

Radiation-Induced Graft Copolymerization of Methacrylonitrile onto Poly (Tetrafluoroethylene-co-ethylene) Film by Discontinuous Method

R. K. Thakur^{1*}, I. Kaur², M. Singh¹, N. Kumar³

¹Department of Chemistry, Vallabh Govt. College Mandi H.P.-175001, India

²Department of Chemistry, H.P. University Shimla-171005, India

³Department of Chemistry, M. L. S.M. College, Sundernagar, Mandi H.P.-175018, India

Received 28 January 2023, accepted in final revised form 16 June 2023

Abstract

An attempt has been made to graft copolymerize the vinyl monomer methacrylonitrile onto poly tetrafluoroethylene-co-ethylene, known as Tefzel film, by the double-irradiation method in aqueous medium. Optimum conditions for attaining the maximum percentage of grafting were evaluated. The maximum percentage of grafting for methacrylonitrile was obtained 128.7 % at an optimum dose of 24.9 kGy using 2.98 mol L⁻¹ of methacrylonitrile. Investigations on the effects of different chain-length aliphatic alcohols, methanol, ethanol, n-butanol, cyclohexanol and amyl alcohol on the grafting percentages of methacrylonitrile have been performed. Characterization of Tefzel and grafted Tefzel films have been performed by infrared spectroscopy and Thermogravimetric Analysis. Methacrylonitrile grafted Tefzel films showed better thermal stability.

Keywords: Copolymer; Grafting; Methacrylonitrile; Monomer; Swelling; Tefzel.

© 2023 JSR Publications. ISSN: 2070-0237 (Print); 2070-0245 (Online). All rights reserved.

doi: <http://doi.org/10.3329/jsr.v15i3.64180>

J. Sci. Res. **15** (3), 855-867 (2023)

1. Introduction

Tefzel is a tough polymer with properties of polyethylene and polytetrafluoroethylene but lacks functional groups in the backbone. This reduces their applicability in various fields where functional groups are required. However, various groups of researchers have successfully modified Tefzel by graft copolymerization using monomers of different functional groups. Grafting has been shown to be a versatile method to bring modifications in polymers [1]. Radiation-induced graft copolymerization of fluorinated polyethylene polypropylene has been observed by many researchers [2-4]. Adequate research has been done on the graft copolymers obtained by radiation-induced grafting of acrylic acid onto poly(tetrafluoroethylene) films [5,6]. Styrene has been grafted onto pre-irradiated fluoropolymer film, which is reported in the literature [7]. The membranes

* Corresponding author: rajthakur1809@gmail.com

possessing sufficient oxidation resistance by grafting of α , α , β trifluoroacrylate onto polyethylene and fluorine-containing films by simultaneous grafting method using γ -rays have also been produced [8]. The effect of various grafting parameters and the effect of aliphatic alcohols of different chain lengths on grafting of acrylonitrile, methacrylonitrile, methylacrylate and ethylacrylate onto Tefzel film by preirradiation method has already been studied in our laboratory [9,10]. Studies have also been done on the graft copolymerization of a monomer combination of an electron donor and an electron acceptor onto Tefzel film [11]. Modification of poly(tetrafluoroethylene-co-ethylene), Tefzel film has been performed by grafting methylmethacrylate by radiation methods, including preirradiation and double-irradiation with improved thermal stability [12]. Monomer styrene affecting the graft copolymerization of acrylonitrile onto deproteinized natural rubber was observed [13]. Also, the effects of monomer contents of styrene, acrylonitrile and radiation doses on various parameters such as thermal stability, chemical structure and physical properties of the graft copolymers were investigated [14]. By using the pre-irradiation approach, a binary combination of 4-vinyl pyridine and methacrylic acid was grafted onto poly (vinyl fluoride) film and ionic bifunctional membranes were created [15, 16]. Styrene and methacrylonitrile co-grafted membranes showed the best results among the tested radiation-grafted membranes [17]. Graft copolymerization of an acrylonitrile-co-*N*-vinylpyrrolidone binary monomer onto low-density polyethylene film has been acknowledged by using a simultaneous irradiation method [18]. A significant advantage of interfacial properties of grafted poly (ethylene-co-tetrafluoroethylene) and polymer electrolyte membranes (ETFE-PEMS) for fuel cell applications has been studied by Hao *et al.* [19].

In the present research work, the grafting of methacrylonitrile has been attempted by discontinuous irradiation with a 4-hour break at room temperature between two consecutive irradiations. An attempt has been made to incorporate nitrile (CN) functional group that would be useful in the separation process. The grafting percentage was studied as a function of the relevant parameters to optimize the conditions.

2. Experimental

2.1. Materials and Method

Tefzel film (5 mm, 127 μ m) was obtained from E.I. DuPont de Nemours, USA. Methacrylonitrile of Merck was distilled and the middle fraction was collected and used. The n-butanol, methanol, ethanol, cyclohexanol and amyl alcohol were distilled before the use. Distilled water was used as the medium to carry out reactions.

2.2. Irradiation of Tefzel film

Tefzel film (4 cm × 2 cm) was washed with methanol and dried under a vacuum. In a Gamma Chamber-900, the film was exposed to gamma rays from a Co⁶⁰ source at a constant dosage rate of 0.52 kGy h⁻¹ for the different duration in the presence of air. The irradiated film was then left at room temperature for a break of 4 h and was re-irradiated for the same time as the initial irradiation, after that, the grafting process on the doubly irradiated film was performed.

2.3. Graft copolymerization

A doubly irradiated and weighed Tefzel film was suspended in a reaction mixture of water and methacrylonitrile in a specific proportion in a round bottom flask. The mixture was refluxed in an oil bath at a constant temperature of 100°C and for a stipulated time. The film was removed from the reaction mixture and thoroughly washed with methanol to completely remove the homopolymer formed during the grafting process. The homopolymer-free grafted Tefzel film was dried and weighed again. The percentage of grafting was determined from the percent increase in the initial weight of the film by applying the following formula;

$$\% \text{ Grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

W_0 and W_1 are the weights of the original and grafted films after completely removing the homopolymer formed during the reaction.

3. Mechanism of Polymerization

In the grafting of methacrylonitrile onto the Tefzel film during the gamma irradiation in the air, carbon-hydrogen bonds undergo cleavage and insert hydroperoxide groups into the Tefzel layer. Hydroperoxide groups provide the sites for grafting of the monomer, the development of such groups and certain alcoholic groups after irradiation has also been reported [20]. The double exposure of the film generates more hydroperoxide groups because, during the exposures, radicals trapped in the bulk of the film get converted to hydroperoxide groups. The four hours time interval provided between the two irradiations aids in the interaction of the embedded radicals with oxygen and their diffusion to the surface of the film. As a result, the two-fold exposure method increases the bulk of the film and the number of surface hydroperoxide groups, increasing the overall grafting percentage. A plausible mechanism for grafting methacrylonitrile onto double-irradiated Tefzel film is proposed in Fig. 1.

The formation of graft copolymers can be carried out by equation 5 or equation 6, involving grafting from and grafting onto processes, respectively. In the former case, hydroxyl radicals formed upon hydroperoxide decomposition are very reactive to initiate polymerization of the monomers and generate propagating radicals that bond directly to macrooxy radicals to give a grafted product. However, graft copolymerization using the procedure described in Equation 5 is less advantageous when thermal grafting is carried out on a pre-irradiated backbone. Thus, the grafting initiation of monomers occurs as in

equation 4, and the growing polymeric chain thus formed reacts with the macrooxy radicals to yield the grafted polymeric product (Eq. 6).

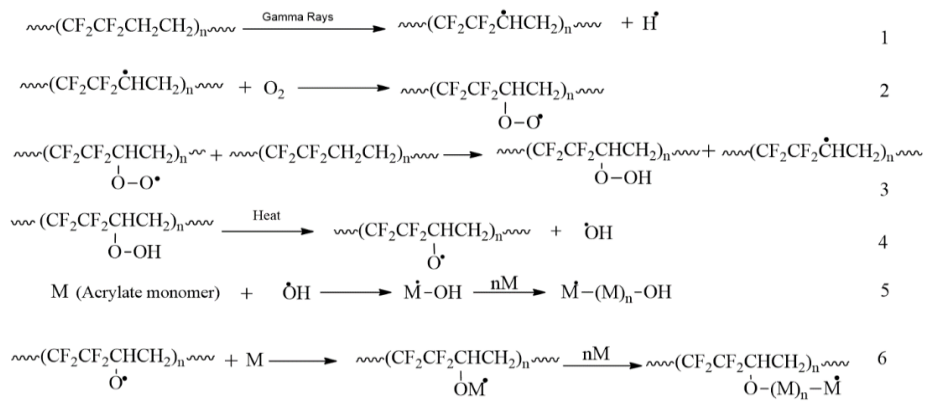


Fig. 1. Plausible mechanism for grafting methacrylonitrile onto double-irradiated Tefzel film.

4. Characterization

4.1. IR spectral analysis

The infrared spectrum of Tefzel-g-poly (methacrylonitrile) (Fig.2) was recorded in Beckman IR-spectrophotometer. The grafted films are observed to exhibit broad peaks in the range of 3000-2800 cm⁻¹ due to the associated hydroxyl and hydroperoxide groups. The sharp peak at 2200 cm⁻¹ is due to the -CN groups of poly(methacrylonitrile), which confirms the grafting of methacrylonitrile onto the Tefzel film.

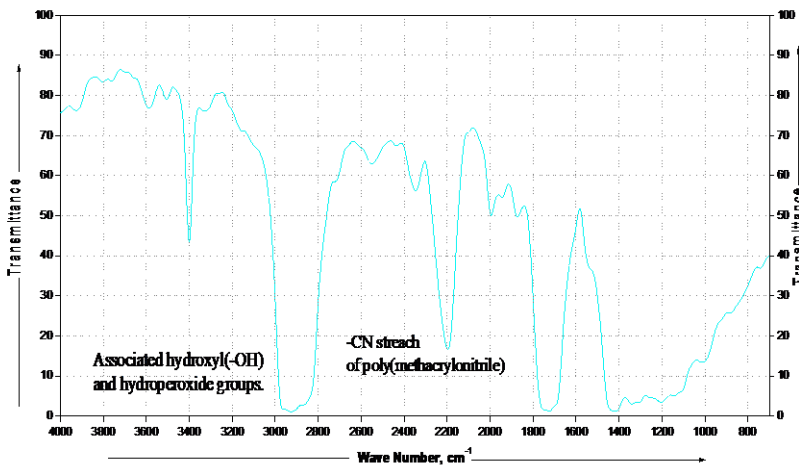


Fig. 2 Infrared spectra of Tefzel-g-poly(methacrylonitrile).

4.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of Tefzel and Tefzel-g-poly(methacrylonitrile) films were recorded at the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in an air atmosphere using a Shimadzu Simultaneous Thermal Analyzer. The primary thermograms of Tefzel and Tefzel-g-poly(methacrylonitrile) films are presented in Fig. 3. The initial decomposition temperature (IDT), final decomposition temperature (FDT) and decomposition temperature (DT) at every 10 % weight loss of both films are given in Table 1.

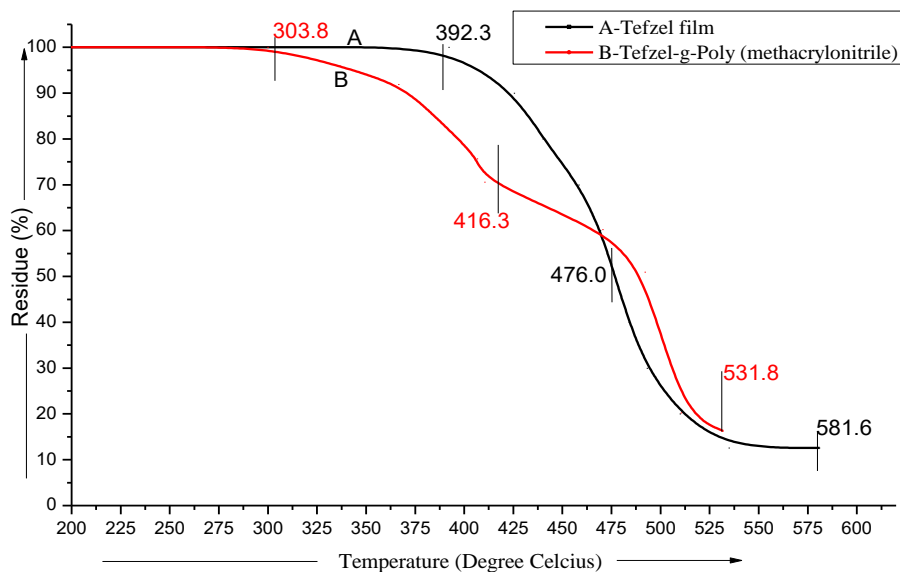


Fig. 3. Primary thermograms of Tefzel film and Tefzel-g-poly(methacrylonitrile).

The original film has a substantially higher IDT ($392.3\text{ }^{\circ}\text{C}$) than Tefzel-g-poly(methacrylonitrile), which has a lower IDT ($303.8\text{ }^{\circ}\text{C}$). The FDT value of the methacrylonitrile grafted film ($510\text{ }^{\circ}\text{C}$) is not much lower than the FDT value of the original film ($535\text{ }^{\circ}\text{C}$). Table 1 shows that, up to a 30 % weight loss, the DT of Tefzel g-poly (methacrylonitrile) is lower than that of the original film for each 10 % weight loss. The DT values for grafted ($468.2\text{ }^{\circ}\text{C}$) and ungrafted ($469.5\text{ }^{\circ}\text{C}$) films are substantially comparable at 40 % weight loss but above 50 % Tefzel g-poly (methacrylonitrile) has a greater DT value than the original film. Tefzel film exhibits single-stage decomposition, with temperature differences between every 10 % weight loss falling in 7 and 18 $^{\circ}\text{C}$ ranges. In contrast, Tefzel-g-poly(methacrylonitrile) film exhibits double-stage decomposition, with temperature differences between 25-60 $^{\circ}\text{C}$ up to 40 % weight loss. Above 40 % weight loss, the temperature difference in DT values for grafted films lies almost within the same range as that of the original film. From these observations, it is

observed that the grafting of vinyl monomers decreases the IDT of the film due to the reason that the grafted chains are affected in preference to the backbone polymer.

Table 1. Thermogravimetric analysis of Tefzel film and Tefzel-g-poly(methacrylonitrile).

Sample	IDT (°C)	FDT (°C)	DT (°C) at every 10 % weight loss (%)									Residue left (%)
			10	20	30	40	50	60	70	80	90	
Tefzel film	392.3	535	425.6	440.2	458.5	469.5	476.8	484.1	493.3	510.0	510.0	12.7
Tefzel-g-poly (methacrylonitri le)	303.8	510.0	354.2	383.3	408.2	468.2	488.2	498.2	504.9	516.6	516.6	16.3

The temperature difference greater than 29 °C between 10-20 % weight losses for methacrylonitrile grafted film compared to less than 20 °C of the ungrafted film indicates thermal stability is gained in the grafted film due to grafting. The difference in temperature behavior at higher weight losses, greater than 50 %, may be because, upon double irradiation, the hydroperoxide groups are also formed in the bulk of the film where grafting occurs, and this would disturb the crystallinity of the backbone polymer. The second stage of decomposition corresponds to the backbone polymer, which decomposes at a higher temperature with a lower temperature difference because of loss of crystallinity.

5. Investigations and Discussion

5.1. Area change of grafted film.

The percentage of area change due to grafting was calculated by using the following formula.

$$A_1 - A_0 / A_0 \times 100$$

A_1 and A_0 represent the area of the grafted and ungrafted films, respectively. The change in the area of the film has been observed as a function of the percentage of grafting, and the results are presented in Table 2 and Fig. 4 for methacrylonitrile grafted Tefzel film.

Table 2. Area change during grafting of methacrylonitrile onto Tefzel film.

Sl. No.	Sample	Percentage of grafting	Area (cm ²)	Percentage of area change
1	Tefzel	0.00	8.00	0.00
2	Tefzel-g-poly(methacrylonitrile)	57.98	10.35	29.37
3	Tefzel-g-poly(methacrylonitrile)	70.27	10.58	32.25
4	Tefzel-g-poly(methacrylonitrile)	70.92	11.76	47.00



Fig. 4. Photographs of Tefzel-g-poly(methacrylonitrile) film.

Fig. 4 shows that the size of the grafted Tefzel films gradually increases as the percentage of grafting increases, but the geometry remains the same. This indicates that the grafting occurs on the film's surface and then proceeds with the diffusion of the monomer into the bulk of the film, thereby increasing the surface area of the film. Therefore, it is possible that the double irradiation procedure with an irradiation break interval of 4 h formed more hydroperoxide groups even in the majority of the backbone polymer. Formation of such groups on both the amorphous and crystalline surfaces of the backbone polymer induces diffusion of monomers into these regions, resulting in a higher grafting percentage which increases the size of the grafted film.

5.2. Swelling behavior

Grafted films of known weight were exposed to dimethylformamide, acetone, benzene and water solvents at room temperature and soaked for 24 h to compare the swelling behaviors of original Tefzel film and Tefzel-g-poly(methacrylonitrile) in relation to various polar and non-polar solvents. The films were taken out, promptly blotted with absorbent paper to remove any liquid that had adhered to their surface, and weighed right away. The degree of swelling was calculated as follows:

$$\text{Percent swelling} = \frac{W_s - W_g}{W_g} \times 100$$

W_s and W_g represent the weight of wet and dry grafted films. Percent swelling has been studied as a function of the percentage of grafting, and the results are shown in Fig. 5 for grafted methacrylonitrile.

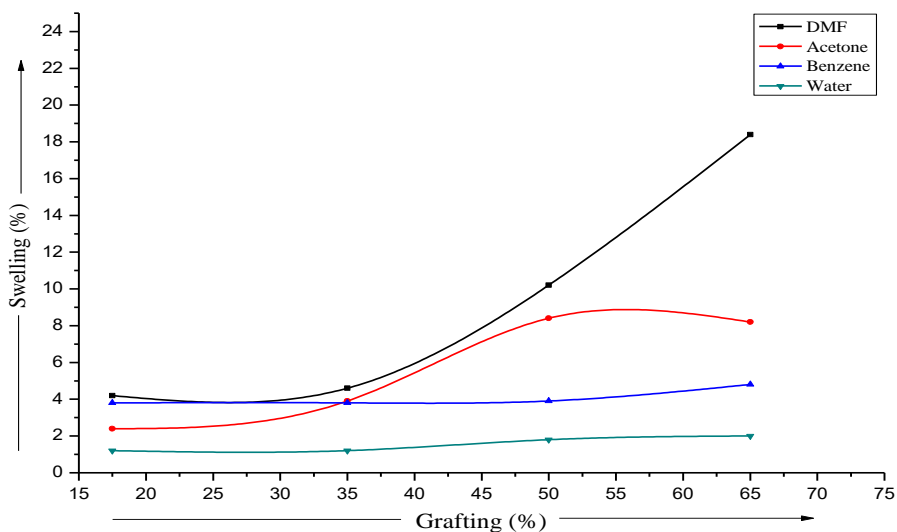


Fig. 5. Effect of grafting on swelling of Tefzel-g-poly (Methacrylonitrile) in different solvents.

Among the above solvents swelling percentage is the maximum in DMF. Tefzel film did not show swelling behavior in any solvents due to its compactness, whereas Tefzel-g-poly(methacrylonitrile) showed swelling behavior in all the solvents except water. This might be the result of solvent interactions with the pendant groups (-CN) grafted onto the backbone, or it might be the result of interactions with the ethylene and fluorinated segments of the backbone film. The higher swelling behavior of the grafted film in DMF and acetone is due to more interactions of these solvents with the polar group (-CN) attached to the grafted film. This stronger interaction exists between the positively charged carbon of the nitrile group bonded with the backbone and the negatively charged oxygen of the ketonic group of the solvents, which increases swelling more in polar solvents like DMF and acetone than in non-polar solvents like benzene (Fig. 6).

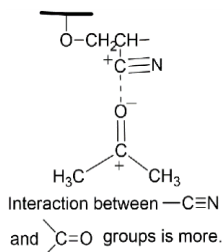


Fig. 6. Interactions between the nitrile and ketonic groups.

Since benzene is a non-polar solvent, its swelling behavior may be explained by interactions between benzene and the non-polar ethylene segment of the backbone film.

Despite being the most polar solvent, water exhibits a negligible swelling behavior that may be caused by its inability to interact with the grafted film's pendant groups or penetrate it. This might occur as a result of the strong intermolecular H-bonding in water molecules, which causes a high number of water molecules to bond together to create macromolecules that might be resistant to interactions and prevent penetration into the grafted layer.

5.3. Effect of the total dose

To determine the effect of varying total doses of monomer on the percentage of grafting, (P_g) methacrylonitrile was grafted onto Tefzel film at various doses (Fig.7). The Tefzel film was exposed to radiation twice, with a four-hour interval in between each exposure. The total dosage administered is calculated by adding the total doses from the two irradiation periods. The moderate initial increase in the grafting rate for the acceptor monomer methacrylonitrile followed by a slight fall and a slight increase at 24.9 kGy, gives a maximum grafting percentage of 57.9 %. At 31.2 kGy, a further increase in the total dose causes the percentage of grafting to decline to 18.08 %. After that, P_g increases as the total dosage rises and remains constant.

This behavior during methacrylonitrile grafting may be brought on by its physical characteristics. The initial rise in P_g corresponds to grafting in the amorphous region and the subsequent rise and fall with a further increase in total dose is due to the diffusion of monomer into the bulk of the film where grafting occurs in the crystalline region. The rise and fall in grafting implies that active sites are created in both the crystalline and amorphous regions and that grafting depends on the diffusion of the monomer into these various regions, which causes a rise and decrease in grafting.

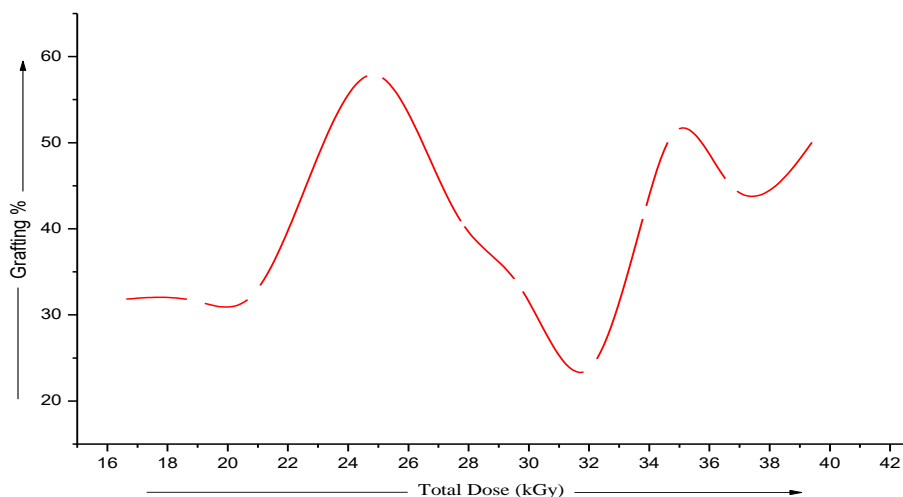


Fig. 7. Effect of total dose on percentage of methacrylonitrile onto Tefzel film.

5.4. Monomer concentration

The percentage of methacrylonitrile grafting has been investigated in relation to the monomer concentration, and the results are shown in Fig. 8. P_g rises as the concentration of monomers rises and plateaus at greater concentrations. However, the rate of increase in P_g is low. This is because the propagation rate (k_p) and termination rate (k_t) are $2.1 \text{ L Mol}^{-1} \text{ s}^{-1}$ and $2.7 \text{ L Mol}^{-1} \text{ s}^{-1}$, respectively. As a result of both being too small, the grafting rate was low and leveled off after reaching the maximum grafting percentage of 128.7 % at a methacrylonitrile concentration of 2.98 Mol L^{-1} . The irregular increase and decrease in P_g were observed because the initial grafting occurred in the amorphous region and later in the crystalline region. The double irradiation with an internal gap of four hours shifts the trapped radicals to the film surface and produces more active sites. The growing polymeric chains attack directly on these active sites to give a higher percentage of grafting with an increase in monomer concentration.

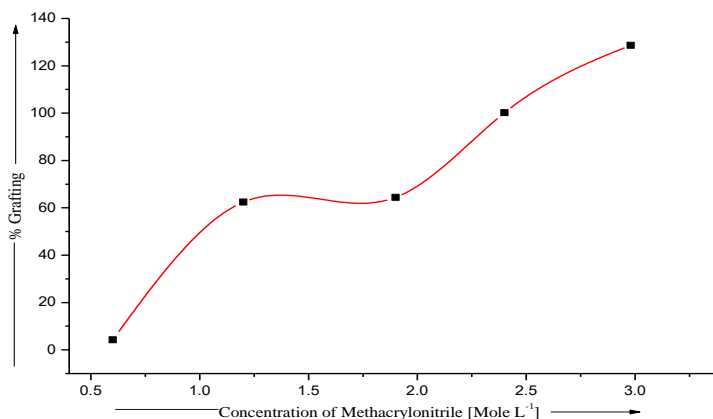


Fig. 8. Effect of amount of methacrylonitrile on percentage of grafting.

5.5. Effect of water content

Grafting of methacrylonitrile was carried in an aqueous medium, and the P_g of methacrylonitrile was studied as a function of the amount of reaction medium also, Fig. 9. It shows that P_g decreases with an increasing amount of water because methacrylonitrile has higher vapor pressure 164 m bar at $40 \text{ }^\circ\text{C}$ [21], hence methacrylonitrile lies more in a vapor state and its accessibility to hydroperoxide group of the backbone is decreased. Thus dilution of monomer decreases the initiation and propagation reactions, decreasing the overall grafting percentage. A similar trend has also been reported in the grafting of acrylonitrile and methacrylonitrile onto Tefzel film by a pre-irradiation method [9].

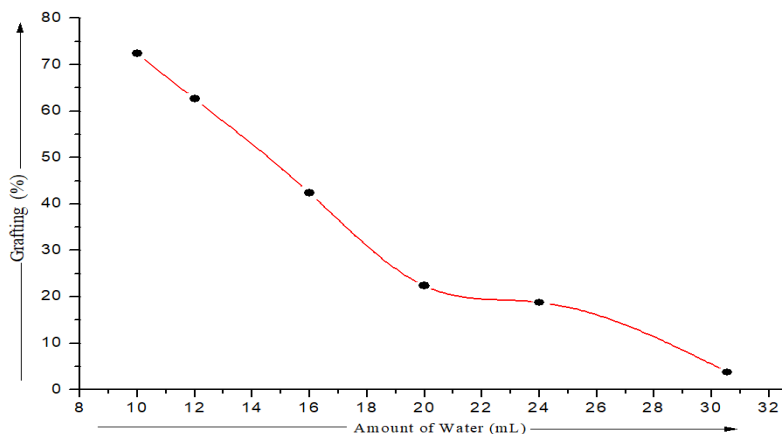


Fig. 9. Effect of amount of water on percentage of grafting of methacrylonitrile onto Tefzel film.

5.6. Effect of alcohols

The effect of the composition of water-alcohol mixed solvents on P_g of methacrylonitrile onto Tefzel film has been studied using n-butanol, methanol, ethanol, cyclohexanol and amyl alcohol, Fig. 10. The P_g in water-alcohol medium shows a decrease in grafting with increasing percentage of alcohol content in the mixture. In the case of an n-butanol mixture, the P_g of methacrylonitrile is found to be a maximum of 47.7 % in 60 % of the n-butanol solution. However, the overall P_g reported is less than that observed in aqueous medium.

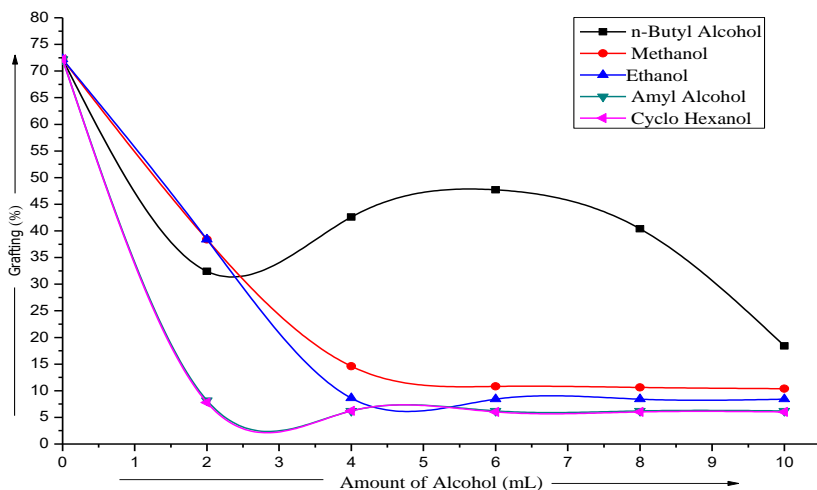


Fig. 10. Effect of amount of alcohol in (alcohol-water) binary mixture on grafting of methacrylonitrile onto Tefzel film.

The H-bonded water structure and the bond between the backbone and water molecules are more likely to be broken by higher alcohols, forming an associated structure between the alcohol and water molecules. The entire procedure and the turbulence in the reaction medium reduce the moment and also the accessibility of the expanding polymeric chains to the active sites, which results in a drop in P_g [9].

6. Conclusion

The polyethylene films can be modified by grafting with various monomers, which incorporates functional groups into the polymer and improves the polymer's suitability for industrial use. The grafting increases the thermal stability of the double-irradiated material and offers excellent longevity and resistance to UV radiations and pollutants. Additionally, they are highly resistant to toxins and outside risks. These grafted films can be laminated, metalized, welded or heat bonded with other chemicals. The swelling of grafted films may make it easier to create new grafted membranes for various requirements.

References

1. A. Bhattacharya and B. N. Mishra, *Prog. Polym. Sci.* **29**, 767 (2004).
<http://dx.doi.org/10.1016/j.progpolymsci.2004.05.002>
2. B. S. Ko, K. Hiroki, A. Yoshimura, and Y. Maekawa, *J. Polym. Sci.* **59**, 108 (2021).
<https://doi.org/10.1002/pol.20200727>
3. H. Wang, Y. Wen, H. Peng, C. Zheng, Y. Li, S. Wang, and X. Zhou, *Polymers* **10**, 503 (2018).
<https://doi.org/10.3390/polym10050503>
4. K. Thinkohkaew, T. Piroonpan, N. Jiraborvornpongsa, and P. Potiyaraj, *Surf. Interf.* **24**, ID 101125 (2021). <https://doi.org/10.1016/J.SURFIN.2021.101125>
5. E. S. A. Hegazy, A. M. Dessouki, N. Assy, N. M. Elsayy, and M. A. A. Elghaffar, *J. Polym. Sci. Part-A* **30**, 1976 (1992). <https://doi.org/10.1002/pola.1992.080300920>
6. E. S. A. Hegazy, A. M. Dessouki, N. M. Elsayy, and M. A. A. Elghaffar, *J. Polym. Sci. A* **31**, 533 (1993). <https://doi.org/10.1002/pola.1993.080310225>
7. U. Lappan, U. Geibler, U. Gohs, and S. Uhlmann, *Radn. Phys. Chem.* **79**, 1072 (2010).
<https://doi.org/10.1016/j.radphyschem.2010.05.001>
8. H. Omichi and H. Okamoto, *J. Polym. Sci.* **20**, 1559 (1982).
<https://doi.org/10.1002/pol.1982.170200616>
9. I. Kaur, R. Kumar, B. Singh, B. N. Mishra, and G. S. Chauhan, *J. Appl. Polym. Sci.* **78**, 1171 (2000).
10. I. Kaur, B. N. Mishra, R. Kumar, and B. Singh, *Polym. Polym. Compos.* **10**, 391 (2002).
<https://doi.org/10.1177/096739110201000506>
11. I. Kaur, B. Singh, and N. Gupta, *Radn. Phys. Chem.* **72**, 489 (2005).
<https://doi.org/10.1016/j.radphyschem.2003.12.050>
12. I. Kaur, V. Sharma, and N. Gupta, *J. Appl. Polym. Sci.* **111**, 2238 (2009).
<https://doi.org/10.1002/app.26308>
13. T. Indah, S. Asep, H. Saputra, S. Bismo, D. R. Maspanger, and A. Cifriadi, *Intern. J. Tech.* **7**, 1164 (2015). <http://dx.doi.org/10.14716/ijtech.v6i7.1266>
14. N. Rimdusit, C. Jubsilp, P. Mora, K. Hemvichian, et al., *Polymers* **13**, 3447 (2021).
<https://doi.org/10.3390/polym13193447>

15. I. Kaur, V. Kumari, B. Sharma, and N. Gupta, *Appl. Radn. Isot.* **79**, 118 (2013).
<https://doi.org/10.1016/j.apradiso.2013.05.004>
16. I. Kaur, S. Rattan, S. Chauhan, and N. Gupta, *Nucl. Instru. Meth. Phys. Res. B* **268**, 1642 (2010). <https://doi.org/10.1016/j.nimb.2010.01.031>
17. Z. Zhang, K. Jetsrisuparb, A. Wokaun, and L. Gubler, *J. Power Sour.* **243**, 306 (2013).
<https://doi.org/10.1016/j.jpowsour.2013.06.009>
18. N. M. El-Sawy, E. A. Hegazy, A. El-Hag, M. S. Ali et al., *Nucl. Instru. Meth. Phys. Res. B* **264**, 227 (2007). <https://doi.org/10.1016/j.nimb.2007.09.028>
19. L. H. Hao, T. D. Tap, D. T. T. Hieu, E. Korneeva, et al., *J. Appl. Polym. Sci.* **139**, 14 (2021).
20. A. Vishwa, Prasad, and R. P. Singh, *J. Macro. Sci., Pure Appl. Chem.* **33**, 91 (1996).
<https://doi.org/10.1080/10601329608010856>
21. I. Kaur, V. Sharma, and N. Gupta, *J. Appl. Polym. Sci.* **111**, 2238 (2009).
<https://doi.org/10.1002/app.26308>