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Radiation-Induced Graft Copolymerization of Methacrylic Acid and Methyl methacrylate onto Polyester.

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Abstract

The radiation-induced graft polymerization of methacrylic acid and methyl methacrylate onto a polyester fabric was investigated with γ-ray as the radiation source, and the rate of grafting was examined.

When acrylic acid, methacrylic acid, and methyl methacrylate were grafted onto a polyester fabric, grafting efficiency was depened upon the dielectric constant of the solvent in the monomer mixture.

The yield of the graft polymerization was related to the total dose, the concentration of the monomer, and the concentration of the swelling agent.

The melting point and the glass transition temperature of MA and MMA grafted copolymers were analysed by means of DTA. Physical properties, such as the moisture regain, the antistatic property, and the wicking time were measured.

요 약

감마선을 이용하여 폴리에스터직포에 methacylic acid와 methyl methacylate를 graft 중합반응시켜서 그 반응성을 보았다.

폴리에스터직포에 acrylic acid, methacrylic acid, methyl methacrylate를 중합반응 시켰을 때 graft 효율은 monomer 혼합용액내에 포함되어 있는 용매의 dielectric constant에 따라 상당한 차이를 나타내었다.

Graft 수율은 방사선 선량과 monomer 농도 및 swelling agent의 농도에 좌우되었다. MA graft copolymer의 glass transition temperature (101°C)와 melting point (238°C)를 측정하였고, 정전기 효과는 frictional electricity 8,000 V에서 half life가 0 sec이었으며, moisture regain는 5.6%, wicking time은 1 sec이었다.

I. Introduction

The modification of textile fibers with ionizing radiation is interesting from the theoretical and practical points of view. Grafting onto fibers is particularly interesting, since it enables the superposition of the grafted side chains onto the fiber without necessarily disturbing the properties of parent fiber. The whole field of the radiation modification of textile fibers has been reviewed in detail by Hoffman[1,2] and recently by Vlagiu and Stannett[3,4].

Studies of the radiation grafting of methacr-

ylate[5] onto wool have been reported by Bendak and his cowrkers[6]. The radiation grafting of acrylic acid has been discussed by Choi and his coworkers.[7] The radiation grafting of acrylic acid and other monomers to polyester fibers has been studied in detail by Sakurada and Okada[8,9,10].

Irradiation of polyester fiber by high-energy radiation[11] or low-energy radiation results in polyester macroradicals which are capable of initiating grafting. Similar polyester radicals can be brought about under the redox system [12,13] and benzoyl peroxide[14].

In this paper, it will be discussed the effects of swelling agents and dose rate on the radiation induced grafting of methacrylic acid and methyl methacrylate to polyester fibers. Melting point and glass transition temperature of graft copolymer will be analysed by means of DTA [15,16].

Ⅱ. Experimental

Materials

Polyester fabric samples were purified by treating with the mixture of 1% sodium carbonate solution, 3% sodium dodecylbenzene sulfonate solution and 0.3% Tween 80 solution (surfactant) at 80°C for 2 hour. Methyl methacrylate (MMA) was washed successively with 5% solution of sodium hydroxide and distilled water, then dried with anhydrous sodium sulfate and distilled under reduced pressure. Methacrylic acid (MA) was purified by vacuum distillation (63°C, 12 mmHg)[17]. All those solvents such as methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, and 1, 2-dichloroethane (DE) were obtained from the Merck Co. and were not purified further.

Procedure

Fabrics (7 cm×7 cm) were placed in test tubes together with the mixture of monomer, solvent and swelling agent. The irradiation were carried out at dose rates ranging from 3.9×10^4 rad/hr to 6.4×10^5 rad/hr in a ^{60}Co radiation source.

The MA grafted fabrics were washed with warm 0.02 N hydrochloric acid solution and dried to constant weight. The MMA grafted fabrics were thoroughly washed with distilled water, repeatedly soxhleted with acetone and dried to constant weight. The increase in weight was recorded as the graft yield. The percentage graft yield was calculated from the following equation;

$$\% \text{ graft yield} = \frac{\text{Weight of grafted polymer}}{\text{weight of original polyester sample}} \times 100$$

Measurement of moisture regain, static charge developing and half life were carried out according to the method reported by Choi and coworkers[7].

Ⅲ. Results and Discussion

1) Effect of dose

The graft polymerization was performed in different monomers; the grafting system consisted of 1, 2-dichloroethane, water, ethyl alcohol

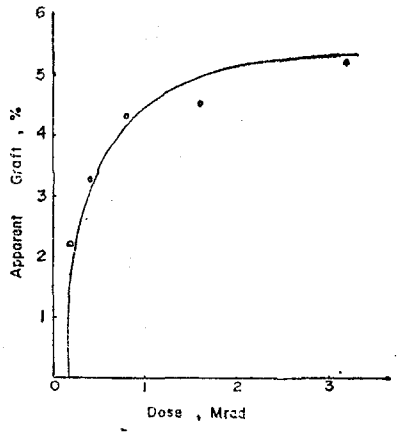

Fig. 1. Effect of total dose on radiation grafting yield at 20°C. Dose rate: 0.16 Mrad/hr. Composition of monomer mixtute: MA-H_2O-DE (10 : 50 : 40 by Vol.)

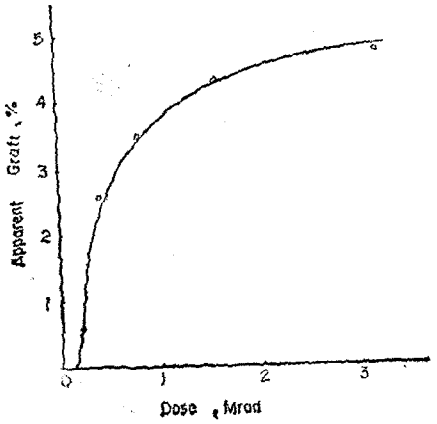

Fig. 2. Effect of total dose on radiation grafting yield at 20°C. Dose rate: 0.16 Mrad/hr. Composition of monomer mixture: MMA-EtOH-DE-H_2O (10 : 45 : 40 : 5 by Vol.)

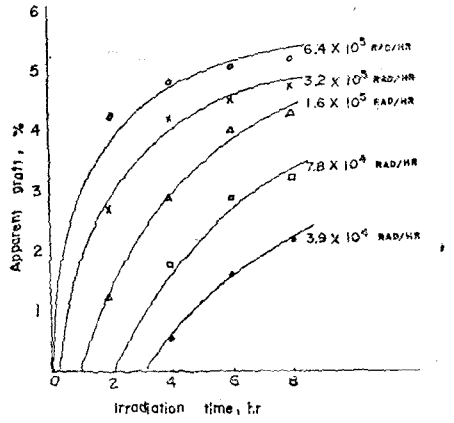

Fig. 3. Grafting of methacrylic acid onto polyester fabric at different dose rate at room temperature. Impregnation: 70°C, 2 hr. Composition of monomer mixture: MA-H_2O-DE (10 : 50 : 40 by Vol.)

and methacrylic acid (or methyl methacrylate).

The percent of graft was found to increase with dose after short induction periods, as shown in Fig. 1.

Fig. 1 and Fig. 2 show clearly that considerable grafting has occured. Comparing the Fig. 1 with the Fig. 2, the induction period of MA was shorter than that of MMA. It is considered that the difference in induction period

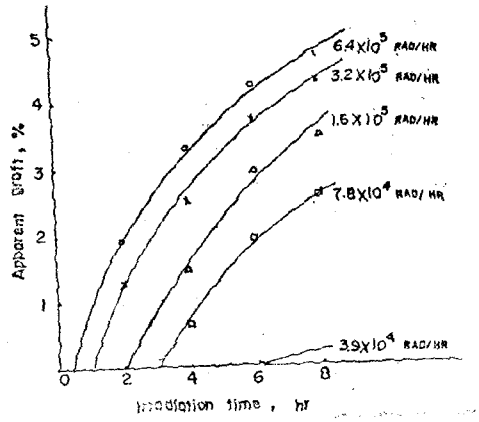

Fig. 4. Grafting of methyl methacrylate onto polyester fabric at different dose rates *at room temperature*. *Impregnation*: 70°C, 2 hr. Composition of monomer mixture: MMA-EtOH-DE-H_2O (10 : 45 : 40 : 5 by Vol.)

is attributed to the polymer stucture.

2) Effect of dose rate on grafting

The percent of graft of MA and MMA onto polyester fabric at different dose rates (3.9×10^4 rad/hr—6.4×10^5 rad/hr) are shown in Fig. 3. and 4 respectively. The percent of graft was found to increase with dose rate in Fig. 3 and Fig. 4. The results suggested that the rate of polymerization of MA was faster than that of MMA, because of steric hindrance of methyl group in ester. At the same does rate, the activation energy of MMA was larger than that of MA. So it is considered that the induction time of MMA is longer than that of MA.

The effect of dose rate on the rate of grafting in MA-DE-water solution is shown as a log-log plot in Fig. 5. The initial rate of grafting was proportional to the power 0.49 for dose intensity. In the case of MMA, the log-log plot of the initial rate of grafting versus dose rate gives a straight line whose slope is the intensity exponent. The rate of grafting was proportional to the power 0.36 for dose intensity (Fig. 6). In the acrylic acid[7], it was reported that rate of grafting was propor-

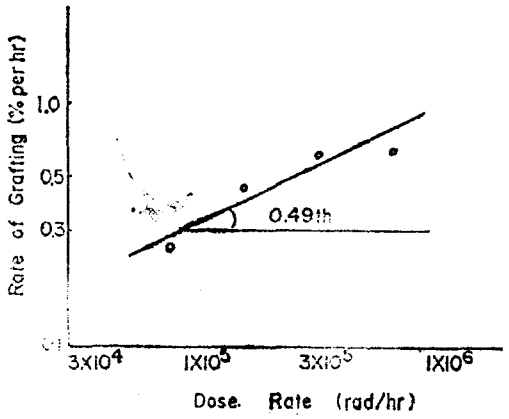

Fig. 5. Effect of dose rate on grafting rate at 20°C. Composition of monomer mixture: MA-H_2O-DE (10 : 50 : 40 by Vol.)

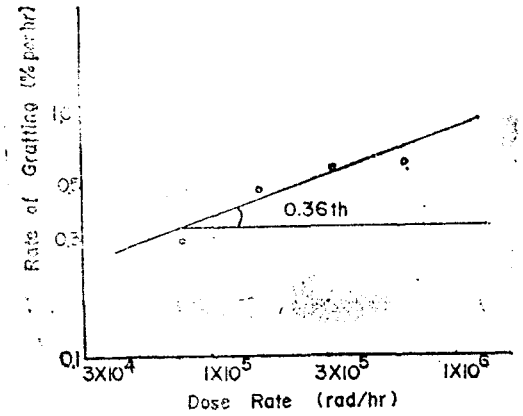

Fig. 6. Effect of dose rate on grafting rate at 20°C. Composition of monomer mixture: MMA-EtOH-DE-H_2O (10 : 45 : 40 : 5 by Vol.)

tional to the power 0.82 for dose intensity. It can be said that the order of grafting is acrylic acid, methacrylic acid, and methyl methacrylate on account of steric effect.

3) Effects of swelling agent and solvents

Polyester fibers were so crystalling that monomers hardly could diffuse into them. The crystalline region were partially converted into the amorphous region by swelling agent. Therefore, it is possible that diffusion rate of monomers is accelerated by swelling agent and that

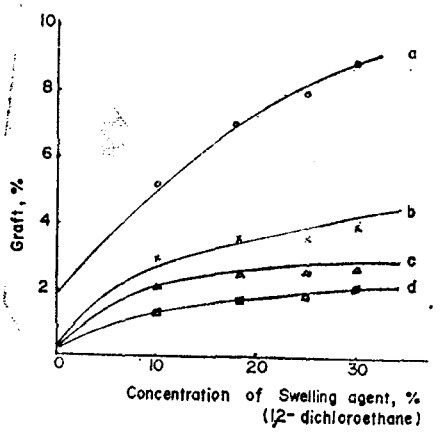

Fig. 7. Dependence of graft on concentration of swelling agent at different solvents.
Solvents: (a) Water
(b) Methyl alcohol
(c) Ethyl alcohol
(d) Isopropyl alcohol
Composition of monomer mixture: MA-Solvent-DE (10 : 80 : DE by Vol.)

monomers are apt to react polymer radicals. When the proportion of swelling agent was increased, the percent of graft was increased in Fig. 7, Fig. 8, and Fig. 9. The role of the swelling agent was complex, since it participated in the partial chain transfer processes as well as facilitating the diffusion of monomers to the active sites.

It is shown in Fig. 10 and Fig. 11 that the nature of solvent affected the extend of grafting. Of the solvents use, water was proved the best solvent for grafting in MA and methyl alcohol in MMA.

Variation of grafting using different solvents could be associated with difference in their i) capability of swelling polyester fiber ii) miscibility with monomer iii) formation of solvent radical from the primary radical species iv) dielectric constant of solvents. The first three factors favored grafting by simplifying access and diffusion of monomer. The order of dielectric constant of solvents (water, 78.54; methyl

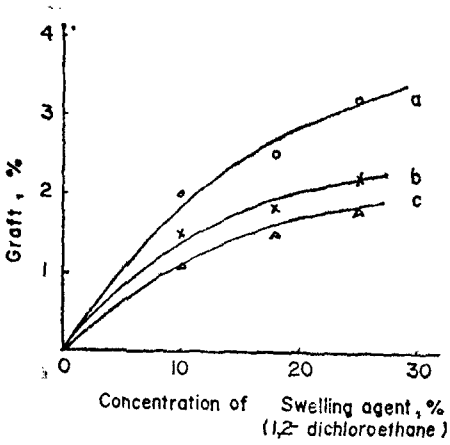

Fig. 8. Dependence of graft on concentration of swelling agent at different solvents.
Solvents: (a) Methyl alcohol
(b) Ethyl alcohol
(c) Isopropyl alcohol
Composition of monomer mixture:
MMA-Solvent-DE (10 : 80 : DE by Vol.)

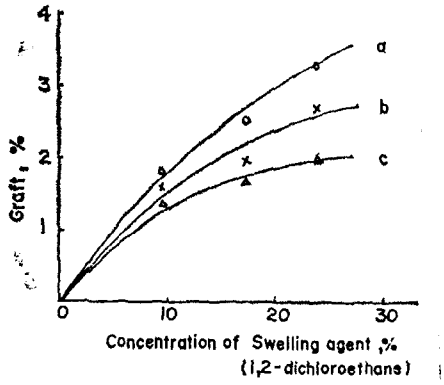

Fig. 9. Dependence of graft of concentration of swelling agent at different solvents containing water.
Solvents: (a) Methyl alcohol
(b) Ethyl alcohol
(c) Isopropyl alcohol

alcohol, 32.35; ethyl alcohol, 25.0; iso-propyl alcohol, 16) was identical with the percent of graft. The influence of the last factor in grafting can't be interpreted with present work.

Incorporation of water in the grafting medium is interesting from both the academic and practical point of view. The presence of water has been reported to increase grafting by swelling and improving the diffusion of monomer within the substance[18,19]. Such a phenomina appeared in Fig. 9.

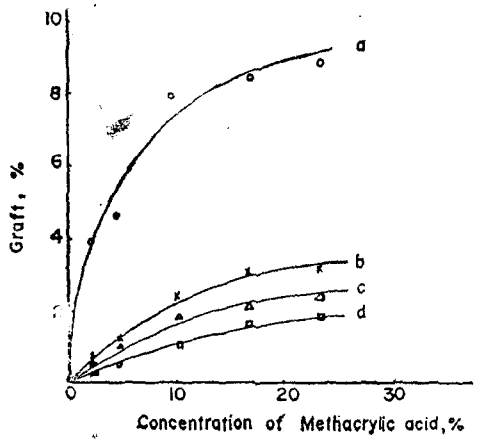

Fig. 10. Dependence of graft on concentration of methacrylic acid at different solvents.
Solvents: (a) Water
(b) Methyl alcohol
(c) Ethyl alcohol
(d) Isopropyl alcohol
Composition of monomer mixture:
Monomer-Solvent-DE (Monomer : 80 : 10 by Vol.)

4) Effect of monomer concentration

Fig. 10 and 11 illustrate the effect of MA and MMA concentration on the extent of grafting. It is seen from the results that the higher the graft yield, the higher concentration of MA. The similar inclination was appeared in MMA, which made a agreement with previous studies [7,20].

5) Physical properties of grafted polyester fabric

The hydrophilic property that was measured by moisture regain versus the percent of graft is shown in Fig. 12. It was showed that polyester fabrics grafted with MA could match the moisture regain properties of polyester and cotton. It has been found from the results that

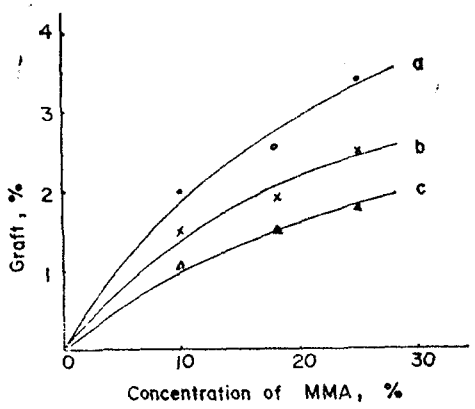

Fig. 11. Dependence of graft on concentration of methyl methacrylate at different solvents.
Solvents: (a) Methyl alcohol
(b) Ethyl alcohol
(c) Isopropyl alcohol
Composition of monomer mixture: Monomer-Solvent-DE (Monomer : 80 : 10 by Vol.)

Table 1. Frictional electricity, half life and wicking time of methacrylic acid grafted polyester fabric at 25°C, 70 % relative humidity.

Apparent graft, %	Frictional electricity, volts	Half life, sec	Wicking time, sec
4.2	40,000	33	1
6.1	39,000	13	1
8.5	34,000	1	1
12.4	8,000	0	1
13.6	8,000	0	1
Original polyester	40,000	300	300
Cotton	12,000	0	0

moisture regaines in 94% relative humidity were increased with the percent of grafting.

The MA grafted polyesters had the high melting point and the improved glass transition temperature. Similar results occured in the MMA grafted polyesters, which are shown in Fig. 13. Copolymers of MA or MMA had a profound influence of the fabric glass transition. The fabric glass transition temperature was

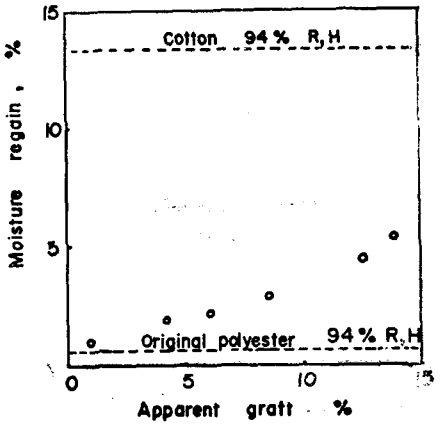

Fig. 12. Moisture regain of methacrylic acid grafted polyester fabric at 20°C, 94 % relative humidity.

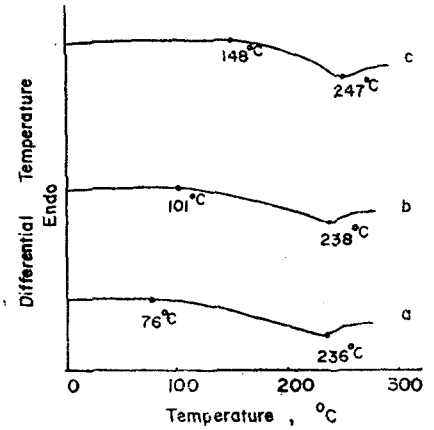

Fig. 13. Thermogram of polyester fabric.
Sample: (a) Original polyester fabric
(b) MA grafted polyester fabric
(c) MMA grafted polyester fabric
Sample Weight: 5 mg
Inert Material: α-Al_2O_3
Atmosphere: Air
Sensitivity: 100 μV
Heating Rate: 10°C/min.
Thermocouple: Pt-Pt. Rh 10%

increased from 76°C to 148°C from the MMA grafted polyester fabric.

Frictional electricity, half life and wicking time of the MA grafted polyester fabric at 25°C, 70% relative humidity are listed in Table 1. The frictional electricity of original polyester

and cotton were 40,000 eV and 12,000 eV respectively. Wicking time and half life of polyester were above 300 sec, and those of cotton were 0 sec. In the MA grafted polyester fabric, the frictional electricity was decreased with the increase of the percent of graft. Half life and wicking time were also decreased with the increase of the percent of graft. When 13 percent of MA was grafted onto polyester fabric, frictional electricity was 8,000 eV and half life and wicking time were below 1 sec.

Ⅳ. Conclusion

The radiation-induced graft polymerization of methacrylic acid and methyl methacylate onto polyester was investigated; the graft yield was largely influenced by the nature of the solvents.

The rate of grafting was proportional to the power of 0.49 for dose intensity in methacrylic acid. In the case of methyl methacrylate, the rate of grafting was proportional to the power 0.36 for dose intensity.

The graft yield is proportional to the concentrations of monomers and swelling agent.

The percent of graft was increased with total dose.

In investigation of DTA, it was found that the glass transition temperature and melting point of graft copolymer were higher than those of original polyester facric.

Polyester fabric treated with methacrylic acid has shown improved properties in the moisture regain and frictional electricity.

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