Graft Copolymerization of Dimethylacrylamide onto AFLAS

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SYNOPSIS

The method of irradiation grafting of DMAA onto AFLAS (alternating copolymer of tetrafluoroethylene and propylene) films was studied. The effect of the solvent on the grafting yield was determined. As a result, it might be important to evaluate the blood compatibility of the films already grafted by using an *in vitro* test. Benzene tests seem to be the most adequate for copolymerization. Grafting yield was better in the monomer 40–60% concentration range. The degree of grafting increases proportionally to dose rate in gamma ray radiation. The graft copolymerization is terminated via unimolecular mechanism. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Grafting of hydrophilic monomer is one of the best methods to improve blood compatibility of commercial plastics and elastomers.[1] We have already reported that blood compatibility of PTFE polytetrafluoroethylene (PTFE) and AFLON (alternating copolymer of tetrafluoroethylene and ethylene) is improved by grafting of dimethylacrylamide (DMAA) under certain conditions.[2,3] Furthermore, we have also found that blood compatibility of natural rubber is improved to a large extent by grafting of DMAA.[4]

In the present work, grafting of DMAA onto AFLAS (alternating copolymer of tetrafluoroethylene and propylene) has been carried out as a series of our research. AFLAS is an elastomer and it contains tetrafluoroethylene units. Thus, this copolymer seems to be very suitable as a substrate for medical applications. In the beginning of our research, γ-irradiation grafting behavior of DMAA onto AFLAS has been investigated. We report the effect of kinetic parameters such as solvent, monomer concentration, and dose rate on the grafting yield of DMAA onto AFLAS.

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EXPERIMENTAL

Materials

AFLAS films were prepared using AFLAS solution, which was supplied by TAIHEI Chemical Co. Ltd. A certain amount of the solution was deposited on a glass plate (100 × 100 mm), and it was kept for 2 days at room temperature to evaporate the solvents. After the plate was dried, AFLAS film that formed was removed and then cut to 2.5- × 2.5-cm pieces for grafting. DMAA was supplied by Kohjin Co. Ltd. and was used without further purification. In addition, all the solvents employed were reagent grade.

Graft Polymerization

A piece of the film and a certain amount of DMAA and solvent were put into a glass ampoule. The ampoule was connected to a vacuum system and was evacuated by freeze-thaw cycle that was repeated five times. After evacuation, the ampoule was irradiated by using γ-rays from a ^{60}Co source at a dose rate of 0.097–1.5 KGy/h at room temperature. The film was then taken out from the ampoule and was washed with water and boiled in water for 6 h to extract the homopolymer. After the film was dried in a vacuum oven for 2 days at room temperature it was weighed. The degree of grafting was determined by the percentage increase in weight of the film.

Table I Effect of Solvents on the Graft Copolymerization of DMAA onto AFLAS[a]

Sample No.	Solvent	Irradiation Time (h)	Degree of Grafting (wt %)
ZPA 1-1	Water	1.30	0.00
ZPA 1-2	MeOH	1.30	0.502
EPA 1-3	EtOH	1.30	0.392
ZPA 2-1	Benzene	1.00	7.33
ZPA 2-7	Ethylacetate	0.20	6.40
ZPA 11-1	Acetone	0.20	1.27

[a] Dose rate, 0.097 KGy/h; irrad. temp., 25°C; DMAA conc., 25 vol %.

RESULTS AND DISCUSSION

Results of the solvent effect on the grafting yield are shown in Table I. Among all the solvents examined, benzene, ethyl acetate, and acetone were more efficient for the grafting compared to the other solvents. This behavior might be explained by the monomer-carrier function that the solvents can realize in grafting. In the case of benzene, ethyl acetate, and acetone, they can promote the swelling of AFLAS, which facilitates the penetration of DMAA molecules inside the polymer chains and, as it is known, this kinetic factor can increase the degree of grafting,[5] specially when the direct method has been used to obtain the graft copolymer.

In close relation with the above mentioned, it is important to comment on the solubility parameter (δ) that these solvents have with respect to those corresponding to the polymers forming AFLAS copolymer (polytetrafluoroethylene and polypropylene). From the values in Table II, it is clear that the chemical interaction to the AFLAS, specially toward the polypropylene part, is higher in benzene, ethyl acetate, and acetone than in the other solvents such as, water, methanol, and ethanol. This is in accord with our results on the influence of the solvent in the degree of grafting.

Table II Solubility Parameters for the Solvents and the Polymers Forming AFLAS[6]

Solvents and Polymer	δ $(cal/cm^3)^{1/2}$
H_2O	23.4
MeOH	14.5
EtOH	12.7
Benzene	9.2
EtAc	9.1
Acetone	9.9
AFLAS	6.2 PTFE–9.2 PP

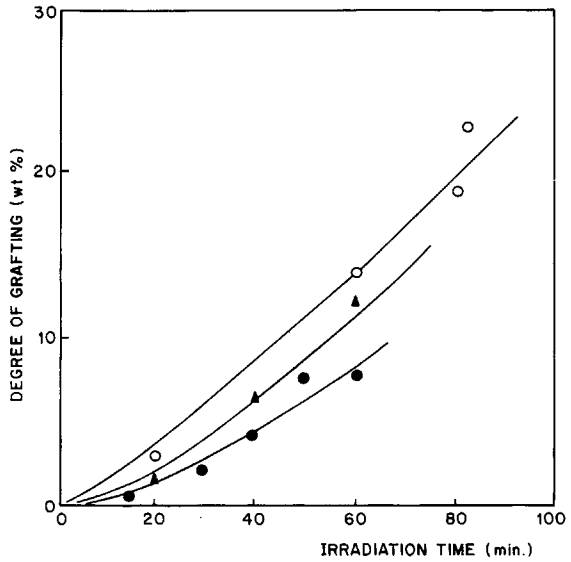

Figure 1 Degree of grafting vs. irradiation time on grafting of DMAA onto AFLAS at various solvents. DMAA conc., 50 vol %; dose rate, 0.10 KGy/h; irrad. temp., 25°C. (●) Benzene, (▲) ethylacetate, (○) acetone.

Thus, by using these solvents, the relation between grafting yield and irradiation time was obtained, as shown in Figure 1, where it is seen that the degree of grafting increased with the time of irradiation for all the solvents examined. Saturation

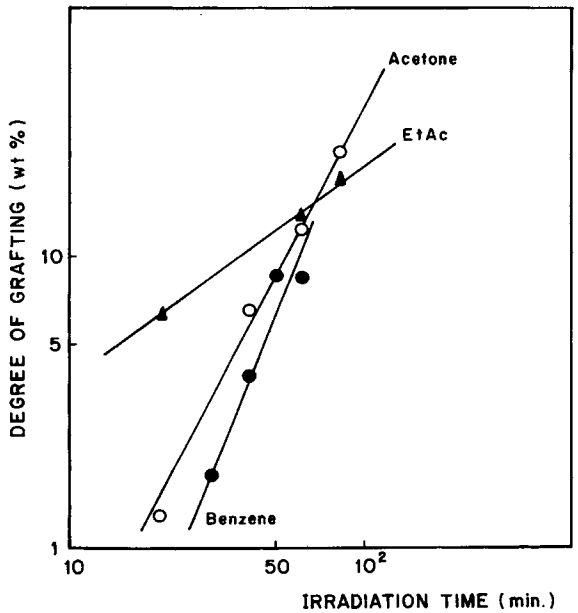

Figure 2 Logarithmic plot of grafting yield and irradiation time at various solvents. DMAA conc., 50 vol %; dose rate, 0.10 KGy/h; irrad. temp., 25°C.

of the grafting was not observed at least until 80 min of irradiation time.

On the basis of Figure 1, three lines could be obtained in log-log coordinates, as shown in Figure 2. From the slope of each line, dependency of grafting yield on irradiation time was obtained as follows:

$$G(\%) \alpha T^{0.76} \quad \text{(ethyl acetate)}$$

$$G(\%) \alpha T^{2.01} \quad \text{(acetone)}$$

$$G(\%) \alpha T^{2.56} \quad \text{(benzene)}$$

where G is the grafting yield and T the irradiation time. The largest exponent of T was found for benzene, which means that this solvent carries on a better carrier function for monomer molecules and elevates swelling of AFLAS. These factors promote a good graft reaction to a less irradiation time than using the other solvents.

Effects of other grafting parameters on the grafting of DMAA onto AFLAS have also been examined by using the above three solvents. Figure 3 shows the effect of monomer concentration of the grafting yield in benzene. Grafting yield is dependent on monomer concentration, and it is relatively higher in the range of 40–60 vol % DMAA in the reactant mixture. Accordingly, the maximum yield seems to be attainable in the same range of DMAA volume percentage.

Dose rate effect on the grafting is shown in Figure 4. This effect was obtained by the graft copolymerization in acetone. Instantaneous rate of the grafting increases as dose rate increased. The exponent of dose rate dependency on the instantaneous rate of the grafting was calculated to be 0.95, that is, the rate of the grafting was found to be proportional to 0.95 power of the dose rate. This value implies that the graft copolymerization is terminated via a unimolecular mechanism.

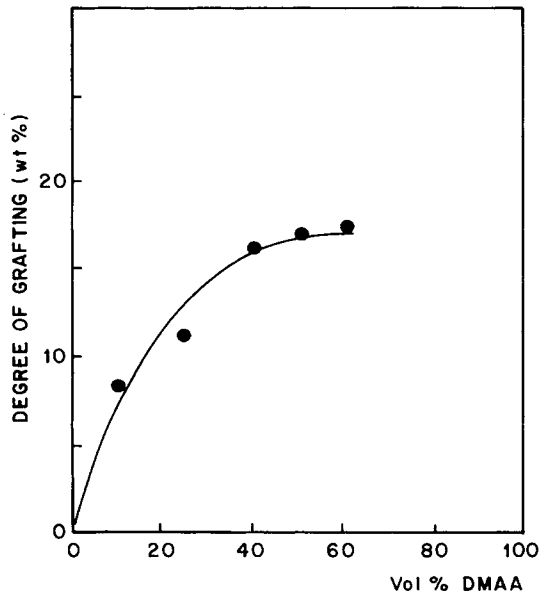

Figure 3 Effect of monomer concentration on grafting of DMAA onto AFLAS in benzene. Dose rate, 0.10 KGy/h; irrad. temp., 25°C.

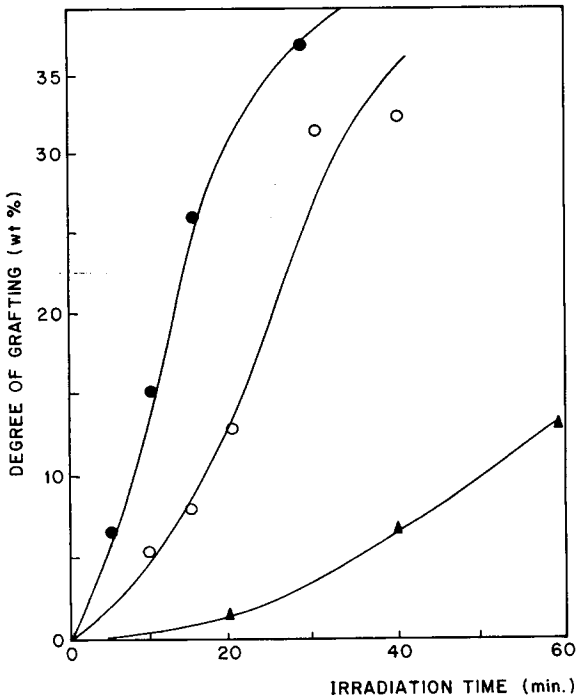

Figure 4 Degree of grafting vs. irradiation time on grafting of DMAA onto AFLAS in acetone at various dose rate. DMAA conc., 50 vol %. (●) 1.50 KGy/h, (○) 0.30 KGy/h, (▲) 0.10 KGy/h.

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