Journal of the Korean Nuclear Society
Volume 5, Number 2, June, 1973

≪Original≫

Radiation Grafting of Hydrophilic Monomers onto Polyester

Jae Ho Choi, Chong Kwang Lee and Kwang Jin Lee

Korea Atomic Enegy Resarch Institute
(Received March 13, 1973)

Abstract

Radiation grafting of acrylic acid and 4-vinylpyridine at room temperature has been studied by an impregnation method to improve the hygroscopic properties, the antistatic behavior and the dyeability of polyester fabric.

Polyester fabric was impregnated with acrylic acid or aqueous emulsion of acrylic acid-4-vinylpyridine by immersion at 25° or 70°C. The impregnated fabric was irradiated under nitrogen gas with γ-rays from Co-60. When acrylic acid grafted polyester fabric was treated with sodium carbonate, calcium acetate and potassium persulfate, tne rate of water absorption was increased and most parts of polyacrylic acid formed were extracted off from the fabric with 0.1% solution of sodium hydroxide at 100°C.

In the case of the impregnation of a mixture of acrylic acid and 4-vinylpyridine the petcent of grafting has been shown to be proportional to the ratio of 4-VP/AA and radiation dose.

Estimating by contact angle measurements of water on the various polymer surfaces, the antistatic behavior was decreased with the increase of grafting percent.

The investigation of electron micrograph disclosed the existence of certain type of discontinuities in the acrylic acid grafted polyester fiber which was treated with various salts.

요 약

본 실험은 방사선을 이용하여 Polyester 직포의 흡수성과 염색성 그리고 대전성을 증진 시키기 위한 연구로서 실온하에서 함침법으로 Acrylic acid 또는 4-vinylpyridine 을 Polyester 직포에 접목시켰다.

Polyester 직포를 25° 또는 70°C 에서 Acrylic acid 나 Acrylic acid 와 4-vinylpyridine 의 emulsion 용액에 함침시켰으며 함침된 Polyester 직포를 질소깨스 존재하에서 Co-60 의 γ-rays 로 조사시켰다.

Acrylic acid 가 접목된 Polyester 직포를 Sodium carbonate, Calcium acetate 또는 Potassium persulfate 로 처리하였을때 흡수율은 더욱 증가하였으며 직포 표면에 형성된 polyacrylic acid 는 0.1% NaoH 용액으로 대부분 추출되었다.

4-vinylpyridine 과 Acrylic acid 의 혼합용액을 함침용액으로 사용하였을 경우 4-

VP/AA의 비율과 방사선 선량이 커짐에 따라 접목율은 점점 증가함을 보여주었다.
여러가지로 처리된 Polyester 직포 표면에 물방울을 떨어 뜨렸을 때의 Contact angle을 측정하여 보니 접목율이 증가함에 따라 대전성은 감소하였다.
Acryli acid가 접목된 Polyester 섬유를 Salt로 처리하여 전자 현미경으로 관찰하여 본 결과 일련의 무정형 형태로 결합되어 있었다.

1. Introduction

Radiation grafting of vinyl monomers has been studied by an impregnation method[1-3] to improve the hygroscopic properties, dyeability, and antistatic behavior of polyester fabric. Polyester fabric was impregnated with acrylic acid, 4-vinyl-pyridine, and aqueous emulsion of acrylic acid-4-vinylpyridine at selected temperature, the impregnated fabric was irradiated under nitrogen with γ-ray from Co-60.

A satisfactory degree of grafts could be obtained when the percent of impregnation solution was in the range of 30-40%. All homopolymer formed on the surface of polyester fabric by the irradiation could not be extracted entirely with water at 100°C, but almost all polymer formed could be extracted with 0.1% solution of sodium hydroxide at 100°C.

The water absorptions of the sodium salts, calcium salts, and potassium salts of the acrylic acid grafts were more excellent than those of acrylic acid grafted polyester fabrics.

In order to enhance the effectiveness for grafting, a mixture of hydrophilic and hydrophobic monomer was used.

The highest value of the degree of grafting could be obtained in the case which the ratio of a mixture of monomer was 90:10, and at this time PH of a mixture was in the range of 7-8.

The purpose of this paper is to describe the preparation of typical hydrophilic grafts on polyester fabric, investigate their structure, and examine some of the unusual properties of these grafts.

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

The antistatic behavior[4] was decreased to the graft, and properties which depend on amorphous aeras, such as water absorption and dyeability, were very enhanced.

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 salts of the acrylic acid grafts was excellent even if it was dyed, basic or disperse dyes in conventional aqueous dye bath at low temperature. Also the dyeability of acrylic acid-4-vinylpyridine grafted polyester fabric was particularly excellent in acid dyes.

The investigation of electron micrograph(by the method of replication and shadow casting) disclosed the existence of certain type of discontinuities in the polyester backbone grafted with monomer. Comparing synthetic fiber to natural fiber, there are a great differences in making use of textile fabric and so grafting of vinyl monomers onto a hydrophobic polymer such as polyester is an effective means of improving the various properties[5].

The technique to prepare graft copolymer using ionizing radiation have been reviewed by Chapiro[6].

2. Experimental

(1) Materials

Polyester fabric was purified by treating with a mixture of 1% solution of sodium carbonate, 3% solution of Na-dodecyl benzenesulfonate, and 0.3% solution of tween 80 at 80°C for 2-3 hrs, and by bleaching with calcium hypochlorite and then washing thoroughly with distilled water.

Distilled water was used without any futher purification. Acrylic acid monomer was purified in the usual manner[7] by distilling under vacuum(56°C, 20 mmHg) and used immediately after distilling or stored -10°C.

4-vinylpyridine monomer was purified by distilling under vacuum (62-65°C, 15-20 mmHg) and used immediatelyafter distillation. Potassium persulfate, calcium acetate, sodium carbonate, hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, formic acid, oxalic acid, acetic acid, and sodium hydroxide used were pure grade.

All the dyes such as acid, 1. Xylene blue AS or Xylene red B as basic, 2. Marine blue RNA, Rhodamine B, or Methyl violet 5B and disperse dyes 3. Kayalong polyester navy blue RSF, Kayalon polyester light yellow 6GSF made in Swiss were used.

(2) Preparation of samples

The impregnation of vinyl monomer into polyester fabric was carried out according to the methods described by Sakurada[1-3]. Purified and bleached polyester fabric was cut into 10×10Cm, weighted exactly.

The sample fabric was impregnated with acrylic acid, 4-vinylpyridine, or a mixture containing acrylic acid and 4-vinylpyridine by immersion at 25°C for 3 hrs. or 70°C for an hour. The impregnated fabric was weighed immedately after the wiping off the solution on the surface of the sample fabric with filter paper. The amount of monomer solutions impregnated was measured to check the condition of experiment.

The impregnated fabric was placed in test tube or stainless steel container, followed with nitrogen and then stoppered quickly.

(3) Irradiation

The irradiation was carried out in a Gamma-cell, an 25,000 Curie Co-60 irradiation facilty, located at Atomic Energy Research Institute. The polyester fabric was irradiated under nitrogen with γ-rays, at a dose rate ranging from 3.7 to 4.1 Mrad/hr., all doses being determined by the ferrous sulfate dosimeter.

The total irradiation dose of a sample was regulated by controlling the total exposure time. Details of a similar irradiation facility are described elsewhere[8].

(4) 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 sample before removing homopolymer formed on the surface of polyester fabric.

The contents weighed were soaked in 0.1% solution of sodium hydroxide to extract the unreacted acrylic acid, 4-vinylpyridine or a part of soluble homopolymer and then extracted continuously at 100°C. Generally the time needed to extract soluble homopolymer was 2-3 hrs., but in the case of heavily grafted polyester fabric the time needed to extract was 4-5 hrs.

The extracted samples were washed with hydrochloric acid (PH=3) and dried in an oven at 100°-105°C for 1 hr. and weighed to determine the extent of grafting. The weigh increase after extraction was taken to be the weight of polyacrylic acid or poly-4-vinylpyridine grafted to the polyester.

The percent grafting[9] is calculated as the ratio of the weight increase to the weight of the original polyester.

$$\%\ \text{grafting} = \frac{\begin{array}{c}\text{bone dry weight of grafted}\\ \text{product—bone dry weight}\\ \text{of original polyester}\end{array}}{\begin{array}{c}\text{bone dry weight of}\\ \text{polyester}\end{array}} \times 100$$

(5) Salt Treatment and Dyeing

1) Salt treatment

The method in preparation of the sodium, calcium, and potassium salts of the acrylic acid grafts, which was originally used by E. E. Magat and J. Zimmerman[17], was applied in the present work to enhance water absorption of polyester fabric.

The sodium salts of the acrylic acid grafts were prepared by agitating grafted fabrics for one hour at 80°C in a 0.1% aqueous solution containing twice the fabric sample weight of sodium carbonate. The calcium salts were prepared by agitating grafted fabrics in a 0.1 % solution of calcium acetate for one hour at 80°C and the potassium salts were prepared by agitating grafted fabrics in a 0.1% solution of potassium persulfate, along with the same method.

2) Dyeing

Acrylic acid or 4-vinylpyridine grafted polyester fabrics were dyed with various dyes in aqueous dye bath. The dyeing methods[10,11] were as follows.

a) 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 10 min. 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.

b) 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, 0.3ml of sulfuric acid and 1.8g of common salt per 700 ml. Starting at 40°C, it was raised to 90-100°C during 20min. and maintained at that temperature for an hour. After cooling to 70°C in the air, it was rinsed and dried.

e) 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.

(6) Physical Tests and Electron Micrographic Investigations

The relative antistatic behavior of acrylic acid grafted polyester fabric was estimated by contact angle measurement of water on the surface of the grafted fabric.

The percents of the relative water absorption of the sodium salts, calcium salts, and potassium salts of the acrylic acid grafts were calculated as the ratio of the weight increase to the weight of acrylic acid grafted polyester fabrics.

The samples were soaked into water at 20°C, taken out after a definite time and the weight increase was determined.

To compare the dyeability of original polyesterfabric to radiation treated polyester fabric such as the acrylic acid grafts, the 4-vinylpyridine grafts, and the salts of the acrylic acid grafts, the samples were dyed with acid, basic, and disperse dyes according to the dyeing methods.

The structures of the surface of original polyester fiber and the surface of radiation-treated fiber such as acrylic acid grafted fiber and fiber of the salt of the acrylic acid grafts were investigated by electron micrographs[12] (X28,000).

3. Results and Dicussion

(1) Grafting *VS.* Time and Temperature

of Impreanation

The relations of the amount of acrylic acid grafted on polyester fabric to the time and temperature of impregnation at radiation dose of 6 Mrad are shown in Table 1.

Table 1. Grafting percent of acrylic acid on temperature and impregnation time.

Temperature (°C)	Graft (%)	Impregnation time	Graft (%)
18	1.7	5min	3.5
30	2.8	10 〃	9.7
50	4.2	1hr	10.6
60	6	2 〃	12.3
70	10.5	3 〃	14
80	8.5	4 〃	8.5
90	7.1	6 〃	7.2
(I)		(II)	

(I) of Table 1 shows the percent of grafting on the temperature of impregnation solution. Polyester fabric was impregnated with acrylic acid monomer for an hour.

The results were obtained at the impregnation temperature ranging from 18° to 90°C when the amount of impregnation was 40%. It is found from the results shown in (I) of the Table that the percent graft is 1.7% when the temperature of inpregnation solution is 18°C, and 2.8% when the temperature of impregnation solution is 30°C, and 10.5% when the temperature is 70°C.

This appears to the result from the basis of a swelling effect which enhances diffusion into polyester fabric. In the case which the temperature of impregnation solution is above 70°C, the percent of grafting is decreased because the formation rate of homo-polyacrylic acid on the surface of polyester fabric is supposed to increase by thermal polymerization.

(II) of Table 1 shows the percent of grafting on the impregnation time. The results were obtained at the impregnation time ranging from 5 min. to 6hrs. when the temperature of impregnation solution was 70°C.

As shown in (II) of Table 1, the percent of grating was 3.5% when the impregnation time was 5min. and 9.7% when the time was 30 min.

The highest value of the degree of grafting was obtained in the case which the time of impregnation was 3 hrs., but above 3 hrs. the percent of grafting was decreased.

It was thought to the result which lots of homo-polyacrylic acid were formed on the surface of polyester fabric on account of long time of impregnation before occuring radiation grafting reaction. The maximum condition of being able to obtain the highest value of the degree of grafting was the case which the time of impregnation was 3 hrs. and the temperature of impregnation solution was 70°C.

(2) water absorption of salts

The results of water absorption of acrylic acid grafted polyester fabric and water absorption of the sodium, caltium, and potassium salts of the acrylic acid grafts are given in Table 2. water absorption was calculated to be the percent increase in the weight of a bone dry sample. The rate of water absorption of polyester fabric untreated with radiation (the percent graft, 0%) was 4.5%.

As shown in Table 2, the rate of water absorption of acrylic acid grafted polyester fabric was 6.5% the percent graft, 6% and 26% (the percent graft, 18%) respectively.

This can be attributed to the fact that at higher levels of grafting, much salt forms in amorphous regions of polyester fabric are built up and the hydrophobic properties of polyester fabric are changed into the hydrophilic properties.

The rate of water absorption of the salt forms was higier than that of water absorption

Table 2. Absorption of water of salts and acrylicacid grafted polyested fabric

Graft (%)	Absorption of water (%)			
	none—salt	Na—salt	Ca—salt	K—salt
6	6.5	12.8	9.6	9.2
9	8.2	20.3	10.4	9.5
11	11	27.9	16.9	11.3
14	15.4	36	19.6	16
16	21	41.2	29	24.2
18	26	47	31	27

of acrylic acid grafted fabric. In the case of the sodium salt, the rate of water absorpton (the percent graft, 6%) was 12.8% and for the calcium salt the rate of water absorption was 9.6% and for the potassium salt the rate of water absorption was 9.2%.

In general, the rates of water absorption of the salt forms increase with the percent of grafting.

This can be attributed to the fact that the salt forms retain much improved hydrophilic properties on account of sodium, calcium, and potassium ions.

In comparing the result of the sodium salts to that of the potassium salts, there were a great differences in the rate of water absorption. Usually acrylic acid homopolymer formed on the surface of polyester fabric is extracted with a dilute solution of strong base. The basicity of 0.1% solution of sodium hydroxide used in present work is lower than that of o.1% solutioun of potassium persulfate and so the rate of water absorption of fabric treated with 0.1% solution of potassium persulfate is supposed to be low.

(3) Grafting *VS.* PH of a Mixture of 4-vinylpyridine and Acrylic Acid

The percent grafts on PH[13] of a mixture of 4-vinylpyridine and acrylic acid or 4-vinylpyridine are shown in Table 3. Polyester fabric was impregnated with 4-vinylpyridine or aqueous emulsion of 4-vinylpyridine and acrylic acid at 70°C for an hour and saturated with nitrogen and then irradiated with Co-60 γ-ray. It is found from the data that in the case of being impregnated with 4-vinylpyridine, the percent of grafting(the ratio of a mixture of monomer, 100:0) is 64% and at this time PH is 7.8, and for a mixture of 4-vinylpyridine-acrylic acid the percent of grafting(the ratio of a mixture of monomer, 90:10) is 89.5% and at this time PH is 7.3. The addition of acrylic acid on the radiation copolymerization of 4-vinylpyridine had a great effect.

Table 3. Grafting of 4-vinylpyridine and acrylic acid to polyester fabric.

Total monomer conc:10% emulsifier conc :0.5% total dosei 6Mrad.

Composition of monemers(4VP/AA) by vol.	PH	Graft (%)
100/0	7.8	64
95/5	7.6	72
90/10	7.3	89.5
80/20	6.5	25
70/30	6	4.4
60/40	5.8	1.2
50/50	5	2.5
20/80	4	4
0/100	2	9.5

On the other hand, the value of the degree of grafting was very low when the solution of a mixture of 4-vinylpyridine and acrylic acid was acidic.

Comparing the percent graft to PH of a mixture, the highest value of the degree of grafting could be obtained in the case which PH was nearly neutral.

(4) Grafts and Effects of Addition of Various Acids

The grafting results of inorganic and organic acids onto polyester fabric imprgnated with

4-vinylpyridine at radiation dose of 6.3 Mrad are shown in Table 4.

When 2cc of lM-acid solution was added to 10cc of 10% aqueous emulsion of 4-vinylpyridine, the percent of grafting was 10.2% in the case of hydrochloric acid, and 15.3% for nitric acid. On the other hand, the percent of grafting in the case of phosphoric acid was 36.5% and at this time PH was in the range of 7-8.

Table 4. Effect of addifion of various acious acids on the grafting of 4-vinyipyridine to polyester fabric.

Totol dose: 6×10^6 rad

Acid	Graft (%)
Hydrochbric acid	10.2
Nifric acid	15.3
Sulfuric acid	9.4
Phosphoric acid	36.5
Formic acid	6.7
Oxalic acid	7.8
Acetic acid	12

The addition of various acids to aqueous emulsion of 4-vinyl-pyridine to enhance grafting onto polyester fabric has been previously reported by Okada[13].

Long and Thompson[18] have observed that the diffusion of organic vapor into plasticized hydrophilic film is faster than into unplsticized facilifilm.

The effect to enhance grafting is believed to be caused by the breaking of hydrogen bonds with various acids, thus providing greater segmenta lmobility of the polymer molecules and tating the diffusion of various acids.

(5) Grafts and Effects of Concentration of Comonomer

Effects of comonomer concentraions of 4-vinylpyridine and acrylic acid, and concentration of acrylic acid on the direct radiation grafting onto polyester fabric are shown in Figure 1.

Concentration of comonomer of 4-vinylpyridine and acrylic acid, and monomer of acrylic acid used in present work were 10%, 5%, 2.5%, and 1%.

Generally the percent graft shown in Figure 1 is seen to increase with increasing concentration of monomer and almost linearly with increasing radiation dose.

Comparing the percent graft of a mixture of 4-vinylpyridine and acrylic acid to that of acrylic acid, the percent graft of comonomer was higher than of acrylic acid monomer.

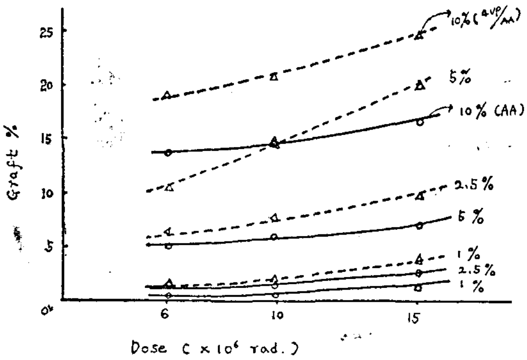


Fig. 1. Effect of comonomer concentration on the grafting of 4-vinylpyridine and acrylic acid to polyester fabric.
comonomer composition: 4-VP/AA=8/2

It is found from the results shown in Figure 1 that the percent graft is 19% at radiation dose of 6 Mrad when the concentration of comonomer is 10%, and 14% when the concentration of acrylic acid monomer is 10%.

On the other hand, the percent of grafting is 25% at radiation dose of 15 Mrad when the concentration of comonomer is 10%, and the perc ent of grafting is 14% for acrylic acid monomer at the same dose.

As a result, a more effective way of enhancing the percent graft is by treating with a mixture of acid and basic monomer, But no logical reason can be given for this behavior.

(6) Grafts VS. Mole Fraction

The results of the percent graft on mole fraction of a mixture of 4-vinylpyridine and acrylic acid are shown in Figure 2. As shown in Figure 2, the percent graft is 60% in the case which mole fraction is zero, and in addition of acrylic acid to 4-vinylpyridine (mole fraction, 0.14) the percent graft is about 90%.

Grafting increases linearly with mole fraction till approximately 90% grafting and then levels off sharply. No grafting was obtained at 0.5 mole fraction, and maximum grafting was obtained at 0.14 mole fraction. At 0.14 mole fraction PH was in the range of 7-8.

Aa a result, the condition of the most effective grafting on a mixture of 4-vinylpyridine and acrylic acid was the case which PH of the mixture was in the range of 7-8.

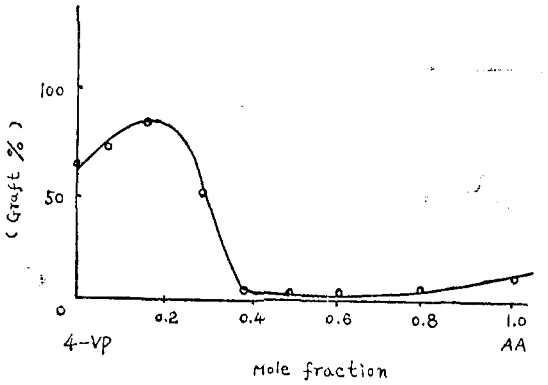


Fig. 2. Grafting of 4-vinylpyridine and acrylic acid to polyester fabric.
4-VP+AA:10%, Emulsifier:0.5%, Total dose:6Mrad.

(7) The Antistatic Behavior

Since the problem of static buildup is generally encountered at low humiditics, the relative antistatic behavior[14,15] is estimated by contact angle measurements of water on the surface of radiation-chemical treated polyester fabric.

The phenomenon of contact angle of water on the surface of acrylic acid grafted polyester fabric is shown in photos of Figure 3, and the degree of contact angle is given in Table 5.

The generation of static charges has been attributed to a variety of causes, most often originating in some form 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[4].

Other possible causes of electron transfer between surfaces include pyroelectric or thermal effects, and piezoelectric or thermal effects, and piezoelectric or pressure effect[16].

It is clear that there is no universally accepted mechanism for electron transfer between surfaces. On the other hand, it has been suggested that in the case of textile meterials the major cause of static charge buildup is ion transfer between one fiber surface and another.

There, improvement of antistatic behavior in polymers has been based on methods which increase the surface conductivity.

The common modification utilized in antistatic chemical treatment to polyester is the depositon within or formation on the polymer surface ef hydrophilic groups.

As shown in Table 5, visual contact angle decreases with increasing of the percent graft.

Figure 3 displays water drops on the surfaces of acrylic acid grafted polyester fabric.

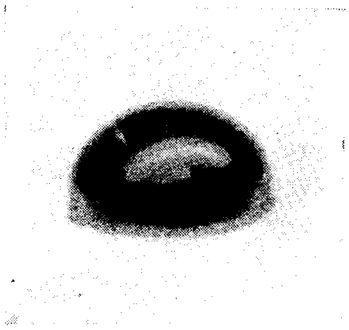
As a result, the lower contact angles on polyester fabric indicate increased ability to dissipate static charges.

Table 5. Relation of grafting % with visual contact angle.

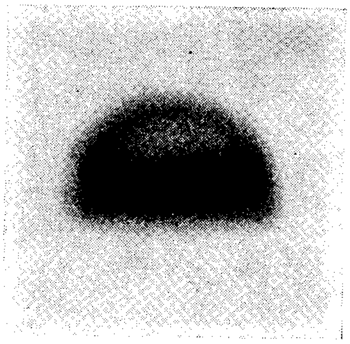
No. of photo	1	2	3	4	5	6
Graft (%)	0	6	8	10	12	14
Contactangle(o)	95	82	65	52	45	27

(8) The Structure of Polyester Fiber by Electron Micrograph and Dyeability

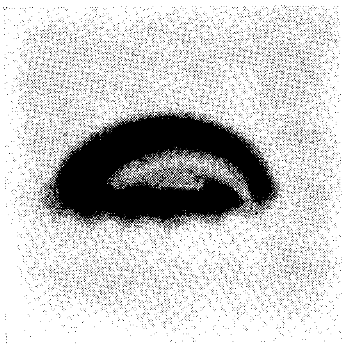
The structures of the surface of original polyester fiber, acrylic acid grafted fiber, and



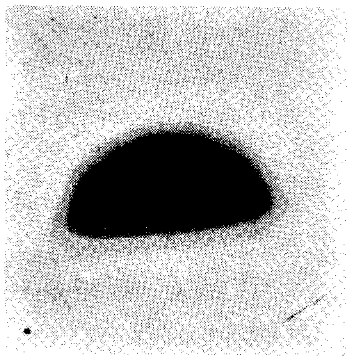
(1) 0%



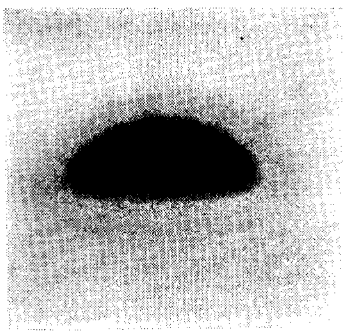
(2) 6%



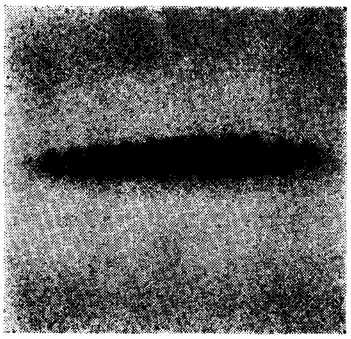
(3) 8%



(4) 10%



(5) 12%



(6) 14%

Fig. 3. Effect of antistatic behavior on visual coutact angle.

the salts such as the sodium, calcium, and potassium salts were examined by replica method in an electron microscope.

Figure 4 shows electron micrographs of original polyeser fiber and of acrylic acid grafted fiber (the percent graft, 10%) at a magnification of 28,000X. We can distinguish the structures of original fiber and acrylic acid grafted fiber because Figure 4(a) provides a marked contrast when compared with Figure 4(b).

As shown in Figure 4, (a) shows the structure ot backbone of original polyester fiber untreated with radiation and (b) shows amorphous structure of acrylic acid grafted fiber.

Figure 5 shows the structure of the salts of the acrylic acid grafts; (a) of Figure 5 shows the structure of the sodium salt, and (b) shows the structure of the calcium salt, and

(a)

(b)

Fig. 4 (a) Electron micrograph of original polyester fiber
(b) Electron micrograph of polyester fiber containing radiation-grafted (10%) polyacrylic acid showing amorphous changes effected during various stages of grafting (×28,000)

(c) the potassium salt. These structures were entitrely different types when compared with those of Figgure 4.

To compare dyeability of original polyester fabric to acrylic acid grafted fabric and the salts of the acrylic acid grafts, the samples were dyed with acid, basic, and disperse dyes.

In general, it is difficult to dye original polyester fabric with all the dyes except disperse dyes. But it was found that the dyeability of acrylic acid grafted fabric was excellent, and that of the salts of the acrylic acid grafts was more excellent. Particularly the dyeability of the sodium salts of the acrylic acid grafts was the most excellent of all the samples even if those were dyed with acid, basic, and disperse dyes at low temperature. This can be attributed to the fact that dyeability is somewhat better probably because of amorphous structure, affinity of sodium ion for dye molecules, and a combination of both chemical and physical factors which have not been investigated sufficiently to permit giving a detailed explanation at present work.

4. Conclusion

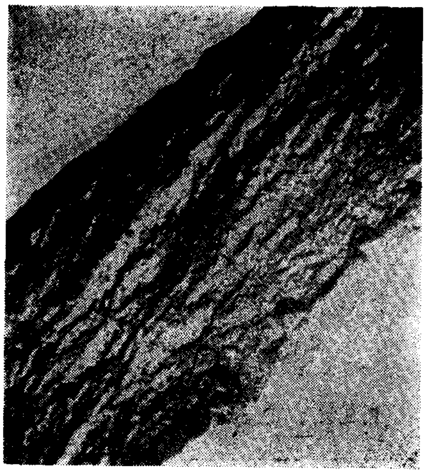
Acrylic acid, 4-vinylpyridine, and aqueous emulsion of 4-vinylpyridine-acrylic acid were used for radiation-induced grafting in order to improve the properties of polyethylene terephthalate (PET).

The percent graft and the formation rate of homo-polyacrylic acid was increased with increasing of the amount of impregnation and so a satisfactory degree of grafting could be obtained when the amount of impregnation was in the range of 30-40%. Control of the amount of grafting was achieved by adjustment of the concentration of monomer, the percent of impregnation, and radiation dose.

Most of polyacrylic acid homopolymer formed on the surface of polyester fabric was extracted with 0.1% solution of sodium hydroxide, but a part of homoplymer of 4-vinylpyridine was insoluble in a solvent of homopolymer due to molecular entanglement.

The maximum condition of being able to obtain the highest value of the degree of grafting was the case which the temperature of impregnation solution was 70°C, and the

(a)



(b)

(c)

Fig. 5 (a) Electron micrograph of polyester fiber radiation grafted (10%) with acrylic acid; treated with 0.1% solution of sodium carbonate
(b) treated with 0.1% solution of calcium acetate
(c) treated with 0.1% solution of potassium persulfate

time of impregnation was 3 hrs.

The acrylic acid grafts on polyester fabric were readily converted to the corresponding sodium, calcium or potassium salts by treatment with sodium carbonate, calcium acetate or potassium persulfate. In contrast to the percents of water absorption of the acrylic acid grafts, those of water absorption of the salts of the acrylic acid grafts were higher.

The sodium salts of the acrylic acid grafts were most hydrophilic. A more effective way to increase the percent of grafting was the case of addition of acidic monomer to basic monomer.

In this case the ratio of 4-vinylpyridine/acrylic acid was 90/10 and PH of the mixture was in the range of 7-8.

The addition of inorganic acids such as phosphoric, sulfuric, and hydrochloric acid or organic acids such as acetic and oxalic acid to 4-vinylpyridine had a great effect on the radiation copolymerization. The combination of ionizing radiation from a Co^{60} source plus chemical treatment in selected reactive solution yields significant reductions in water contact angles on polyester surfaces. The magnitude of the reduction in contact angle was shown to be approximately proportional to the rate of water absorption of acrylic acid grafted polyester fabric.

The lower contact angles on polyester surfaces indicate increased ability to dissipate static charges.

In contrast to dyeability of acrylic acid grafted polyester fabric, that of the salts of the acrylic acid grafts was well. Particularly the dyeability of the sodium salts of the acrylic acid grafts was excellent.

The investigation of electron micrograph reveals that certain types of discontinuities on the surfaces of the grafted fiber exist. It has been demonstrated experimentally that the medified fabric posseses excellent dyeability, that water absorption is increased, and that the antistatic behavior is decreased.

In conclusion, we wish to state that the radiation-induced grafting of acrylic acid onto polyester seems to be a practical solution to the general problem of conferring dyeability, wettability, the antistatic behavior, etc. to fabric made from such material.

References

1) Sakurada, JAERI **5026**, 74 (1969)
2) Sakutada, JAERI **5026**, 46 (1969)
3) Sakurada, JAERI **5026**, 56 (1969)
4) A.S. Hoffman and G.R. Berbeco, Textile Research Journal, (975-982) November, 1970
5) Toshio Okada and Ichiro Sakurada, JAERI **5027**, 4 (1971)
6) Chapiro, A., Radiation Chemistry of Polymer System, New York, pp. 569-691 (1962)
7) R.Y.-M. Huang, B. Immergut, J. of Pol., Sei., Part A vol. **1**, pp. 1257-1297 (1963)
8) Rice, F.G., Ind. Eng. Chem., 52, 5, 52A(1960)
9) R.Y-M. Huang, W.H. Rapson, J. of Pol. Sci., Part C, No. 2, PP. 169-188
10) Won Kyu Jung, Dyeing Method (1965)
11) Diserens L, The Chemical Technology of Dyeing and Printing, Vol. **1**, **11**
12) R.F. Stamm, E.F. Hosterman, J. of Applied Polymer Science, Vol. **7**, pp. 753-782 (1963)
13) Toshio Okada, Yasue Suzuki JAERI **5018**, 5 (1968)
14) Bikerman, J.J., Ind. Eng. Chem. Anal. 13 PP. 443-444 (1941)
15) Shashona, V. E., J. Polymer Sci. **33**, 65-85 (1958)
16) Henry, P.S.H., Survey of Generation and Dissipation of Static Electrictricity, Brit. J. Appl. Phys. Suppl. No. 2, S6-S10 (1953)
17) E.E. Magat and J. Zimmerman, J. of Polymer science; Part C, No. 4, PP. 615-629 (1663)
18) Long, F. A., and L. J. Thompson, J. Polymer Science, **14**, 321 (1954)