

# Functionalization of Poly(tetrafluoroethylene-co-ethylene) Film by Radiation-Induced Graft Copolymerization

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**ABSTRACT:** To introduce functional moieties to Tefzel film, a copolymer of tetrafluoroethylene and ethylene, graft copolymerization of vinyl monomers such as acrylonitrile (AN) and methacrylonitrile (MAN) was attempted by a preirradiation method in aqueous medium. Optimum conditions for obtaining the maximum percentage of grafting have been evaluated for both monomers. Maximum grafting of AN (52.2%) and MAN (77.7%) is obtained at a total dose of 3.14 and  $2.69 \times 10^4$  Gy, respectively, using  $[AN] = 3.018$  mol/L and  $[MAN] = 1.177$  mol/L in 10 mL of water. The effect of aliphatic alcohols of varying chain length, such as methanol, ethanol, isopropanol, *n*-butanol, and cyclohexanol, on percentage add-on of AN and MAN has also been studied. It has been found that all the alcohols decreased the percentage of grafting. Characterization of Tefzel and grafted Tefzel films has been carried out by IR spectroscopy and thermogravimetric analysis. Grafted Tefzel film has been found to have improved thermal resistance. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1171–1178, 2000

**Key words:** functionalization; Tefzel; acrylonitrile; methacrylonitrile; alcohols; thermogravimetric analysis

## INTRODUCTION

Tefzel, a product from DuPont, is a copolymer of tetrafluoroethylene and ethylene with the repeat unit  $-(CF_2-CF_2-CH_2-CH_2-)_n-$ . It is a tough polymer with properties of both polyethylene and poly(tetrafluoroethylene). Its uses in various fields, where functional groups are required, however, are restricted. Very little work has been carried out on modification of Tefzel by the graft-copolymerization method. However, grafting onto polyethylene, polytetrafluoroethylene (PTFE, Teflon), and Teflon-FEP (fluorinated ethylene-propylene) film has been studied successfully. AN has been radiochemically grafted onto PTFE film by Chapiro and coworkers.<sup>1</sup> Radiation grafting of acrylic acid and 4-vinyl pyridine onto thin PTFE

film has been carried out by Jendrychowska-Bonamour and Millequant<sup>2</sup> and the grafted films were evaluated for transport properties. Bifunctional membranes, containing both carboxylic and pyridine groups, were obtained by successive grafting of acrylic acid and 4-vinyl pyridine onto thin films of PTFE.<sup>3</sup> Structural investigation on proton-exchange membranes, obtained by the radiation grafting of styrene onto Teflon-FEP films and subsequent sulfonation, was carried out by differential calorimetry.<sup>4</sup> Preparation of the Teflon-FEP-polypyrrole (Teflon-FEP-PPy) composite, using a two-step process involving grafting of acrylic acid to insulating Teflon-FEP backbone and subsequent formation of polypyrrole over the grafted film matrix, has been reported.<sup>5</sup> A study has been made on the graft copolymers obtained by radiation-induced grafting of acrylic acid onto poly(tetrafluoroethylene ethylene) (ET) films by Hegazy and coworkers.<sup>6</sup> The conversion of the graft copolymer into metal acrylate copolymer

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was carried out by treatment with different metal salts, to study such characteristics as electrical conductivity, swelling behavior, and mechanical properties. We have successfully grafted Teflon-FEP films by radiation-induced graft copolymerization of acrylic acid.<sup>7</sup> In the present study, we report on grafting of AN and MAN onto Tefzel film by a preirradiation method, to introduce functional moieties that would be useful in separation processes.

## EXPERIMENTAL

### Materials and Method

Tefzel film (5-mil) was obtained as a gift from Dupont (USA). Acrylonitrile (Merck, München) and methacrylonitrile (Merck, München) were used as received. All alcohols were distilled before use. Distilled water was used as a reaction medium.

### Irradiation of Tefzel Film

Tefzel film was washed with methanol and dried in a vacuum oven. The film (4 × 2 cm) was irradiated from a Co<sup>60</sup> source housed in a Gamma Chamber-900 at a constant dose rate of 0.056 × 10<sup>4</sup> Gy/h for different time periods.

### Graft Copolymerization

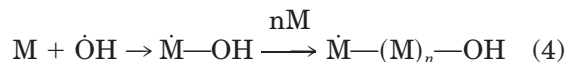
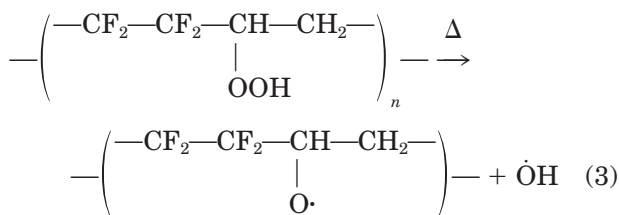
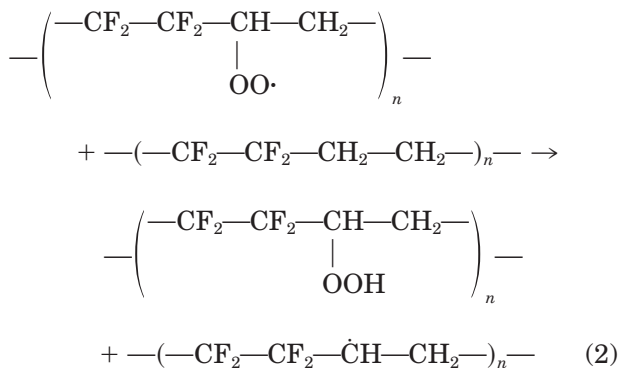
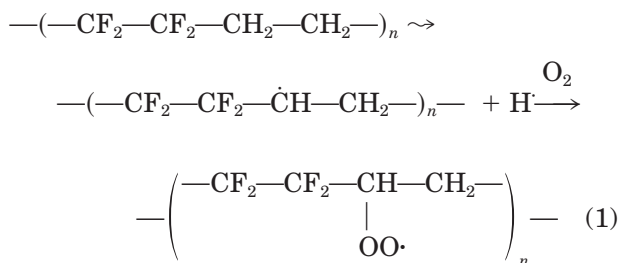
Irradiated and weighed Tefzel film was suspended in a round-bottomed flask, to which was added a known amount of water and the monomer (AN/MAN). The reaction mixture was refluxed at a constant temperature in an oil bath, maintained at 100°C for a specific time period. After the stipulated time, the film was removed from the mixture, washed thoroughly with an appropriate solvent [DMF for Poly(AN) and MeOH for Poly(MAN)] for removal of the homopolymer formed during the reaction. The grafted homopolymer-free Tefzel film was dried and weighed. Percentage add-on was calculated as follows:

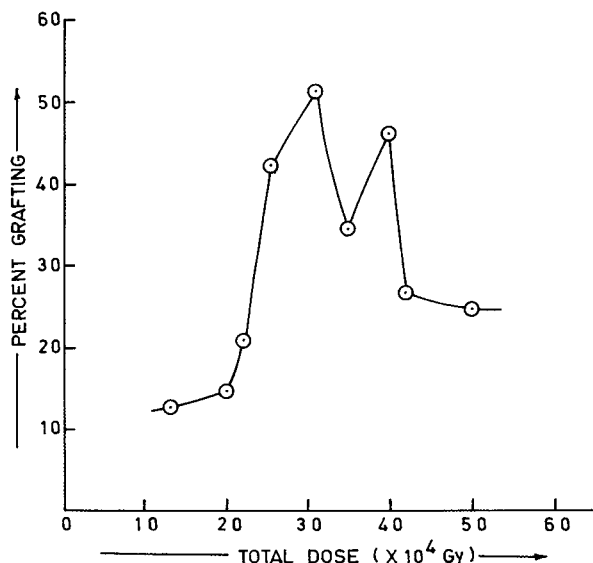
$$\% \text{ add-on} = \frac{w_1 - w_0}{w_0} \times 100$$

where  $w_0$  and  $w_1$  are the weights of original film and grafted film after complete removal of the homopolymer.

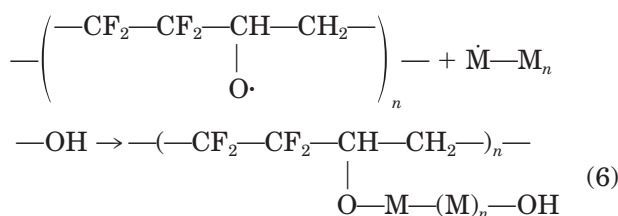
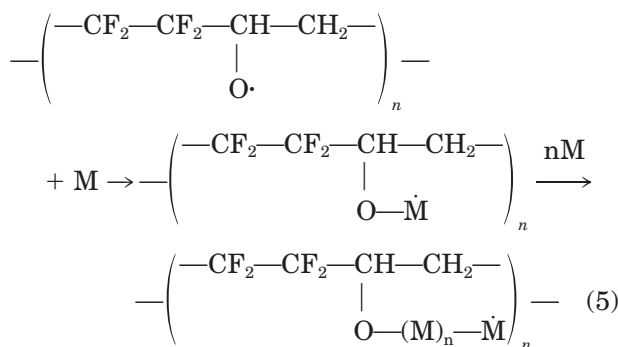
## RESULTS AND DISCUSSION

When Tefzel is irradiated in air, formation of hydroperoxide groups occurs. The formation of these groups, along with some alcoholic groups, on the surface of Tefzel on irradiation with  $\gamma$  rays has been observed by Singh and Prasad<sup>8</sup> in the FTIR spectrum. The hydroperoxide groups offer sites for grafting when they decompose on heating, to form macro free radicals (Tefzel- $\dot{O}$ ) and hydroxyl radicals ( $\dot{O}H$ ), capable of initiating homopolymerization and graft copolymerization. Based on this, the following plausible mechanism is suggested for grafting of AN and MAN onto Tefzel film.





**Figure 1** Effect of total dose on percentage grafting of AN.

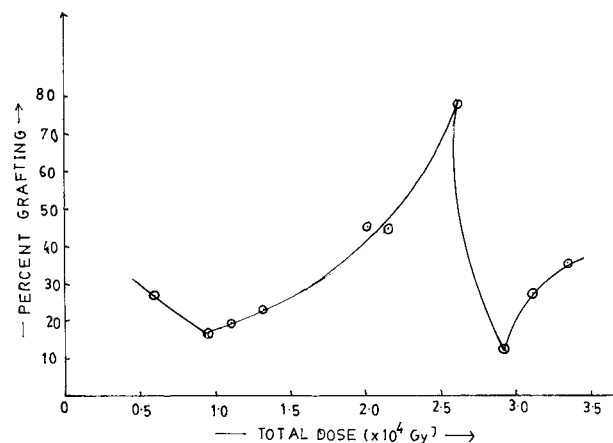


Thus, the formation of graft copolymer can take place by either grafting *from* or grafting *onto* method. The grafting onto would be more probable, as compared to grafting from, since the initiation of monomer by hydroxyl radical is a faster process than the initiation by the macro polymeric radical. Once the hydroperoxide groups are formed, the grafting can be achieved on heating the irradiated backbone in the presence of vinyl monomer. The formation of graft copolymer is influenced by different reaction parameters and, to optimize the conditions, grafting of AN and

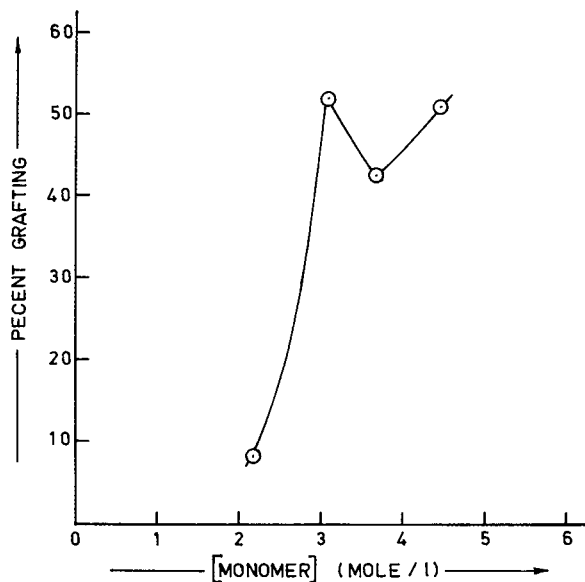
MAN has been studied as a function of different parameters. The results are discussed in the light of the proposed mechanism.

### Effect of Total Dose

Percentage of grafting of AN and MAN has been studied as a function of total dose and the results are presented in Figures 1 and 2. From the figures, one observes that the percentage add-on of both AN and MAN increases with increasing total dose, reaches a maximum, and decreases thereafter. The rate of increase in percentage add-on with AN is steep, giving the maximum (52.2%) at a total dose of  $3.14 \times 10^4$  Gy and falls to 30% at  $3.81 \times 10^4$  Gy. With a further increase in the total dose beyond  $3.81 \times 10^4$  Gy, a rise and fall in percentage add-on are observed. With MAN, the increase in percentage add-on is steady; the maximum add-on of 77.7% is obtained at  $2.69 \times 10^4$  Gy and then sharply decreases to 12.5% at  $2.91 \times 10^4$  Gy. An even further increase in total dose increases percentage add-on. A similar rise and fall in percentage grafting have also been observed during grafting of vinyl monomers onto polyethylene film.<sup>9</sup> Such a trend in grafting has been explained on the basis that initial grafting occurs in the amorphous region and then proceeds into the crystalline region with an increase in total dose. Formation of random macroradicals on radiation-induced degradation of fluoropolymers in both crystalline and amorphous regions has also been observed by Seguchi and Keizo.<sup>10</sup> The diffusion of radicals from the crystalline region to other sites is difficult because of the tightly



**Figure 2** Effect of total dose on percentage grafting of MAN.

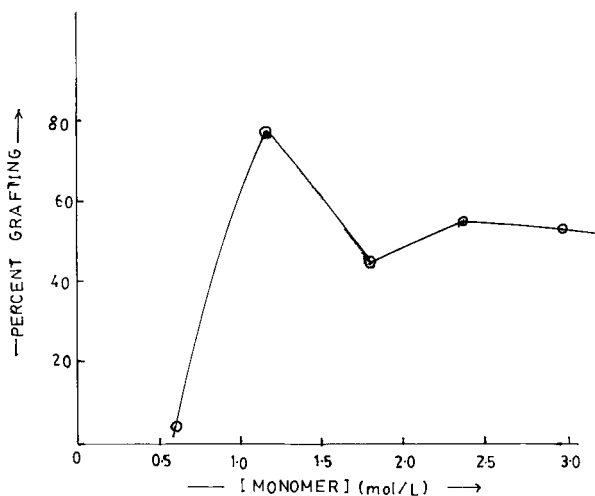


**Figure 3** Effect of monomer concentration on percentage grafting of AN.

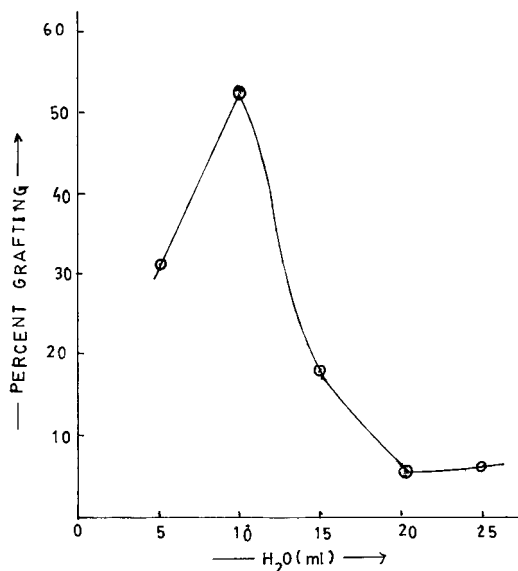
packed chains. Therefore, radiation-induced reactions are expected to occur predominantly in the amorphous region and, as such, an increase in percentage add-on is observed. With increases in reaction time and total dose, the diffusion of the monomer into the crystalline region takes place, although before this happens, percentage grafting initially falls. Formation of the grafts in the crystalline regions again increases the percentage add-on.

#### Effect of Monomer Concentration

The effect of concentration of the monomers AN and MAN on the percentage of grafting has been



**Figure 4** Effect of monomer concentration on percentage grafting of MAN.

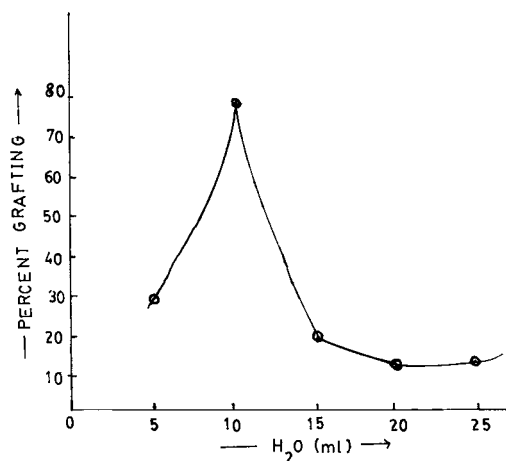


**Figure 5** Effect of amount of water on percent grafting of AN.

studied and the results are presented in Figures 3 and 4. Percentage grafting of both monomers shows a jump in the grafting region from 8.3 to 52.2% for AN and 3.9 to 77.7% for MAN; the rise is sharper with AN than with MAN. Beyond the maximum grafting, a fall in percentage add-on is observed in both cases. A further increase in monomer concentration again increases percentage grafting. In the case of AN, the second rise in grafting percentage is higher (56.6%) than the first maximum (52.2%), but in the case of MAN, the second rise in grafting is marginal. The steep rise in the case of AN may be attributed to a gelling effect that is not observed with MAN. The irregular rise and fall in grafting percentage result from the fact that grafting initially occurs in the amorphous region and then proceeds to the crystalline regions of the film.

#### Effect of Liquor Ratio

Figures 5 and 6 represent the results of percentage of grafting of AN and MAN, respectively, as a function of amount of water. Percentage grafting under optimum conditions increases with a concomitant increase in the amount of water from 5 to 10 mL, giving maxima of 52.2 and 77.7% for AN and MAN, respectively. With a further increase in the amount of water, the percentage of grafting of both monomers decreases. The decrease in grafting is sharper in the case of AN than for MAN; the

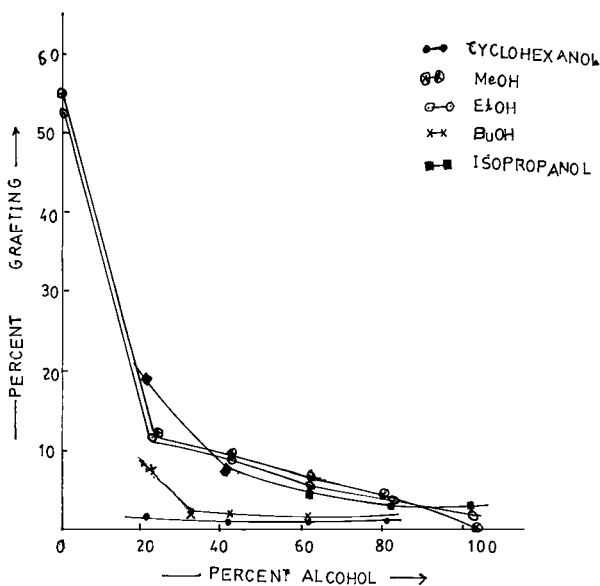


**Figure 6** Effect of amount of water on percentage grafting of MAN.

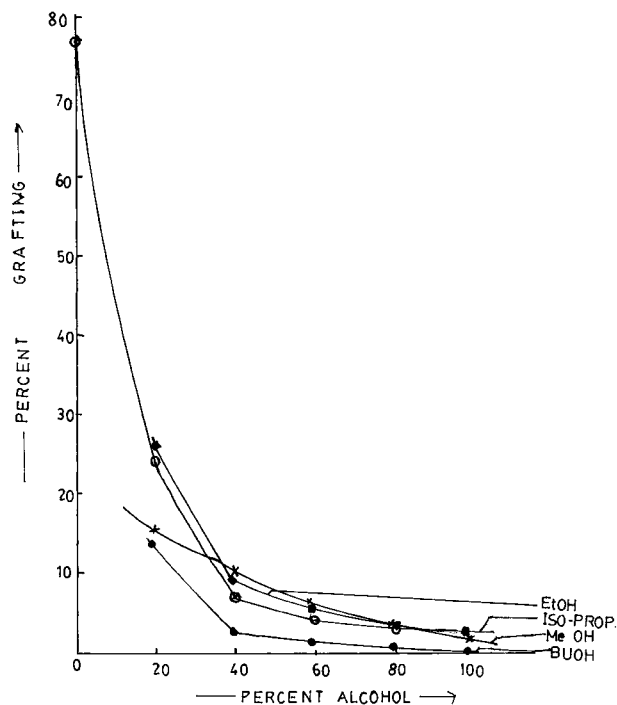
grafting percentage finally levels off in both cases. The dilution of the monomer decreases the initiation and propagation reactions, thereby decreasing the overall percentage of grafting.

#### Effect of Alcohols

To study the effect of different alcohols as additives, graft copolymerization of AN and MAN has been carried out in the presence of binary solvent, comprising a mixture of water and alcohol. Alcohols of varying chain lengths, starting from methanol to butanol and cyclohexanol, have been added to water



**Figure 7** Effect of alcohols on percentage of grafting of AN.



**Figure 8** Effect of alcohols on percentage of grafting of MAN.

to study their effect on percentage add-on; results are presented in Figures 7 and 8. It is observed that, in the presence of all the alcohols, percentage of grafting of both AN and MAN decreases. This is expected, since alcohols act as breakers of the associated structures between macrohydroperoxy groups and water, which reduces the accessibility of the monomer to the grafting sites. Yasuda and co-workers<sup>11</sup> have also observed that, with the addition of a small amount of surfactant or ethanol (50 vol %), the surface configuration change decreases according to the decrease in the surface tension of the liquid. This change would certainly change the reaction pattern of the growing polymeric chains toward grafting. In addition, alcohols assist chain-transfer reactions and, as a result, decrease the overall grafting percentage.

Among the alcohols, the following reactivity patterns toward grafting of AN and MAN, respectively, were observed:

Isopropanol > MeOH > EtOH

> *n*-BuOH > cyclohexanol

and

Isopropanol > EtOH > MeOH > *n*-BuOH

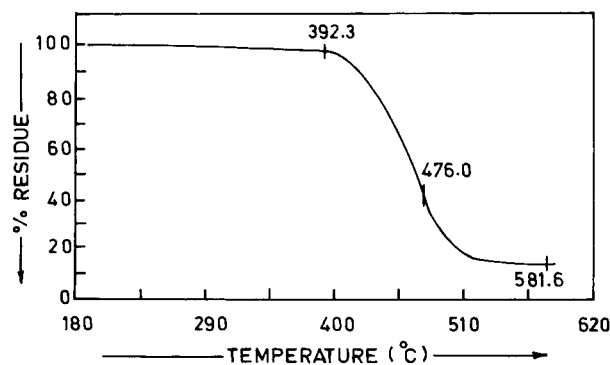
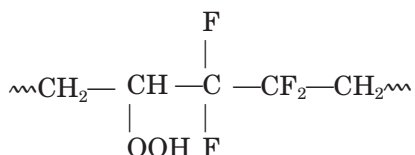


Figure 9 Primary thermogram of Tefzel film.

Earlier studies, involving nonfluorinated backbones, revealed that isopropanol, which has a higher chain transfer constant value, decreases percentage of grafting. In the present case, however, isopropanol was found to promote grafting, as compared with other alcohols. This indicates that the structure of the backbone polymer plays some role in influencing grafting in the presence of alcohols. The active sites presumably are generated onto the polyethylene segment of Tefzel. The macrohydroperoxide groups may form hydrogen bonds with neighboring fluorine atoms as shown in the following schematic:



It appears that isopropanol is more effective in breaking this structure, thus releasing hydroperoxide groups where grafting occurs.

## Evidence of Grafting

### Spectral Analysis

Infrared spectra for Tefzel and Tefzel grafted with AN and MAN have been taken on a Beckman Spectrophotometer. The IR spectra of these films show that the grafted films have broad peaks in the range between 3700–3200  $\text{cm}^{-1}$  because of associated hydroxyl and hydroperoxide groups. The peaks at 2220 and 2210  $\text{cm}^{-1}$  result from the —CN groups of grafted Poly(AN) and Poly(MAN), respectively. The absence of these peaks in the ungrafted Tefzel film confirms the formation of the graft.

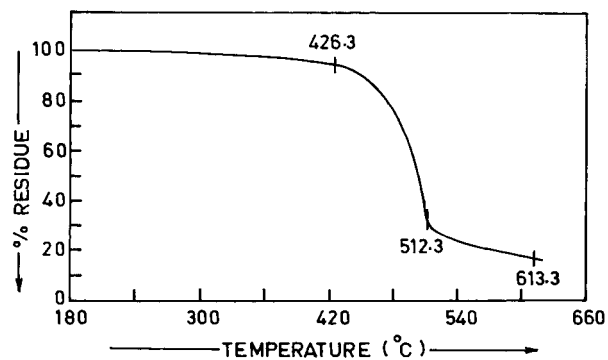


Figure 10 Primary thermogram of Tefzel-g-Poly(AN).

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of Tefzel, Tefzel-g-Poly(AN), and Tefzel-g-Poly(MAN) was carried out on a Shimadzu Simultaneous Thermal Analyzer in air, at a heating rate of 10°C/min. The primary thermograms of the films are presented in Figures 9–11. It is observed from the primary thermograms that the decomposition of the grafted films begins quite late, as compared to the original film, with the result that the initial decomposition temperature for both grafted films is quite high (426.3°C), whereas for Tefzel film it is 392.3°C. With a further increase in temperature, the decomposition of the films is observed and is found to be more stable with the grafted films than with the original Tefzel film. The decomposition temperature at every 10% weight loss is higher for the grafted films than for the original. Finally, the decomposition curve takes a turn where final decomposition of the film starts. In Tefzel film, final decomposition begins from 501°C and continues up to 581.6°C, with 12.7% residue left. The final decomposition of the grafted films begins at a higher temperature:

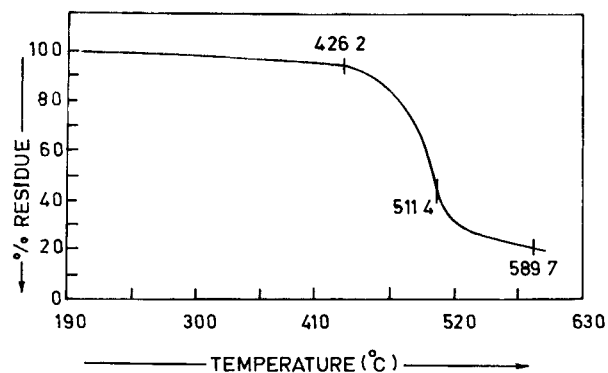


Figure 11 Primary thermogram of Tefzel-g-(MAN).

**Table I** Optimum Conditions of Grafting of AN and MAN onto Tefzel Film

Sample	Total Dose ( $\times 10^{-4}$ Gy)	[M] (mol/L)	H <sub>2</sub> O (mL)	% Grafting
Tefzel-g-Poly(MAN)	0.576	1.177	10	77.7
Tefzel-g-Poly(AN)	0.672	3.018	10	56.6

512.3 to 613°C and 511.4 to 589.7°C for Tefzel-g-Poly(AN) and Tefzel-g-Poly(MAN) with a percentage residue of 15.5% and 19.3%, respectively.

All the data show that the grafted films become thermally stable. It has been observed by Prasad and Singh<sup>8</sup> during their studies on the effect of irradiation on Tefzel, that with increasing time of irradiation, crystallinity of the polymer increased; this would certainly increase the thermal stability. The higher IDT value for Tefzel-g-Poly(AN) and Tefzel-g-Poly(MAN) is the result of the stability of the grafted Poly(AN) and Poly(MAN) toward a rise in temperature. Both polyacrylonitrile<sup>12</sup> and poly(methacrylonitrile)<sup>13</sup> undergo color changes only at approximately 200°C. Between 250–280°C, Poly(AN) gives off 12% of the volatile products, whereas the remaining products are involatile; Poly(MAN) on the other hand, gives off 50–100% monomer. Poly(acrylonitrile) is still stable and the rise of temperature between 280–450°C gives off the major volatile products cyanogen, HCN, CH<sub>3</sub>CN, AN, and vinyl acetonitrile, and the remaining nonvolatile residue remains. Thus, grafting of thermally stable Poly(AN) and Poly(MAN) raises the IDT of the Tefzel film *after* grafting. After the initial decomposition, a further increase in temperature causes degradation of both the ungrafted film and the grafted film, but from the primary thermograms it is observed that the decomposition temperature of the grafted films is higher than that of ungrafted Tefzel film. The data thus support the conclusion that the grafting of AN and MAN improves thermal stability of the Tefzel film.

#### Comparison of Reactivity of AN and MAN toward Grafting onto Tefzel Film

From the foregoing discussion, it is observed that methacrylonitrile produces more grafting as compared to acrylonitrile. Table I provides the optimum conditions for both monomers toward grafting.

#### CONCLUSIONS

Both total dose and monomer concentration for MAN are less than for AN. In other cases, MAN

has been found to be less reactive than AN. This means that the backbone polymer, that is, a copolymer of polytetrafluoroethylene and polyethylene, has some role to play in changing the reactivity of the two monomers. From the literature, it was found that the rate of propagation  $k_p$  for MAN<sup>14</sup> is too small (26 L mol s<sup>-1</sup>) as compared to that of AN,<sup>15</sup> which is 14,500 L mol s<sup>-1</sup> at 25°C in water medium. Since MAN is insoluble in water, this may be expected. AN, on the other hand, is soluble in water and propagates at a very high rate; therefore, the gelling effect is observed. MAN, which has no interaction with water, involves itself with the backbone polymer, at which site the vinylic methyl groups and the nitrile group interact with the hydrocarbon and hydroperoxy parts of the backbone, thus exposing the backbone for grafting. The rate of termination  $k_t$  for MAN is low (21), whereas for AN, the value of  $k_t$  is high—on the order of 200 L mol s<sup>-1</sup>. The lower value of total dose and monomer concentrations for MAN may result from the fact that, as the number of hydroperoxy groups will be less, the interaction of the monomer with the polyethenic segment of the polymer will be more. As a result, for the monomer in the vicinity of the grafting site, a higher amount of graft is produced, but in lower concentration. On the other hand, the growing polymeric chains of acrylonitrile, which also terminate at a higher rate, have to diffuse to the active sites to produce the graft. Therefore, a higher total dose and higher monomer concentration of AN is required to produce maximum percentage of grafting under optimum conditions.

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