Title	Properties of Graft Copolymerized Cellulose Fiber. (II) : Butadiene Grafted Cotton and Rayon (Special Issue on Physical, Chemical and Biological Effects of Gamma Radiation, VI)
Author(s)	Tsuji, Waichiro; Imai, Masazo; Kadono, Yoriko; Ichikawa, Kimiko
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1965), 43(1): 94-101
Issue Date	1965-03-25
URL	http://hdl.handle.net/2433/76049
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Properties of Graft Copolymerized Cellulose Fiber. (II)

Butadiene Grafted Cotton and Rayon

Waichiro TSUJI, Masazo IMAI, Yoriko KADONO
and Kimiko ICHIKAWA*

(Tsuji Laboratory, Institute for Chemical Research Kyoto University)

Received January 30,1965

Butadiene, butadiene-styrene or butadiene-acrylonitrile were graft copolymerized onto cotton or rayon using high energy radiation and some properties of the grafted fibers were studied.

It was found that elasticity, heat-settability, abrasion-resistance, adhesion to rubber were markedly improved and the coefficient of friction of fabric was decreased by the grafting.

INTRODUCTION

We have reported that excellent thermoplasticity, dimensional stability and water repellency were given to cotton cloth by the graft copolymerization of styrene[1], but elasticity (crease recovery) was not remarkably improved. In respect of this point it is expected that the graft copolymerization of diene monomer such as butadiene will show more interesting effect.

It has been found by Sakurada[2] that butadiene, butadiene-styrene or butadiene-acrylonitrile could be easily graft copolymerized onto cellulose fiber using high energy radiation, if the graft reaction was carried out in the presence of water or methanol. In the present work these results were applied and various properties of grafted rayon or cotton were studied.

EXPERIMENTAL AND DISCUSSION

The cellulose fibers used in this work are an ordinary viscose rayon staple fiber and the cotton cloth which is the same as used in our previous work. The graft copolymerization was carried out by the mutual or simultaneous irradiation grafting method using Co^{60} γ-ray. The dose rate was 8.5×10^3r/hr and the irradiation temperature was 30°C.

1. Tensile and Elastic Properties of the Grafted Rayon

Rayon staple fiber was immersed in the methanol solution of butadien (Bt) and irradiated by Co^{60} γ-ray at 30°C under vacuum of 10^{-4}mm Hg. Monomer concentration, total dose and % grafting are shown in Table 1. The homopolymer was removed by benzene extraction.

Next, butadiene-styrene (Bt-St) and butadiene-acrylonitrile (Bt-AN) were

* 辻和一郎, 今井政三, 門野順子, 市川喜美子

graft copolymerized onto rayon fiber using methanol solution of monomers. % grafting thus obtained are shown in Tables 2 and 3.

Using some of these grafted rayon fiber, tensile and elastic properties were examined. Results obtained are shown in Table 4.

In Table 4 the value of the elastic recovery of nylon 6, polyester, acrylic and acetate fibers were given for comparison.

It is shown that up to about 200% grafting the decrease of fiber tenacity is comparatively slight. Even in the case of more than several hundred % grafting, about 60% of original fiber tenacity is retained. The elongation is remarkably

Table 1. Grafting of butadiene onto rayon fiber.

Sample No.	Total dose (r)	Monomer conc. (Wt.%)	% Grafting (%)
A-896	1.39×10^{6}	14.7	29.5
A-885	1.35×10^{6}	82.0	48.0
A-884	9.9×10^{6}	56.4	72.5
a′-1	—	—	86.3
a′-2	1.5×10^{6}	—	161

Table 2. Grafting of butadiene-styrene onto rayon fiber.
(total dose 1.35×10^{6}r)

Sample No.	Bt/Bt+St (Wt.%)	Monomer conc. (%)	% Grafting (%)
A-886	75.6	78.8	66.4
A-884	57.4	77.6	126.3
A-889	52.2	82.6	170.1
A-890	34.3	80.6	233.6
A-891	24.7	80.8	615.4
A-892	17.6	81.4	1601.7

Table 3. Grafting of butadiene-acrylonitrile on to rayon fiber.

Sample No.	Bt/Bt+AN (Wt.%)	Monomer conc. (%)	Total dose (r)	% Grafting (%)
A-918	36.0	44.3	2.1×10^{5}	97.2
A-923	32.2	46.8	3.8×10^{5}	435
A-919	44.1	47.6	6.0×10^{5}	3245
A-920	37.6	49.2	7.5×10^{5}	6340
A-880	47.2	49.5	9.9×10^{5}	9329
A-924	54.1	45.9	2.1×10^{5}	77.1
A-925	63.7	45.7	8.0×10^{5}	1885
A-930	55.6	47.0	9.4×10^{5}	2714
A-881	51.0	64.5	9.9×10^{5}	9111
A-931	63.9	43.5	9.4×10^{5}	13023

Table 4. Tensile and elastic properties of grafted rayon fiber.

Sample No.	Monomer	Bt in monomer (Wt.%)	% Grafing (%)	Tenacity[a] (g)	Elongation (%)	Elastic recovery(%)[b] Immed. after Unloading	After 2 min
Untreated	—	—	0	4.56	18.0	50.6	59.8
A-885	Butadiene	100	48.0	3.62	30.4	52.2	61.2
A-884			72.5	3.66	20.6	—	—
a'-1			86.3	—	—	57.2	74.2
a'-2			160.8	—	—	67.3	82.3
A-886	Butadiene + Styrene	75.6	66.4	3.75	35.8	55.4	70.8
A-888		57.4	126.3	3.83	32.3	64.0	79.0
A-889		52.2	170.1	4.88	33.6	71.2	87.8
A-891		24.7	615.4	2.33	31.0	—	—
A-924	Butadiene + Acrylonitrile	54.1	77.1	4.26	29.6	61.4	76.2
A-918		36.0	97.2	4.24	28.0	65.2	80.0
A-923		32.2	435	2.96	37.1	—	—
A-925		63.7	1885	2.93	130.0	91.3[c]	94.1[c]
nylon 6						95.3	100.0
Tetoron[d]						77.8	86.3
Acrylic						69.8	87.0
Actate						76.3	88.2

[a] Tensile strength was measured on the fiber tester called K.S. Type Senimeter, using a gauge length of 1cm. The mean value of about 10 readings was taken.
[b] Elastic recovery of elongation was measured at 5% elongation, using a gauge length of 2cm. The mean value of 5 readings was taken.
[c] In the case of A-925 (Bt+AN) the elastic recovery at about 100% elongation was shown.
[d] Polyethylene terephthalate fiber Japan.

increased by grafting.

When % grafting exceeds about 100%, the elastic recovery is considerably increased and reaches the level of acrylic, acetate or polyester fibers. It seems that the butadien-acrylonitrile grafting is most effective for the improving of the elastic recovery. It is interesting that the rayon fiber which has 1885% grafted butadiene-acrylonitrile (A-925) has 130% elongation and more than 90% elastic recovery when released from 100% extension. When % grafting reaches up to several thousands, the fiber becomes rather brittle, though the fiber form is still retained.

Another experiments were carried out using rayon and polyvinyl alcohol (PVA) fiber (unheat-treated and unformalized). Results obtained are shown in Table 5.

On the grafted rayon results almost similar to Table 4 are shown. The increase of the elastic recovery of PVA fiber is not remarkable, because the unheat-treated and unformalized PVA fiber has originally rather good elasticity.

Next the wet and knot tenacities of the grafted rayon were examined using another samples. The condition of grafting and the properties of grafted fibers are shown in Tables 6 and 7.

Table 5. Tensile and elastic properties of grafted rayon and PVA fiber.

Fiber	Sample No.	Monomer solution	Total dose (r)	% Grafting (%)	Tenacity (g)	Elongation (%)	Elastic recovery (%) Immed. after Unloading	Elastic recovery (%) After 2 min
Rayon	Untreated	—	—	0	4.50	18.6	56.8	66.8
	A-3	MeOH: Bt:St 20:2:8	3.5×10^5	46.1	4.80	32.0	55.5	66.7
	A-4		5.5×10^5	113	5.00	33.6	55.3	65.8
	A-6	MeOH: Bt:AN 5:3:2	2.0×10^5	117	5.00	32.3	64.7	79.0
	A-7		5.9×10^5	490	3.65	28.7	73.2	88.0
	A-8		3.9×10^6	131	4.71	24.1	67.8	82.3
PVA	Untreated	—	—	0	7.74	32.3	61.5	87.0
	PVA-5	MeOH: Bt:AN 5:3:2	5.9×10^5	155	7.30	71.8	62.2	89.2
	PVA-6		8.9×10^5	279	7.78	74.1	65.5	90.0
	PVA-7		3.9×10^5	54	7.08	42.7	62.7	84.8

Table 6. Grafting onto rayon fiber.

Sample No.	Monomer	Pretreatment	Monomer solution (cc) Methanol	Bt	AN	Total dose[a] (r)	% Grafting (%)
B- 275	Butadiene	Water Swelling	0	10	0	3.5×10^5	31.5
A-1528			0	10	0	4.8×10^6	224
B- 279	Butadiene + Acrylonitrile	Water Swelling	0	6	6	2.1×10^5	159
A-1524		None	4.5	9	9	4.1×10^5	458
B-282		Water Swelling	0	6	6	4.0×10^5	537
A-1526		None	3	6	6	4.4×10^5	679
B- 280		Water Swelling	0	6	6	4.6×10^5	795

[a] Dose rate-Butadien 2.1×10^4r/hr, Butadiene-acrylonitrile 8.5×10^3r/hr,

Table 7. Tensile properties of grafted rayon fiber.

Sample No.	Monomer	% Grafting (%)	Tenacity (g) Standard	Wet	Knot	Elongation (%) Standard	Wet	Knot
Untreated A	—	0	4.50	—	—	18.6	—	—
Untreated B			4.62	4.08	3.28	19.7	35.1	14.7
B- 275	Butadiene	31.5	4.99	3.05	3.20	36.2	46.4	21.2
A-1528		224	3.59	2.36	2.47	37.7	66.4	27.3
B- 279	Butadienen + Acrylonitrile	159	5.35	3.35	4.03	41.7	64.0	22.5
A-1524		458	3.00	2.04	3.29	25.6	53.8	26.7
B- 282		537	4.96	3.46	4.55	32.0	76.4	36.0
A-1526		679	2.53	1.84	2.67	26.9	75.0	41.6
B- 280		795	5.66	3.69	5.24	58.7	157.4	82.9

Table 8. Elastic properties of grafted rayon fiber.

Sample No.	Monomer	% Grafting (%)	Elastic recovery (%) Immed. after Unloading	Elastic recovery (%) After 2 min.
Untreated A	—	0	50.5	59.8
Untreated B	—	0	48.8	59.0
A-1528	Butadiene	224	71.6	86.0
B- 279	Butadiene + Acrylonitrile	159	60.6	83.8
B- 282	Butadiene + Acrylonitrile	537	75.7	93.0
B- 280	Butadiene + Acrylonitrile	795	80.3	99.2

The wet and knot tenacities are not remarkably changed by the grafting. Elastic recovery of the grafted rayon fiber is excellent as shown in Table 8.

2. Properties of the Grafted Cotton

Various properties of the butadiene and butadiene-acrylonitrile grafted cotton were examined. The conditions of grafting are shown in Table 9.

a) **Tensile and elastic properties.** Thensile and elastic properties of the warp yarn of the grafted cotton cloth were measured. The results obtained are shown in Table 10. On some samples tensile tests were carried out using fibers pulled out from the warp yarn.

It is shown that the tenacity of warp yarn decreases somewhat larger than the fiber. It may be due to the decrease of the coefficient of friction by grafting as shown later. The elastic recovery of butadiene grafted yarn is excellent.

b) **Stiffness and crease recovery.** Stiffness and crease recovery of grafted cotton cloth were measured. As shown in Table 11, the stiffness of cloth is increased by the grafting, but can be decreased to almost the same level as ungrafted cloth by the rubbing with fingers in the soap solution. The crease recovery is fairly increased by butadiene-acrylonitrile.

c) **Thermoplasticity (Heat settability).** The butadiene grafted cloth (E-1 and E-2; test piece 1×4 cm; the larger dimension in warp direction) was folded at the

Table 9. Grafing of butadiene and butadiene-acrylonitrile onto cotton fabric.

Sample No.	Monomer	Pretreatment	Monomer solution	Total dose[a] (r)	% Grafting (%)	Shrinkage of fabric during grafting Warp	Shrinkage of fabric during grafting Filling
E- 1	Butadiene	Water swelling[b]	Butadiene[b]	6.0×10^5	39.6	14	4
E- 2	Butadiene	Water swelling[b]	Butadiene[b]	1.2×10^6	77.4	18	4
E-21	Butadiene	Water swelling[b]	Butadiene[b]	5.6×10^5	44.3	14	6
E-25	Butadiene	Water swelling[b]	Butadiene[b]	6.2×10^5	45.6	12	4
E-11	Butadiene + Acrylonitrile	None	MeOH:Bt:AN 5:3:2	2.0×10^5	39.6	6	2
E-12	Butadiene + Acrylonitrile	None	MeOH:Bt:AN 5:3:2	5.9×10^5	77.6	12	2
E-13	Butadiene + Acrylonitrile	None	MeOH:Bt:AN 5:3:2	3.9×10^6	65.3	12	6

a) Dose rate 8.5×10^3 r/hr:30°C

b) Water swelled fabrics were irradiated with γ-ray in butadien under vacuum. The degree of water swelling of E-1, E-2 and E-25 were 105, 82.7 and 99.0%.

Table 10. Tensile and elastic properties of grafted cotton.

Sample No.	Monomer	% Grafting (%)	Warp yarn[a)] Tenacity (g)	Warp yarn[a)] Elongation (%)	Fiber[b)] Tenacity (g)	Fiber[b)] Elongation (%)	Elastic recovery (%)[c)] Immed. after Unloading	Elastic recovery (%)[c)] After 2 min.
Untreated	—	0	282	6.9	4.43	4.3	82.8	89.0
E- 1	Butadiene	39.6	105	10.2	3.01	4.7	99.7	100.0
E-21	Butadiene	44.3	211	9.8	4.49	8.2	—	—
E- 2	Butadiene	77.4	153	10.3	—	—	83.1	90.8
E-11	Butadiene + Acrylonitrile	39.6	252	10.8	4.94	8.0	—	—
E-13	Butadiene + Acrylonitrile	65.3	241	8.9	—	—	—	—
E-12	Butadiene + Acrylonitrile	77.6	229	10.9	—	—	—	—

a) Gauge length 5 cm; mean value of 20–30 readings.
b) Gauge length 1 cm; mean value of 30 readings.
c) Elastic recovery of warp yarn from 3% extension; gauge length 5 cm; mean value of 5–6 readings.

Table 11. Stiffness and crease recovery of grafted cotton cloth.

Sample No.	Monomer	% Grafting (%)	Stiffness[a)]	Crease recovery (%)[b)] 500g Weight	Crease recovery (%)[b)] 50g Weight
Untreated	—	0	3.67	37.2	46.7
E- 1	Butadiene	39.6	2.94	46.5	49.6
E-21	Butadiene	44.3	23.88	30.7	36.0
E-21[c)]	Butadiene	〃	3.93	40.9	41.4
E- 2	Butadiene	77.4	26.62	44.0	51.8
E-11	Bt+AN	39.6	8.26	54.8	57.0

a) Measured with Clark Softness Tester; values of L^3W.
b) Measured with Monsanto Type Tester: 500 or 50 g weight was loaded for 5 min. and crease angle was measured 2 min. after the removing of the weight.
c) The grafted cloth was rubbed with fingers in 0.5% water solution of Marseilles soap at 50°C, then washed with water and dried.

center of its long direction and was pressed with iron for 1 min., which weighed 5 lb. and was heated to 170–175°C. Then the iron was removed and the pleat angle was observed after keeping the sample for 30 min. in air at room temperature or immersing it in water of room temperature for 10 min. and drying. The pleat angle was almost zero degree in either cases. Even when the water was heated to boil, the change of pleat form was slight. Thus it was known that the butadiene grafted cotton had excellent heat settability as styrene grafted cotton. The sticking of grafted cloth was not found when it was pressed with hot iron.

d) **Flex-abrasion test.** Flex-abrasion test of the butadiene grafted cotton cloth was carried out using Universal Type Fabric Wear Tester. Sample No. E-25 was used for this test. Test piece was 1cm width. The compression load of 0.5 lb. and tension load of one lb. were applied. As shown in Table 12, the flex-abrasion resistance was found to be increased by butadiene grafting especially the softening treatment was applied.

e) **Coefficient of friction of the butadiene grafted cloth.** The butadiene grafted cotton cloth had some slippery feel, so its coefficient of friction was measured using D.S. Type Tester of the coefficient of friction of fabric. The load of 400g was applied on the test piece, the dimension of which was 5×7cm. The pulling velocity was 10cm/min. As shown in Table 13, butadiene grafted cloth (E-25) has lower value of static and dynamic coefficient of friction.

f) **Adhesion of styrene and butadiene grafted cotton cloth to rubber.** It is interesting to examine the adhesion of grafted cellulose fiber to rubber. It was reported that the adhesion of rayon cord to rubber was increased 76% by grafting of styrene[3]. So we examined the adhesion of styrene and butadien grafted cotton cloth to rubber. These tests were carried out in the laboratory of Bando Rubber Manufacturing Co. through their kindness.

The procedure of the test is as follows:

Grafted cloth → resorcine-formaldehyde resin (RF) treatment → rubber paste coating → bonding to top rubber sheet → vulcanisation → stripping test.

Results obtained are shown in Table 14. The increase of adhesion by grafting is generally recognized.

g) **Dyeability of butadiene grafted cotton cloth.** Dyeability of butadiene grafted cotton cloth with various kinds of dyes was examined by Professor R. Tanaka, Kyoto Technical University, in co-operation with the authors. It was found that the butadiene grafted cotton, even if % grafting reached up to about 50%, could be dyed with direct, vat or azoic dyes nearly as well as the ungrafted cotton, similarly to the case of styrene grafted cotton.

Now, as described above, butadiene grafted cellulose fibers have various interesting properties, but the yellowing in grafting is a problem remained in future,

Table 12. Flex-abrasion resistance of butadiene grafted cotton cloth (Sample No. 25; % grafting of butadiene is 45.6%)

Sample	Flex-abrasion life (cycles)
Untreated	188
Grafted cloth	907
After softening[a]	5185

[a] The softening treatment of the grafted cloth is the same as described in Table 11 (c).

Table 13. Coefficient of friction of butadiene grafted cotton cloth.

Sample	Coefficient of friction	
	Static	Dynamic
Between untreated clothes	1.07	0.78
Between untreated and grafted clothes[a]	1.06	0.79
Between grafted clothes[a]	0.85	0.59

[a] Sample No. E-25. % grafting of butadiene is 45.6%

Table 14. Adhesion of grafted cotton cloth to rubber

Grafted monomer	% Grafting (%)	RF Treatment	Rubber paste[a]	Top rubber sheet[a]	Adhesive strength (kg/15mm)
Styrene	0	None	NR	NR	2.0~2.1
	43.6				2.2~2.3
	0	Treated	NR	NR	3.7~3.9
	43.6				4.2~4.3
	0	None	SBR	SBR	4.4~4.5
	43.6				5.8~6.0
	0	Treated	SBR	SBR	7.8~7.9
	43.6				8.3~8.4
Butadiene (E-21)	0	None	NR	NR	4.0~4.5
	44.3				4.3~5.3
	0	Treated	NR	NR	4.2~5.4
	44.3				4.5~5.5
	0	None	SBR	SBR	5.0~5.6
	44.3				6.3~6.6
	0	Treated	SBR	SBR	6.7~7.4
	44.3				9.1~9.2

[a] NR: natural rubber, SBR: styrene-butadiene rubber.

though the discoloration can be prevented to some extent by the use of the protecting agent such as phenyl-β-naphthylamine.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor I. Sakurada for his suggestion and discussion; to Dr. T. Okada and Dr. F. Kimura for the preparation of grafted fiber samples.

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

REFERENCES

(1) W. Tsuji, M. Imai and Y. Kadono, This Bulletin, **42**, 68 (1964).

(2) I. Sakurada, T. Okada nad F. Kimura, *Reports of the Institute of Chemical Fiber, Kyoto University*, **19**, 21 (1962) ; *J, Polymer Sci.*, Part C, No.4, 1233 (1963)

(3) K.H.U. Usmanov, B.I. Aikhodhaev and U. Azizov, *J Polymer Sci.*, **53**, 87 (1961)