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GRAFTING PARAMETERS IN THE COPOLYMERIZATION BY IRRADIATION OF N,N-DIMETHYL ACRYLAMIDE (DMAA) ONTO AFLON FILMS

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The radiation-induced grafting has been studied to modify chemical structures and physical properties of polymers (Allen et al, 1955).
In the synthesis of biocompatible membranes is specially useful to impart hydrophilic property to the originally hydrophobic polymers by grafting monomer such as DMAA, HEMA, AAm, etc.
In this work the parameters for the grafting of N,N-Dimethylacrilamide (DMAA) onto poly(ethylene-co-tetrafluoroethylene) (AFLON) films were studied.
The swelling degree of AFLON in DMAA and ethylacetate indicated them to be, respectively, the more suitable monomer and solvent for the process. A grafting degree of 24,67% was achieved with 30 vol% DMAA at a dose rate of 0,045 KGy/hr after 10 hours irradiation at 25ºC. The grafting degree showed to be dependent of dose rate and temperature.
The infrared spectroscopy (IR) analysis of the grafted film showed a peak at 1640 cm^{-1} due to the C=O groups of the monomer. There was a linearity between grafting and water absorption degree.

Ref.

1. ALLEN P.W.; MERRET F.M.; SCANLAN J. The interaction of polymerizing systems with rubber and its homologues. Trans. Faraday Soc., 51, 95-106, 1955.

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INTRODUCTION

The radiation-induced grafting has been studied to modify chemical structures and physical properties of polymers (Allen, 1955).

It is specially useful to impart hydrophilic property to the originally hydrophobic polymers by grafting monomers such as DMAA, HEMA, AAm, etc. In this way biocompatible materials were synthesized and has been used widely in medical field (Ikada et al, 1981).

In our laboratory, synthesis of biocompatible surfaces has been studied particularly by using radiation-induced tecnique.

In this work, we have studied the effect of grafting parameters such as solvent, dose rate and temperature on the grafting of DMAA onto AFLON.

EXPERIMENTAL

Materials

N,N-dimethylacrylamide (DMAA) supplied by Wako Pure Chemical Industries Ltda was used as received.

AFLON films of 50 μm thickness (2.5 X 2.5 cm) were used in the grafting polymerization after being washed with detergent and rinsed with ethanol and distilled water. They were dried for 6 hours under vacuum.

Other chemicals were reagent grade and used without further purification.

Graft Polymerization

The AFLON film and a certain amount of DMAA and ethylacetate were put into a glass ampoule. The ampoule was connected to a vacuum system and it was evacuated by freeze-thaw cycle which was repeated five times.After evacuation, the ampoule was irradiated by using gama rays from a ^{60}Co source at a dose rate of 0.033 KGy/hr to 0.468KGy/hr at room temperature. The film was taken out from the ampoule and it was immersed in water for 24 hours. The extraction of polydimethylacrylamide from the film was carried out in boiled water for 8 hours. After the film was dried in a desiccator under vacuum at room temperature, it was weighed. The degree of grafting was determined by percentage in weight of the film.

Surface Characterization

The wettability of the grafted film was measured immersing it into distilled water for 24 hours at room temperature. Then, it was taken out and the excess water attached on the surface of it was removed by a blotting paper and the film was weighed quickly. Swelling percent of the film was determined as follows:

$$\text{Swelling } (\%) = \frac{W_w - W_d}{W_d} \cdot 100$$

were W_d and W_w represent the weights of dry and wet films, respectively.

Infrared Spectroscopy

A spectrophotometer Perkin-Elmer model 735 B was used for the characterization of the grafted surface.

RESULTS AND DISCUSSION

To obtain a high grafting efficiency, particularly in the simultaneous irradiation, the monomer shall be as close as possible to the active center created in the polymer backbone (Tabata, 1977). The grafting is very affected by diffusion of monomer and solvent in to the polymeric matrix.

The diffusion was studied by the swelling degree of the AFLON films in monomers and solvents as show in Tables I and II. The swelling percent of AFLON by DMAA and ethylacetate were higher compared to others monomers and solvents studied.

To increase the diffusion of monomer in the polymeric surface various concentrations of DMAA in ethylacetate were prepared. The difference in the graft level obtained at various concentrations of DMAA in ethylacetate is shown in Figure 1. The grafting of DMAA onto AFLON was carried out at a dose rate of 0.045 KGy/hr and room temperature. Degree of grafting in ethyl acetate increased with monomer concentration became maximum at a monomer concentration of 30 vol%.

Effect of other grafting parameters, such as dose rate and temperature

on the grafting yield was examined.

Only ethylacetate was used as solvent since it is the most suitable solvent for the grafting in all solvents examined here.

TABLE I

Swelling* ability of AFLON in various monomers

Monomer	Swelling Ability (%)
N-Vinyl-2-Pyrrolidone	3,57
Styrene	6.07
Nonaethylenoglycoldiacrylate (A 9G)	5.34
N,N-Dimethylacrylamide (DMAA)	7.13
Methoxynonaethyleneglycoldiacrylate (M 9G)	5.73
Tetradecaethyleneglycoldiacrylate (A 14G)	5.77
Hidroxyethylmetacrylate (HEMA)	4.43

*swelling conditions:

The AFLON films was immersed into the monomers for 24 hours at temperature of 27ºC.

TABLE II

Swelling** ability of AFLON in various solvents

Solvent	Swelling ability (%)
Water	0
Methanol	0
Ethanol	0.47
Buthanol	0.65
Carbon Tetrachloride	3.89
Ethylacetate	4.16

**Swelling conditions:

The AFLON films was immersed into the solvents for 24 hours at temperature of 27ºC.

Figure 2 shows dose rate dependency of the grafting of DMAA onto AFLON in a region of dose rate from 0.033 KGy/hr to 0.468 KGy/hr.

According to these results, we can say that lower dose rate is more effective to obtain higher graft level. In generally, the same tendency would be expected in the simultaneous irradiation method because for higher dose rate the rate of homopolymerization becomes higher, and because of this, satured graft level would be decreased.

Temperature dependency of graft copolymerization is shown in Figure 3,in the range of temperature of 4 to 67ºC. The inicial rate of grafting increases with temperature. The temperature dependence of the initial rate of grafting can be understood by the diffusibility of monomer into polymer matrix. It was reported that crystalline regions of polymers undergoes a series of transitions and that there is a higher internal friction (Mccrum, 1959). It is concluded that the increase in diffusibility of monomer into AFLON matrix results in the lowering of the activation energy in the temperature ranging from 25 to 67ºC.

The infrared spectroscopy showed absorption peak at 1640 cm^{-1} due to carbonyl group of the grafted monomer. The presence of this absorption peak (Fig.4) conclusively proves that grafting of dimethylacrilamide onto AFLON has taken place.

Figure 5 shows the results of swelling test of DMAA-g-AFLON. By this test percentage of swelling in water increased linearly withthe degree of grafting.

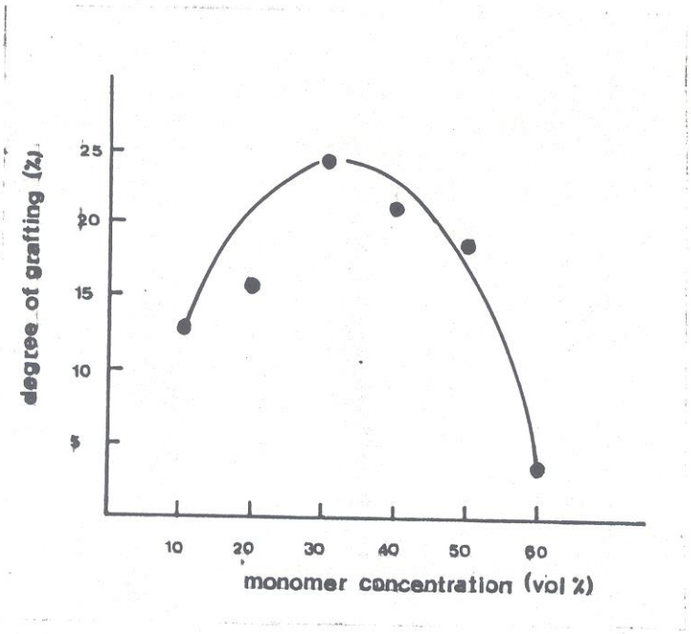

Fig.1- Effect of monomer concentration on degree of grafting. Irradiation time, 10 hr; grafting temp., 27ºC; dose rate, $4.46.10^{-2}$ KGy/hr.

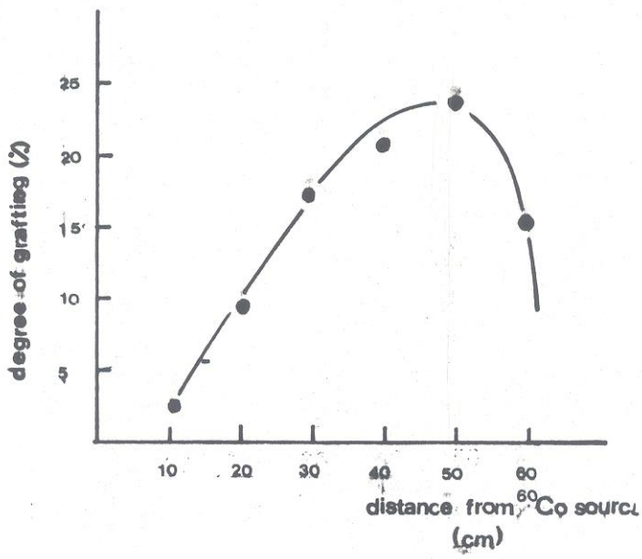

Fig.2- Relation between degree of grafting and distance from a ^{60}Co source: 10 cm, $4.68.10^{-1}$KGy/hr; 20 cm, $1.96.10^{-1}$KGy/hr; 30 cm, $1.03.10^{-1}$KGy/hr; 40 cm, $6.4.10^{-2}$KGy/hr; 50 cm, $4.5.10^{-2}$KGy/hr; 60 cm, $3.3.10^{-2}$KGy/hr; irradiation time, 10 hr; grafting temperature, 27ºC; monomer concentration, 30 vol%.

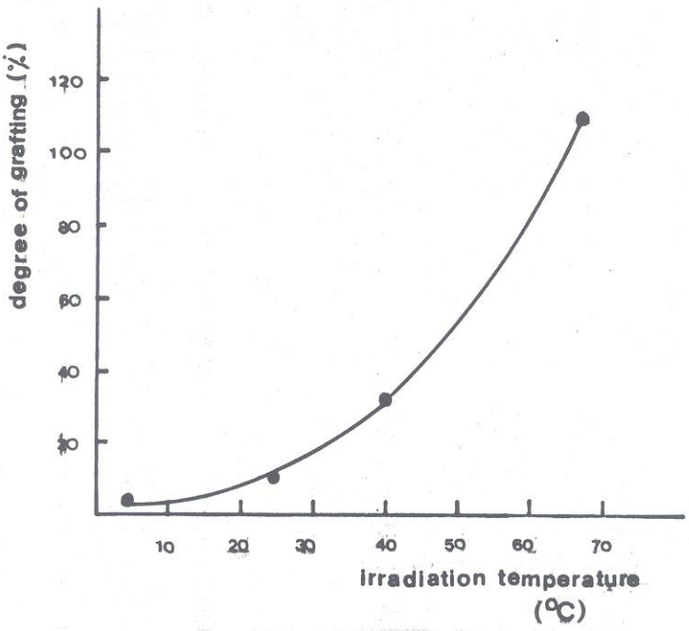

Fig.3- Grafting yield of DMAA onto AFLON at various temperatures. Dose rate, 0,063 KGy/hr; film thickness, 50 μm; concentration DMAA/ethylacetate, 30 vol%; time of irradiation, 2 hours.

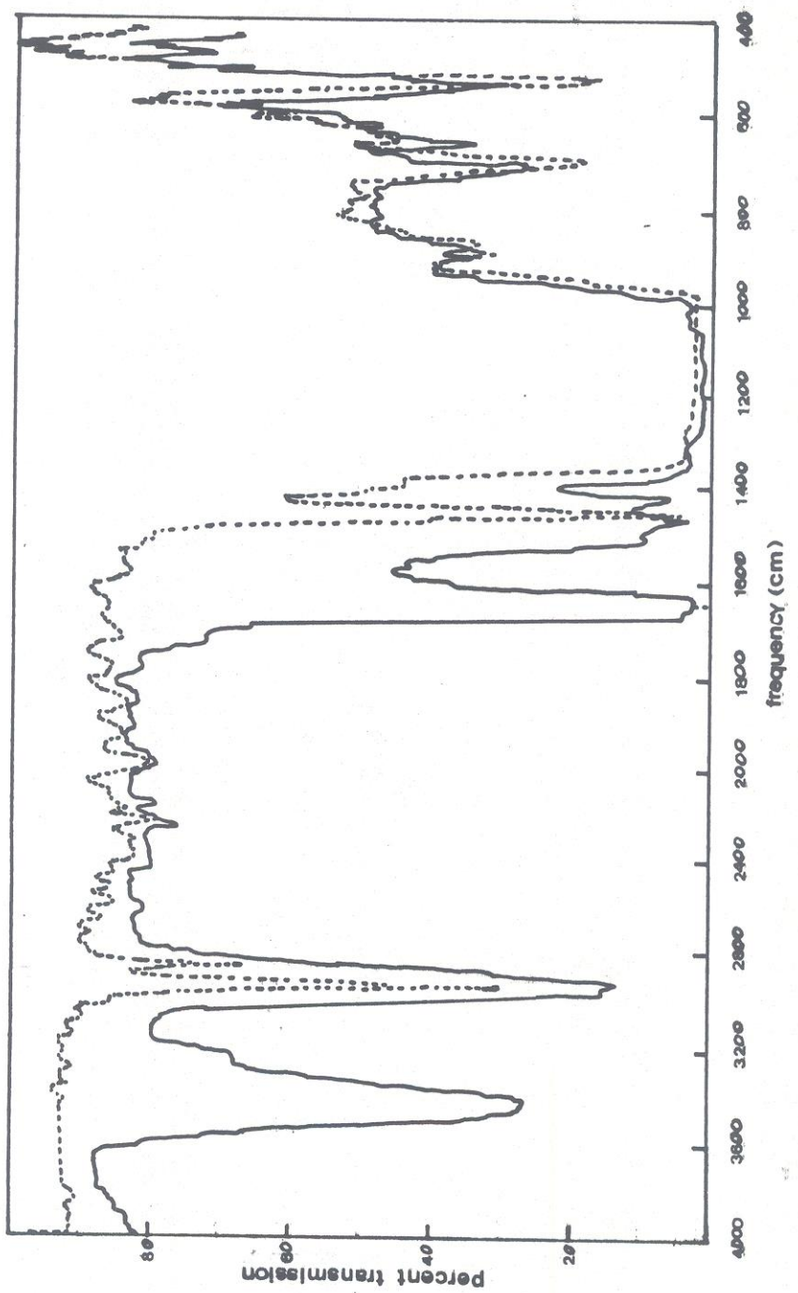

Fig. 4- Infrared spectrum of N,N-dimethylacrylamide grafted AFLON by radiation.

——— DMAA-g-AFLON. Degree of grafting, 24.69%.

----- Virgin AFLON.

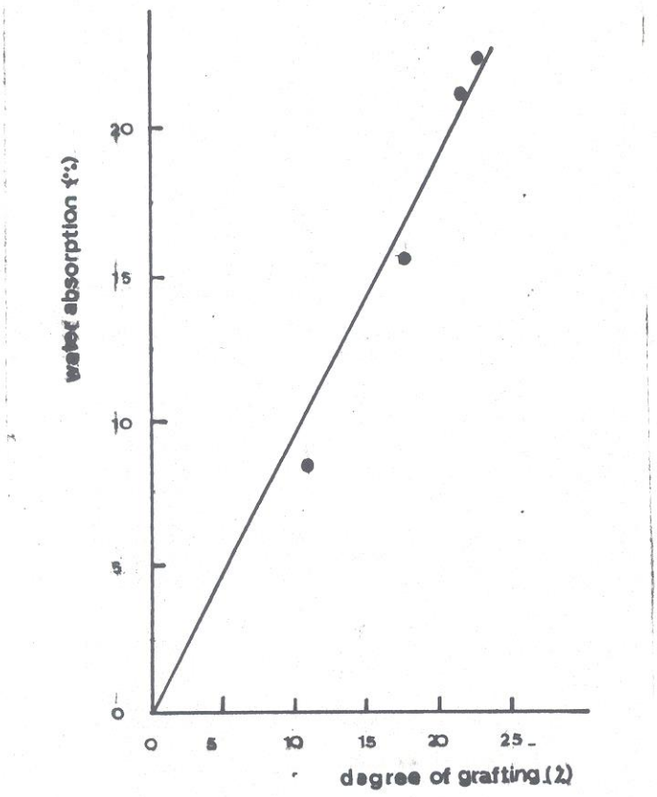

Fig.5- Relation between water absorption and degree of grafting (%). Irradiation time, 10 hours; irradiation temperature, 27ºC; monomer concentration, 30 vol%.

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ALLEN P. W.; MERRET F.M.; SCANLAN J. The interaction of polymerizing systems with rubber and its homologues. Trans. Faraday Soc., 51 : 95-106, 1955.

IKADA Y.; SUZUKI M.; TANIGUCHI M.; IWATA H.; TAKI W.; MIYAKE H.; YONEKAWA Y.; HANDA H. Interaction of blood with radiation-grafted materials. Radiat. Phys. Chem., 18, (5) (6), 1207-1216, 1981.

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