

Grafting of Vinyl Monomers onto Crosslinked Polymers. I. Grafting of Methyl Methacrylate onto Fibers Spun from Polymer Blends of Polyvinyl Alcohol and Its Partially *N*-Methylolcarbamoylethylated Products*

MICHIHARU NEGISHI, YOSHIO NAKAMURA, and RYOZO KITAMARU†

Faculty of Technology, Gumma University, Kiryu, Japan

INTRODUCTION

It is generally accepted that shrink-proofing and elastic recovery of fiber materials are improved by a certain degree of crosslinking. However, too many or too short crosslinks will be at a sacrifice of not only the softness but also the thermosetting property. For example, wool fibers impart a thermosetting property by breaking disulfide crosslinks, and cotton fibers increase the crease resistance and lessen shrinkage but are apt to lose softness by the formal crosslinking. On the other hand, it is known that graft copolymerization of vinyl monomers imparts a thermoplasticity to backbone polymers and occasionally improves the elastic recovery to some extent.¹ Therefore, we have attempted to improve the thermosetting property, the elastic recovery, and the shrink-proofing in boiling water of polyvinyl alcohol fibers by the concerted effects of both crosslinking and graft copolymerization.

Conventional polyvinyl alcohol fibers (Vinyon) have become shrink-proof in boiling water by heat treatment and successive formalization after spinning. Unfortunately, however, the formalization is always accompanied by a decrease in the elastic recovery. In our previously reported paper,² it was observed that fibers spun from polymer blends containing polyvinyl alcohol (PVA) and its partially (about 20 mole-%) *N*-methylolcarbamoylethylated product (PVM) in a weight ratio of 90:10 gave almost sufficient shrink-proofing in boiling water and an appreciable improvement of the elastic recovery without loss in the tensile strength and knot strength by a lower degree of formalization after heat treatment. These effects

were considered to be due to the formation of a longer chain of intermolecular crosslinks between methylol groups or PVA-OH and methylol groups.

Here, by grafting of hydrophobic vinyl monomers, without formalization the crosslinked fibers mentioned above would be expected to impart a further improvement in elastic recovery as well as less of shrinkage in boiling water. At the same time, the thermosetting property would be given to some extent. In the present paper, grafting of methyl methacrylate (MMA) by ceric ion method is discussed.

EXPERIMENTAL

Materials

Partially *N*-methylolcarbamoylethylated PVA used for spinning was prepared from the commercial PVA ($\bar{P} = 1480$) by cyanoethylation, carbamoylethylation, and *N*-methylolation by previously reported methods.³⁻⁵ The degrees of cyanoethylation and carbamoylethylation in the intermediates were 16.13 and 15.50 mole-%, respectively. The degree of methylolation in the final products was 14.85 mole-%.

Spinning of the Fibers

The aqueous solutions containing both PVA and PVM were spun into fibers in the same way as in the conventional Vinyon fibers using a 100-hole nozzle (0.09 mm. in diam.) and a spinning bath of aqueous saturated sodium sulfate solution. The total concentration of polymers in the spinning solution was 15% by weight and PVM/PVA weight ratios were 0/100, 10/90, 15/85, and 20/80. The fibers formed were drawn twice at 180°C. and successively dry heated under tension for 100 sec at 220-225°C. As previously reported, although

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† Now with the Institute for Chemical Research, Kyoto University.

the intermolecular crosslinks between methylol groups or PVA-OH and methylol groups may be formed to some extent by the heat treatment, occasionally for the purpose of its further formation, the subsequent acid treatment was performed in a solution of 200 g./liter of sulfuric acid and 300 g./liter of sodium sulfate at 60°C. for 60 min. Before grafting, the fibers were washed with a water-methanol mixture (25/75 by volume) and cold water at room temperature, to remove sodium sulfate.

Choice of the Solvent Used for Graft Copolymerization

Graft copolymerization was carried out by means of ceric ion redox system using ceric ammonium nitrate reported by Mino and Kaizerman.⁶ First, choice of the organic solvent necessary to add to increase the solubility of MMA monomer was made from the standpoint of the stability of ceric ions; namely, the consumption of ceric ions was investigated in the distilled water and the mixtures of water and aldehyde-free or nonfree acetone or methyl alcohol (1:1 by volume). In addition, in order to ascertain the difference in stability of ceric ions for primary and secondary OH groups, *n*-propyl alcohol and isopropyl alcohol were compared as solvents. In any case, the concentration changes of ceric ions were studied in the initial concentration of 0.0017–0.0019 mole/liter of ceric ions and 0.02 mole/liter of nitric acid from 10 to 180 min. at room temperature. The analysis was carried out according to the ferrous ammonium method using an *o*-phenanthroline indicator re-

TABLE I

Changes of Ce⁴⁺ Concentration with Time in Distilled Water and Mixtures of Water and Aldehyde-Free or Nonfree Acetone or Methyl Alcohol (1:1 by Volume)^a

Time, min.	Dis-tilled water	Ace-tone/water	Alde-hyde-free ace-tone/water	Methanol/water	Alde-hyde-free metha-nol/water
0	1.90	1.90	1.90	1.90	1.90
10	1.85	1.20	1.82	0.36	0.83
15	1.85	1.18	1.85	0.38	0.80
30	1.90	1.17	1.85	0.36	0.77
45	1.90	1.18	1.80	0.33	0.75
60	1.80	1.15	1.77	0.33	0.80
120	1.84	1.17	1.77	0.25	0.72
180	1.80	1.14	1.73	0.20	0.68

^a Concentration of Ce⁴⁺ in solvents, 10⁻³ mole/liter.

TABLE II

Changes of Ce⁴⁺ Concentration with Time in Distilled Water and Mixtures of Water and *n*-Propyl Alcohol or Isopropyl Alcohol (1:1 by Volume)^a

Time, min.	Distilled water	<i>n</i> -Propyl alcohol/water	Isopropyl alcohol/water
0	1.70	1.70	1.70
10	1.68	0.73	0.85
15	1.70	0.73	0.88
30	1.70	0.71	0.82
45	1.66	0.68	0.84
60	1.70	0.70	0.85
90	1.66	0.66	0.78
120	1.67	0.64	0.79
180	1.64	0.58	0.74

^a Concentration of Ce⁴⁺ in solvents, 10⁻³ mole/liter.

ported by Mino et al.⁷ The results are shown in Tables I and II.

It was observed that ceric ions were apt to be remarkably reduced by aldehyde and alcohol and almost unaffected in acetone or water. Also, it is noted that ceric ions are a little more stable in secondary alcohol than in primary alcohol. This means that the OH groups of primary alcohol have a greater facility of free radical formation in the ceric ion redox system.

From the above results, the system of mixing aldehyde-free acetone and a small amount of water was adopted for graft copolymerization. This system increases the moisture in the fibers to some extent and is also favorable for removing homopolymers which may be formed with the graft polymers, since acetone is a solvent for poly-methyl methacrylate.

Grafting Procedure

Commercial acetone was dehydrated and distilled after being freed from aldehyde by silver nitrate. As usual, the MMA monomer was purified by distillation. Before mixing, nitrogen gas was passed through acetone, monomer, and water.

The composition of monomer solution used for graft copolymerization was acetone 70, MMA 45 and water 10 parts by volume containing 0.001 mole/liter of ceric ammonium nitrate and 0.01 mole/liter of nitric acid. The reaction vessel held the fiber bundles loosely. The cycle of degassing to vacuum was repeated three times (below 1 mm. Hg) then replaced by gaseous nitrogen. Next, a monomer solution was poured in. Polymerization was carried out at 30°C. from 0.5 to 15 hr. bubbling the nitrogen gas in atmosphere throughout the

TABLE III
Effects of Reaction Time on MMA Grafting onto PVA and PVM/PVA (15/85) Fibers and Fiber Shrinkage by Grafting

Composition PVM/PVA	Time of reaction, hr.	Extent of grafting, %	Shrinkage by grafting, %
0/100	0.5	15.0	2.3
	1.0	30.1	2.8
	2.0	60.2	6.6
	3.0	95.3	8.2
	5.0	150.2	11.3
	15.0	330.7	12.6
15/85	0.5	90.5	11.7
	1.0	148.7	12.4
	2.0	253.0	14.0
	3.0	385.0	13.0
	5.0	575.0	13.5
	15.0	1045.5	17.7
15/85, acid treated	0.5	35.0	4.8
	1.0	62.7	6.7
	2.0	117.5	10.7
	3.0	160.0	11.4
	5.0	245.2	12.2
	15.0	533.3	14.0

duration of reaction. The turbidity of the liquid system appeared to increase with the duration of reaction indicating the formation of homopolymers. After the reaction period, the fibers were first washed with acetone/water (1:1 by volume), then water, and finally Soxhlet-extracted with acetone for about 20 hr. to remove the homopolymers as much as possible. The extracted fibers were again washed with water, dried, and weighed. The extent of grafting was expressed as the weight per cent increase based on the original weight of the fibers. The extent of homopolymer removal from within the fibers could not be ascertained. The shrinkage of the fibers by grafting was measured.

Physical Testing

The test to determine mechanical properties and moisture was performed at 20°C. and 65% relative humidity. The tensile strength and elongation, the knot strength and knot elongation, and the elastic recovery at 30 sec. after unloading were determined by the Senimeter. The stress vs. strain curves were recorded by the Tensilon UTM-II tester.

The degree of shrinkage of the fiber bundles was measured after immersing the fibers in water at 96°C. for 60 min. under the minute load of 0.2 mg./denier.

As a measure of the thermosetting property, the following test was carried out: The fiber bundles

were wound around a stainless steel plate (150 mm. long, 10 mm. wide, and 1 mm. thick), sandwiched between two metal plates preheated (150°C.), and set at 150°C. for 2 min. under a 25-g. load. After setting, many pieces in the shape of isosceles triangle were obtained by cutting off the fiber bundles along the length of stainless steel plate. The angle of opening between two sides of the triangle was measured after 20 min. or immersing in water at 50 or 80°C. for 10 min. and occasionally air drying. The per cent angle of opening to 180° should decrease with increasing thermosetting property. The dyeing properties were also tested briefly.

RESULTS AND DISCUSSION

Effects of Reaction Time on Grafting

The effects of the reaction time on the extent of grafting onto the PVA, PVM/PVA (15/85), and acid-treated PVM/PVA (15/85) fibers are shown in Table III and Figure 1. The acid-untreated PVM/PVA (15/85) fibers gave the most grafting and the PVA fibers gave the lowest grafting in the overall duration of the reaction. Since the acid-untreated PVM/PVA fibers are considered to have a lower crystallinity or coarser texture because of

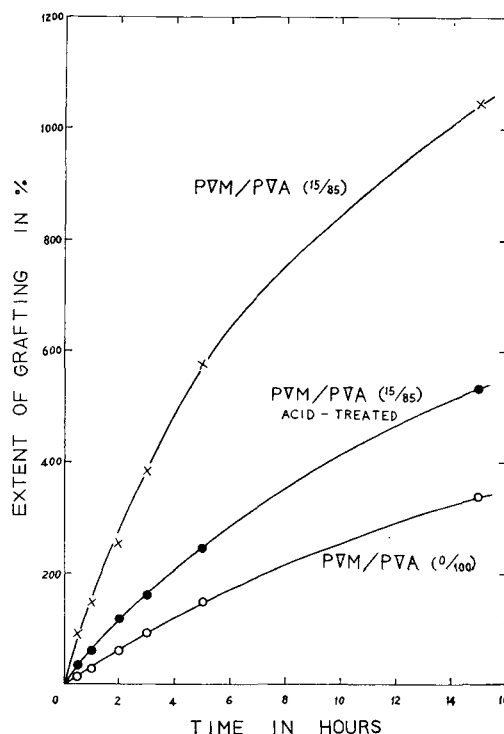


Fig. 1. Effects of reaction time on MMA grafting onto PVA and acid-treated or acid-untreated PVM/PVA(15/85) fibers.

polymer blending, the easier impregnation of monomers might accelerate the grafting. In addition, assuming less stability of ceric ions in primary alcohol as obtained above, the methylol groups as the reducing agent (primary OH groups) in the PVM component might produce more effective redox systems by ceric ions than the hydroxyl groups (secondary OH groups) in the PVA component. The lowering of grafting in the acid-treated PVM/PVA fibers may be ascribed to the further formation of the crosslinked structure between methylol groups or PVA-OH groups and methylol groups causing the difficulty of swelling and a decrease of methylol groups.

Effects of Polymer Blend Ratios in Fibers on Grafting

The effects of PVM/PVA blend ratios on grafting for 3 hr. are shown in Figure 2. The grafting of the acid-untreated PVM/PVA fibers reached a maximum at PVM 15% blending and then sharply decreased. This abnormality was verified by repeated experiments. On the other hand, the grafting of the acid-treated PVM/PVA fibers showed a linear increase with increasing PVM component. The fact that a maximum of grafting was exhibited may be due to the competitive effects of the increase of the structural accessibility or methylol groups and the crosslink formation with

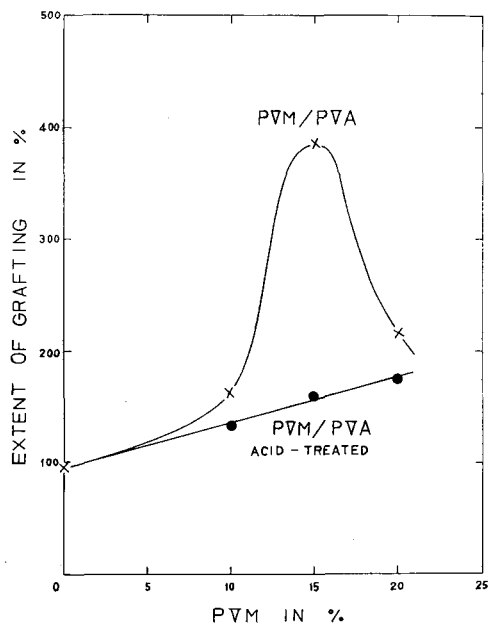


Fig. 2. Effects of PVM/PVA blend ratios on MMA grafting for 3 hr.

increasing PVM component. In the moisture regains of ungrafted fibers, similar behaviors seem to be present, as shown in Table IV.

TABLE IV
Moisture Regains of Ungrafted PVA and PVM/PVA Fibers at 20°C. and 65% Relative Humidity

Composition PVM/PVA, wt.	Acid treatment	Moisture regain, %
0/100	None	5.85
10/90	None	6.20
15/85	None	6.33
20/80	None	6.15
10/90	Treated	5.97
15/85	Treated	6.02
20/80	Treated	6.10

Moisture Regains

Moisture regains of the PVA and acid-treated or -untreated PVM/PVA fibers by varying the extent of grafting are shown in Table V. Moisture regains decrease with increasing graft fraction. In the same grafting, the moisture regains of PVM blend fibers are highest, falling slightly when acid treated before grafting, and the moisture regains of PVA fibers are lowest as shown in Figure 3. In each case, moisture regains appeared to be greater than the additive values of backbone and graft polymers. By ignoring a very small moisture

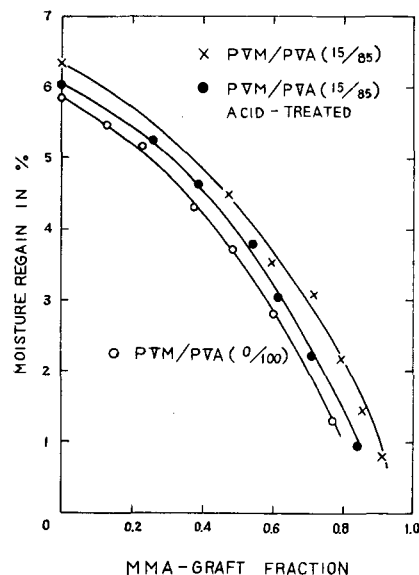


Fig. 3. Moisture regains plotted against MMA-graft fraction for PVA and acid-treated or acid-untreated PVM/PVA (15/85) fibers.

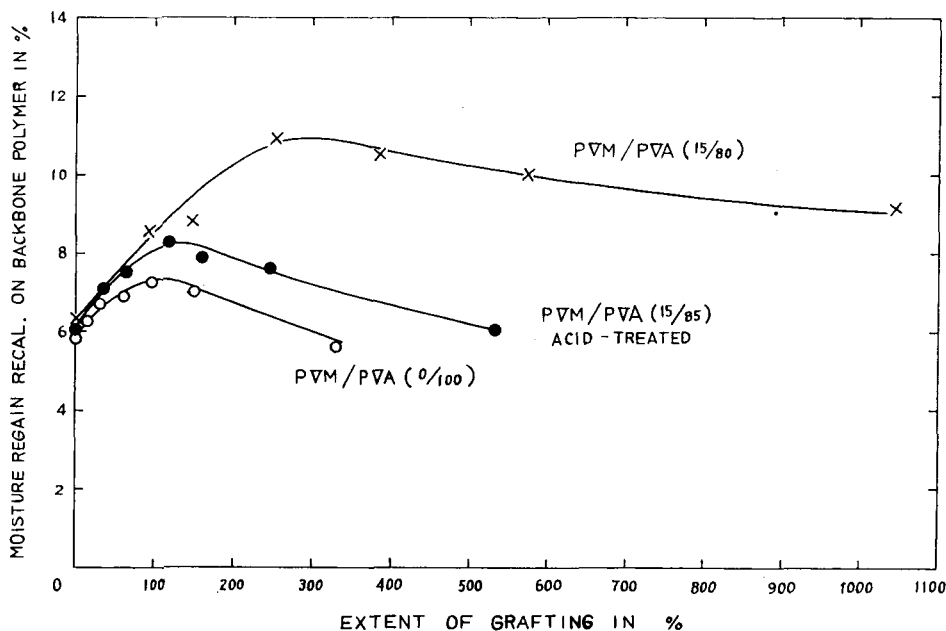


Fig. 4. Moisture regains recalculated on backbone polymers vs. MMA grafting for PVA and acid-treated or acid-untreated PVM/PVA (15/85) fibers.

TABLE V

Moisture Regains at 20°C. and RH 65% of PVA and Acid-Treated or Acid-Untreated PVM/PVA (15/85) Fibers Obtained by Varying the Extent of Grafting

Composition PVM/PVA, wt.	Extent of grafting, %	Moisture regain, %
0/100	0	5.85
	15.0	5.45
	30.1	5.15
	60.2	4.28
	95.3	3.70
	150.2	2.80
	330.7	1.30
15/85	0	6.33
	90.5	4.50
	148.7	3.54
	253.0	3.09
	385.0	2.17
	575.0	1.48
	1045.5	0.80
15/85, acid treated	0	6.02
	35.0	5.25
	62.7	4.63
	117.5	3.80
	160.0	3.02
	245.2	2.20
	533.3	0.95

regain of graft polymer (PMMA) and recalculating the moisture regain on the backbone polymer, a significant relationship was obtained between

moisture regains and grafting as shown in Figure 4; namely, in the PVA and acid-treated or -untreated PVM/PVA fibers, a maximum of moisture regain was exhibited at about 100, 150, and 300% graft-on, respectively. This was most likely due to the competition between the coarsening of the backbone structure caused by a chemical heterogenization and the hydrophobization by the chemical blocking or physical screening of the hydroxyl groups.

Shrinkage in Boiling Water

Shrinkage in boiling water of the grafted fibers at varying PVM content and MMA grafting are shown in Table VI. Generally, as the extent of grafting increases the shrinkage in boiling water decreases. However, the PVA fibers did not show sufficient nonshrinkage since there was always an agglutinated or brittle state after boiling in water. These results, which have been also reported by Tsuji et al.,¹ show little possibility of the formation of crosslinked MMA polymers.

In the PVM/PVA fibers, there was a significant decrease in shrinkage with increasing PVM composition which reached a desirable value of below 10% at about 50% graft-on (see Fig. 5). Especially, in the acid-treated PVM/PVA fibers a greater improvement in less shrinkage was obtained. From these results, it appears necessary to consider the contributions of crosslinking between methylo

TABLE VI

Shrinkage in Boiling Water of PVA and Acid-Treated or Untreated PVM/PVA Fibers at Varying PVM Content and MMA Grafting

Composition PVM/PVA, wt.	Extent of grafting, %	Shrinkage in boiling water, %
0/100	0	Dissolved
	10.0	31.8 ^a
	22.7	29.4 ^a
	45.5	22.1 ^a
	56.0	17.6 ^a
	70.0	14.3 ^b
	130.0	10.9 ^b
10/90	0	30.5 ^a
	13.1	20.0 ^a
	32.5	13.7
15/85	0	20.0 ^a
	65.5	7.3
	132.9	5.8
	200.9	4.6
	225.4	3.3
	250.0	3.0
	331.2	1.4
20/80	0	16.3 ^a
	34.6	7.0
	76.6	3.0
10/90, acid treated	0	23.0 ^a
	9.4	17.3
	27.8	13.0
15/85, acid treated	0	17.0 ^a
	33.9	8.3
	71.5	6.0
	129.2	5.2
	143.5	4.0
	160.0	3.0
	197.6	2.5
20/80, acid treated	0	14.0 ^a
	19.8	12.0
	54.0	3.0
20/80, formalized under mild condition	0	6.5 ^c
0/100, conventional vinylon	0	3.5 ^d

^a Agglutinated in a rubber-like state after testing in boiling water.

^b Altered to a brittle state after testing in boiling water.

^c Formalized in H₂SO₄ 50 g./liter at 60°C. for 60 min.

^d Formalized in H₂SO₄ 250 g./liter at 60°C. for 60 min.

groups or PVA-OH groups and methylol groups as well as MMA grafting in order to obtain less shrinkage.

Also, as shown in Table III, the shrinkage of fibers occurs to a certain degree in processes of the

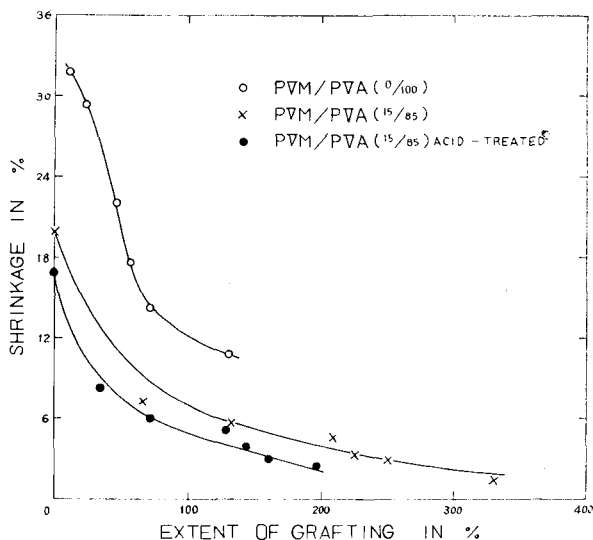


Fig. 5. Shrinkage in boiling water vs. MMA grafting for PVA and acid-treated or acid-untreated PVM/PVA (15/85) fibers.

graft reaction and tends to level above a 100% graft-on independent of the composition of fibers; however, it is certain that less shrinkage in boiling water of the grafted fibers is predominantly due to the effect of MMA grafting itself. It is noteworthy that the PVM/PVA fibers are capable of imparting sufficient shrink-proofing by MMA grafting without formalization.

Tensile Properties

Generally, the inherent tenacity and elongation of the grafted fibers increase slightly with increasing graft-on or denier except at a very high grafting, whereas the tensile strength in grams per denier decreases with increasing graft-on, as shown in Table VII and Figure 6. By plotting the inherent tenacity against the increase of denier in the PVA and PVM/PVA (15/85) fibers (as shown in Fig. 7) an approximately linear relation was achieved. Previously, Negishi and Arai⁸ found the following for the silk fibers into which acrylonitrile was polymerized:

$$F = F_0 + f(d - d_0)$$

where F_0 and F are the inherent tenacities; d_0 and d are the deniers of ungrafted and grafted fibers, respectively; and f is a tenacity increasing coefficient per denier giving the value of about 0.5. However, in the higher grafting the deviation of falling from the above relation occurs. Also, similar behaviors seem to be present in the elongation.

TABLE VII
Fineness, Inherent Tenacity, Tensile Strength, and Elongation and Knot Strength and Knot Elongation of Grafted PVA and PVM/PVA Fibers

Composition PVM/PVA, wt.	Extent of grafting, %	Fineness, denier	Inherent tenacity, g.	Tensile strength, g./denier	Tensile elongation, %	Knot/normal ratio, %	
						Strength	Elongation
0/100	0	4.25	20.7	4.87	30.4	—	—
	22.7	5.61	21.3	3.79	32.3	93.5	95.0
	56.0	7.30	22.2	3.07	29.9	85.0	93.0
	70.0	8.00	23.3	2.91	34.5	90.7	91.5
	150.2	13.4	21.4	1.60	38.4	—	—
	330.7	21.4	20.1	0.93	34.4	—	—
10/90	0	5.87	19.8	3.38	24.3	—	—
	32.5	7.92	23.6	2.99	32.1	95.4	96.3
10/90, acid treated	0	5.75	18.8	3.27	25.0	—	—
	27.8	6.66	22.3	3.35	29.6	97.0	96.0
15/85	0	5.66	21.9	3.87	25.9	—	—
	65.5	9.53	22.8	2.39	27.7	95.3	96.6
	132.9	13.7	23.5	1.73	29.1	93.0	97.3
	225.4	18.5	27.8	1.50	32.5	94.0	95.0
	250.0	23.8	28.5	1.20	34.7	90.0	93.0
	575.0	38.0	26.8	0.69	31.5	—	—
15/85, acid treated	0	5.73	20.0	3.49	24.0	—	—
	33.9	8.21	22.0	2.71	28.3	95.5	95.8
	71.5	9.45	23.2	2.46	31.5	97.7	97.0
	143.5	16.7	27.0	1.62	39.4	94.3	91.0
	160.0	15.5	25.1	1.51	34.7	99.0	98.0
	533.3	37.0	22.0	0.59	24.4	—	—
20/80	0	5.41	21.7	4.02	23.6	—	—
	34.6	6.61	22.5	3.41	28.0	96.3	97.7
	76.6	8.24	21.8	2.65	37.6	99.0	99.2
20/80, acid treated	0	5.50	19.8	3.42	24.8	—	—
	54.0	7.21	21.5	2.98	32.1	97.0	96.3
20/80, formalized under mild condition ^a	0	5.35	20.5	3.84	22.5	82.7	91.8
0/100, conven- tional Vinylon ^b	0	4.20	20.0	4.78	29.0	96.0	90.2

^a Formalized in H₂SO₄ 50 g./liter at 60°C. for 60 min.

^b Formalized in H₂SO₄ 250 g./liter at 60°C. for 60 min.

It is interesting that the grafting at which the deviation occurs seems to be about 100, 150, and 300% in the PVA, acid-treated PVM/PVA, and acid-untreated PVM/PVA fibers, respectively, corresponding to the behavior of the moisture regains recalculated on backbone polymers as mentioned above (see Fig. 4). At very high grafting, a heavy destruction in the fiber texture of backbone polymers will perhaps occur. However, it is likely that the coarser texture of backbone fibers, the harder it is to change by grafting. Moreover, since a graft reaction of about 3 hr. has been required for the above graft-on in every case (as shown in Fig.

1), the falling deviation in the tenacity and elongation may be due not only to the destruction of the fiber texture by MMA grafting but also to the oxidation degradation of the backbone polymer chains by ceric ions.

The knot strength and knot elongation are retained at above 90% to the normal strength and elongation as shown in Table VII.

Elastic Recovery

Some of the determined results of the degree of elastic recovery of the grafted PVA and PVM/PVA fibers are shown in Figures 8, 9, and 10. It is

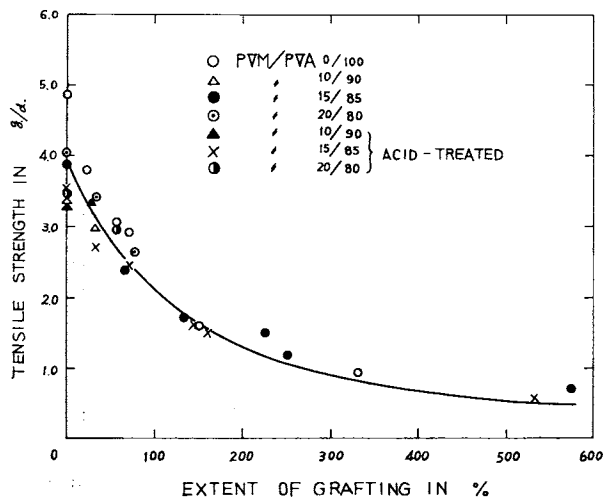


Fig. 6. Effects of MMA grafting on the tensile strength of PVA and PVM/PVA fibers.

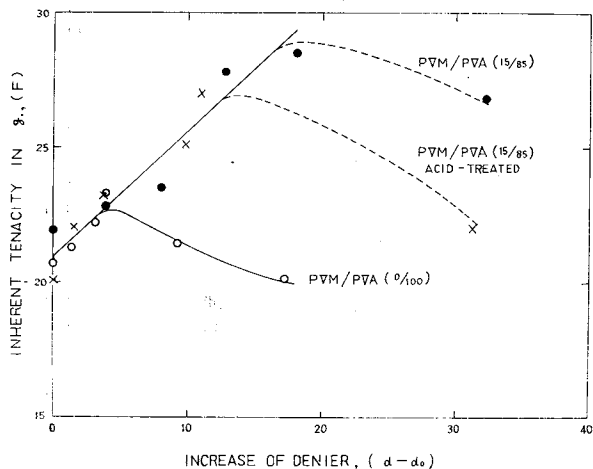


Fig. 7. Inherent tenacity vs. increase of denier for MMA-grafted PVA and PVM/PVA fibers.

observed that the elastic recovery of the grafted fibers is considerably improved as compared to the conventional Vinylon fibers. The improvements in the grafted PVM/PVA fibers are significantly greater. The elastic recovery of the grafted PVM/PVA fibers in the range of lower extension below 5% is undoubtedly superior to the ungrafted PVA or PVM/PVA fibers as shown in Figure 9. Moreover, it should be noted that, generally, the increase of elastic recovery with increasing graft-on is not so great. This shows a significant improvement above and below the 50% graft-on where nearly sufficient shrink-proofing in boiling water is obtained as mentioned above. Although the PVM/PVA fibers impart considerably high shrink-proofing and elastic recovery by formalization

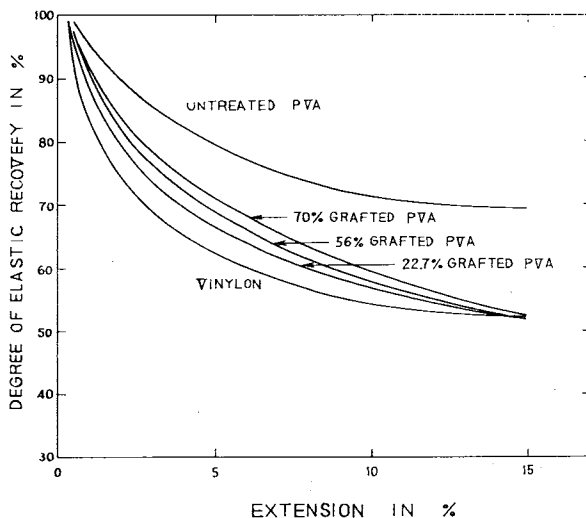


Fig. 8. Elastic recovery vs. extension for PVA fibers at varying MMA grafting.

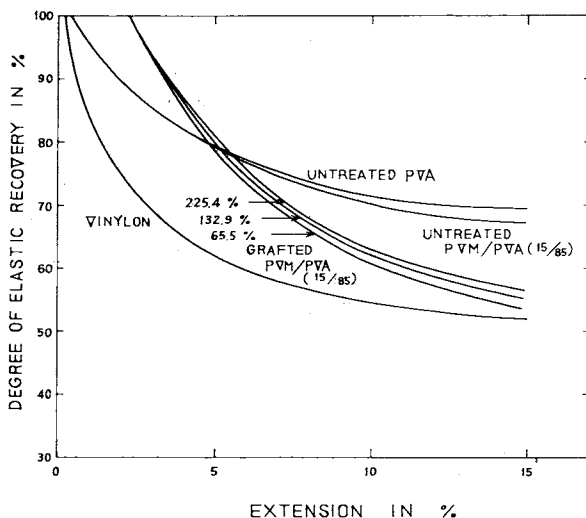


Fig. 9. Elastic recovery vs. extension for acid-untreated PVM/PVA (15/85) fibers at varying MMA grafting.

under a mild condition as reported in a previous paper,¹ the MMA grafting brings about greater improvement without formalization making the most of the characteristics of crosslinked PVM/PVA polymers (see Table VI and Fig. 10).

Also, acid treatment and the increase of PVM content in the PVM/PVA fibers seem to give a little more increase in elastic recovery by grafting (see Figs. 9 and 10)

Stress-Strain Curves

The stress-strain curves of the conventional Vinylon fibers and the PVM/PVA (20/80) fibers

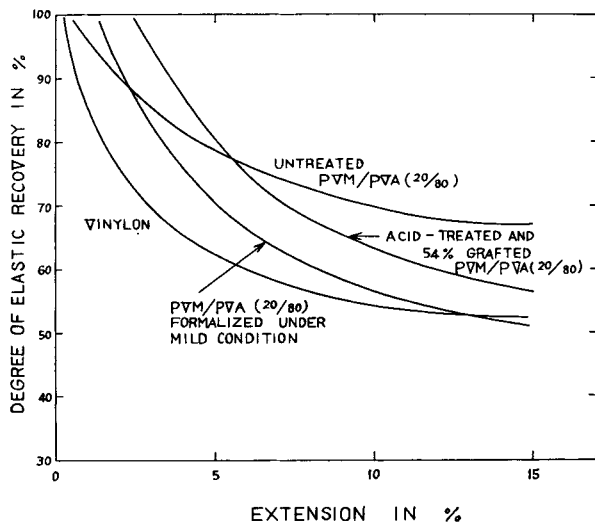


Fig. 10. Elastic recovery vs. extension for PVM/PVA (20/80) fibers acid treated and MMA grafted or formalized under mild condition.

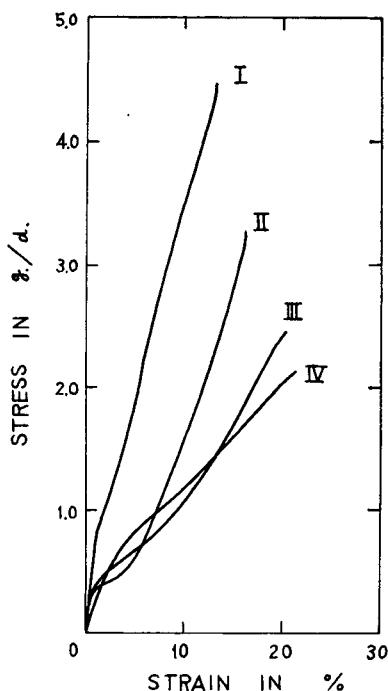


Fig. 11. Stress-strain curves of the conventional Vinylon fibers and the PVM/PVA (20/80) fibers formalized or MMA grafted. [Curves I, II, III, and IV are those of the Vinylon fibers, the formalized under mild condition, the acid-treated and MMA-54% grafted, and the MMA-76.6% grafted PVM/PVA (20/80) fibers respectively.]

formalized mildly or MMA grafted by 54.0% or 76.6% after or without acid treatment are shown in Figure 11.

It is to be noted that by MMA grafting the characteristic curve in the PVM/PVA fibers tends

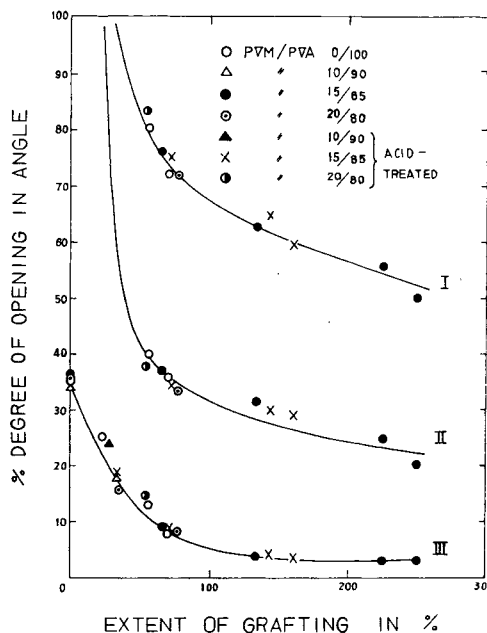


Fig. 12. Per cent angle of opening between two legs of the heat-set fibers at varying MMA grafting. (Curves I, II, and III were determined in the air-dry state after 10 min. immersion in 80°C. water, in the wet state after 10 min. immersion in 50°C. water, and in 20 min. left in air immediately after heat-setting and cutting.)

TABLE VIII
Initial Modulus of Elasticity of MMA-Grafted PVM/PVA (20/80) Fibers at 20°C. and 65% Relative Humidity

Sample	Extent of grafting, %	Initial modulus of elasticity, g./denier
Conventional Vinylon	0	47.5
PVM/PVA (20/80) fiber formalized under mild condition	0	31.9
MMA grafting	34.6	25.2
MMA grafting	76.6	16.3
MMA grafting after acid treatment	54.0	23.6

to turn into a more acceptable type raising the yield point and decreasing the initial modulus of elasticity as shown in Table VIII.

Thermosetting Property

Figure 12 shows the per cent angle of opening between two legs of the heat-set fibers plotted against the amount of grafting. It is observed that the angle of opening decreases with increasing graft-on and is greater in warm water than in air. These results show clearly that the thermosetting property is imparted appreciably by MMA grafting.

as expected. However, it was not expected to find the angle of opening almost independent of the PVM component or acid treatment by which the degree of intermolecular crosslinking was considered to be varied. It may be due to less crosslinking.

Dyeing Properties

The affinities for the direct dye (Direct Scarlet B), basic dye (Rhodamine G), and acid dye (Lanasyn Blue GL) of the PVM/PVA fibers were almost unaffected up to about 50% graft-on at which there was little decrease of moisture regain as mentioned above. Naturally, either PVA or PVM/PVA fiber was readily dyeable by disperse dyes over all grafting.

Our unpublished data of grafting by gamma radiation have also shown the similar improvements in physical properties as already mentioned.

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Synopsis

Improvements in physical properties of polyvinyl alcohol fibers were attempted by means of both crosslinking and graft copolymerization. By using the ceric iron redox system on synthetic fibers spun from polymer blends containing polyvinyl alcohol (PVA) and its partially (about 15 mole-%) *N*-methylolcarbamoyl ethylated products (PVM) in which the blend ratios were 0/100, 10/90, 15/85, and 20/80 in the aldehyde-free acetone-water system after crosslinking by heat treatment or successive acid treatment. Grafting increases with increasing PVM component. This may be ascribed to the coarsening of the fiber texture caused by polymer blending and the increasing of methylol groups as a

reducing agent. Moisture regains decrease with increasing graft fraction, but these appear to be greater than the additive values of backbone and graft polymer. Less shrinkage in boiling water is obtained with the increase of PVM component and grafting; the decreased shrinkage is significant in the acid-treated PVM-PVA fibers, and it reaches a nearly sufficient value at about 50% graft-on. The PVA fibers do not give sufficient shrink-proofing. The inherent tenacity and elongation of the grafted fibers increase slightly with increasing graft-on or denier except at the high grafting above about 100, 150, and 300 in the PVA, acid-treated, and acid-untreated PVM/PVA fibers, respectively; whereas the tensile strength in grams/denier decreases with grafting. Although at high grafting, a destruction in the fiber texture will perhaps occur, the coarser the texture of backbone fiber, the harder the change by grafting. The knot/normal ratios in tensile strength or elongation of the grafted fibers have been retained at above 90%. The elastic recovery of the grafted fibers is considerably improved as compared to the conventional Vinylon fibers. The improvements in the acid-treated and grafted PVM/PVA (20/80) fibers are significantly greater above and below 50% graft-on, especially in the range of lower extension. As expected, the thermosetting property is also appreciably imparted with grafting. In the conventional Vinylon fibers, the formalization for shrink-proofing is usually at a sacrifice of elastic recovery. But MMA grafting in the PVM/PVA fibers gives a fairly good elastic recovery and less shrinkage in addition to thermosetting property, making the most of the characteristics in the longer intermolecular crosslinkages formed between methylol groups or PVA-OH groups and methylol groups.

Résumé

Des améliorations des propriétés physiques des fibres d'alcool polyvinyliques ont pu être réalisées, tant par pontage que par copolymérisation par greffage. A la surface des fibres synthétiques filées aux dépens de mélanges de polymères contenant de l'alcool polyvinylique (PVA) et ses produits partiellement mélangés (environ 15 mole%) *N*-méthylolcarbamoyléthylés (PVM), dans lesquels le rapport en poids était 0/100, 10/90, 15/85 et 20/80, on a greffé du méthacrylate de méthyle (MMA) à 30°, en se servant à cet effet d'un système oxyde réducteur contenant des ions cériques; ce greffage a lieu dans un système acétone-eau dépourvu d'aldéhydes, après pontage par un traitement à chaud ou par traitement avec des substances acides progressivement plus fortes. Le greffage progresse en augmentant le composant PVM et peut être attribué à la rudesse de la texture des fibres, occasionnée par le mélange des polymères et par l'accroissement des groupes méthyloliques, agissant comme agents réducteurs. Les gains d'humidité diminuent avec l'augmentation de taux de greffage et paraissent plus grands que prévus sur la base de la composition de la chaîne principale et des greffons. L'infroissabilité dans l'eau bouillante augmente avec un accroissement en composant PVM et greffé; elle est la plus prononcée dans les fibres PVM/PVA traités avec de l'acide et atteint une valeur suffisante dans la pratique à environ 50% de greffage, tandis que les fibres PVA n'ont jamais été citées comme étant suffisamment infroissables. La tenacité inhérente et l'élongation des fibres greffées aug.

mentent lentement avec un accroissement de greffage, sauf à des degrés de greffage élevés (au-dessus d'environ 100, 150 et 300% dans le PVA traité à l'acide et les fibres PVM/PVA non-traitées), tandis que la résistance à la traction (gramme par denier) diminue par greffage. Bien qu'à greffage poussé, une destruction de la texture des fibres peut se reproduire, on peut admettre que, plus la texture de la fibre principale est rude de nature, plus il est difficile de la changer par greffage. Les rapports pour la résistance à la traction ou l'élongation des fibres greffées sont maintenus jusqu'à concurrence de plus de 90%. L'élasticité des fibres greffées est toujours considérablement améliorée par rapport aux fibres conventionnelles Vinyon et les améliorations réalisées dans le domaine des fibres PVM/PVA (20:80) traitées à l'acide et par greffage sont de façon significative plus grandes à des taux de greffage de 50%, spécialement dans le domaine des extensions plus faibles. Par greffage le thermdurcissement est également renforcé de façon appréciable comme prévu. Dans les fibres conventionnelles Vinyon le traitement au formol en vue de l'infroissabilité a généralement été fait aux dépens de l'élasticité. Par ailleurs on a conclu que le greffage par le MMA dans les fibres PVM/PVA a révélé non seulement une bonne élasticité et les infroissabilité, mais également des propriétés de thermdurcissement. Ces propriétés constituent peut-être les caractéristiques principales dans les pontages intermoléculaires les plus longs entre des groupes méthyloliques ou groupes PVA-OH et les groupes méthyloliques.

Zusammenfassung

Verbesserungen der physikalischen Eigenschaften von Polyvinylalkoholfasern wurden sowohl durch Vernetzung als auch durch Pfcopolymerisation versucht. Unter Verwendung eines Cerionenredoxsystems wurde bei 30°C Methylmethacrylat (MMA) auf synthetische Fasern, die aus Polymermischungen von Polyvinylalkohol (PVA) und dessen teilweise (ca 15 Mol-%) *N*-methylolcarbamoyläthylierten Produkten (PVM) mit Mischungsverhältnissen von 0/100, 10/90, 15/85 und 20/80 (Gewichtsverhältnis) gesponnen wurden, in aldehydfreiem Aceton-Wasser-System nach Vernetzung durch Hitzebehandlung oder darauffolgender Säurebehandlung aufgepfropft. Die Aufpfropfung steigt mit zunehmender PVM-Komponente an. Das kann

der durch das Mischen der Polymeren verursachten Vergrößerung der Fasertextur und der Zunahme an reduzierenden Methylolgruppen zugeschrieben werden. Mit zunehmender Aufpfropfung nimmt die Feuchtigkeitsaufnahme ab; sie scheint aber grösser zu sein, als einer Additivität von Hauptkette und aufgepfropftem Polymeren entsprechen würde. Die Schrumpffestigkeit in kochendem Wasser steigt mit Zunahme der PVM-Komponente und der Aufpfropfung in der für säurebehandelte PVM/PVA-Fasern charakteristischen Weise an und erreicht bei einer Aufpfropfung von ca 50% einen für die Praxis genügenden Wert, während bei der PVA-Faser eine genügende Schrumpffestigkeit überhaupt nicht erreicht wird. Die spezifische Zähigkeit und Dehnung der Pfcopfasern steigt mit zunehmender Aufpfropfung oder Denier leicht an, ausser bei hoher Aufpfropfung von über 100, 150 und 300% bei säurebehandelten PVA-, bzw. nicht mit Säure behandelten PVM/PVA-Fasern, wo hingegen die Zugfestigkeit in g./d. mit steigender Aufpfropfung abnimmt. Obwohl bei hoher Aufpfropfung vielleicht eine Zerstörung der Fasertextur stattfindet, ist es wahrscheinlich umso schwieriger, die Textur der Hauptkettenfaser durch Aufpfropfen zu verändern, je gröber sie von Natur aus ist. Das Verhältnis zwischen Verknüpfung und normaler Zugfestigkeit oder Dehnung wurde bei den Pfcopfasern zu mehr als 90% beibehalten. Die elastische Rückfederung der Pfcopfasern ist im Vergleich zu den begräuchlichen Vinyonfasern stets wesentlich verbessert und diese Verbesserungen sind bei den mit Säure behandelten und aufgepfropften PVM/PVA-(20/80)-Fasern oberhalb und unterhalb 50% Aufpfropfung, besonders im Bereich geringer Dehnung, merklich grösser. Auch die Wärmehärtung wird durch Aufpfropfung merklich verbessert. Bei den handelsüblichen Vinyonfasern konnte die Schrumpffestigkeit durch Formalisierung gewöhnlich nur bei gleichzeitigem Verlust an elastischer Rückfederung erreicht werden. Im Gegensatz dazu liefert die MMA-Aufpfropfung eine recht gute elastische Rückfederung und Schrumpffestigkeit zusätzlich zu einem wärmehärtenden Verhalten. Für dieses Verhalten sind vielleicht die zwischen Methylolgruppen oder zwischen PVA-OH- und Methylolgruppen gebildeten längeren Vernetzungen besonders charakteristisch.

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