cloth is somewhat increased when the % grafting is lower than 50%, but decreased for higher % grafting.

In the case of 50 g weight similar results were obtained, but the degree of increase of the crease recovery due to grafting was more remarkable than in the case of 500 g weight.

3. Thermoplasticity (Heat Settability)

It may be expected that excellent thermoplasticity (heat settability) will be given to cotton by St grafting.

To examine this property, the sample cloth (1×4 cm; the larger dimension in warp direction) was folded at the center of its long direction and was pressed with iron for 1 min., which weighted 5 lb and was about 175°C. Then the iron was removed and the pleat angle was measured after keeping the cloth for 30 min. in air at room temperature or immersing in the water of room temperature for 10 min. and drying.

The result obtained for a sample of 44.2% grafting (see Table 2) is shown in Table 6.

Table 6. Heat settability of styrene grafted cotton cloth.

% Grafting (%)	Pleat angle after hot ironing	
	30 min. after ironing	After immersing in water
0	30°	79°
44.2	7°	2°

The pleat of the St grafted cotton cloth does not change even if it is immersed in water. So it was found that the St grafted cotton had very excellent heat settability. Even if the water was heated to boil, the change of pleat form was little.

It is very interesting that the adhesion of St grafted cotton cloth did not occur when it was pressed with hot iron, even if the % grafting was 81.3%.

Next, the following experiment was carried out in the same way using St grafted cotton cloth of various % graftings to study the relation between heat settability and % grafting. The results obtained are shown in Table 7. Though the heat settability is unsatisfactory when the % grafting is less than 20%, it is very excellent in the case of % grafting more than about 40%.

Table 7. Heat settability of styrene grafted cotton cloth of various % grafting[a].

% Grafting (%)		0	7.8	18.0	49.0	60.7	72.3
Pleat Angle	30 min. After Ironing	19°	13°	11°	3°	1°	0°
	After Immersing in Water	66°	35°	21°	6°	6°	5°

[a] Described in Table 4.

When the cloth is immersed in the water solutions of soap or various surfactants after pleated with hot iron, the effect of soap or surfactant was slight.

4. Tearing Strength

The tearing strength of St grafted cotton cloth was measured by tongue method using 1×3.5 cm sample cloth.

As shown in Table 8, the tearing strength of the grafted cloth was somewhat lowered. However, it is probable that this decrease of the tearing strength is, to some extent, due to the stiffening of cloth owing to St grafting. So, as will be described later, the softening treatment was given to the grafted cloth and it was found that the tearing strength of the grafted cloth was improved by the softening treatment.

Table 8. Tearing strength of styrene grafted cotton cloth[a].

% Grafting (%)	Tearing strength (g)
0 (Untreated)	1239
0 (Irradiation only)	903
7.8	735
18.0	750
49.0	677
60.7	623
72.3	643

[a] Described in Table 4.

5. Flex Fatigue Test

The flex-life of the single fiber taken out from the St grafted cotton cloth was measured using the Franz-Henning type flex-life tester. As is shown in Table 9 the grafted fiber showed somewhat low flex-life.

Table 9. Flex fatigue test of styrene grafted cotton fiber[a].

% Grafting (%)	Flex-life (cycles)[b]
0 (Untreated)	4286
7.8	1289
18.0	1405
49.0	933
60.7	669
72.3	935

[a] Described in Table 4.
[b] Applied load : 0.5 g.

6. Flex-Abrasion Test

Flex-abrasion test of the St grafted cotton cloth was carried out using Universal type Wear Tester. The sample cloth for this test was St grafted by electron beam pre-irradiation method. Test piece was 1 cm width. The

compression load of 0.5 lb. and tension load of 1 lb. were applied. Standard test was carried out in the air of 20°C, RH 61%. Wet test was performed after immersing the sample cloth in water of 70°C for 10 min. and further in water of room temperature for 20 min. and then wiping the surface of cloth with filter paper. As is shown in Table 10, the flex-abrasion resistance was found to be increased by St grafting.

Table 10. Flex-abrasion test of styrene grafted cotton cloth.

% Grafting (%)	Flex-abrasion life (cycles)	
	Standard	Wet
0 (Untreated)	358	181
0 (Irradiation only)	332	126
29.2	374	211
57.3	609	295
83.1	1772	1078

7. Shrinkage of St Grafted Cloth by Hot Water

St grafted cotton cloth was immersed in the boiling water and, after drying the shrinkage of the cloth was estimated. As is shown in Table 11, no shrinkage was observed for St grafted cloth. From this result and the excellent heat settability as described before, it can be said that the St grafted cotton has satisfactory dimensional stability.

Table 11. Shrinkage in boiling water.

% Grafting (%)[a]	Shrinkage (%)	
	Warp	Filling
0 (Untreated)[b]	1.8	3.5
0 (Irradiation only)	0	2.2
44.2	0	0
83.1	0	0

[a] Sample clothes are the same as described in Table 2.
[b] Washed with methanol.

8. Absorption of Water and Water Vapor and Drying Property

The absorption of water and water vapor, and drying property of St grafted cotton cloth were measured.

The sample cloth was immersed in the water of 19.5°C and weighed immediately after the wiping off the water on the surface of cloth with filter paper. It was weighed again after being kept in room temperature for 30 min. Further it was weighed after storing for 2 days in a desiccator at RH 65%. Finally its bone-dried weight was measured. The results obtained are shown in Table 12. It is found that, by St grafting, the absorption of water and water vapor are decreased, and the drying velocity is increased.

Table 12. Absorption of water and wates vapor and drying property of styrene grafted cotton cloth.

% Grafting (%)	Absorption of water (%)		Absorption of water vapor (%) (RH 65%)
	Immediately after wiping	After keeping 30 min. in room	
0	91.56	13.11	9.22
44.2	74.62	12.26	6.77
83.1	47.86	8.55	3.85

9. Water Repellency

It was found that St grafted cotton cloth does not easily sink into water at room temperature, so its water repellency was examined.

The testing method used are as follows:

(1) Spray method: JIS L1004 Testing method for cotton fabric.

(2) Water drop method: JIS L1005 Testing method for rayon staple fabric. 0.1 cc of distilled water of 20°C is dropped down from a height of 2 cm. on the sample cloth laid horizontally, and the time required for the permeation of the water drop into cloth is measured.

(3) Sinking method: Sample cloth (1×1 cm) is put on the surface of distilled water (20°C) and the time required until the cloth starts to sink down into water is measured.

As shown in Table 13, the St grafted cotton cloth showed remarkable water repellency.

Table 13. Water repellency of styrene grafted cotton cloth.

% Grafting (%)	Spray method	Sinking method	Water drop method
0	0	0 sec.	0 sec.
21.2[a]	50	> 2 hr.	>2 hr.
0	0	1 min.	
7.8[b]	0	>20 hr	
18.0[b]	50	>20 hr	
49.0[b]	50	>20 hr	
72.3[b]	50	>20 hr	
60.7[b]	50	>20 hr	

[a] Mutual irradiation grafting method.

[b] Pre-irradiation grafting method.

10. The Softening Treatment of the St Grafted Cotton Cloth

By the St grafting the stiffness of the cloth is increased. Below a % grafting of about 30% the increase of the stiffness is comparatively small, but the 40% grafted cloth is fairly stiff and the 60% grafted cloth becomes very stiff. As this stiffening might be attributed to some extent to the mechanical fixing or sticking of fabric structure due to the swelling and shrinkage of

cloth, so the grafted cloth was rubbed to soft by hand in soap solution.

The stiffness, crease recovery and tearing strength of the St grafted cotton cloth estimated before and after rubbing by hand about 20 times in 0.5% water solution of Marseilles soap at 50°C are shown in Table 14.

Table 14. The Effect of the softening treatment on the properties of styrene grafted cotton cloth.

	Stiffness[a] (Warp)				Crease recovery[b] (Warp) (%)				Tearing strength[c] (g)	
% Grafting (%)	0	45.4	69.2	89.8	0	45.4	69.2	89.8	0	63.9
Untreated	1.62	5.78	>18	>18	38.8	39.7	32.2	29.5	767	653
Treated	—	1.98	7.52	11.7	—	48.3	45.6	43.2	—	854

[a] Measured with Clark Softness Tester ; values of L^3W.

[b] 500g weight for 5 min. ; measured 2 min. after weight is removed.

[c] Tongue method.

It is found that the stiffness of the grafted cloth can be remarkably decreased by this softening treatment and crease recovery and tearing strength are improved.

11. Dyeability of the St Grafted Cotton Cloth

St grafted cotton clothes (% grafting 0-77%) were dyed with various direct, vat, azoic, reactive and disperse dyes.

It was found that the St grafted cotton, even if the % grafting reached up to about 50%, could be dyed with direct, vat or azoic dyes as well as the ungrafted cotton, and moreover could be fairly dyed with disperse dye.

These study of the dyeing of St grafted cotton were carried out by Professor R. Tanaka, Kyoto Technical University in cooperation with authors and may be reported in detail in another paper.

SUMMARY

1. Study on the properties of cotton graft copolymerized with styrene by high energy irradiation was carried out.

2. The graft copolymerization was done by the irradiation of total dose $2\text{-}3\times10^6$r. The decrease of fiber strength was slight.

3. When the % grafting reaches to about 40%, the grafted cotton cloth shows excellent heat settability. It does not shrink in boiling water. Its dimensional stability is excellent.

4. The tearing strength of cotton cloth and the flex-life of cotton fiber were somewhat lowered by grafting, but the flex-abrasion resistance was improved.

5. The absorption of water and water vapor were decreased by styrene grafting, and the drying velocity was increased.

6. Styrene grafted cotton cloth showed remarkable water repellency.

7. Styrene grafted cotton fabric has fairly stiff hand, but by rubbing by

hand in warm soap solution, it can be remarkably softened, and the crease recovery and tearing tearing strength are increased.

8. Styrene grafted cotton fabric can be easily dyed with direct, vat, azoic dyes and also with disperse dye.

ACKNOWLEDGEMENTS

The authors are pleased to express their thanks to Professor I. Sakurada for his suggestion and discussion; to Dr. T. Okada and Dr. F. Kimura for their preparation of grafted cotton cloth.

This work is a part of the research carried out by request of Japan Cotton Technical Institute and under the aid of Toyo Spinning Company. The authors wish also to thank them.

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