

## ◀Original▶ Radiation-Induced Graft Copolymerization of Hydrophilic Monomers to Polyester

Chong Kwang Lee and Jae Ho Choi

Chemistry Division, Atomic Energy Research Institute, Seoul, Korea

(Received March 20, 1972)

### Abstract

Radiation grafting of acrylic acid to polyester fabric has been studied by an impregnation method to render its surface more hydrophilic. Impregnated fabric was irradiated under nitrogen with gamma-ray from Co-60.

The homopolymer formed usually could be extracted with water at 100°C. Graft-fabric exhibited a good acceptability to acid, basic or disperse dyes in conventional aqueous dye bath at moderate temperature.

### 요 약

Polyester 織布 表面을 親水化하기 위하여 含浸法에 의하여 acrylic acid를 방사선 graft 共重合시켰다. 이때 含浸된 織布를 窒素에서 Co-60 감마선으로 照射하였다. 生成된 Homopolymer는 100°C의 물에 의하여 大體로 抽出되었다.

Graft된 織布는 산성, 염기성 또는 분산염료에 對하여 在來式 低溫 侵染法에 의해서 염색이 잘 되었다.

### 1. Introduction

Radiation grafting of acrylic acid at room temperature has been studied by an impregnation method<sup>1-3)</sup> to improve the hygroscopic properties of polyester fibers. Polyester fabric was impregnated with acrylic acid or acrylic acid solution by immersion at 25° or 70°C, the impregnated fabric was irradiated under nitrogen with  $\gamma$ -ray from Co-60.

Not only the use of swelling agents such as dimethyl formamide, dimethyl sulfoxide and

formic acid but also the use of water are effective to conduct the grafting up to 18% graft.

The satisfactory graft could be obtained when the percent of impregnation solution of acrylic acid-swelling agent was in the range of 30-40%.

All homopolymer formed could be extracted with water at 100°C but at higher levels of acrylic acid in impregnation solution almost all polymer formed by the irradiation could not be extracted with water at 100°C.

This indicates that the polyacrylic acid formed in the crystalline polyester matrix can hardly be extracted with water due to entanglement of their long chain molecules between the crystalline parts of matrix polymer and is observed as apparently grafted onto polyester. One of the intriguing possibilities opened up by radiation induced grafting is the preparation of polymers combining the hydrophobic properties of polyesters and hydrophobic properties of selected vinyl monomers<sup>4)</sup>.

The resulting graft polymers lend themselves to characterization in comparison to unmodified polyesters because modification occurs mainly in the amorphous areas of the polyester substrate.

As a result, tensile strength and thermo-plasticity are increased in the graft, and properties which depend on amorphous areas, such as moisture regain and dyeability, are very enhanced.

Acrylic acid was chosen because it was a potentially strong hydrogen bond<sup>5)</sup>. Also it polymerizes readily and as a result forms grafts composed of long polymeric chains.

The highest value of the degree of grafting was 25% at a dose of 6-7 Mrad under nitrogen.

Generally it is difficult to dye polyester fabric with all the dyes except disperse dyes at low temperature.

But it was found that the dyeability of the acrylic acid grafted polyester fabric containing the hydrophilic properties was excellent even if it was dyed with acid, basic or disperse dyes in conventional aqueous dye bath at low temperature. The investigation of electron micrograph disclosed the existence of certain type of discontinuities in the acrylic acid grafted polyester fabric which was dyed with various dyes.

The various techniques to prepare graft

copolymer using ionizing radiation have been reviewed by Chapiro<sup>6)</sup>.

## 2. Experimental

### Materials

Polyester fabric was purified by treating with a mixture of 1% Na<sub>2</sub>CO<sub>3</sub>, 3% Na-dodecyl benzene sulfonate and 0.3% tween 80 at 80°C for 2-3 hrs. and then washing thoroughly with water.

Acrylic acid monomer was purified in the usual manner<sup>11)</sup> by distilling under vacuum (56°C, 20 mmHg) and used immediately after distillation or stored at -10°C.

Dimethyl formamide, dimethyl sulfoxide, carbon tetrachloride and formic acid used were pure grade.

Distilled water was used without any further purification.

All the dyes such as acid, 1. Xylene blue as basic 2. Marine blue RNA and disperse dyes 3. Kayalon polyester navy blue RSF made in Swiss were used.

### 3. Preparation of Samples

Purified polyester fabric was cut into strips 15×10cm, weighed exactly. The sample fabrics were impregnated with acrylic acid or acrylic acid solution by immersion at 25° or 70°C for an hour.

Dimethyl formamide, dimethyl sulfoxide, formic acid, carbon tetrachloride and water were employed as solvents of acrylic acid for acrylic acid solution. The sample fabric was weighed immediately after the wiping off the solution on the surface of the sample fabric with filter paper. The impregnated sample was placed in test tube, followed with nitrogen (5cm<sup>3</sup>/sec) and then stoppered quickly.

### 4. Irradiation

The irradiation was carried out in a Gamma-cell, an 25,000 Curie Co<sup>60</sup> irradiation facility, located at the office of Atomic Energy.

All experiments in this paper were carried out at dose rates ranging from 3.7 to 4.1 Mrad/hr.

The total irradiation dose of a sample was regulated by controlling the total exposure time. All experiments were conducted in air.

Details of a similar irradiation facility are described elsewhere<sup>7)</sup>.

### 5. Separation of Homopolymer and Determination of percent Grafting

After irradiation, the test tube was opened and weighed. Percentage of the weight increase was determined by weighing a mixture before removing soluble homo-polyacrylic acid.

The contents were soaked in water to extract the unreacted acrylic acid and a part of the homo-polyacrylic acid, and then extracted continuously in water at 100°C for 2-3hrs. The extracted samples were dried in an oven at 100-105°C for 1 hr. and weighed to determine the extent of grafting. The weight increase after extraction was taken to be the weight of polyacrylic acid grafted to the polyester.

The percent grafting was calculated as follows:

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

### 6. Dyeing

Acrylic acid grafted polyester fabric was dyed with various dyes in aqueous dye bath. The dyeing methods<sup>8-9)</sup> were as follows

#### 1) Disperse Dyes

17g of a sample fabric was treated previously in a solution of Sandopan D. T. C. (1g/1) at 40-60°C for 30 min., and then wetted in a bath containing 1.5g of Dilatin DPA and 1.5g of Disper VGO per a half liter for 10min. at 50°C, and next, 0.85g of dyes (previously

dissolved in hot water) was added into the bath.

The temperature was raised to 90-100°C in 30 min. and maintained for 90 min. at that temperature.

After dyeing, soaping, and rinsed, it was dried.

#### 2) Acid Dyes

17g of a sample fabric was wetted in warm water at about 50°C. Dyed in a bath containing 1.45g of dyes, 0.3 ml of sulfuric acid and 1.8g of common salt per 700 ml.

Starting at 40°C, it was raised to 90-100°C during 20 min. and maintained at that temperature for an hour.

After cooling to 70°C in the air, it was rinsed and dried.

#### 3) Basic Dyes

16g of a sample fabric was wetted in warm water.

Dyed in a bath containing 1.3g of dyes, 1.6g of common salt and 0.2g of sodium carbonate per a half liter.

It was raised to 70-80°C and maintained at that temperature for an hour, and proceeded to rinsing, soaping, rinsing and drying.

### 7. Physical Tests and Electron Micrographical Investigations

The tensile strength and elongation of acrylic acid grafted polyester fabric were measured by Instron using 2×8 cm sample fabric.

The percent of absorption of water was calculated as the ratio of the weight increase to the weight of acrylic acid grafted polyester fabric (dry basis).

In this case the sample was soaked into water at 20°C, taken out after a definite time and the weight increase was determined.

Thermoplasticity of acrylic acid grafted polyester fabric was measured as follows:

The sample fabric was folded at the center of its long direction and pressed with hot iron

(115-125°C) for 1 min. .

Then the iron was removed and the pleat angle was measured.

The fastness of the samples dyed with various dyes was measured. The testing methods used were as follows:

Light fastness: KSK 0700 testing method

Abrasion fastness: KSK 0650 testing method

Wash fastness. ASK 0641 testing method

Sweat fastness. ASK 0715 testing method

The structures of the surface of acrylic acid grafted polyester fabric and acrylic acid grafted polyester fabric dyed with various dyes were investigated by electron micrographs (X20,000).

**8. Results and Discussion**

**1) Grafting VS. Dose**

The relation of the amount of acrylic acid grafted on polyester fabric to the total dose of radiation at room temperature is shown in figure 1.

Points were obtained at radiation dose ranging from 3 to 7 Mrad when the percent of impregnation was 35%.

The percent graft increases almost linearly with radiation dose.

This can be attributed to the fact at higher

levels of grafting the reaction becomes diffusion controlled.

Practically no grafting occurred when the radiation dose was below 3 Mrad. It is probably because acrylic acid is a potentially strong hydrogen bonder and so free radicals can not be formed on the polyester backbone in low radiation dose.

On the other hand, the percent graft increased with the percent of impregnation, but at higher levels of impregnation it was difficult to extract the homo-polyacrylic acid formed on the surface of polyester fabric.

**2) Grafts VS. a Mixture of Acrylic Acid Swelling Agents**

The grafting results of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid (AA)-dimethyl formamide (DMF) at radiation dose of 6.3 Mrad are shown in (I) and (II) of Table 1. After impregnation of polyester fabric in AA-DMF solution at 70°C for an hour (I) or 25°C for three hrs. (II). (I) of Table 1 was the case when the sample was saturated with nitrogen for 30 sec. (5cm<sup>3</sup>/sec), but (II) not saturated with nitrogen.

When the sample was not saturated with nitrogen, a little grafting occurred as compared

**Table 1. Grafting of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid-dimethyl formamide. Dose rate 90 rad/sec, total dose 6.3 Mrad, irradiation temperature 18°C.**

Comp. of mixture DMF/AA by vol.	Pick up of mixt %	Weight increase %(C)	Apparent graft %(D)	$\frac{D}{C} \times 100$	Note
16/4	40	38	2	5	(I)
12/8	42	36	4	11	
10/10	43	35	7	20	
8/12	38	34	12	35	
6/14	41	37	18	50	
16/4	43	38	2	5	(II)
12/8	41	39	3	8	
10/10	40	37	4	10	
8/12	40	38	5	13	
6/14	40	36	5	14	

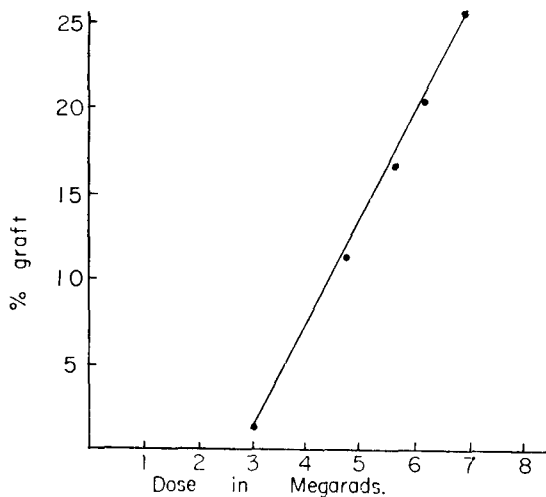


Fig. 1. Relation of percent graft and total dose in 35% impregnation of acrylic acid monomer at 25°C

to the considerable amount of grafting obtained after the saturation of nitrogen.

The decreased grafting can be attributed to the effects of oxygen and swelling at low temperature of impregnation solution.

Also this appears to result from the formation of homo-polyacrylic acid by thermal polymerization.

It is found from the results shown in Table 1 that the % grafting is 18% when the ratio of DMF/AA is 6/14, and the highest value of the efficiency of graft, D/C, is 50%.

Next, the grafting results of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid-dimethyl sulfoxide (DMSO) at radiation dose of 6.3 Mrad are

shown in Table 2.

Polyester fabric was impregnated with a mixture of AA-DMSO at 70°C for an hour and then saturated with nitrogen.

After irradiation, the sample was extracted with water at 100°C. Most of the unreacted acrylic acid, dimethyl sulfoxide and homo-polyacrylic acid was extracted, but some parts of homo-polyacrylic acid were not extracted.

Generally the weight increase of the sample was 37% when the percent of impregnation was 40%.

The % grafting increases with the decreasing ratio of DMSO/AA.

It is found from the results shown in Table 2 that the % grafting is 15% when the ratio of DMSO/AA is 16/4, and the highest value at the efficiency of graft, D/C, is 40%.

Next, the grafting results of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid (AA)-carbon tetrachloride (CCl<sub>4</sub>) at radiation dose of 6 Mrad are shown in Table 3.

After impregnating polyester fabric in AA-CCl<sub>4</sub> solution at 25°C for three hour (I) or 70°C for an hour (II), it was not saturated with nitrogen.

Table 3 shows the value of a nearly certain graft.

The addition of CCl<sub>4</sub> in acrylic acid monomer had little effect on the radiation copoly-

Table 2. Grafting of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid (AA)-dimethyl sulfoxide (DMSO). Dose rate 90 rad/sec, total dose 6.3 Mrad, irradiation temperature 18°C.

Comp. of mixture DMSO/AA by vol.	Pick up of mixt. %	Weight increase % (C)	Apparent graft % (D)	$\frac{D}{C} \times 100$
16/4	42	38	2	5
12/8	40	37	8	21
10/10	39	35	10	28
8/12	40	36	12	33
6/14	43	38	15	40

**Table 3. Grafting of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid (AA)-carbon tetrachloride(CCl<sub>4</sub>). Dose rate 90 rad/sec, total dose 6 Mrad, irradiation temperature 18°C.**

Comp. of mixture CCl <sub>4</sub> /AA by Vol.	pick up of mixt. %	weight increase %(C)	Apparent graft %(D)	$\frac{D}{C} \times 100$	Note
16/4	33	30	7	23	(I)
12/8	34	30	8	25	
10/10	32	29	8	26	
8/12	38	34	8	25	
6/14	39	33	8	24	
16/4	38	34	8	24	(II)
12/8	36	33	9	27	
10/10	37	32	9	28	
8/12	39	33	9	27	
6/14	38	34	9	26	

**Table 4. Grafting of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid-water. Dose rate 90 rad/sec, total dose 6.3 Mrad, irradiation temperature 18°C.**

Comp. of mixture H <sub>2</sub> O/AA by Vol.	pick up of mixt. %	weight increase %(C)	Apparent graft %(D)	$\frac{D}{C} \times 100$	Note
16/4	43	30	4	13	(I)
12/8	41	32	8	25	
10/10	38	33	13	39	
8/12	41	33	15	43	
6/14	39	31	18	59	
16/4	39	30	4	13	(II)
12/8	41	32	18	56	
10/10	40	32	20	60	
8/12	41	34	22	64	
6/14	42	35	24	68	

**Table 5. Grafting of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid-formic acid. Dose rate 90 rad/sec, total dose 6.3 Mrad, irradiation temperature 18°C.**

Comp. of mixture FA/AA by Vol.	pick up of mixt. %	weight increase %(C)	Apparent graft %(D)	$\frac{D}{C} \times 100$	Note
16/4	33	28	4	14	(I)
12/8	30	24	8	33	
10/10	31	24	10	41	
8/12	33	25	13	52	
6/14	30	26	15	57	
16/4	30	26	4	15	(II)
12/8	33	28	9	32	
10/10	33	26	14	52	
8/12	35	30	16	53	
6/14	34	30	18	60	

merization when the sample was not saturated with nitrogen.

This appears to result from the formation of homo-polyacrylic acid on account of the effect of oxygen.

The percent graft and the formation rate of homo-polyacrylic acid increase with temperature of the impregnation solution, and so temperature used in present work was below 70°C.

Next, the grafting results of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid (AA)-water (H<sub>2</sub>O) at radiation dose of 6.3 Mrad are shown in Table 4.

Polyester fabric was impregnated with a mixture of acrylic acid-water at 25°C for three hour (I) or 70°C for an hour (II) and then saturated with nitrogen (5cm<sup>3</sup>/sec) for 30 sec.

Table 4 shows that the percent graft increases with the decreasing ratio of H<sub>2</sub>O/AA, but practically at higher levels of grafting it was difficult to extract all the homo-polyacrylic acid with water at 100°C.

The addition of water to acrylic acid monomer to enhance grafting onto polyester fabric has been previously reported by Sakurada.

The amount of water added has been expressed on a ratio basis of AA-solvent solution.

The addition of water on the radiation copolymerization of acrylic acid had a great effect. This appears to the result from the endless solubility of water in acrylic acid and the basis of a swelling effect which enhances diffusion into the polymer, polyester fabric.

It is found from the results shown in Table 4 that the % grafting is 24% when the ratio of H<sub>2</sub>O/AA is 16/4, and the highest value of the efficiency of graft, D/C, is 59%.

Next, the grafting results of acrylic acid onto polyester fabric impregnated with a mixture of acrylic acid (AA)-formic acid (FA) at radiation dose of 6.3 Mrad are shown

in Table 5.

Polyester fabric was impregnated with a mixture of acrylic acid-formic acid at 25°C for three hours (I) or 70°C for an hour (II) and then saturated with nitrogen (5cm<sup>3</sup>/sec) for 30 sec.

It is found from the results shown in Table 5 that the % grafting is 18% when the ratio of FA/AA is 16/4, and the highest value of the efficiency of graft, D/C, is 60%.

### 3) Absorption of Water

The results of water absorption of acrylic acid grafted polyester fabric are shown in Table 6.

The sample fabric was immersed in the water of 22°C for 5 min. and wiped off the water on the surface of fabric with filter paper.

It was weighed after being kept at room temperature for 15 min.

Water absorption was calculated to be the present increase in the weight of a bone dry sample.

As shown in Table 6, the rate of water absorption of untreated polyester fabric (the percent graft, 0%) is only 0.5%. On the other hand, the rate of water absorption of treated polyester fabric (the percent graft, 22%) is 62%.

This value is high as compared to the considerable amount of water absorption of original cotton cloth<sup>10)</sup> (the rate of water absorption, 91%) untreated with radiation.

It is found from the results shown in Table 6 that the rate of water absorption is excellent when the percent graft is in the range of 17-22%.

This can be attributed to the fact that at higher levels of grafting, much amorphous regions in polyester fabric are formed and the hydrophobic properties of polyester fabric are changed into the hydrophilic properties by radiation-induced grafting.

**Table 6. Absorption of water of acrylic acid grafted polyester fabric at room temperature.**

Sample No.	Graft %	Absorption of water (%) after keeping 15 min. in room
10-1	0	0.5
10-2	9	2
10-3	11	5
10-4	14	24
10-5	17	35
10-6	22	62
10-7	25	34

**4) Thermoplasticity (Heat Settability)**

The results of thermoplasticity of acrylic acid grafted polyester fabric are shown in Table 7.

This experiment was carried out to study the relation between heat settability and the percent graft.

To examine this property, the sample fabric (1×4cm, the larger dimension in warp direction) was folded at the center of its long direction and was pressed with iron (115°-125°C) for 1 min., which weighed about 4 kg.

And then the iron was removed and pleat angle was measured after keeping the fabric for 30 min. in air at room temperature.

Though the heat settability is unsatisfactory when the percent graft is less than 9%, it is excellent in the case of the percent graft more than 17%.

**5) Tensile Properties**

The results of the tensile properties of acrylic acid grafted polyester fabric are shown in Table 8.

It is found from the data that excellent tensile properties are given to polyester fabric by acrylic acid grafting.

To examine this properties, the sample fabric was cut into strips 2×8cm.

**Table 7. Thermoplasticity of acrylic acid grafted polyester fabric.**

Sample No	Graft %	Pleat angle (°) 30 min. after ironing
10-1	0	28
10-2	9	21
10-3	11	19.5
10-4	14	19
10-5	17	17
10-6	22	13
10-7	25	11

**Table 8. Tensile strength and elongation of acrylic acid grafted polyester fabric.**

Sample No.	Graft %	Tensile strength (g)	Elongation (%)
10-1	0	3,500	20
10-2	9	4,560	23
10-3	11	4,810	24
10-4	14	5,440	26
10-5	17	5,690	26.5
10-6	22	5,250	28
10-7	25	5,130	31

Tensile strength and elongation were measured with an Instron using 100 mm/min. rate of chart speed and 10 mm/min. rate of Cross Head speed.

As shown in Table 8, tensile strength rises to a maximum at 17% grafting, and then falls off with the increase of the percent graft.

On the other hand, elongation increases with the percent graft. This appears to result from the complexity of the structure because of entanglement.

**6) The Structure of Grafted Polyester Fiber by Electron Micrograph.**

The structure on the surface of acrylic acid grafted polyester fiber was examined by



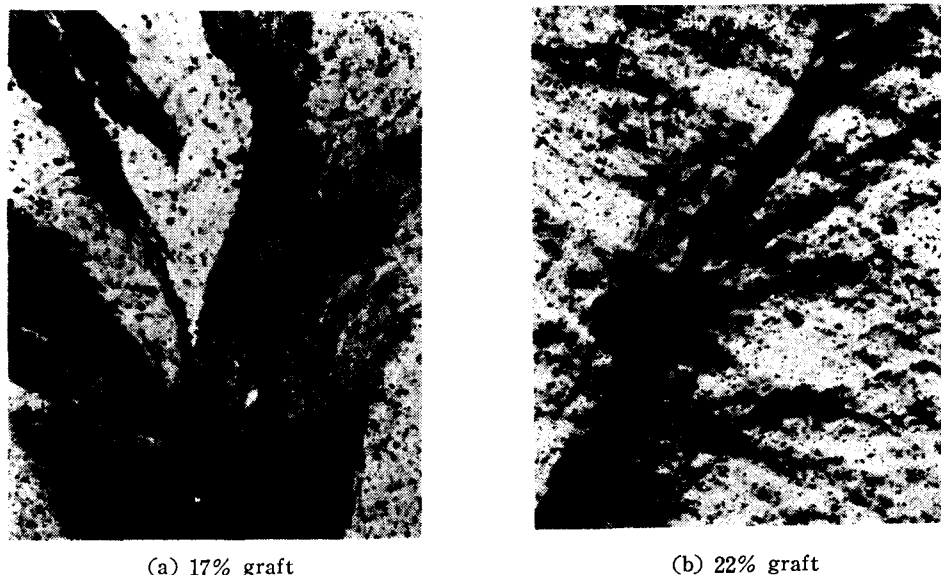


Fig. 2. Electron micrograph of polyester fiber (by replica) containing radiation-grafted polyacrylic acid showing amorphous changes effected during various stages of grafting.

(a) Dose rate 90 rad/sec, total dose 4.4 Mrad.

(b) Dose rate 90 rad/sec, total dose 6 Mrad.

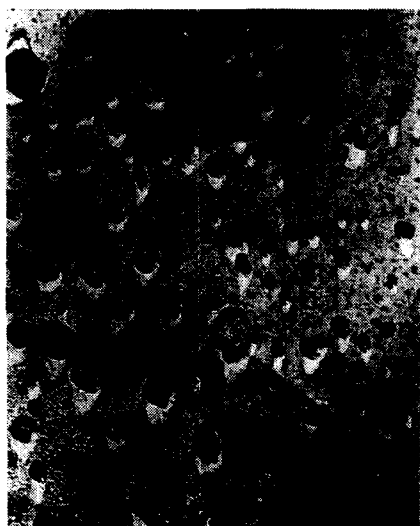


Fig. 3. Electron micrograph of heavily grafted sample of polyester fiber (25% by weight of acrylic acid graft) obtained by an impregnation method. 20,000X

replica method in an electron microscope.

The sample of fiber whose electron micrographs had been swollen in acrylic acid solution at 70°C for an hour and irradiated ( $\text{Co}^{60}$   $\gamma$ -ray, 4.4 Mrad or 6 Mrad).

At a magnification of 20,000X, the electron micrographical investigation of the various percent graft disclosed the existence of certain types of discontinuities on the surface of grafted fiber.

We can distinguish the structure of acrylic acid grafted polyester fiber because Figure 2(a) provides a marked contrast when compared with Figure 2(b).

Figure 3 shows an electron micrograph of heavily-grafted sample of polyester fiber (25% by weight of acrylic acid graft).

As shown in Figure 3, a homogeneous structure seems to exist throughout the entire surface of heavily-grafted polyester fiber.

The specks seen on the surface of polyester fiber appear to be craters rather than voids. This can be attributed to the specks formed when the reaction of copolymerization was taken place by radiation.

Figure 3 shows good agreement with previous work by Stamm and Hosterman<sup>4</sup>, but the

**Table 9. Fastness of various dyes**

Item Sample	Light fastness (degree)	Abrasion fastness (degree)		Washing fastness (degree)		Perspiration fastness (degree)			
		dry	moisture	decolor- ation	contam- ination	acid		alkali	
						decolor- ation	contam- ination	decolor- ation	contam- ination
A	4	4-5	4	4	4-5	4-5	4-5	4-5	4-5
B	1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
C	1	4-5	4	4	3-4	4	2-3	4	2-3

Note (1) : A=Disperse dyes  
 B=Basic dyes  
 C=Acid dyes

Note (2) : Light fastness: KSK 0700 testing method  
 Abrasion fastness: KSK 0650 testing method  
 Wash fastness: KSK 0641 testing method  
 Sweat fastness: KSK 0715 testing method

appearances of specks, if any, seems to be different.

**7) Dyeability and Structure**

The results of fastness of acrylic acid grafted polyester fabric dyed with acid, basic and disperse dyes are shown in Table 9.

It has been demonstrated experimentally that the modified fabric possess excellent dyeability, that true shades are obtained, that good dye penetration is achieved, and that the dyed fabric manifest excellent Wash fastness, Abrasion fastness and Sweat fastness.

As shown in Table 9, light fastness of disperse dyes is good when compared with those of acid and basic dyes.

In Sweat fastness degree of acid dyes is lower than those of basic and disperse dyes.

The data from Table 9 show that the dyeability is somewhat better probably because of a combination of both chemical and physical factors which have not been investigated sufficiently to permit giving a detailed explanation at this time.

Next, the structure on the surface of acrylic acid grafted polyester fiber which was dyed with various dyes was examined by replica method in an electron microscope.

This structure was an entirely different type

when compared with that of figure 2.

At a magnification of 20,000X, electron microscopical investigation disclosed the existence of amorphous structure resulting from the dyeing operation.

Figure 4 shows amorphous structure of acrylic acid grafted polyester fiber dyed with disperse dyes (a) and basic dyes (b).

Next, Figure 5 shows an electron micrograph of heavily-grafted sample of polyester fiber dyed with acid dyes.

At higher levels of grafting, particles of acid dyes seem to go into the amorphous regions of acrylic acid grafted polyester fiber and give the more random structure.

Investigation of photomicrograph<sup>4)</sup> (350X) revealed that the fibers were ring dyed, but investigation of electron micrograph (20,000X) disclosed that the fibers were dyed nonuniformly because of the difference in magnification.

**9. Conclusion**

Direct radiation grafting onto polyester fabric is believed to take place through free radicals which are formed on the polyester backbone.

Practically it was found that not only grafting of acrylic acid but also homo-polymerization took place when drawn crystalline

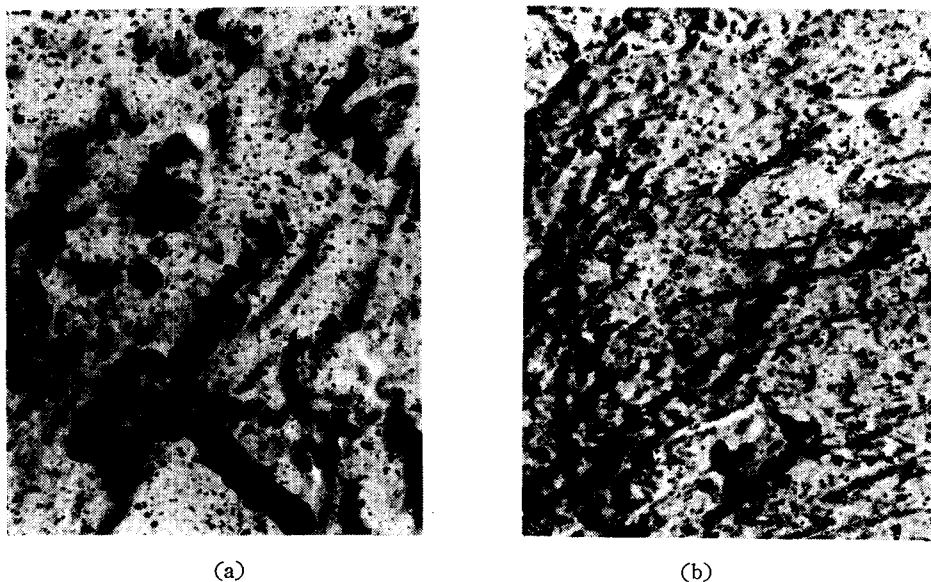


Fig. 4. (a) Electron micrograph of polyester fiber radiation-grafted (18%) with acrylic acid; dyed in aqueous bath for 90 min. at 90–100°C, Kayalon polyester Navy Blue RSF:  
 (b) (18% graft) dyed in aqueous bath for an hour at 70–80°C, Marine Blue RNX



Fig. 5. Electron micrograph of polyester fiber radiation-grafted (22%) with acrylic acid; dyed in aqueous bath for 2 hrs. at 90–100°C, Xylene Blue As. 20,000X

polyester fibers were irradiated with  $\text{Co}^{60}$   $\gamma$ -rays.

Accordingly to our investigation, the main fraction of the apparent graft is truly chemically combined with the backbone polymer,

but fairly much fraction is not a graft copolymer but a homopolymer formed in the matrix of the backbone polymer and is insoluble in a solvent of the homopolymer due to molecular entanglement.

The reaction of polymerization is supposed to increase with the radiation dose. At a low radiation dose (below 3 Mrad) a substantial degree of grafting could not be obtained.

In present work the most useful percent of impregnation was in the range of 30–40%.

When polyester fabric was impregnated with a mixture of acrylic acids–swelling agents such as DMF, DMSO, FA and water, the highest value of the degree of grafting could be obtained in the case which the ratio of a mixture of monomer and swelling agent was 16:4.

As shown in Table 4, strong swelling agent such as water produced even higher levels of grafting than was obtained with other swelling agents.

The effectiveness of these polar liquids in promoting diffusion and grafting appears to

depend mainly on their swelling power for polyester fabric.

It was found in the results of this work that the presence of air during irradiation affected very markedly on the degree of grafting, because the presence of oxygen has an inhibiting effect (Table 4).

The investigation of electron micrograph reveals that certain types of discontinuities on the surface of the grafted fibers exist, and heavily-grafted sample of polyester fiber shows a continuous structure containing an occasional specks of impurity.

It has been demonstrated experimentally that the modified fabric possess excellent dyeability and thermoplasticity, that water absorption and tensile properties are increased, and that the dyed fabric manifest excellent Wash fastness, Abrasion fastness and Sweat fastness.

In conclusion, we wish to state that the radiation-induced grafting of acrylic acid onto polyester can be carried out easily and seems

to be a practical solution to the general problem of conferring dyeability, wetability, thermoplasticity, tensile strength, *etc.* to fabric made from such materials.

#### References

- 1) Sakurada, JAERI **5026**, 74 (1969)
- 2) Sakurada, JAERI **5026**, 46 (1969)
- 3) Sakurada, JAERI **5026**, 56 (1969)
- 4) R. F. Stamm, E. F. Hosterman, J. of Applied Polymer Science, Vol. **7**, pp. 753-782 (1963)
- 5) James K. Rieke, Gerald M. Hart, J. of Pol. Sci., Part C, No. 4, pp. 589-604 (1963)
- 6) Chapiro, A., Radiation Chemistry of Polymer Systems, New York, pp. 596-691 (1962)
- 7) Rice, F. G, Ind. Eng. Chem., 52, **5**, 52A (1960)
- 8) Won Kyu Jung, Dyeing Method (1965)
- 9) Diserensl, The Chemical Technology of Dyeing and Printing. Vol. **I. II.**
- 10) Waichiro Tsuji, Masazo Imai, Report of Institute for Chemical Research, Kyoto University. Vol. **42**, 1, 68-76 (1964)
- 11) R. Y-M. Huang, B. Immergut, J. of Pol. Sci., part A, Vol. **1**, pp. 1257-1297 (1963)