

## 《Original》 Radiation-Induced Graft Copolymerization of Hydrophilic Monomer onto Nylon 6

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### Abstract

Radiation grafting of acrylic acid onto nylon fabric has been studied by "simultaneous irradiation" method to render its surface more hydrophilic. Nylon fabric immersed in monomer solution was irradiated in air or under vacuum with gamma-rays from Co-60. Most parts of polyacrylic acid formed on the surface of the fabric were extracted off from the fabric with 0.1% solution of sodium hydroxide at 100°C. The chemical components of the grafted product have been determined. By comparing graft polymer with ungrafted polyamide, the rate of water absorption and antistatic behavior are improved.

### 요 약

Nylon 직포의 표면을 친수화 하기 위하여 동시조사법으로 Acrylic acid를 방사선 graft 중합시켰다.

Monomer 용액속서 침지된 Nylon 직포를 공기중 또는 진공하에서  $\gamma$ -선으로 조사시켰다.

직포 표면에 형성된 Polyacrylic acid는 100°C의 sodium hydroxide 용액(0.1%)으로 대부분 추출되었다.

접목 반응된 생성물의 화학적 조성을 측정하였다. 접목반응된 Polymer와 방사선 처리를 하지 않은 polyamide를 비교하여 물에 흡수성이라든가 대전성은 증진되었다.

### 1. Introduction

Radiation grafting<sup>1-9)</sup> of acrylic acid monomer at room temperature has been studied by "simultaneous irradiation" method to improve the hygroscopic properties of nylon fabric. Nylon fabric was impregnated with an acrylic acid solution and the impregnated fabric was

irradiated under vacuum or in air with gamma-rays from Co-60. The purpose of this paper is to describe the preparation of typical hydrophilic grafts on polyamide, determine their components, and examine some of the unusual properties of these grafts. It was reported by Jimmerman<sup>10)</sup> that tensile properties, such as tenacity and stiffness, are retained in the graft, and that properties which depend on

amorphous areas, such as moisture regain and dyeability, are improved because modification occurs mainly in the amorphous areas of the polyamide substrate.

The polyamide selected for this work was nylon 6 fabric produced by acid-catalyzed polymerization of  $\epsilon$ -caprolactam.

Acrylic acid was chosen because it was a potentially strong hydrogen bonder<sup>11)</sup>. Also it polymerizes readily and as a result forms grafts composed of long polymeric chains. This paper will be concerned mainly with the acid grafts as prepared, the sodium salts which are typical of hydrophilic grafts, and calcium salts which exemplify ionically crosslinked networks. It was found that antistatic behavior was increased with the increase of the percent graft, and the water absorptions of the sodium salt and the calcium salt of the acid graft were more excellent than those of acrylic acid grafted nylon fabric.

## 2. Experimental

### 1) Materials

Nylon fabric was purified by treating with a mixture of 1% solution of sodium carbonate and 3% solution of sodium dodecyl benzene sulfonate at 80°C for 2-3 hrs., and bleaching with calcium hypochlorite (5g/l) at room temperature for 40 min.

And it was treated with solution (0.5g/l) of sulfuric acid at 70°C for 40 min. and treated with 1% solution of sodium thiosulfate and then washed thoroughly with distilled water.

Acrylic acid monomer was purified in the usual manner<sup>12)</sup> by distilling under vacuum (20mmHg, 56°C) and used immediately after distillation or stored at -10°C.

Calcium acetate, sodium hydroxide, formic acid, phenol, hydrochloric acid, sodium

carbonate, calcium chloride, calcium hypochlorite, sulfuric acid, sodium thiosulfate and acetone were reagent grade.

### 2) Preparation of Samples.

Purified and bleached nylon fabric was cut into strips 4×8 cm, weighed exactly. The fabric was placed in a test tube with a aqueous solution of acrylic acid at room temperature and then stoppered or placed in an evacuated sealed tube (10<sup>-3</sup>mmHg).

Control of the amount of acrylic acid grafted was achieved by adjustment of the concentration of acrylic acid or the radiation dosage.

### 3) Irradiation

The irradiation was carried out in a Gamma-Cell, an 25,000 Curie Co-60 irradiation facility, located at Korea Atomic Energy Research Institute. The total irradiation dose of a sample was regulated by controlling the total exposure time. All experiments were conducted in air or under vacuum. Details of a similar irradiation facility are described elsewhere.<sup>13)</sup>

### 4) Separation of Homopolymer and Determination of Percent Grafting.

The irradiated samples were soaked in 0.1% solution of sodium hydroxide to extract the homopolyacrylic acid formed on the surface of the fabric, and then extracted continuously in the same concentration of sodium hydroxide at 100°C.

The extracted product was converted to the free acid form from the sodium salt by heating at 90°C. with 5% solution of acetic acid, and washed with distilled water, and dried at 105°C.

The weight increase after extraction was taken to be the weight of polyacrylic acid grafted to the nylon.

The percent grafting was calculated as follows.

$$\% \text{ grafting} = \frac{\text{bone dry weight of grafted product} - \text{bone dry weight of original nylon}}{\text{bone dry weight of original nylon}} \times 100$$

#### 5) Separation of Ungrafted Acrylic Acid Homopolymer.

A 1g sample was placed in a glass-stoppered Erlenmeyer flask and 50g of 85% formic acid added.

After the sample was dissolved completely, 50ml of water was added dropwise to the solution from a buret.

The solution was stirred with a magnetic stirrer during addition of the precipitant. The final mixture was allowed to stand overnight at room temperature to accomplish complete precipitation of the nylon homopolymer and the N-AA graft copolymer.

The precipitate was collected by filtration, washed free of acid, dried at 80°C and weighed. The polyacrylic acid homopolymer content of the sample was calculated from the difference in weight between the final precipitate and original sample.

#### 6) Separation of Ungrafted Nylon and graft Copolymer.

A 6g sample was added to 200ml of 10% Na<sub>2</sub>CO<sub>3</sub> solution and heated at 90°C for 15min. After washing free of carbonate with distilled water, the sample was heated at 90°C for 15 min. in 10% calcium chloride solution.

The sample in the form of the calcium salt was washed free of chloride ion and dried at 50°C. The sample was then combined with 30 ml of phenol at 80°C. and stirred for 15min. The mixture was filtered through coarse fritted glass. Extraction of the residue with fresh 30ml portions of phenol was repeated until a drop of the phenol extract no longer formed a precipitate when added to 10ml of acetone.

The combined phenol extracts were added to a volume of acetone equal to ten times the volume of the extract.

After precipitation was complete, the residue was collected by filtration and washed free of phenol with acetone.

The nylon homopolymer content of the original sample was calculated from the weight of the phenol-soluble fraction.

The phenol-insoluble residue (graft copolymer) was washed free of phenol with acetone and converted to the free acid form from the calcium salt by heating at 90°C with 200ml of 5% acetic acid solution.

After washing free of excess acid with water, the product was dried to constant weight at room temperature in a vacuum desiccator.

The graft copolymer content of the original sample was calculated from the weight of this fraction.

#### 7) Separation of Polyacrylic Acid Branches from Nylon Backbone of Graft Copolymer.

An amount of graft Copolymer was heated with concentrated hydrochloric acid in an evacuated sealed tube for a period of 20-24hrs.

After cooling to room temperature, the sample was diluted with water and placed in a cellophane dialysis tube.

The sample was dialyzed for a period of 4 days in a stream of distilled water. The contents of the tube were transferred to a titration flask and titrated with standard NaOH as a phenolphthalein indicator. The amount of polyacrylic acid present was calculated from this titration.

### 3. Results and Discussion

#### 1) Grafts VS. Acrylic Acid Concentration

The relation of the amount of acrylic acid

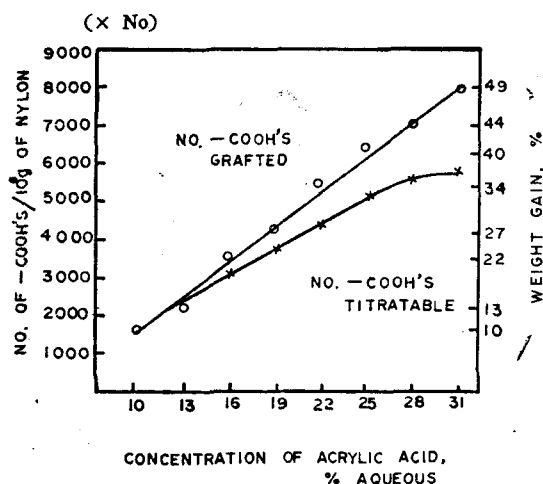


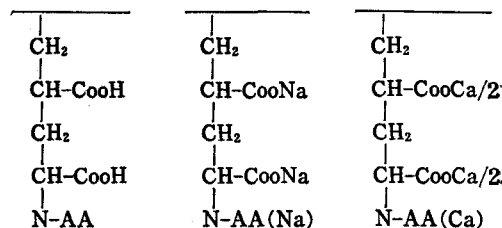
Fig. 1. Acrylic acid grafted vs. acrylic acid concentration (Total dose; 6Mrad)

grafted on nylon fabric to acrylic acid concentration at room temperature is shown in Figure 1.

The amount of acrylic acid grafted were measured by weight gain and titration of carboxyl groups in the grafted nylon.

The number of carboxyl groups was calculated from the ratio of polyacrylic acid to nylon in the graft copolymer. The discrepancy between the titrated number of  $\text{CooH}$  groups and that measured by weight gain can be ascribed to the polyelectrolyte effect as the acid graft is converted to the sodium salt during titration with sodium hydroxide solution.

The percent graft increases with the increase of acrylic acid concentration, but at higher levels of acrylic acid concentration (beyond 35%) it was not able to measure the percent graft because nylon backbone was dissolved. The following nomenclature will be used in the rest of the paper to refer to the various salts: N-AA denotes acrylic acid graft on nylon; N-AA(Na) denotes the sodium salt of N-AA, and N-AA(Ca) denotes calcium salt of N-AA.



## 2) Grafts VS. Radiation Dose

The relation of the amount of acrylic acid grafted onto nylon fabric to radiation dose is shown in Figure 2.

The amounts of acrylic acid grafted were measured by weight gain in the grafted nylon at radiation dose ranging from 1 to 7 Mrad when the concentration of acrylic acid was 15%.

The percent graft increases almost linearly with radiation dose.

As shown in Figure 2, the percent graft was 10% when radiation dose was 1 Mrad and 28% when radiation dose was 7 Mrad.

This can be attributed to the fact that at higher levels of grafting the reaction becomes diffusion controlled.

## 3) Grafts under Vacuum or in Air.

The grafting results of acrylic acid onto nylon fabric immersed in a mixture of AA-

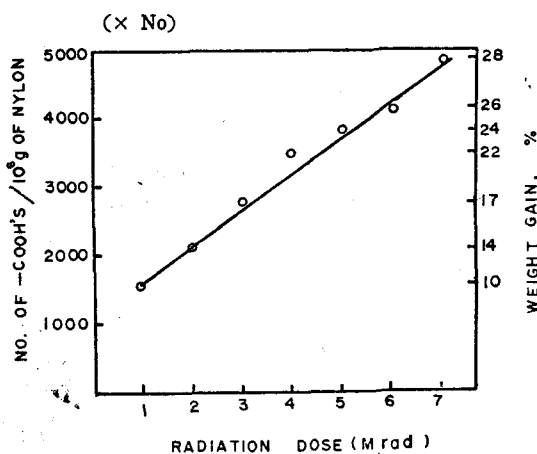


Fig. 2. Acrylic acid grafted vs. radiation dose (AA concn.; 19%)

**Table 1.** Grafting of acrylic acid onto nylon fabric immersed in a mixture of AA-H<sub>2</sub>O. Dose rate: 247rad/sec, Total dose: 6 Mrad

Comp. of Mixture H <sub>2</sub> O/AA by Vol.	Apparent Graft (%)	
	in air	under Vacuum
94/6	8	8.4
91/9	10	11
88/12	12	14
85/15	25	31
82/18	36	40
79/21	40	45

H<sub>2</sub>O at radiation dose of 6 Mrad are shown in Table 1.

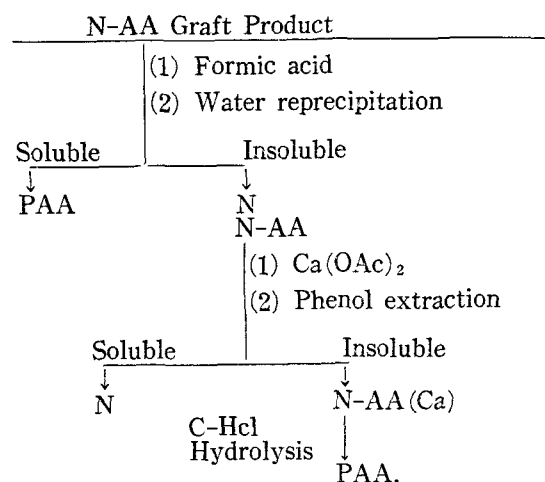
It is found from the results shown in Table 1 that the percent graft (the ratio of a mixture of AA-H<sub>2</sub>O, 6:94) is 8% in air and 8.4% under vacuum. On the other hand, the percent graft (the ratio of a mixture of AA-H<sub>2</sub>O, 21:79) is 40% in air and 45% under vacuum. Generally the percent graft is seen to increase with the increase of acrylic acid concentration. Comparing the percent graft in air with that under vacuum, slightly higher degree of grafting has been found under vacuum. This appears to the result from the basis of a scavenger effect which reduces radicals formed in nylon fabric by radiation.

#### 4) Chemical Components of N-AA Graft.

The results of N-AA graft product analyzed by the Jimmerman's method<sup>10)</sup> are shown in Table 2.

Results shown in the table pertain to the 18% graft.

Note that the grafted product analyzed represents the final grafted fabric and not the crude product which could be obtained immediately after irradiation. The separation scheme is outlined in Figure 3.

**Fig. 3.** Separation scheme.

The polyacrylic acid homopolymer fraction is separated by dissolving the graft in 85% formic acid. By addition of water, the ungrafted nylon and graft copolymer are precipitated and the polyacrylic acid homopolymer remains in solution. The polyacrylic acid homopolymer content of the sample was calculated from the difference in weight between the final precipitate and original sample. The percent polyacrylic acid in the graft is obtained from the weight gain of the nylon on grafting. The nylon acid portion of the graft is hydrolyzed away from the polyacrylic acid by treatment with concentrated HCl at 100°C.

The hydrolysis products are removed by

**Table 2.** Composition of nylon-acrylic acid grafted product (18% weight gain)

Composition of N-AA Grafts	Weight (%)
PAA homopolymer	1
Nylon, ungrafted	40
Nylon-PAA graft	58
Nylon portion in graft	43
PAA portion in graft	15

dialysis, and the final weight of the polyacrylic acid are determined by titration with standard NaOH to phenolphthalein endpoint.

As shown in Table 2, the polyacrylic acid homopolymer fraction entangled in the graft is about 1%, and ungrafted nylon content in the graft is about 40%. Nylon-PAA portion in the graft is about 58% (nylon portion of nylon-PAA graft; 43% and PAA Portion of nylon-PAA graft; 15%).

### 5) Hydrophilic Properties of N-AA Grafts

The results of water absorption in acrylic acid grafted nylon fabric are shown in Figure 4. The sample fabric was immersed in the water of 20°C for 5 min. and wiped off the water on the surface of the fabric with filter paper. It was weighed after being kept at room temperature for 1 hr.

The percent of water absorption was calculated from the increase in the weight of a bone dry sample. Generally the percent of water absorption of the samples are increased with the increase of the percent grafting. This can be attributed to the fact that the hydrophobic properties of the nylon fabric are changed into the hydrophilic properties by

radiation-induced grafting. It is seen from Figure 4 that the percents of water absorption of the calcium- and sodium salt of the acrylic acid graft are much higher than that of the acrylic acid graft. Particularly the percent of water absorption of the sodium salt was the highest of all the samples. This appears to be the result from the affinity of sodium ion for water molecule.

### 6) Recovery Properties of N-AA Grafts.

The results of crease recovery properties of the acrylic acid graft and the calcium- and sodium salt of the acrylic acid graft are shown in Figure 5. The test sample of nylon 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 2min., then the weight was removed and after a definite time the crease angle was measured.

The dry recovery properties of nylon fabric grafted with acrylic acid are not essentially different from that of ungrafted nylon fabric. In the wet, however, the picture is quite different. The crease recovery of the sodium salt of the acrylic acid graft rises sharply at

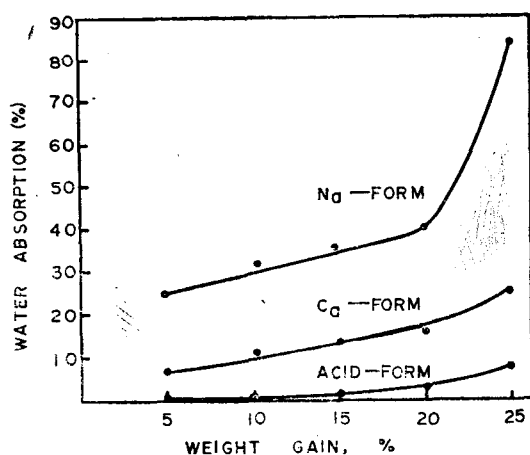


Fig. 4. Water absorption of nylon fabric grafted with acrylic acid and its salts

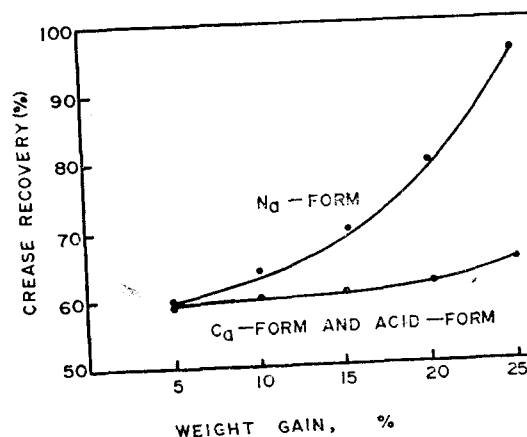


Fig. 5. Crease recovery of acrylic acid grafted nylon fabric of various % grafting

25% of the grafting to assume a value of 95% while wet (the rate of water absorption; 15%) as compared to 60% for the free acid form of the graft or the calcium form. The high wet crease recovery of the sodium form of the acrylic acid graft has been explained in terms of ionic forces which come into play when the fabric is immersed in water. As in the case of polyelectrolytes, the salt groups are ionized and the polyacrylic acid side chains on the nylon backbone behave like anionic polyelectrolytes in which the electrical charges mutually repel each other, thereby extending the chains and resisting folds or other configurational restrictions. The calcium form of

the graft does not have wet crease recovery properties since calcium polyacrylate is insoluble in water and is not ionizable.

#### 7) The Antistatic Behavior

Since the problem of static build up is generally encountered at low humidities, the relative antistatic behavior<sup>14-15)</sup> is estimated by contact angle measurement of water on the surface of radiation-chemical treated nylon fabric. The phenomenon of contact angle of water on the surface of acrylic acid grafted nylon fabric is shown in photos of Figure 6, and the degree of contact angle is given in Table 3.

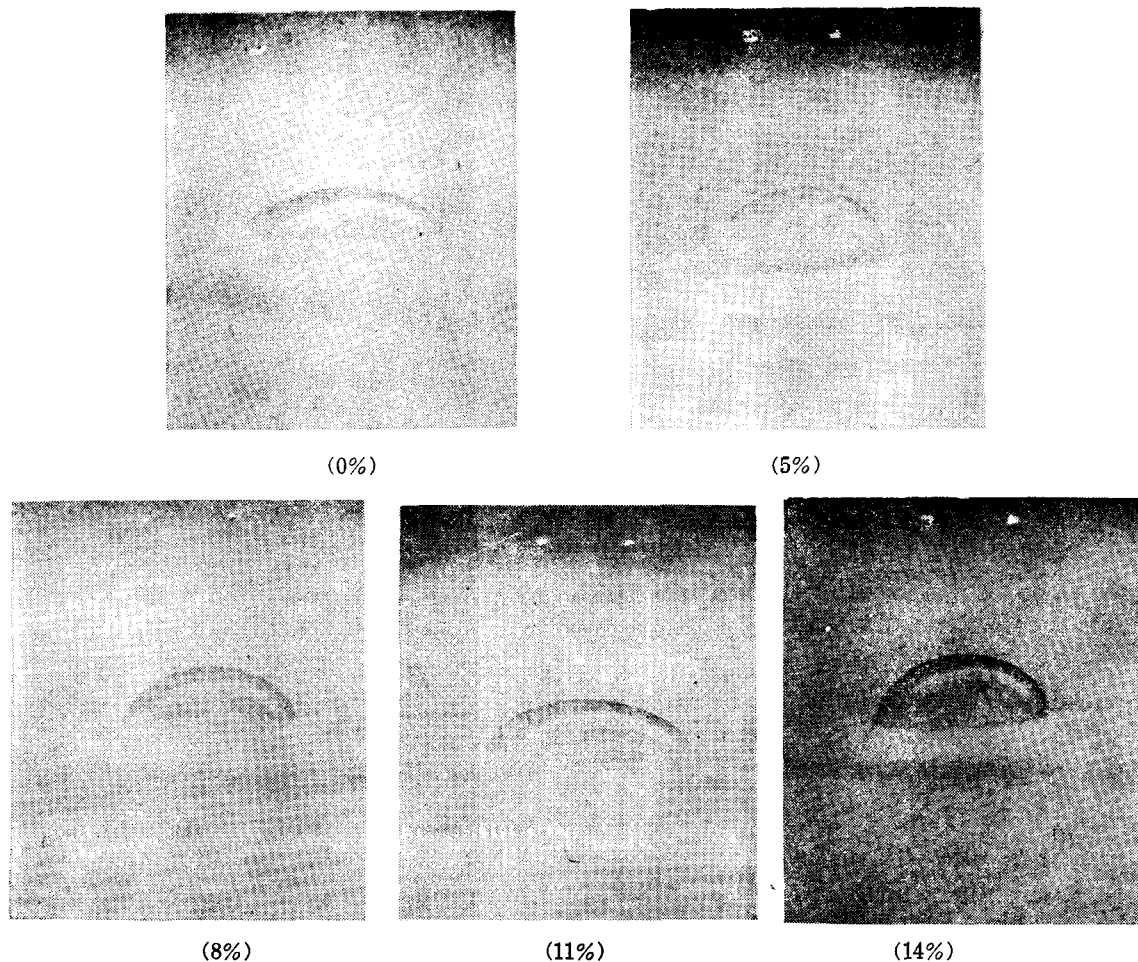


Fig. 6. Effect of antistatic behavior on visual contact angle.

**Table 3.** Effect of percent grafting on visual contact angle

Graft (%)	0	5	8	11	14
Contact angle (°)	65	60	50	45	36

The generation of static charges has been attributed to a variety of contact between two dissimilar surfaces.

One possible cause involves the transfer of electrons from the conduction or valence bands of one material to the empty conduction bands of the other insulator<sup>5)</sup>.

As shown in Table 3, visual contact angle decreases with the increase of the percent graft. Figure 6 displays water drops on the surfaces of acrylic acid grafted nylon fabric. It is found from the results that the combination of ionizing radiation from Co-60 plus chemical treatment in especially-prepared compositions yields significant reduction in contact angles of water on polyamide surfaces.

These lower contact angles indicate increased ability to dissipate static charges and increased ability to release oily stains from the surfaces in aqueous solutions. As a result, the use of irradiation plus chemical treatments should impart longer lifetimes *i.e.* greater permanence to these improved fabric properties.

#### 8) Tensile Properties of N-AA Grafts

The results of the tensile properties of acrylic acid grafted nylon fabric are shown in Table 4.

To examine this properties, the sample fabric was cut into strips 2×8cm. Tensile strength and elongation were measured with an Instron using 100mm/min. rate of chart speed and 10mm/min. rate of Cross Head speed.

It is found from the data that excellent

**Table 4.** Tensile properties of N-AA grafts

Sample	Grafting, %	Tensile strength(g)	Elongation, %
Nylon	0	18000	27
N-AA	14	21500	33
N-AA(Na)	14	24000	43
N-AA(Ca)	14	27500	39
N-AA	22	26100	33
N-AA(Na)	22	22000	40
N-AA(Ca)	22	27700	44

tensile properties are given to nylon fabric by acrylic acid grafting or salt treatments of the acrylic acid grafts.

The effect to enhance tensile strength and elongation is probably thought to be caused by the breaking of hydrogen bonds, and by cross linking, and by side chains of polyacrylic acid coated on nylon fabric.

#### 4. Conclusion

Nylon 6 has been grafted with a solution of acrylic acid.

The percent graft and the formation of homo-polyacrylic acid was increased with the increase of the concentration of acrylic acid and radiation dose.

Most of polyacrylic acid homopolymer formed on the surface of nylon fabric was extracted with 0.1% solution of sodium hydroxide, but at higher levels of grafting it was difficult to extract the homopolymer entirely. Our investigation shows that the main fraction of the apparent graft is chemically combined with the backbone polymer, but the least unavoidable fraction is a homopolymer formed in the matrix of the backbone polymer.

Considering the chemical components of



acrylic acid grafted product, it is found that the graft polymerization is not homogenous reaction. The acrylic acid grafts on nylon fabric are readily converted to the corresponding sodium- or calcium salts by treatment with sodium carbonate or calcium chloride.

The various acid and salt forms are readily interconvertible. The sodium salt of the acrylic acid graft is highly hydrophilic as measured by the rate of water absorption, and also the crease recovery of the sodium salt rises sharply at higher levels of grafting.

The lower contact angles on surfaces of nylon fabric indicate increased ability to dissipate static charges.

It has been demonstrated experimentally that the modified fabric possesses excellent antistatic properties and crease recovery properties, and that water absorption and tensile properties are increased.

In conclusion, we wish to state that the radiation-induced grafting of acrylic acid onto nylon fabric can be carried out easily and seems to be a practical solution to the general problem of conferring wettability, antistatic behavior, high wet crease recovery, tensile properties, etc. to fabric made from such materials.

## References

- 1) Bruce s. Bernstein; J. of Pol. Sci., Part A, **3**, 3405-3412 (1965)
2. J.K. Thomas; J. of Pol. Sci., **55**, 721-729 (1961)
3. John A. Rusnock; J. of Pol. Sci., Part A, **3**, 647-658 (1965)
4. A.S. Hoffman; Textil Vereldung 2, **6**, 327-331 (1967)
5. A.S. Hoffman and G.R. Berbeco; The Textile Research Joucrnal, 971-982, Nov. (1970)
6. Hiroshi Ishibashi; Textile Research Institute of Osaka Prefecture, **26**, 331-336 (1969)
7. Adolf Heger; Faserforschung und Textiltechnik, **17**(10), 439-444 (1966)
8. Adolf Heger; Faserforschung und Textiltechnik, **20**(1), 21-30 (1969)
9. Adolf Heger; Monatsber. Deut. Akad. Wiss. Berlin **7**(12), 917-923 (1965)
10. J. Jimmerman, J. of Pol. Sci., Part C, **4**, 515-629 (1963)
11. James K. Rieke, and Gerald M. Hart; J. of Pol. Sci., Part C, **4**, 539-604 (1963)
12. R.Y. -M. Huang, and E. Immergut; J. of Pol. Sci., Part A, **1**, 125701297 (1963)
13. Rice, F.G.; Ind. Eng. Chem., **52**, 5, 52A. (1960)
14. Bikerman, J.J.; Ind. Eng. Chem. Anal. Ed. **13**, 443-444 (1941)
15. Shashona, V.E.; J. of Pol. Sci., **33**, 65-85 (1958)