

Radiation Induced-Grafting of Acrylic Acid onto Polyvinyl Chloride Fibers

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Abstract

The grafting of acrylic acid in aqueous solution to polyvinyl chloride fibers has been studied in the presence of ferrous, ferric, and cupric salts.

The mutual irradiation technique was adopted using a Co-60 source or a Van de Graaff accelerator.

The grafting and homopolymerization were suppressed by the cations. Particularly the grafting was suppressed by the cations in the following order of effectiveness: $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Cu}^{+}$.

The rate of grafting (in %/hr) was proportional to the 0.76th power of the dose rate over the range from 8.5×10^3 rad/hr to 1.4×10^5 rad/hr.

The apparent activation energy for the grafting was determined to be 6.1 Kcal/mole between 25° and 75°C for the mixture of $\text{AA-H}_2\text{O}-(\text{CH}_2\text{Cl})_2$, containing Mohr's salt, 4×10^{-3} mole/l.

The increase of the grafting was observed when total dose and dose intensity were raised, or when ethylene dichloride as a swelling agent was saturated in the monomer mixture.

The grafted polyvinyl chloride fibers showed considerable improvement in moisture regain, heat shrinkage, and melting properties, but tensile properties were not significantly affected by grafting.

개 요

Polyvinyl Chloride 섬유에 Acrylic acid (AA)를 방사선을 이용하여 Graft 중합 반응시킬 때 Homopolymer의 방지제인 Ferrous, Ferric, Cupric salt을 첨가시켰다.

방사선 선원으로서는 Co-60의 γ -선 또는 Van de Graaff 가속기를 사용하였으며 조사방법으로는 상호조사법을 이용하였다.

Graft 중합반응과 Homopolymerization은 반응계에 첨가시킨 Cation에 의해서 영향을 받았으며 그 효율은 $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Fe}^{3+}$ 의 순서였다.

Graft 중합반응속도는 방사선 선량율이 8.5×10^3 부터 1.4×10^5 rad/hr 사이에서 선량율의 0.76 중에 비례하였고 Craft 중합반응에 대한 활성화 에너지는 25° 부터 75°C 사이에서 6.1 Kcal/mole 이었다. 이 때 중합반응 용액은 $\text{AA-H}_2\text{O}-(\text{CH}_2\text{Cl})_2$ 로서 Homopolymer inhibitor의 농도는 4×10^{-3} mole/l 이었다. Graft율은 총선량과 선량율을 클 때 증가하였거나 또는 Polymer 팽윤제인 Ethylene dichloride가 mono-

mer 혼합용액에 포화되었을 때 증가되었다.

Acrylic acid 가 Craft 된 Polyvinyl Chloride 섬유는 흡습율, 열수축성, 용융성이 크게 증진되었고 Tensile properties 는 original 과 별차이를 나타내지 않았다.

1. Introduction

Most radiation grafting studies have involved the copolymerization of a monomer in the gaseous or liquid phase with a solid polymer¹⁻⁹ and are heterogeneous in nature.

A few reports have appeared on homogeneous system in which the polymer is dissolved in the liquid monomer¹⁰.

In this work radiation grafting of acrylic acid onto drawn polyvinyl chloride fibers was carried out with a direct irradiation immersion technique using γ -rays from a Co-60 source. For comparison, some of experiments were performed with an impregnation technique using electron beams from a Van de Graaff accelerator.

The rates of grafting and homopolymerization of acrylic acid were suppressed by salts such as Mohr's salt, cupric sulfate, and ferric chloride. In the absence of these salts gel formation was proceeded very rapidly and prevented separation of grafting fibers from gelled homopolymer.

The presence of ethylene dichloride in the monomer mixture was observed to accelerate the grafting. Particular low concentration of homopolymer inhibitor was effective in raising the graft efficiency. The graft efficiency also depends on the extent of the swelling of polyvinyl chloride fibers.

For the grafting systems, most parts of the grafting rates were increased sharply in the initial stage of the copolymerization.

The kinetics of the grafting of acrylic acid and 4-vinylpyridine to poly (tetrafluoroethylene) were studied by Chapiro¹¹.

Although no quantitative studies appear to have been made on the effect of metal ions on radiation grafting, the situation with respect to their role in γ -initiated solution polymerization has been clarified in the report by Huglin and Johnson¹², which provide a useful basis for this note concerned with the mutual irradiation of aqueous acrylic acid-polyvinyl chloride fibers in the presence of the three cations.

In investigating mechanisms for the process of chain termination by transition metal ions, a quantitative studies were carried out.

2. Experimental

2-1. Materials

Drawn polyvinyl chloride fiber denoted by Teijin Ltd., Osaka, Japan, was utilized in slacked state or stretched state without any purification.

Acrylic acid monomer was made inhibitor-free by vacuum distillation. All reagents used in this work such as Cupric sulfate, Mohr's salt, Ferric chloride, Sodium bicarbonate, and Calcium acetate were pure grade.

2-2. Irradiation

Radiation was effected by γ -rays from 2000- and 10000-Curie Co-60 source, or by electron beam from a Van de Graaff accelerator at Osaka Atomic Energy Research Institute, located in Japan.

Dose rate of γ -rays was from 8.5×10^3 rad/hr to 1.4×10^5 rad/hr, and that of electron beams was 0.1 Mrad/sec.

2-3. Procedure

Sample tube containing Ca, 0.1 g of poly-

vinyl chloride fiber and 4 ml of a solution composed of 50% acrylic acid, 40% aqueous salt solution, and 10% ethylene dichloride was circulated by nitrogen gas.

The overall concentrations of salts added were varied to the condition of the work, the values being 4×10^{-4} , 1×10^{-3} , 1×10^{-2} , 4×10^{-2} , and 8×10^{-2} mole/l.

Sample tube was sealed under nitrogen gas, and kept in refrigerator overnight before irradiation.

After irradiation, each tube was opened immediately after removal from the source to minimize post irradiation effect. Sample was extracted with hot water at 50°C for 5 hr, and dried to constant weight in vacuum.

In the case of electron beams, sample immersed in a solution of monomer mixture was wiped off with filter paper, kept in aluminum foil, sealed, and irradiated at the dose rate of 0.1 Mrad/sec.

Another procedure was then adopted to determine the per cent of homopolymerization.

After irradiation, all the reactants were poured in petri dish, and dried in Hood for 2-3 hr, and then dried in vacuum at 50°C for overnight.

After weighing the dried reactants, homopolymer was extracted with the method mentioned above.

The amount of the salt solution added was also considered in determining the per cent of homopolymer.

3. Results and Discussion

3-1. Effect of Inhibitor Concentration on Grafting

Preliminary experiments of grafting of acrylic acid to polyvinyl chloride fiber resulted in a crosslinked gel. The separation of the entrapped fiber from the gel for graft percent-

tage was a difficult and lengthy procedure.

Various metal salts such as Mohr's salt, Cupric sulfate, and Ferric chloride were utilized as a scavenger to reduce the homopolymer formation.

The results of the effects of Mohr's salt and Cupric sulfate on grafting at the dose rate of 1.4×10^5 rad/hr are shown in Fig. 1. and Fig. 2. It is seen that grafting first increases sharply with irradiation time and finally tends to level off with further increase in the irradiation time, except at the concentration of Mohr's salt, 1.4×10^{-4} mole/l.

It is seen in Fig. 1. that the per cent of graft increases with diluting the concentration of Mohr's salt.

This may be due to "gel effect". Namely, under low concentration of homopolymer inhibitor, the termination rate is low because the viscosity of the reaction medium is high and the mobility of the macroradicals is restricted. And so the net result would be an increase in the grafting yield.

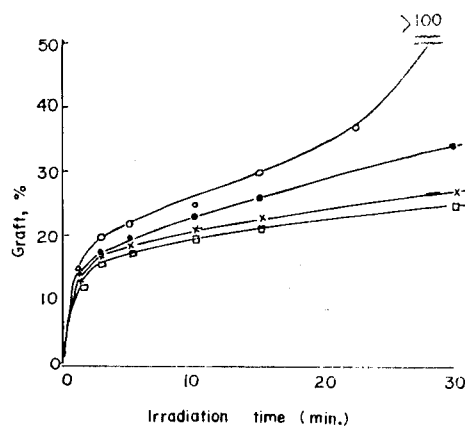


Fig. 1. Effect of Mohr's salt on the grafting of acrylic acid onto polyvinyl chloride fiber at the dose rate 1.4×10^5 rad/hr. Concn. of Mohr's salt; (O) 4×10^{-4} mole/l, (●) 1×10^{-3} mole/l, (X) 1×10^{-2} mole/l, (□) 4×10^{-2} mole/l. Monomer mixture; AA: H_2O : $(\text{CH}_2\text{Cl})_2$ = 50:40:10, Irradiation temp.; room temp.

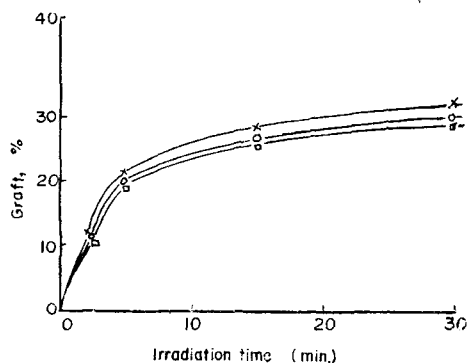


Fig. 2. Effect of cupric sulfate on the grafting of acrylic acid onto polyvinyl chloride fiber at the dose rate 1.4×10^5 rad/hr.

Concn. of cupric sulfate: (X) 4×10^{-4} mole/l, (O) 1×10^{-3} mole/l, (□) 4×10^{-2} mole/l.

Monomer mixture; AA: H_2O : $(CH_2Cl)_2$ = 50:40:10, Irradiation temp.; room temp.

It is shown in Fig. 2 that unlike Mohr's salt, diluting the concentration of Cupric sulfate did not result in a significant difference in the grafting yields. Acrylic acid grafted samples were slightly bluish in color. This may be due to the complex formation of $CuSO_4$ with polyacrylic acid.

3-2. Effect of Concentrations of Swelling Agent and Monomer

The effects of acrylic acid and swelling agent on grafting were studied.

When ethylene dichloride as a swelling agent was added in the monomer mixture, the per cent of grafting at a given radiation dose was increased considerably according to the solubility of ethylene dichloride.

The result of the solubility of ethylene dichloride in the monomer mixture is shown in Fig. 3. Preliminary study on grafting with monomer mixture-ethylene dichloride indicated that above solubility of swelling agent, the fiber is damaged due to over-swelling.

In this experiments, hence, the concentration of ethylene dichloride in the monomer mixture was not beyond the solubility.

The grafting yield was raised with increasing acrylic acid concentration in the saturated solution of ethylene dichloride (Fig. 4).

It is supposed that the swelling of polyvinyl chloride fiber is caused mainly by sorption of ethylene dichloride, and consequently the amorphous regions loosen and become accessible to monomer and result in increasing the grafting yields.

3-3. Effect of Inhibitor and Radiation Dose on Grafting with Electron beams

Polyvinyl chloride fibers were impregnated with aqueous solution of the monomer mixture and irradiated with electron beams from a Van de Graaff accelerator, which is placed in Osaka Atomic Energy Research Institute.

The results of effects of homopolymer inhibitors such as ferrous and ferric ions on grafting are shown in Table 1. The per cent of grafting was increased with the total dose over the range of 0.1–0.8 Mrad.

Comparing the effects of ferrous ions with those of ferric ions on grafting, no significant differences in the grafting yield, monomer-conversion, and graft efficiency were

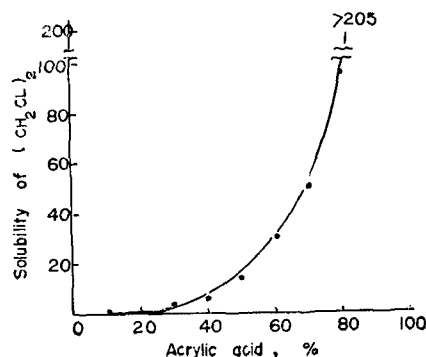
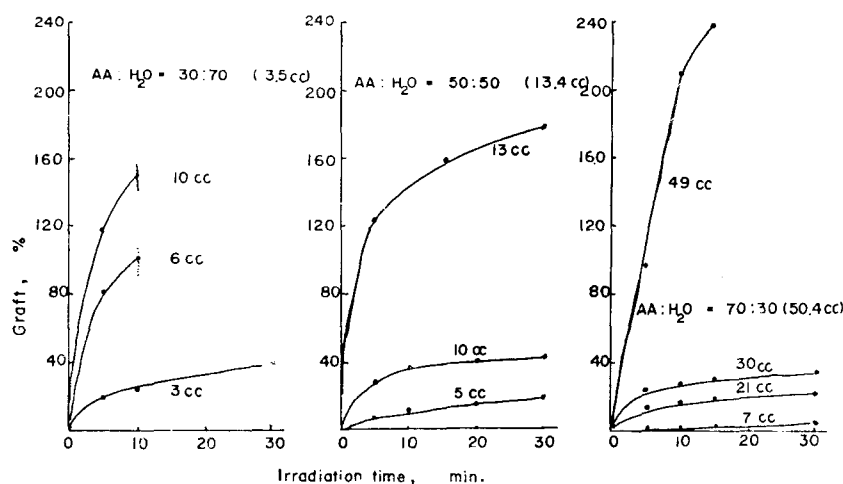


Fig. 3. Solubility of ethylene dichloride added in acrylic acid solution.

Table 1. Effects of inhibitors on the grafting of acrylic acid onto polyvinyl chloride fibers with Van de Graaff electrons (1.5 MeV).Monomer mixture; AA: H₂O: (CH₂Cl)₂=60:20:20Concn. of inhibitor: 2×10^{-3} mole/l, Dose rate; 0.1 Mrad/sec.

	Dose	Pick up of mixt.	Pick up of AA	Weight increase	Apparent graft	Conversion	Utilization	Graft efficiency
	Mrad	% (A)	% (B)	% (C)	% (D)	% (C/B)	% (D/B)	% (D/C)
(Fe ⁺⁺)	0.1	62.6	37.6	12.3	7.5	32.7	19.9	61.0
	0.2	43.7	26.2	28.4	21.4	100	81.7	75.4
	0.4	54.8	32.9	35.6	30.2	100	91.8	84.8
	0.8	61.3	36.8	38.4	32.6	100	88.6	84.9
(Fe ⁺⁺⁺)	0.1	51.9	31.1	18.0	12.0	57.9	38.6	66.7
	0.2	47.7	28.6	29.1	22.4	100	78.3	77.0
	0.4	65.9	39.5	38.2	31.7	96.7	80.3	83.0
	0.8	54.5	32.8	36.2	29.4	100	87.6	81.2

**Fig. 4. Effect of ethylene dichloride on the grafting of acrylic acid onto polyvinyl chloride fiber.**

Concn. of Mohr's salt in acrylic acid solution; 2×10^{-3} mole/l, dose rate; 1×10^6 rad/hr. The numbers on the curves mean ml of ethylene dichloride added to 100 ml of aqueous solution of acrylic acid.

noticed.

To investigate monomer-utilization on grafting with electron beams, the following two procedures were tried.

In the first procedure (process A), sample immersed in the monomer mixture was picked up, kept in aluminum foil, and irradiated with electron beams for the grafting (process A).

In the second procedure (process B), sam-

ple picked up in the monomer mixture was wiped off with filter paper, kept in aluminum foil, and irradiated for the grafting.

The results are shown in Table 2. It was found from the results that the per cent of grafting in process A is higher than that in process B. However, monomer-utilization, monomer-conversion, and graft efficiency were higher in process B than those in process A.

Table 2. Impregnation grafting of acrylic acid onto polyvinyl chloride fibers with Van de Graaff electrons (1.5 MeV).Monomer mixture; AA : H₂O : (CH₂Cl)₂=60 : 20 : 20Concn. of inhibitor; 2×10^{-3} mole/l, Dose rate; 0.1 Mrad/sec.

	Dose	Pick up of mixt.	Pick up of AA	Weight increase	Apparent graft	Conversion	Utilization	Graft efficiency
	Mrad	% (A)	% (B)	% (C)	% (D)	% (C/B)	% (D/B)	% (D/C)
A*	0.2	326	196	55.3	31.9	28.2	16.3	57.7
	0.4	358	215	91.3	45.4	42.5	21.1	49.8
	0.8	296	178	144.4	81.4	81.1	45.7	56.4
B*	0.2	43.5	26.1	28.4	21.4	100	81.9	75.4
	0.4	43.0	25.8	28.5	24.9	100	96.5	87.4
	0.8	58.5	35.1	35.7	31.3	100	89.2	87.7

A* = Carrying out in impregnated state

B* = Padding method

It was supposed that wiping off monomer mixture with filter paper, homopolymerization is considerably reduced and so this leads to higher utilization percentage in polyvinyl chloride fibers swollen in monomer mixture and consequently higher conversion percentage and grafting efficiency.

3-4. Mechanisms of Cation Ions on Grafting

The salts utilized were ferrous ammonium sulfate, ferric chloride, and cupric sulfate. The three cations display similar characteristics (Fig. 5), the reduction in homopolymerization being greater the higher the ion concentration (mole/l).

At very high concentration (8×10^{-2} mole/l) the suppression is almost complete, but this practical advantage is obtained at the expense of grafting efficiency (Fig. 6).

The broken vertical lines (in ferric ions) denote the points for which a marked increase in viscosity was observed, and above the broken lines (1×10^{-2} mole/l) reaction heat was raised sharply although the irradiation was carried out at room temperature.

In the absence of any metal cations gel formation was proceeded very rapidly and

prevented any estimation of homopolymerization and grafting.

From Fig. 6 it is supposed that the cations decrease the grafting in a similar fashion to homopolymerization.

The order of effectiveness in suppressing grafting is $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Fe}^{3+}$ and we are accordingly studying the kinetics of grafting in the presence of 10^{-3} mole/l ferrous ions. This concentration of ferrous ions is eminently suitable, for at lower ones the homopolymerization is excessive, while the suppression of grafting is too great at higher ones.

In the simultaneous procedure, the radiolysis of all components of the solution are factors in initiating graft copolymerization.

It was reported by Huglin¹²⁾ that the radiolysis products of water (in the absence of oxygen: OH, H and $e^-_{aq.}$) may be expected to play a significant role as the reaction medium comprises 90% (V/V) of water.

Below pH 3, the solvated electron has a very short lifetime and as the pH of the medium is 2.5–3.0, solvated electron reactions will be omitted from consideration.

In this work the reaction medium comprised 40% (V/V) of water, and the irradiation was not carried out under vacuum, and so it is supposed that the radiolysis products of water

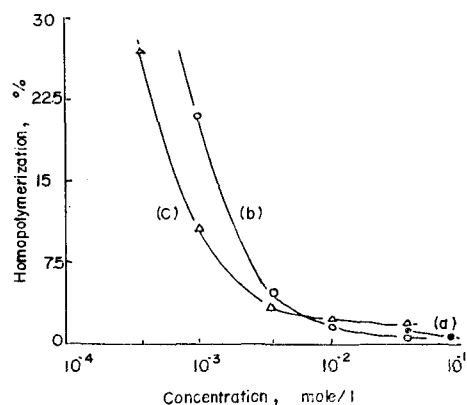


Fig. 5. Dependence of homopolymerization on concentration of added cation ions: (a) Fe^{3+} , (b) Fe^{2+} , (c) Cu^{2+}
Dose rate; 1.4×10^5 rad/hr
Irradiation time and temp.; 30 min. and room temp.
Monomer mixture; AA : H_2O : $(\text{CH}_2\text{Cl})_2$ = 50 : 40 : 10

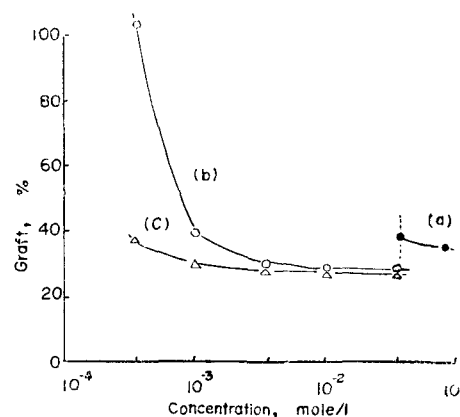


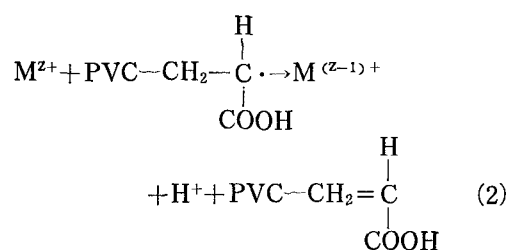
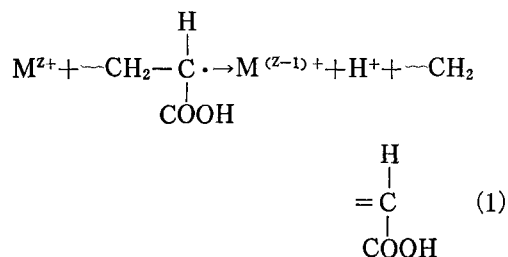
Fig. 6. Dependence of grafting on concentration of added cation ions: (a) Fe^{3+} , (b) Fe^{2+} , (c) Cu^{2+}
Dose rate; 1.4×10^5 rad/hr
Irradiation time and temp.; 30 min. and room temp.
Monomer mixture: AA : H_2O : $(\text{CH}_2\text{Cl})_2$ = 50 : 40 : 10

may not be expected to play a significant role on grafting.

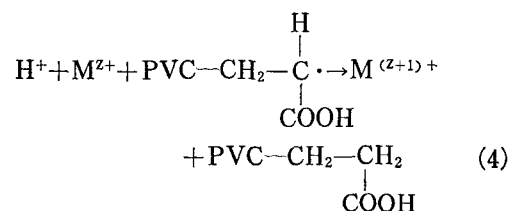
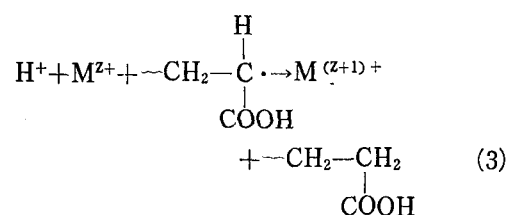
The effect of Cu^{2+} and Fe^{3+} on the γ -initiated polymerization of aqueous acrylamide in acid medium has been investigated by Collison et al.¹³⁾, who suggested that radical termination occurs by an electron transfer process from a propagating polymer to a d-orbital of the cation.

In the light of these and our own findings it is proposed that termination by metal (M) cations in a similar fashion as Nylon¹²⁾ proceeds as shown in eqs. (1) and (2) for the cupric and ferric systems and as shown in eqs. (3) and (4) for the ferrous systems.

For the cupric and ferric systems



For the ferrous systems



3-5. Effect of Dose Rate on Grafting

The intensity dependence of grafting was investigated for the dose rate range, 8.5×10^3

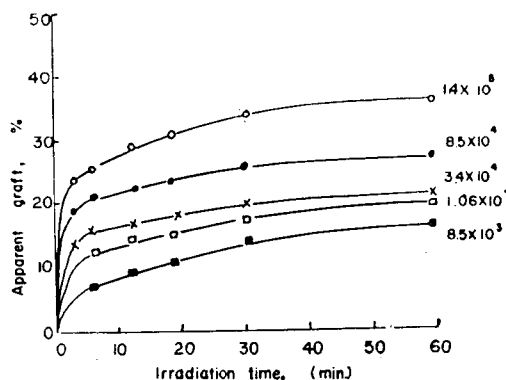


Fig. 7. Grafting of acrylic onto polyvinyl chloride fibers at 25°C at different dose rates in the presence of the ethylene dichloride.

Monomer mixture; AA : H₂O : (CH₂Cl)₂ = 50 : 40 : 10, containing Mohr's salt, 4×10^{-3} mole/l.

-1.4×10^5 rad/hr.

The results are shown in Fig. 7. During grafting with acrylic acid, no induction period was noticed. This could possibly be due to either the faster diffusion of acrylic acid solution into the fiber which is swollen by ethylene dichloride or due to the absence of any trace impurities in a monomer mixture which could react with the radicals initially produced by radiation.

It is shown in Fig. 7 that the per cent of grafting is increased with increasing dose rate, and that grafting first increases sharply with time and finally tends to level off with further increase in the irradiation time. The log-log plot of the initial rate of grafting versus intensity gives a straight line whose slope is the intensity exponent (Fig. 8).

It is shown in Fig. 8 that intensity exponent value is 0.76 for Mohr's concentration of 4×10^{-3} mole/l. Thus the initial rate of grafting (in %/min.) is proportional to the power 0.76 for dose intensities.

3-6. Activation Energy Determination

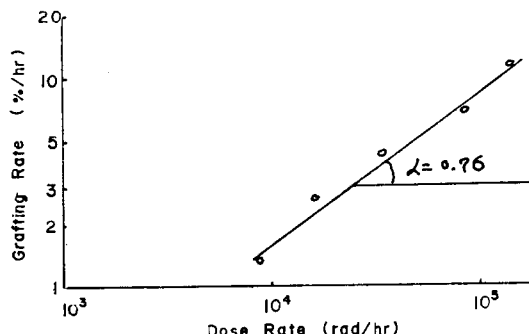


Fig. 8. Effect of dose rate on the grafting rate of acrylic acid onto polyvinyl chloride fibers.

Monomer mixture; AA : H₂O : (CH₂Cl)₂ = 50 : 40 : 10, containing Mohr's salt, 4×10^{-3} mole/l.

The effect of temperature on the grafting kinetics as well as the homopolymerization kinetics is important, particularly in this work in using ferrous and cupric ions as inhibitor of homopolymerization.

The grafting runs were carried out in sealed tubes immersed in water to help control the temperature of the tubes.

The results of the effect of temperature on grafting at the dose rate of 8.6×10^4 rad/hr are shown in Fig. 9. The results show that the per cent of grafting of acrylic acid was not significantly altered in the reaction temperature over the range of 25°–70°C.

The log-log plot of the per cent of grafting versus the irradiation time gives nearly straight line, which is a basis of calculating the rate of grafting R_G (in %/hr). Arrhenius plot of the initial rate of grafting R_G (in %/hr) versus temperature gives a straight line whose slope is a basis of determining the activation energy (Fig. 10). The activation energy for grafting of acrylic acid was determined to be about 6.1 Kcal/mole over the range of 25°–70°C.

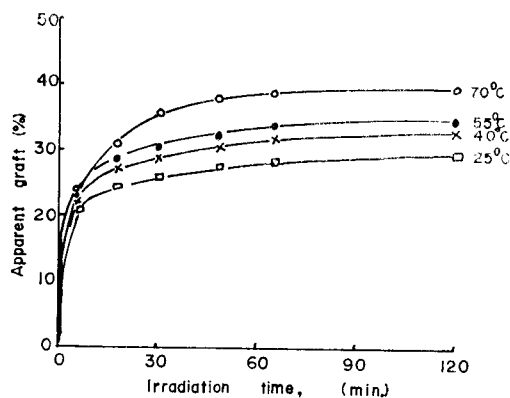


Fig. 9. Grafting of acrylic acid onto polyvinyl chloride fibers at dose rate of 8.6×10^4 rad/hr at different temperatures in the presence of ethylene dichloride.

Monomer mixture; AA : H₂O : (CH₂Cl)₂ = 50 : 40 : 10, containing Mohr's salt, 4×10^{-3} mole/l.

It was reported by Sakurada¹⁴⁾ that the apparent activation energy for grafting of acrylic acid onto polyethylene tetrathalate fiber is 8 Kcal/mole between 18°C and 40°C.

It is supposed from the results that the grafting time of acrylic acid depends upon the activation energy, the value in activation energy being lower the shorter the induction period.

3-7. Properties of the Grafted Fibers

Polyvinyl chloride fibers of varying graft add-on such as the acid-, calcium-, and sodium form, were prepared and evaluated for heat shrinkage, moisture regain, and tensile properties.

1) Heat Shrinkage

Polyvinyl chloride fibers of the acid- and calcium form were tested for heat shrinkage in a glass apparatus which heating temperature is controlled by silicon oil.

The results are shown in Fig. 11 and Fig. 12. Comparing the results of original polyvinyl chloride fibers with acrylic acid grafted poly-

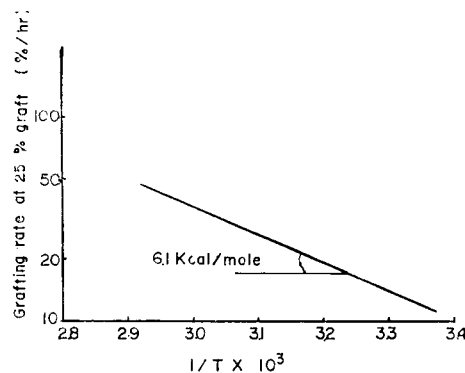


Fig. 10. Arrhenius plot of the grafting rates of acrylic acid onto polyvinyl chloride fibers.

Monomer mixture; AA : H₂O : (CH₂Cl)₂ = 50 : 40 : 10, containing Mohr's salt, 4×10^{-3} mole/l.

mer, the rate of heat shrinkage was decreased with the increase of the per cent of grafting. The rate of heat shrinkage of original polyvinyl chloride fibers was 70% at 17°C, but in the case of the calcium salt the rate (per cent of grafting, 58%) was 10% at 170°C.

It is also seen from Fig. 12 that fibers of the calcium form (per cent of grafting, 17%) retained its fibrous structure up to 330°C, the maximum temperature studied, whereas corresponding untreated fibers melted at 187°C.

2) Tensile properties

Acrylic acid grafted polyvinyl chloride fibers were tested for tensile strength and elongation. Denier, tenacity, and young's modulus of the graft polymer were determined.

The results are shown in Table 3.

Comparing the results of untreated polyvinyl chloride fibers with those of grafted samples, there is no loss either in strength or elongation by treatment.

3) Moisture Regain

Polyvinyl chloride possesses low equilibrium moisture regain which makes it uncomfortable

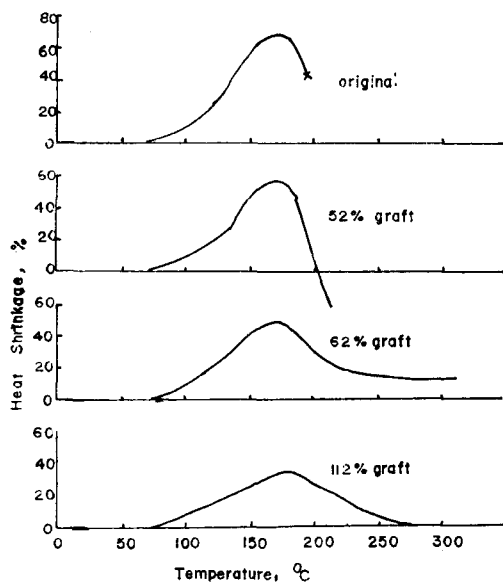


Fig. 11. Heat shrinkage of AA graft of polyvinyl chloride fiber.

for wear.

Moisture regains of the acid—, calcium—, and sodium form were determined respectively by allowing the samples to attain equilibrium moisture at 23°C and 66% or 94% relative humidity.

The results are shown in Fig. 13 and Fig. 14.

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

Table 3. Tensile properties of AA-graft of polyvinyl chloride fiber.

Apparent graft (%)	Denier	Strength (g)	tenacity (g/d)	Elongation (%)	Initial Young's modulus (kg/mm ²)
0	2.61	10.7	4.10	35.2	417
22.9	3.51	12.6	3.58	33.8	390
32.0	3.54	10.0	2.82	39.6	378
39.8	3.93	9.3	2.37	41.3	272
52.1	4.50	11.3	2.51	39.8	297
62.0	4.59	10.5	2.28	35.0	274
85.0	5.60	9.5	1.70	34.2	214

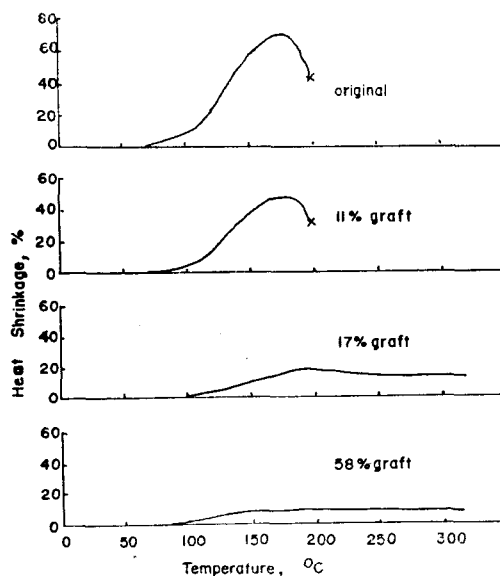


Fig. 12. Heat shrinkage of AA-Ca graft of polyvinyl chloride fiber.

It is also seen that moisture regain of the sodium form gave the highest yields compared to those of the acid—, and calcium form.

This could possibly be due to water affinities of sodium ions.

Conclusions

Most experiments were carried out with a direct immersion method using γ -rays. For comparison, some of experiments were performed with the impregnation method using electron beams from a Van de Graaff accelerator.

The aim of this work was to modify the properties of polyvinyl chloride fibers such as moisture regain, melting, and heat shrinkage, and to investigate mechanisms of grafting and polymerization of acrylic acid onto polyvinyl chloride fibers.

Increasing grafting yields was observed when the swelling agent such as ethylene dichloride was saturated in the monomer mix-

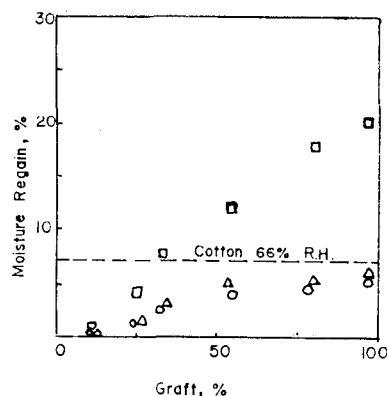


Fig. 13. Moisture regain of acrylic acid grafted polyvinyl chloride fibers at 23°C.
 Acid form; 66% R. H. (○)
 Ca form; 66% R. H. (△)
 Na form; 66% R. H. (□)

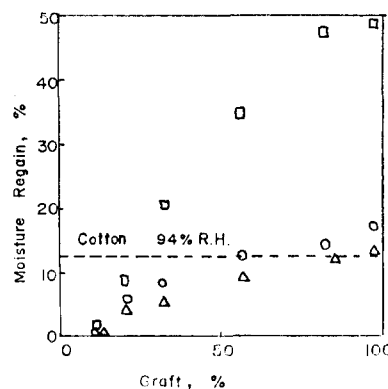


Fig. 14. Moisture regain of acrylic acid grafted polyvinyl chloride fibers at 23°C.
 Acid form; 94% R. H. (○)
 Ca form; 94% R. H. (△)
 Na form; 94% R. H. (□)

ture containing homopolymer inhibitor (Mohr's salt, Cupric sulfate, and Ferric chloride), or when the total dose and dose intensity was increased.

The grafted polyvinyl chloride fibers showed considerable improvement in moisture regain, heat shrinkage, and melting properties, but comparing to those of untreated fibers, there was very little difference in tensile strength and elongation.

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

It was also observed that the three cations (Fe^{2+} , Fe^{3+} , Cu^{2+}) displayed similar characteristics, the reduction in homopolymerization being greater the higher the concentration of cations.

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

As mentioned on mechanisms of cations in discussion, it is assumed that in the presence of cations termination of grafting and polymerization occurs mainly by electron transfer

with the cation.

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