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Radiation-Induced Graft Copolymerization of Acrylic Acid onto Polyester

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Abstract

The radiation-induced graft polymerization of acrylic acid onto polyester fabric was investigated with accelerated electron beams as ratiation source at high dose rates.

Homopolymerization was suppressed by addition of cations which is known as homopolymerization inhibitor, but this practical advantage was obtained at the expense of grafting efficiency. The rate of grafting (%/sec) was proportional to the 0.82th power of dose rates over the range from 1.6×10^6 to 10×10^6 rad/sec.

The grafted polyester fabric showed considerable improvement in moisture regain and antistatic properties.

요 약

High dose rates의 전자선을 이용하여 polyester 직포에 acrylic acid를 중합 반응시켰다.

Homopolymerization inhibitor로서 cation을 첨가시키면 homopolymerization 뿐만 아니라 graft효율도 감소되었다. Graft 중합 반응 속도는 선량율이 1.6×10^6 rad/sec에서부터 10×10^6 rad/sec 사이에서 선량율의 0.82승에 비례하였다.

Acrylic acid가 graft 중합 반응된 polyester 직포는 흡습성, 제전성 효과 등이 크게 증진되었다.

1. Introduction

Radiation grafting of acrylic acid[1-10] onto polyester fibric was carried out by an impregnation technique using electron beams from a 300 KeV, 25mA electron accelerator.

The possibility opened by radiation-induced grafting is the preparation of polymers combining the hydrophobic properties of polyester with hydrophilic properties of polyacrylic acid.

Highly crystalline polyester fiber prevented the monomer molecules from diffusing into the interior of polyester fiber, and so the polyester fiber was swollen by swelling agents such as 1,1-dichloroethane or 1,1,2-trichloroethane.

Inhibitors such as Mohr's salt or cupric sulfate were used to suppress the homopolymerization of acrylic acid monomer.

A possible mechanism for the reactions of propagating polymer radicals and cations (homopolymerization inhibitor) has been studied and the properties of the grafted copolymer was investigated.

The basic data were obtained at various radiation doses, dose rates and the relation of dose rate to grafting rate were obtained by the simultaneous irradiation of acrylic acid-polyester fiber in the presence of the different cations.

2. Experiment

2-1 Materials

Polyester fabric samples were purified by treating with a mixture of 1% solution of sodium carbonate, 3% solution of sodium-dodecylbenzene sulfonate and 0.3% solution of Tween 80 (surfactant) at 80°C for 2-3 hours.

Acrylic acid monomer (AA) was purified by vaccum distillation[11] (20 mmHg, 56°C) and used immediately after distilling or stored below 0°C.

Sodium carbonate, Mohr's salt, cupric sulfate, 1,1-dichloroethane, 1,1,2-trichloroethane, sodium nitrate, potassium nitrate were EP reagent grade and were not purified further.

2-2 Irradiation

Irradiation was done by electron beam from electron accelerator of the Korea Atomic Energy Research Institute.

Dose rate of electron beams was in the range of 1.6-10 Mrad/sec.

The radiation dose was measured with CTA (cellulose triacetate) film or polycarbonate film as standard.

2-3 Preparation of Samples and Graft Copolymerization

Purified polyester fabric was cut into suitable strips and weighed exactly.

The sample fabirc was immersed in the mixed solution which was composed of acrylic acid, homopolymerization inhibitor such as Mohr's salt or cupric sulfate and swelling agents such as 1,1-dichloroethane or 1,1,2-trichloroethane.

The amount of the mixed solution containing polyester fabric was controlled by padding method.

The sample was irradiated with electron beams in air or nitrogen.

The fiber was graft-copolymerized in the simultaneous irradiation at a dose rate ranging from 2.6 to 9.2 Mrad/sec. at room temperature.

The fibric samples obtained after the grafting step, was kept immersed in warm water at 50°C for 3-5 hours and dried in oven.

This treatment appears to be sufficient to remove the unreacted monomer and all of the polyacrylic acid homopolymer during the irradiation.

The graft polymer content of the original fibric sample was calculated from weight deviation.

The per cent grafting was obtained from the weight gain of the polyester on grafting.

2-4 Measurement of Water Absorption and Moisture Regain.

When a drop of distilled water was dropped on the surface of the polyester fabric at 2cm height and was completely absorbed on the fabric, the difference of absorption time between the original and the graft-copolymerized fabric was measured.

The moisture regain of the acid form and sodium salt form of the grafted polymers was determined respectively by allowing the samples to attain moisture absorption equilibrium at 23°C and 66% or 94% relative humidity (RH).

2-5 Measurement of the Static Charge developed and Half Life

The humidity control chamber and electrostatic tester were used to determine the static charge developed in 45% relative humidity at 20°C.

The half life is the time repuired to fall into half value of the static charge developed.

The difference of half life between original and graft copolymerized fabric was determined by electrostatic tester.

3. Results and Discussion

3-1 Effect of Acrylic Acid Concentration and Oxygen on Grafting

The Polyester fabric was kept immersed in the solution, which was composed of acrylic acid, Mohr's salt solution (4×10^{-2} mole/*l*) and 1, 1-dichloroethane (20% by volume ratio) at 30-35°C for one hour.

The per cent pick up of acrylic acid was controlled to approximately 100% by the padding method.

The treated fabric was irradiated at the dose rate of 7.5 Mrad/sec in air or nitrogen condition.

As shown in Table 1, the per cent of grafting was increased with increasing concentrations of acrylic acid.

The per cent of grafting of acrylic acid onto polyester in air was almost equal to the per cent of grafting in nitrogen.

It is considered from such a result that oxygen has no sufficient time to attack the propagating radicals because of the short irradiation time at high dose rates.

It was clear that there was little effect of oxygen at high dose rate used.

3-2 Effect of Swelling Agent on Grafting

The effect of 1, 1-dichloroethane in impregnating solution on the grafting of acrylic acid onto polyester fabric in air or nitrogen is shown in Table 2.

The per cent of grafting was increased with increasing concentrations of the swelling agent.

It is shown from Table 2 that the per cent of grafting in solution containing 1, 1-dichloroethane (20% by volume ratio) was

Table 1. Grafting of acrylic acid onto polyester fabric by impregnation method.
Impregnation: 35°C, 24hr: Concn. of Mohr's salt, 4×10^{-3} mole/l
Swelling Agent: Ethylene dichloride (ED)
Irradiation: Electron beams; total dose, 7.5 Mrad

Comp. of Monomer Mixt. AA/H_2O/ED by Vol.	Apparent graft, %	
	Air	Nitrogen
70/10/20	12.4	15.8
60/20/20	8.8	10.0
50/30/20	6.8	6.8
40/40/20	5.7	6.4
30/50/20	5.4	5.5
20/60/20	4.0	4.9

Table 2. Effect of ethylene dichloride in impregnating solution on the grafting of acrylic acid onto polyester fabric.
Impregnation: 35°C, 24hr:Concn. of Mohr's salt, 4×10^{-3}mole/l
Irradiation: Electron beams: total dose, 7.5 Mrad

Comp. of Monomer Mixt. AA/H_2O/ED by Vol.	Apparent graft, %	
	Air	Nitrogen
60/40/ 0	1.8	2.3
60/40/10	2.9	4.3
60/40/20	4.5	6.2
60/40/30	4.5	5.5
60/40/40	4.9	5.7

2-3 times larger than the per cent of grafting in the solution containing no 1, 1-dichloroethane.

It is supposed that the swelling of polyester fiber is caused mainly by sorption of 1, 1-dichloroethane and the crystalline regions, and the diffusion rate of monomer is accelerated and so monomers are apt to react polymer radicals and result in increasing the grafting yields.

Effect of impregnation time on the grafting of acrylic acid onto polyester fabric by two-step method is shown in Fig. 1.

After polyester fabric was impregnated with 1, 1-dichloroethane solution by immersion at 70°C for one hour, the impregated fabric was immersed in 50% solution of acrylic acid containing Mohr's salt (6×10^{-3} mole/l) for various hours at 30°C.

Irradiating the treated fabric with electron beams (total dose 7.5 Mrad) from electron accelerator at room temperature, the per cent of grafting has reached a plateau at one hour of impregnation time.

From the results it is considered that the limiting value of the impregnation time-monomers diffuse into the amorphous area of the fabric—is one hour in this system.

3-3 Effect of Dose on Grafting

Effect of radiation dose on the grafting of acrylic acid onto polyester fabric with impregnating solution containing 1, 1-dichloroethane is shown in Table 3.

Table 3 shows that the per cent of grafting, conversion and utilization were increased with increasing dose rate.

It is supposed that the dense radical sites are generated in prepolymer (polyester) high dose rate and the copolymerization proceeds with monomers within the life time of radicals.

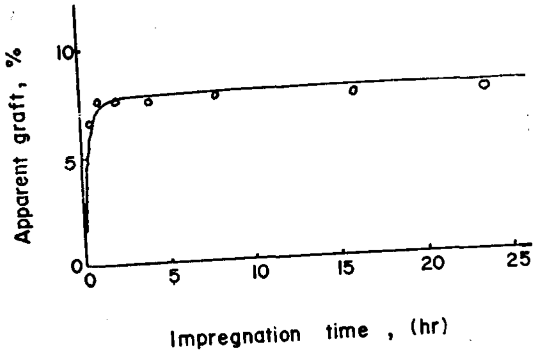

Fig. 1. Effect of impregnation time on the grafting of acrylic acid onto polyester fabric by two-step method

Pre-treatment: 70°C, 1hr in swelling agent (ED)

Impregnation: 30°C, 50% aqueous solution of acrylic acid containing Mohr's salt, 6×10^{-3}mole/l

Irradiation: Electron beams; total dose, 7.5 Mrad

Effect of radiation dose on the grafting of acrylic acid with impregnating solution containing 1, 1, 2-trichloroethane is shown in Table 4.

It is shown from Table 4 that the per cent of grafting, conversion and utilization were increased with increasing dose rate.

Comparing 1, 1-dichloroethane (Table 3) with 1, 1, 2- trichloroethane (Table 4) as swelling effect, 1, 1-dichloroethane was more effective than 1, 1, 2-trichloroethane.

While the different swelling agents were used, the per cent of conversion was plotted against the dose as given in Fig. 2.

Comparison of the per cent of conversion of polymerization of acrylic acid in the 1, 1-dichlorothane with that in the 1, 1, 2-trichloroethane, 1, 1-dichloroethane was more efficient than 1, 1, 2-trichloroethane.

It can be said that 1, 1- dichloroethane was found to be tha most effective swelling agent in this system.

Table 3. Effect of radiation dose on the grafting of acrylic acid onto polyester fabric with impregnation solution containing 1,2-dichloroethane

Impregnation: 30°C, 24hr; AA-H_2O-$(CH_2Cl)_2$ (60 : 40 : 20, by Vol.) containing Mohr's salt, 4×10^{-3} mole/l

Irradiation: Electron beams

Dose, Mrad	Pickup of AA, %	Wt. increase, %	Apparent graft, %	Utilization, %	Conversion, %	Graft efficiency, %
0.5	22	5.4	1.4	6.2	24.5	25
1.0	21.5	7.5	2.7	12.6	35.0	36
2.2	26	7.2	3.6	13.8	27.6	50
3.2	21	9.4	4.0	19.0	45.0	42
5.1	20	11.4	4.9	24.6	56.7	43
7.5	20.5	13.5	5.2	25.6	66.0	38

Table 4. Effect of radiation dose on the grafting of acrylic aicd onto polyester fabric with impregnating solution containing 1,1,2-trichloroethane

Impregnation: 30°C, 24hr; AA-H_2O-$CHCl_2CH_2Cl$ (60 : 40 : 20, by Vol.) containing Mohr's salt, 4×10^{-3} mole/l

Irradiation: Electron beams

Dose, Mrad	Pick up of AA, %	Wt. increase, %	Apparent graft, %	Utilization, %	Conversion, %	Graft efficiency, %
0.5	21.2	3.8	1.2	5.7	17.8	32
1.0	15.4	5.2	1.9	12.2	33.8	36
2.2	16.3	6.0	2.7	16.5	36.8	44
3.2	16.1	6.7	3.5	21.8	41.6	52
5.1	23.3	10.5	4.6	19.8	44.2	44
7.5	23.2	10.7	5.3	22.8	46.2	49

3-4 Effect of Cations on Grafting and Homopolymerization

It is interesting to investigate the dependence of homopolymerization and grafting on the concentration of added cation (Mohr's salt, cupric sulfate) in the grafting of acrylic acid onto polyester fabric.

The results are shown in Fig. 3 and Fig. 4.

The cations display similar characteristics (Fig. 3), the reduction in homopolymerization being greater the higher the ion concentration (mole/l).

At very high concentrations the suppression was almost complete, but this practical advantage was obtained at the expense of grafting efficiency (Fig. 4).

In the absence of cations gel formation was proceeded rapidly and prevented any estimation of homopolymerization and grafting.

From Fig. 4 it is supposed that the cations decrease the grafting in a similar fashion to homopolymerization.

The mechanism of cations[13] which react with the homopolymer radicals or copolymer radicals is shown in Fig. 5.

It is thought that in the absence of cations the propagating homopolymer radicals could produce the long chain of polymer.

As shown in Fig. 5 it is also thought that in the presence of cations terminations of homopolymerization and graft copolyme-

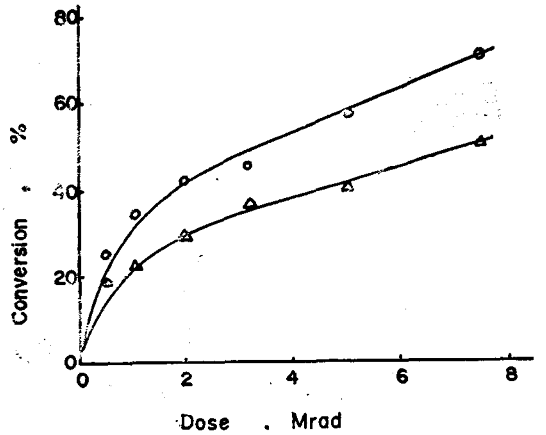

Fig. 2. Conversion curves of polymerization of acrylic acid in the process of impregnation grafting with different swelling agents

○ : 1,2-dichlorethane
△ : 1,1,2-trichloroethane

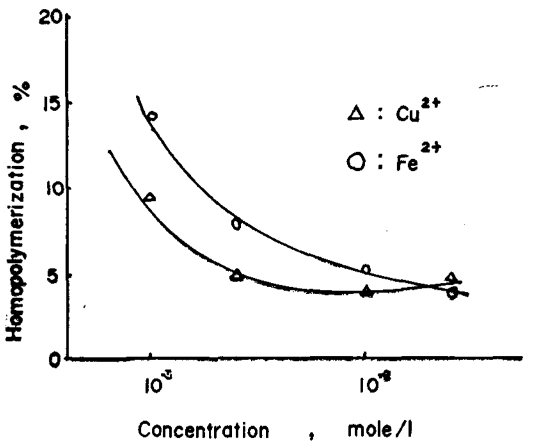

Fig. 3. Dependence of homopolymerization on the concentration of added cation on the grafting of acrylic acid onto polyester fabric

Impregnation: 30°C, 1hr
Monomer Mixt.: AA-H_2O-$(CH_2Cl)_2$ (50:40:10, by Vol.) containing different concentrations of cation
Irradiation: Electron beams; total dose, 7.5 Mrad

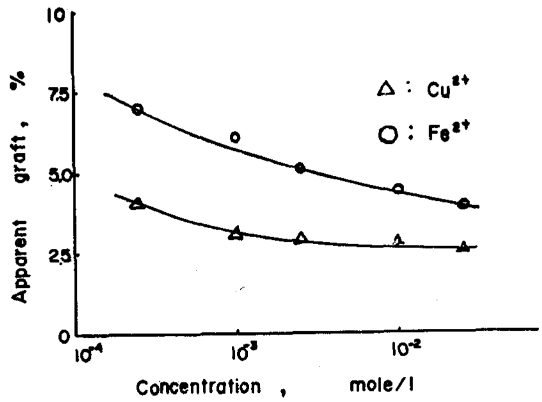

Fig. 4. Dependence of the grafting on the concentration of added cation on the grafting of acrylic acid onto polyester fabric

Impregnation: 30°C, 1hr
Monomer Mixt.: AA-H_2O-$(CH_2Cl)_2$ (50:40:10, by Vol) containing different concentrations of cation
Irradiation: Electron beams; total dose, 7.5 Mrad

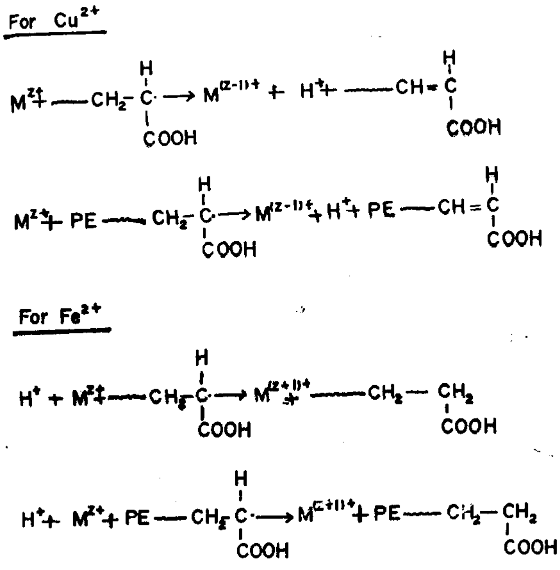

Fig. 5. Mechanisms of cation inhibition of polymerization

rization occur by an electron transfer process from a propagating polymer to the cations.

It is proposed that the mechanism of grafting of acrylic acid onto polyester fabric (Fig. 5) is similar to that of Nylon fabric[12-13] having been found previously.

3-5 Effect of Dose Rate on Grafting

The per cent of grafting of acrylic acid

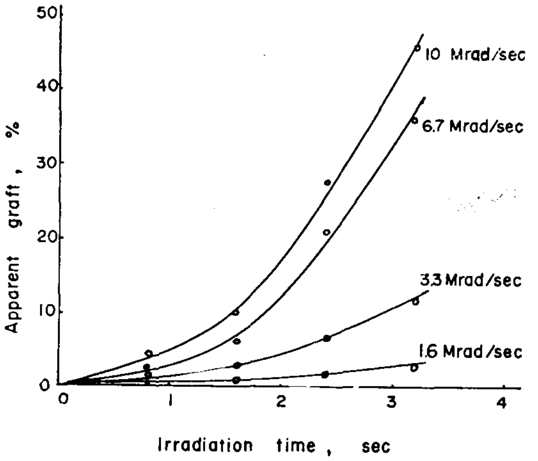

Fig. 6. Grafting of acrylic acid onto polyester fabric at different dose rate at room temperature
Impregnation: 30°C, 1hr
Monomer Mixt. : AA-H_2O-$(CH_2Cl)_2$ (50:40:10, by Vol.) containing Mohr's salt, 4×10^{-2} mole/l

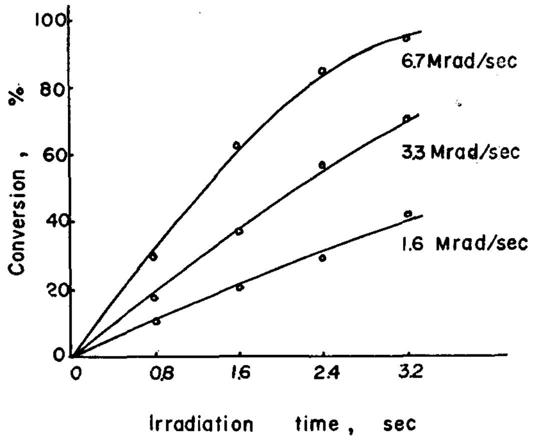

Fig. 8. Conversion curves of polymerization of acrylic acid in the process of impregnation grafting at different dose rates of electron beams
Impregnation: 30°C, 1hr
Monomer Mixt. : AA-H_2O-$(CH_2Cl)_2$ (50:40:10, by Vol.) containing Mohr's salf, 4×10^{-3} mole/l

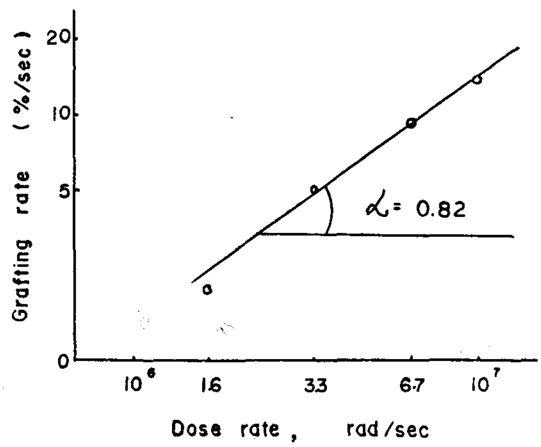

Fig. 7. Effect of dose rate on the grafting of acrylic acid onto polyester fabric
Impregnation: 30°C, 1hr
Monomer Mixt. : AA-H_2O-$(CH_2Cl)_2$ (50:40:10, by Vol.) containing Mohr's salt, 4×10^{-3} mole/l

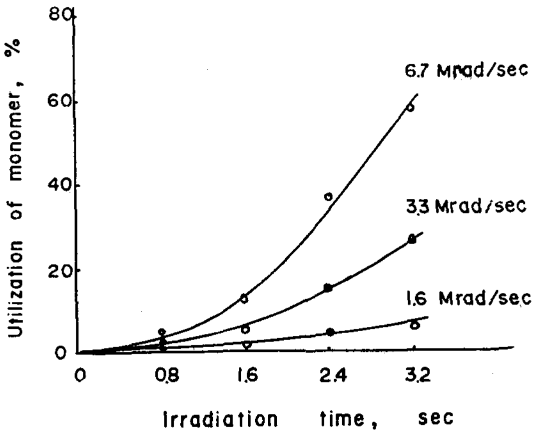

Fig. 9. Utilization curves of acrylic acid in the process of impregnation grafting at different dose rates of electron beams
Impregnation: 30°C, 1hr
Monomer Mixt. : AA-H_2O-$(CH_2Cl)_2$ (50:40:10, by Vol.) containing Mohr's salt, 4×10^{-3} mole/l

onto polyester fabric at different dose rates at room temperature is shown in Fig. 6.

The polyester fabric was immersed in the mixture solution followed padding.

The mixture solution was composed of acrylic acid, Mohr's salt and 1, 1-dichloroethane(50:40:10 by volume ratio).

Treated fabric was irradiated to different dose rates(1.6 Mard/sec-10Mrad/sec).

It is shown in Fig. 6 that the per cent of grafting is increased with increasing dose rate.

Effect of dose rate on the grafting of acrylic acid onto polyester fabric is shown in Fig. 7.

The log-log plot of the initial rate of grafting versus dose rate gives a straight line whose slope is the intensity exponent.

The intensity exponent value is 0.82 for Mohr's concentration of 4×10^{-3} mole/l (Fig. 7).

Thus the rate of grafting (in %/sec) is proportinal to the power 0.82 for dose intensity.

3-6 Dose Rate vs. Conversion % and Utilization %

Conversion curves of polymerization of acrylic acid in the process of impregnation grafting at different dose rates of electron beams are shcwn in Fig. 8.

Utilization curves of acrylic acid in the process of impregnation gragting at different dose rates are shown in Fig. 9.

The per cent of conversion—the amount of graft copolymer and homopolymer—was increased with increasing dose rate (Fig. 8).

The per cent of utilization—the amount of graft copolymer—was increased with increasing dose rate.

At the high dose rate of 6.7 Mrad/sec., 70% of the monomers were converted to graft copolymer, while 30% were converted to homopolymer.

At the low dose rate of 1.6 Mrad/sec., 13% of the monomers were converted to graft copolymer, while 87% were converted to homopolymer.

The high dose rate of electron beams gives higher utilization efficiency.

3-7 Frictional Electricity of Grafted Polyester Fabric

Frictional electricity, half life and wicking time of acrylic acid grafted polyester fabric at 20°C, 45% relative humidity are listed in Table 5.

The sodium salt of acrylic acid grafts was prepared by treating the fabric for 2-3 hours at 80°C in a 10% solution of sodium bicarbonate.

The physical properties of acid form and sodium form were measured.

It is shown from Table 5 that the frictional electricity of original polyester and cotton were 54,000 Volts, 20,000 Volts respectively and the half life of original polyester and cotton were above 300 sec., 0 sec respectively.

The term "Half life" is time required to fall into half value of the frictional electricity in second.

In both the acid-and sodium form the frictional electricity was decreased with the increase of per cent of graft.

Half life and wicking time were also decreased with the increase of per cent of graft.

Frictional electricity, half life and wicking time of the sodium form of acrylic acid grafts were lower than those of the acid form.

3-8 Graft vs. Moisture Regain

Moisture regains of the acid form and sodium form were determined respectively by allowing the acrylic acid grafted polyester fabric at 23°C and 66% or 94% relative humidity.

The results are shown in Fig. 10 and Fig. 11.

It is seen from the results that moisture regains in 66% or 94% relative humidity are increased with the per cent of grafting.

Moisture regains of the sodium form and acid form were almost equal in 66% relative

Table 5. Frictional electricity, half life and wicking time of acrylic acid grafted polyester fabric at 20°C, 45% relative humidity

Apparent graft, %	Frictional electricity, volts		Half life, sec		Wicking time, sec	
	Acid-form	Na-form	Acid-form	Na-form	Acid-form	Na-form
2	55,000	50,000	>300	>300	>300	>300
4	50,000	54,000	18	9	190	220
8	32,000	30,000	0	0	18	18
16	21,000	22,000	0	0	22	6
22	20,000	12,000	0	0	15	6
30	15,000	7,000	0	0	30	2
Original Polyester	54,000		>300		>300	
Cotton	20,000		0		0	

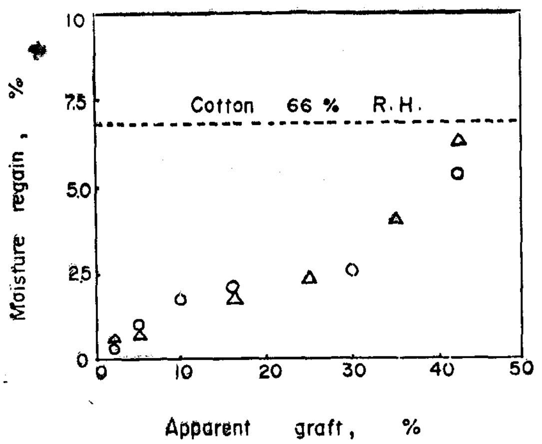

Fig. 10. Moisture regain of acrylic acid grafted polyester fabric at 23°C
Acid form: 66% R.H. (○)
Sodium form: 66% R.H. (△)

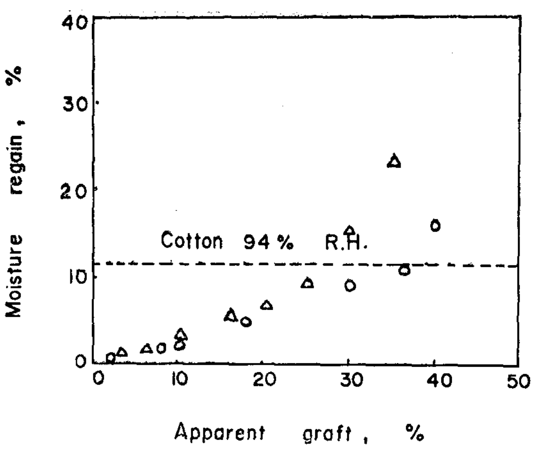

Fig. 11. Moisture regain of acrylic acid grafted polyester fabric at 23°C
Acid form: 94% R.H. (○)
Sodium form: 94%R.H. (△)

humidity

But Moisture regain of the sodium form gave the higher yields compared to that of the acid form in 94% relative humidity

The reason could be due greater to water affinities of sodium ions.

4. Conclusion

The per cent of conversion and utilization were increased with increasing the dose rate of electron beams.

The suitable condition for experiment is sought by controlling the condition of swelling agent, homopolymer and monomer.

It was observed that the cation added as homopolymerization inhibitor depressed the grafting as well as the formation of homopolymer.

At very high concentrations of cations the suppression was almost complete, but the practical advantage was obtained at the expense of grafting efficiency.

As mentioned on mechanism of cations in discussion, it is supposed that in the presence of cations termination of grafting and polymerization occurs mainly by electron transfer with the cation.

Generally the frictional electricity, half life and wicking time were decreased with the increase of the per cent of grafts.

When the per cent of the grafts was above 20%, the physical properties of modified polyester fabric were similar to those of cotton.

It is considered from the results that grafting of hydrophilic monomer onto hydro phobic polyester with electron beams at high dose rate can produce the proposedly modified copolymer with various physical properties.

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