

Preparation and Characterization of Teflon–FEP Films Grafted with Acrylic Acid by Radiochemical Method

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SYNOPSIS

In an attempt to prepare permselective membrane, grafting of acrylic acid (AAc) onto Teflon–fluorinated ethylene-propylene (FEP) film was studied in aqueous medium by the preirradiation method in air. Grafting was carried out by heating a mixture of AAc, water, and preirradiated Teflon–FEP film in air at 93°C for definite time periods. Percentage of grafting was determined as a function of total dose, monomer concentration, reaction time, and amount of water. Maximum percentage of grafting (60.17%) was obtained at a total dose of 4.8 Mrad using 0.07M [AAc]. Evidence of grafting was obtained from the physical appearance and swelling behavior of the grafted film in polar solvents. Infrared spectroscopic and thermal analysis of the grafted film provided additional evidence for grafting. A plausible mechanism for grafting of AAc onto preirradiated Teflon–FEP film in air has been proposed.

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INTRODUCTION

Permselective membranes have attracted much attention in recent years due to their individual importance. These membranes are particularly suitable for separating various liquid mixtures including azeotropes by employing a new technique called pervaporation. Liquid mixtures can be separated by partial vaporization through a nonporous permselective membrane. Preparation of permselective membranes from numerous hydrocarbon polymers such as polyethylene (PE), polypropylene (PP), Teflon, and Teflon–fluorinated ethylene-propylene (FEP) films can be conveniently carried out by incorporating polar groups onto the backbone polymer. Among various methods available for functionalization of polymeric backbones, radiation induced grafting of polar vinyl monomers appears to be feasible. Grafted membranes obtained from PE or PP films were not suitable for separating organic liquid mixtures by pervaporation. These membranes rup-

tured under operational conditions. There is an ongoing search for methods of preparing stronger membranes. Teflon is a stronger polymer but its enormous toughness imposes severe limitations in its processing. Teflon–FEP copolymer is fairly strong and at the same time it is processable. This is why Teflon–FEP film has been utilized for preparing permselective membranes. Chapiro and Gupta¹ have recently reported the preparation of permselective membranes from peroxidized PE films by radiation induced grafting of acrylic acid (AAc) by the mutual method in vacuum. Very little work on grafting of polar vinyl monomers on Teflon–FEP films has been reported. Jendry Chowska–Bonamour and Millegnant² reported the preparation of non-ionizable membranes by radiation grafting of *N*-vinyl pyrrolidone onto the film of polytetrafluoroethylene. Gupta and Chapiro³ reported on the preparation of ion exchange membranes by grafting AAc onto Teflon–FEP film in vacuum by the mutual method. Chapiro et al.⁴ have recently been successful in preparing permselective membranes from Teflon–FEP film by grafting 4-vinyl pyridine and vinyl imidazole using the mutual irradiation method in vacuum. In the present study we report on grafting of AAc onto Teflon–FEP film by the preirradiation method.

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EXPERIMENTAL

Materials and Methods

Teflon-FEP film (0.05 mm; DuPont, obtained courtesy of Prof. A. Chapiro of CNRS, Thiais, Paris) was washed several times with MeOH and dried under suction. The dried Teflon-FEP film (4 × 2 cm) was weighed and then irradiated in air by γ -rays from a Co^{60} (2100 Ci) source (Bhabha Atomic Research Centre, Bombay) at a constant dose rate of 0.01 Mrad/h.

Graft Copolymerization

Irradiated Teflon-FEP film in air was suspended in a definite amount of water and a known volume of the monomer (AAc) was added. The reaction mixture was heated at 93°C for appropriate time period. After the completion of the reaction the grafted film was washed with water several times to completely remove the homopolymer, poly(AAc) (PAAc). The grafted film was dried in a vacuum oven at 50°C until the constant weight was obtained. Percentage of grafting was calculated from the increase in weight of the film in the following manner:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are, respectively, the weights of the original film and the grafted film after complete removal of the homopolymer.

Evidence of Grafting

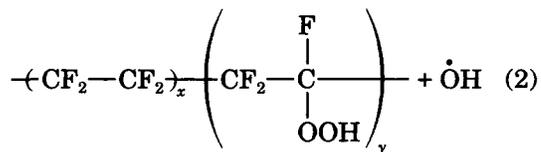
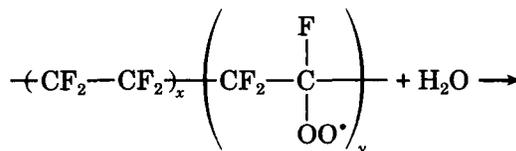
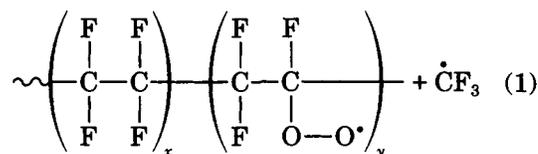
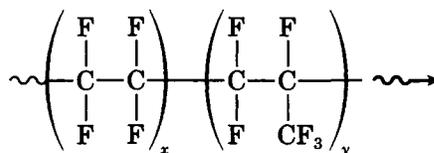
1. The IR spectrum of grafted film in comparison with that of Teflon-FEP film showed additional peaks at 1700 cm^{-1} and a broad peak between 2700 and 3600 cm^{-1} . The peak at 1700 cm^{-1} was attributed to $>\text{C}=\text{O}$ of grafted acrylic acid. The broad peak between 2700 and 3600 cm^{-1} was attributed to the hydrogen bonded $-\text{COOH}$ group in the grafted film.
2. Physical appearance of the films revealed that the ungrafted film was transparent and the grafted film was opaque.
3. Swelling behavior of ungrafted and grafted Teflon-FEP film was studied in water and dimethylformamide (DMF) and it was found that the ungrafted film did not swell but the

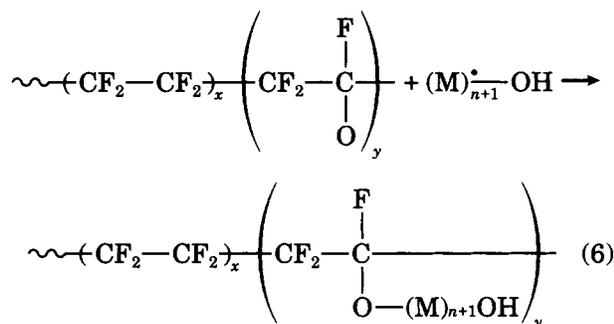
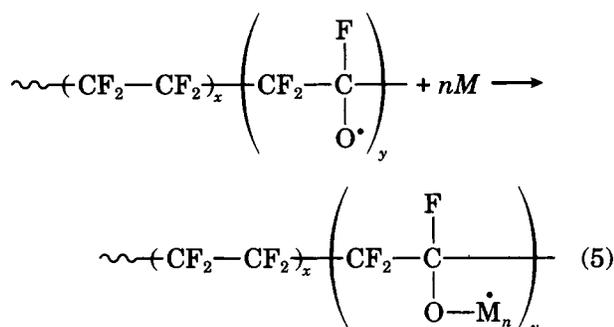
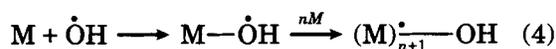
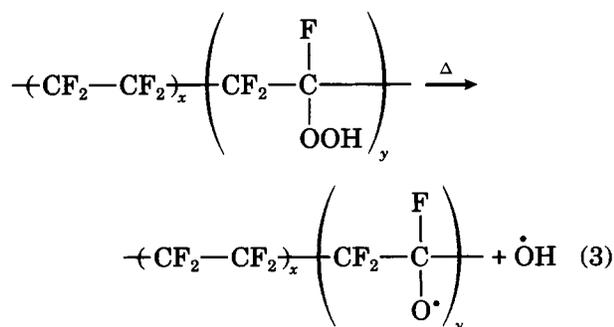
grafted film swelled appreciably in these solvents.

4. Upon grafting, an increase in the dimension of the film was observed.

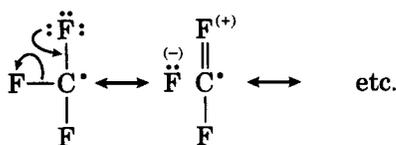
RESULTS AND DISCUSSION

A plausible mechanism for grafting of AAc onto Teflon-FEP film by the preirradiation method is suggested in an analogy with the mechanism of grafting vinyl monomers onto preirradiated isotactic polypropylene (IPP). IPP contains a large number of labile tertiary hydrogen atoms that upon irradiation in air easily form hydroperoxides. Upon heating the hydroperoxides generate active sites on the polymer backbone where grafting of appropriate vinyl monomer can lead to the formation of the graft copolymer.⁵ Teflon-FEP, on the other hand, does not contain any labile hydrogen atom. However, the following mechanism is suggested involving the generation of the diperoxy radical on Teflon-FEP film upon irradiation in air. The preirradiated film containing diperoxy radical upon treatment with water gives hydroperoxides that when heated in the presence of water produces graft copolymer:





In the above postulated mechanism, expulsion of trifluoromethyl radical, $\dot{\text{C}}\text{F}_3$, is assumed on the basis of the fact that $\dot{\text{C}}\text{F}_3$ is stabilized by the reverse hyperconjugative effect⁶ as shown below:

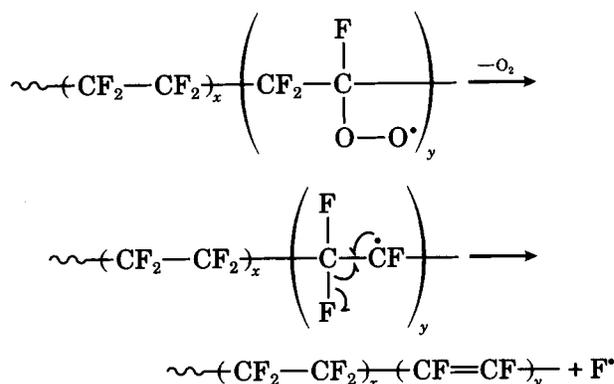


Once the formation of stable $\dot{\text{C}}\text{F}_3$ is rationalized, it becomes easier to explain the grafting by the above postulated mechanism involving generation of the active site on expulsion of the $\dot{\text{C}}\text{F}_3$ radical.

Effect of various reaction parameters that influence grafting has been explained on the basis of the above mechanism.

Effect of Total Dose

Percentage of grafting of AAc has been studied as a function of total dose and the results are presented in Figure 1. It is observed from the figure that the percentage of grafting of AAc increases rather slowly with increasing total dose and reaches maximum (33.34%) at an optimum total dose of 4.8 Mrad, beyond which it decreases. This may indicate that beyond 4.8 Mrad, active sites on the backbone polymer are depleted by the following process leading to a decrease in percentage of grafting



Effect of Monomer Concentration

Figure 2 represents the effect of concentration of AAc on percentage of grafting. Maximum percentage of grafting (60.17%) occurred at $[\text{AAc}] = 0.07M$. Beyond this concentration, percentage of grafting decreased. This is explained by assuming that with the progress of the reaction, some of the homopolymer formed was soluble in water, which raises the viscosity of the medium.

Diffusion of growing polymeric chains to the active sites in a highly viscous medium becomes difficult and as a consequence, grafting decreases.

Effect of Amount of Water

In Figure 3 the results of the effect of amount of water on percentage of grafting of AAc are presented. It is observed from the figure that maximum percentage of grafting under optimum conditions occurred when 10 mL of water was used. A further increase in the amount of water decreased the percentage of grafting. This is explained by the fact that with an increased amount of water, AAc becomes entrapped in water due to extensive hydrogen

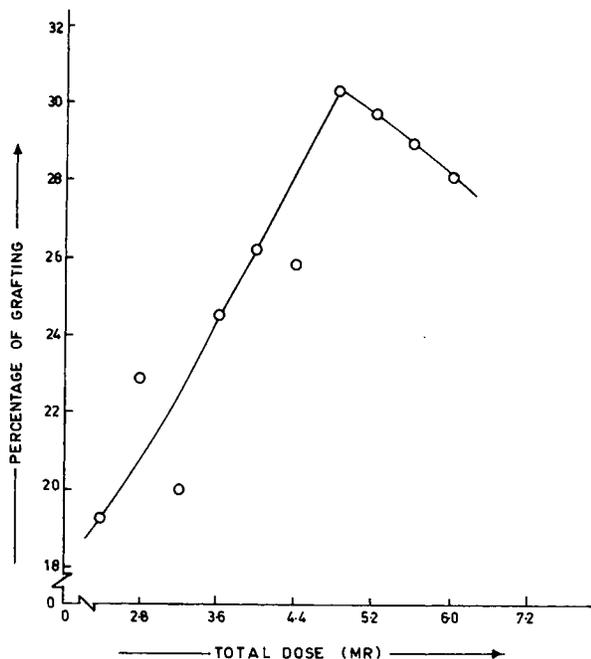


Figure 1 Effect of total dose on percentage of grafting of AAc onto Teflon-FEP film.

bonding. The hydrogen bonded monomer cannot diffuse easily to the active sites leading to a decrease in percentage of grafting.

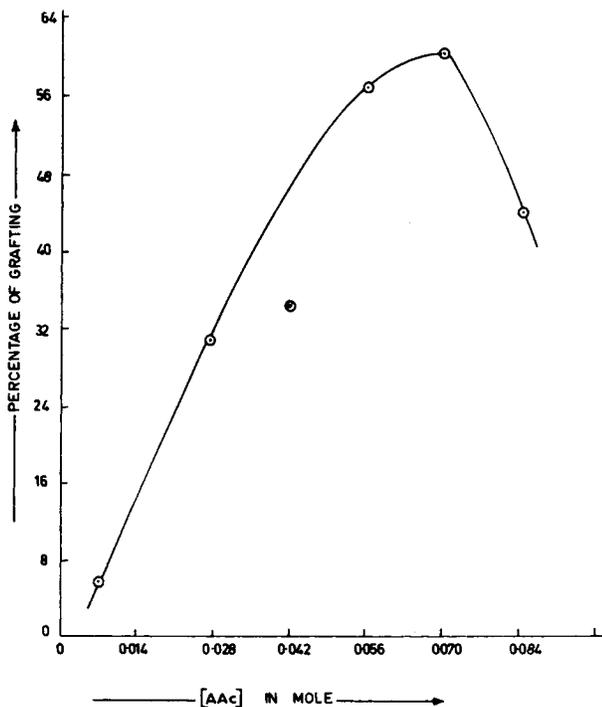


Figure 2 Effect of [AAc] on percentage of grafting.

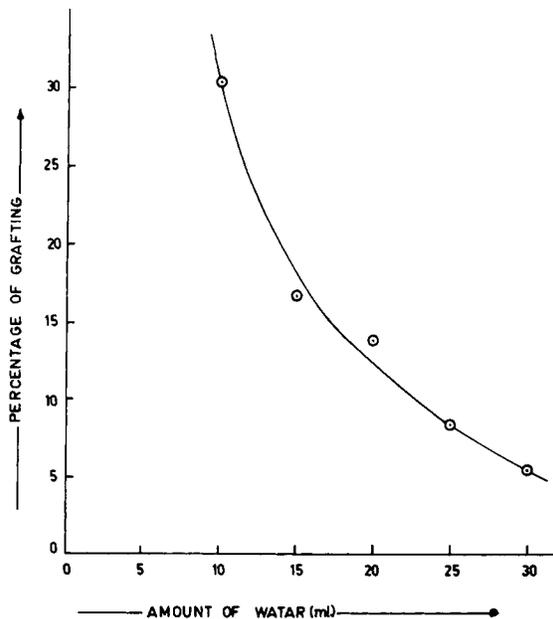


Figure 3 Effect of amount of water on percentage of grafting onto Teflon-FEP.

Effect of Reaction Time

It is observed from Figure 4 that the percentage of grafting increases with increasing reaction time and reaches maximum (60.17%) within 120 min under optimum conditions. A further increase in the re-

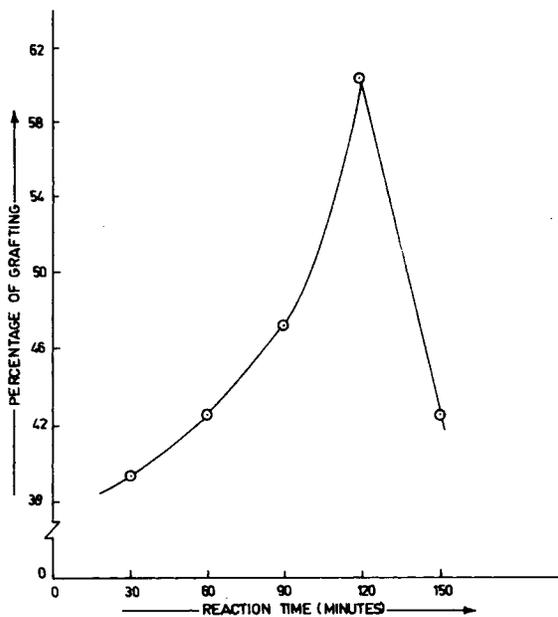


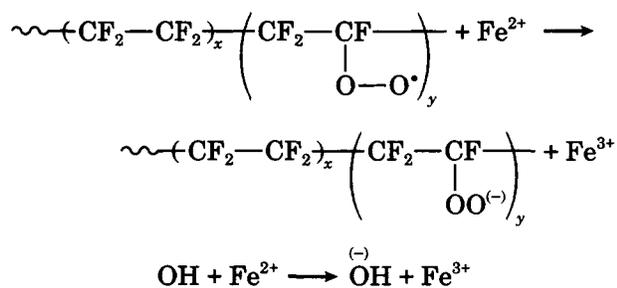
Figure 4 Effect of time of reaction on percentage of grafting of AAc onto Teflon-FEP film.

action time decreases the percentage of grafting. It appears that within 120 min, all the active sites are exhausted and mutual annihilation of growing polymeric chains occurs, leading to a decrease in percentage of grafting.

Effect of Ferrous Ammonium Sulfate

Fe^{2+} is known to suppress homopolymerization and therefore its effect was studied and the results are presented in Figure 5. In the present study, Fe^{2+} did not promote grafting.

This is explained by assuming that Fe^{2+} enters into redox reaction with the Teflon-FEP peroxy radical and the hydroxy radical formed during the reaction to generate anions that do not contribute toward grafting:



Swelling Behavior of Grafted Film

Percent swelling of Teflon-FEP-g-PAAc was determined in water and DMF, and the results are presented in Table I. It is observed from the Table I

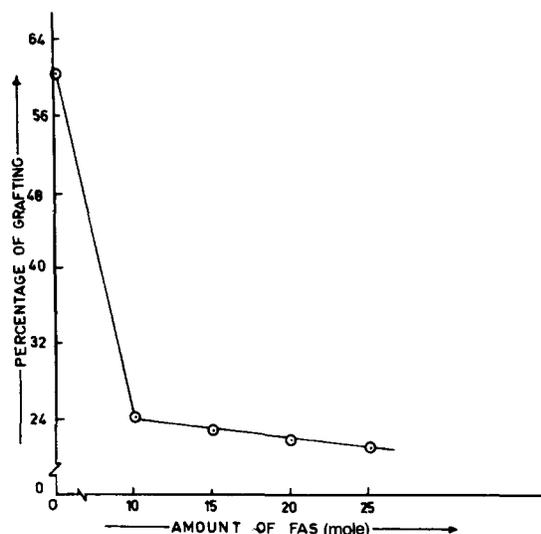


Figure 5 Effect of $[\text{Fe}^{2+}]$ on percentage of grafting of AAc onto Teflon-FEP.

Table I Swelling Behavior of Teflon-FEP-g-PAAc Films

Serial No.	Percentage Grafting of Grafted Film	% Swelling	
		Water	DMF
1	1	0	2.2
2	10	2	7
3	15	2	11.8
4	20	6.1	12.5
5	25	8.1	21
6	30	8.2	21.1
7	40	15.6	35.5
8	60.17	30.7	42.2

that in both the solvents percent swelling increases with an increase in percentage of grafting. DMF was found to be more effective than water in swelling the grafted film. It appears that there exists a critical amount of water for affording maximum swelling beyond which swelling does not increase. This is explained by assuming that water forms extensive hydrogen bonding with the pendant carboxylic acid groups of grafted AAc. Diffusion of water through hydrogen bonded complex becomes difficult. No such hydrogen bonded complex is formed between DMF and the graft and therefore swelling is enhanced in DMF.

Thermogravimetric Analysis

Thermogravimetric (TG) analysis was carried out on a DTG-40 (simultaneous DTA-TG module, Shimadzu Corporation) thermal analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ in air. The film was cut into small pieces before the analysis. The TG and dy-

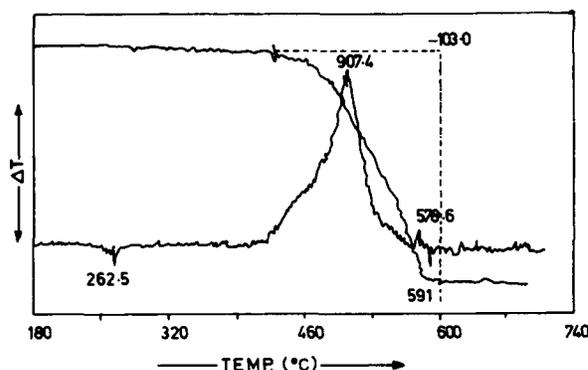


Figure 6 TGA and DTA curve for Teflon-FEP film.

ing to 85% weight loss. This indicates grafting has marginally improved thermal stability of the Teflon-FEP film. This is also confirmed by comparing the decomposition temperature values (Table I) of the grafted and ungrafted films where it is seen that for the same amount of decomposition, that is 10–40% weight loss, the grafted film requires much higher temperature (from 280 to 490°C with a difference of 210°C) than the ungrafted film (from 480 to 520°C, temp. diff. 40°C) and also for 50–90% decomposition again, the grafted film requires much higher temperature (i.e., from 497 to 640°C, temp. diff. 143°C) whereas for the same amount of decomposition the ungrafted film requires lower temperature (i.e., from 540 to 580°C, temp. diff. only 40°C). Further examination of Table II reveals that the DT values up to 80% decomposition for the ungrafted film are higher than the corresponding values of the grafted film. Beyond 80% decomposition, DT values of grafted film are higher than that of ungrafted film. It may be mentioned that the ungrafted film decomposes completely at 590°C but the grafted film leaves a residue of 10% at 640°C. The lower DT values of the grafted film between 10 and 80% weight loss is explained by the fact that upon grafting, both the amorphous and crystalline regions of Teflon-FEP film are disturbed and also upon heating the grafted PAAc chains will undergo facile decompositions at lower temperature. However, at the higher temperature region, the higher DT value of the grafted film may be due to the cyclization reactions leading to anhydride formation and some other oxidative reactions forming charred residues.

DTA Curve of Teflon-FEP Film

Figure 6 shows an endothermic peak at 262–265°C that is attributed to the melting temperature of the

film. Beyond this temperature the film does not show any decomposition up to 410°C. Upon further heating a broad exothermic peak between 420 and 580°C is observed that is attributed to the oxidative degradation of the Teflon-FEP film. The DTA curve of the grafted film, however, shows a different trend. No peak corresponding to melting of the grafted film is observed; rather a mild exothermic peak is observed between 110 and 250°C corresponding to removal of adsorbed moisture. Another broad and mild exothermic peak is observed between 250 and 458.9°C indicating the onset of dehydration of the pendant carboxylic groups of the grafted chains. This reaction is completed within the temperature range of 460–535°C as evidenced from the sharp exothermic peak in the region.

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