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## Radiation–Induced Graft Copolymerization Of Methyl Acrylate Onto Poly (Tetrafluoroethylene–Co–Ethylene) Film By Discontinuous Method

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### ABSTRACT

Co-polymerization of methyl acrylate, a vinyl monomer, onto Tefzel film is done by discontinuous gamma ray double irradiation in an aqueous medium. Tefzel however is a polymer having the properties of polyethylene and poly (tetrafluoroethylene). In the ideal condition, the highest percent of grafting for methacrylate was obtained which was 684.9% and it was obtained using 33.2 kGy dose and 2.3 mol L<sup>-1</sup> concentration of methyl acrylate. The impact of alcohols such as methanol, ethanol, n-butanol, cyclohexanol, and amyl alcohol on the grafting proportion of methacrylate onto Tefzel film has also been investigated. IR spectroscopy and thermogravimetric analysis were performed to characterize Tefzel and grafted Tefzel film. Nevertheless, the Tefzel film with high grafting showed a good thermal behavior which can be employed in many other applications.

**Key Words:** Monomer, Copolymerization, Grafting, Swelling and Tefzel

film

## INTRODUCTION

Although Tefzel possesses two functional groups in its monomer, both are buried inside the backbone, thus, Tefzel is a resistant polymer with characteristics of Poly(tetrafluoroethylene) and Polyethylene. Consequently, its use in different domains, where functional groups are necessary, is almost negligible. However, modifications onto Tefzel have been successfully done by a different group of workers using monomers of changed functional groups. Hegazy and workers drew attention to radiation-induced grafting of acrylic acid onto poly(tetrafluoroethylene), which for the first time can be attributed to ozonolysis of alkene groups in the manufacture of fluoropolymers. A Bhattacharya et. accounted for the altered by of the polymer chains by the grafting method. Irradiation of styrene has been performed along pre-irradiated fluoropolymer films by U Appy Lappanet. al [ 4]. Iijima &Takeuchi [5] prepared membranes of TFA (tri furyl acetate) being placed on PE and fluorine-containing films through  $\alpha$ ,  $\alpha$ ,  $\beta$  grafting method by  $\gamma$ -ray irradiation using their Patent who showed good resistance against oxidation. Kaur et. al. [6,7] recorded the grafting of acrylonitrile, methacrylonitrile, methyl acrylate and ethyl acrylate all vinyl monomers onto Tefzel film along with the effect of different grafting parameters by a pre-irradiation method. Modification of Tefzel film to be used as the membrane was carried out by graft copolymerization of acrylonitrile and methacrylonitrile by I Kaur *et al* [8]. Electron donor and electron acceptor monomer blend graft on Tefzel film [9] by I Kaur *et al*. Grafting of methylmethacrylate onto Tefzel film by using simultaneous and consecutive irradiation methods has shown increased thermal stability by Inderjeet Kaur et al [10]. The interaction of styrene monomer by graft copolymerization of acrylonitrile onto deproteinized real rubber was investigated by Tuti Indah Sari et al [11]. Methacrylic acid and 4-vinyl pyridine copolymerization onto poly (vinyl fluoride) film have been studied by Inderjeet Kaur et al. [12] by using the pre-irradiation process. The development of ionic bifunctional membranes using grafting of the binary blend of methacrylic acid (MAAc), 4-vinyl pyridine (4-VP) on a Teflon-FEP film by the pre-irradiation technique has been studied by the researcher [13]. As for styrene/methacrylonitrile co-grafted membranes, there is an increased performance between the radiation-grafted membranes which is the best compared to others [14]. Acrylonitrile-co-N-vinylpyrrolidone, a binary monomer, was grafted onto low-density-polyethylene (LDPE) film by concurrent irradiation method by N. M. El-Sawy *et al* [15]. Possibly, grafting methacrylate was performed by intermittent irradiation for three hours at room temperature by an obvious pause between the two consecutive irradiations; one kind of functional group such as ester (-COOR) can be utilized for the separation purpose. The dependence of % grafting on all the relevant factors was studied to reach the optimum grafting condition which was done by experiments.

## EXPERIMENTAL

### Materials and Method for Polymerization.

The Tefzel film that was sourced from E.I. Dupont de Nemours, United States of America was washing down with methanol, wiped under a vacuum, and used for the externalization of methyl acrylate. The Cobalt-60 source was placed in a Gamma Chamber-900 at a persistent dosage amount of 0.52 kGy h<sup>-1</sup> for a specific period. The film, of dimensions 4 cm × 2 cm, was placed in the open air and irradiated discontinuously with gamma rays. After irradiation, the sample film was stored at 22–25 °C for 4 hrs & irradiated similarly again. Hence, the film would be positioned in a round-bottomed flask with a predetermined extent of distilled water. A specific extent of methyl acrylate monomer was added to the flask contents and in fixed ratios. To get the monomer



is through pathway 6. The preparation of graft copolymer is affected by many reaction parameters, and thus, methacrylate grafting was carried out under varying conditions to find the optimum situation.

## Evidence of Grafting

### 1. Infrared Spectroscopy Analysis

IR spectra of both 'unnitrated' and 'Tefzel-g-poly(methacrylate)' films were acquired on Beckman Spectrophotometer Fig. 2. Spectral assignments indicate that there is a general point in the range of between 3000–2800  $\text{cm}^{-1}$  that can be attributed to hydroxyl and hydroperoxide groups. Carbonyl peaks appear at 1710, confirming the presence of a poly(methacrylate) group. As opposed to the IR spectra of ungrafted, no such peaks present in the spectra suggest the pattern of the graft.

### 2. Thermo gravimetric Analysis

The TGA test of Tefzel and Tefzel-g-poly(methacrylate) film was performed upon Shimadzu Simultaneous Thermal Analyzer in air using a  $10^\circ \text{C min}^{-1}$  heating rate. In Fig. 3 and Fig. 4, these are the main thermograms

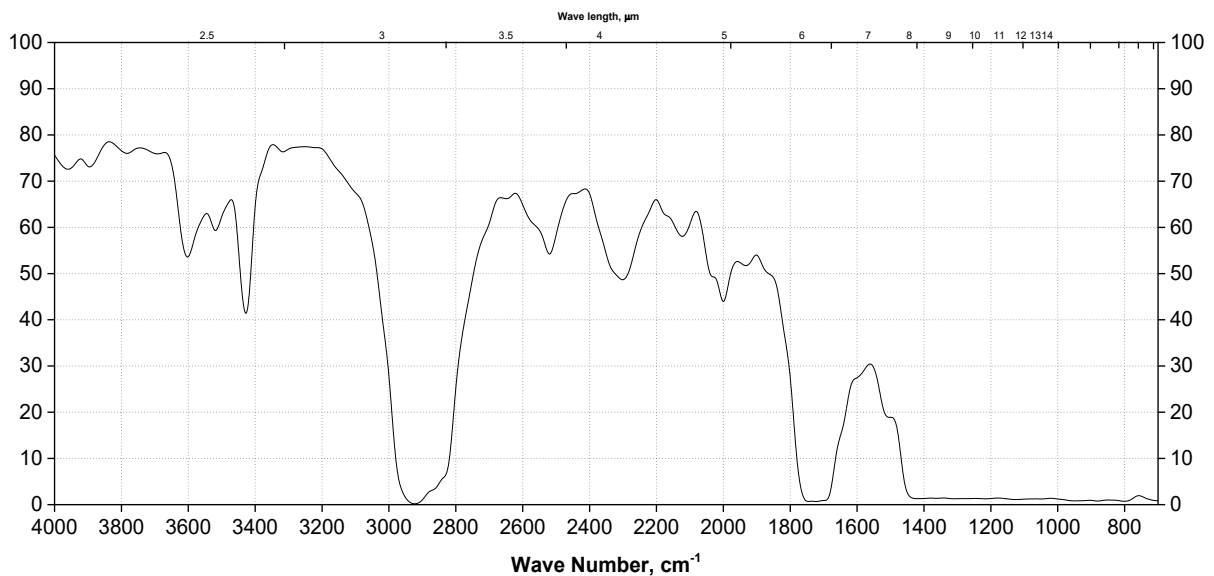


Fig. 2 IR Spectra of Tefzel-g-Poly(methacryalte)

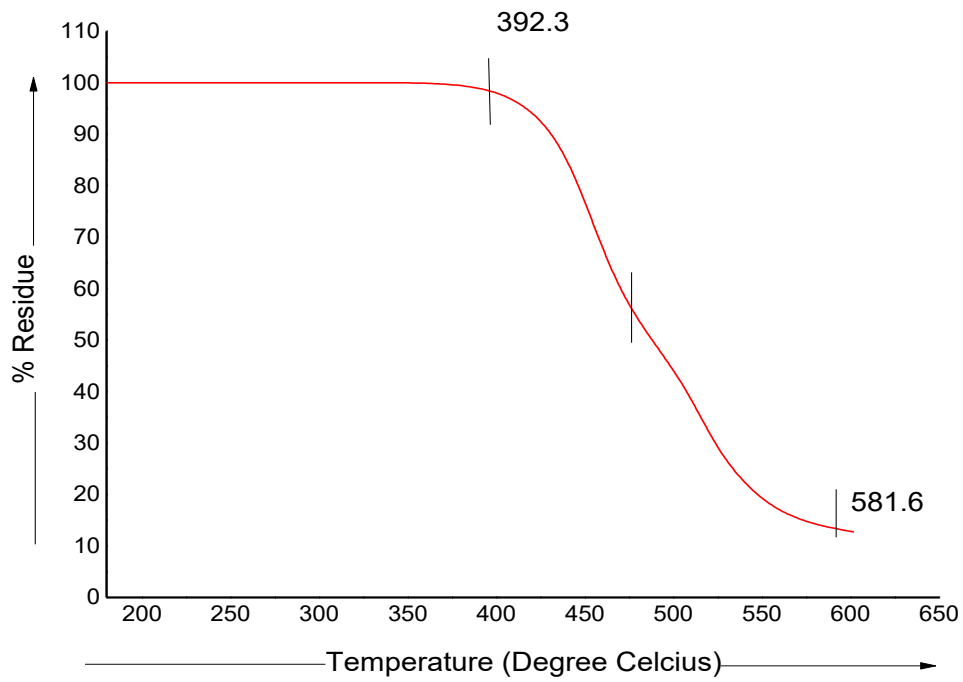


Fig. 3 Primary Thermogram of Tefzel Film

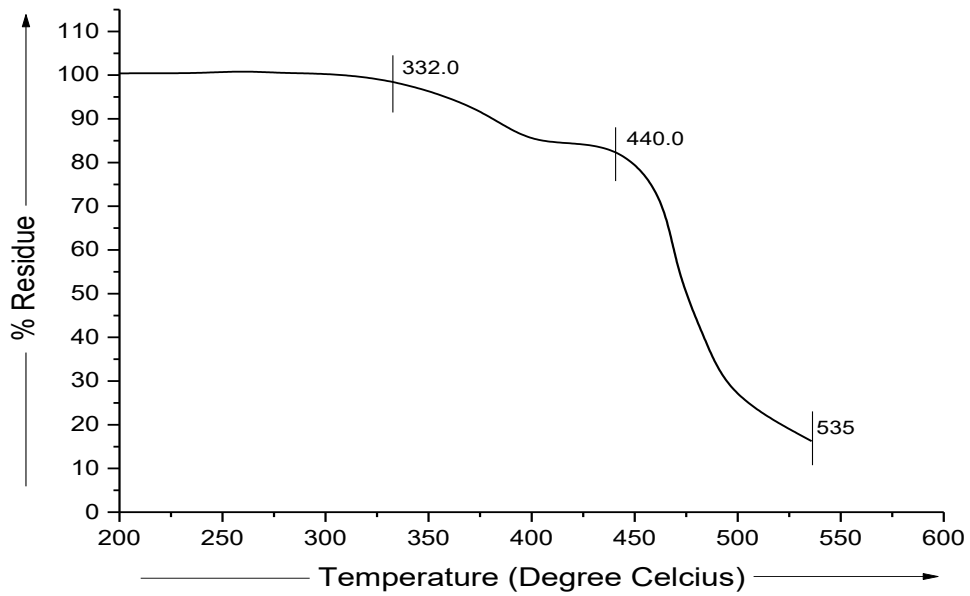


Fig. 4 Primary Thermogram of Tefzel-g-Poly (Methacrylate)

Listed in Table1 are the Initial Decomposition Temperature, Final Decomposition Temperature, Decomposition Temperature at each 10% of weight loss.

Table 1: Thermo gravimetric Analysis of Tefzel Film and Tefzel-g-poly (MA)

Sample.	IDT.	FDT.	DT(°C) at every 10% weight loss (%)

	(°C)	(°C)	10	20	30	40	50	60	70	80	90	Residue left (%)
Tefzel Film	392.3	535	425.6	440.2	458.5	469.5	476.8	484.1	493.3	510	–	12.7
Tefzel-g-poly (MA)	332	511.1	384.5	428.7	469.7	483.5	491.1	497.7	504.3	522.5	–	16.2

The Table 1 shows very clearly that the high of dramatic decrease of the IDP Thermos Brasileiro from 392.3°C of prime ungrafted Tefzel film is significantly lower than that of IDP of Tefzel-g-polymethacrylate at just 332°C. Although the value for the FDT of the methacrylate grafted film (511.1°C) is not greatly less than the value for the FDT of the unmodified film, 535°C, yet it is acceptable value for practical uses. Poly(methacrylate) DT of Tefzel-g-poly(methacrylate) at each 10% loss of strength is low and up to 20% weight loss the DT values were lower and from the 30% beyond the DT appears higher up to 80% loss as associated to the initial ungrafted film. Difference is about 3.5% (3.5%) for grafted MPMrP-gr Film which is higher than the initial rate of 12.7% for ungrafted Film. The thermograms for the first decomposition of the Tefzel are concise and possess similar temperature ranges for 10% latency at a time. The Tefzel-g-poly methacrylate film displays the two stages of degradation with 44.2 C and 410 C are the highest temperatures of Tefzel-g-poly then the original membrane in the same ranges for 10–20% and for 20–30% weight loss respectively. Besides all these values, the temperature variation interval for the area of grafting is around 60–80% weight loss, about the unchanged as that of the initial film, though the grafted DT values are considerably less than that of the non-grafted film. It can be noticed from these results that the grafting of vinyl monomer affects way of the decrease in the film IDT through the effect of the grafted chains rather than the main polymer chains. If we observe a temperature loss significant than 40°C in 10–20% of weight for methacrylate in grafted film, whereas, about 20°C of ungrafted film, this is a clear indication that this grafting raises the thermal stability in the grafted film. The higher magnitude of the DT in the case of films with a weight loss greater than 30% from the ungrafted ones may be attributed to the formation of anhydrides from the degradative chain of the polymethyl acrylate.

When the thermal data of methacrylate graft conjointly irradiated to Tefzel film covers mechanical data of methacrylate that is grafted into materials prepared with pre-irradiation method 7, it can be detected that IDT values of the film have gone up from 298.8°C to 332°C for methacrylate grafted film with The weight loss for 10% decreased density of MA grafted film, which was doubly irradiated showed the higher values compared to those of the grafted film prepared by the pre-irradiation method. On the other side, the temperature differences become marked from 20% (till 40%) weight loss for the methacrylate grafted film during which temperature reaches the level far developed than that of the irradiated once obtained single methacrylate grafted film. This could be the case because the grafted chain in the twice-as-grafted methacrylate film has narrowed grafting on the external but more so on most of the film so that a clearer temperature difference is observed in the measuring instrument used. Nevertheless, the difference over an intervening 10% of weight loss from 40% onwards between the doubly irradiated and the grafted films are almost like that of the ungrafted film. Here, for methacrylate single film grafted by ions the gap is clear only within 40–50% loss of the weight and from which it becomes practically the same as for other grafted films. In the higher weight loss following two irradiation periods, we can see how the hydroperoxide radical formed bonds in the middle polymer where grafting happens which disturbs the crystallinity of the backbone polymer. The 2<sup>nd</sup> phase of the breakdown involves the backbone polymer which is the higher temperature at a lesser temperature difference. This is attributed to the deficit of its crystallinity.

### Area Change in Grafted Film.

Value of methacrylate grafted film size has been shown as an operational state in the percentage of grafting. Table 2 is followed by Fig. 5. Area of the sample resulting from grafting and ungrafted series was determined as a rate of the growth area and compared with others. As presented in Fig. 5, the physical size of the insulator made of Tefzel plasmolyzed cellulose enhances as the percentage of grafting becomes higher, while the shape persists always the unchanged one. The phenomenon says that the grafting takes place firstly on the external of the film and on the next stage with the diffusion into most of the film involving more film zone.

The Tefzel film percent area ground is higher with increasing percent-addon of methacrylate and even begins to level off. The percent change area correlates quite well with the percent methacrylate grafting. This varied trend in a monomer may result in any difference in grafting conditions.

**Table 2: Area Change During Grafting of Methacrylate onto Tefzel Film**

SN.	Sample.	Percentage of Grafting	Area (cm <sup>2</sup> )	Percentage of Area Change
1	Tefzel.	.0	8.0	.0
2	Tefzel-g-poly(methacrylate)	83.40	11.75	46.87
3	Tefzel-g-poly(methacrylate)	94.60	12.40	55.75
4	Tefzel-g-poly(methacrylate)	129.10	13.26	65.75



**Fig. 5 Photographs of Tefzel-g-Poly(methacrylate)**

The irradiation technique "pre-irradiation process" will be discussed via its monomer reactivity, which is based on physical properties. Here it is different, but also features that with the exception that the cord irradiation is repeated but with a difference of four hours between irradiations.

Besides this, the oxidation by double irradiation is most probably accompanied by the appearance of more hydroperoxide sites in the bulk of the film in addition to the film surface. It is believed that it is this diffusion which enables the formation of the film in the conditions of film formation. According to research results, this will result in an increased grafting frequency and that has been proven to occur. Acrylate methyl due to the fact that it possesses high vapors, takes slow time to either polymerize or diffuse shifts in percentages of the provided area.

### Swelling Behavior

To determine the alteration in surface activity of the initial Tefzel film and grafted poly (methacrylate) in polar and nonpolar solvents, established and weighed grafted films was engaged in the different solutions at 37 °C for 24 hours. The pictures was eliminated, and quickly stained

with paper tissues to get rid of the water clinging on the surface, and immediately the beaker with film apparatus was weighed. The swelling extent is obtained by dividing the film weight in a swollen state to its weight in dry film. A percentage swelling graph as a function of a percentage of grafted methacrylate monomers is shown here as the results of Fig. 6.

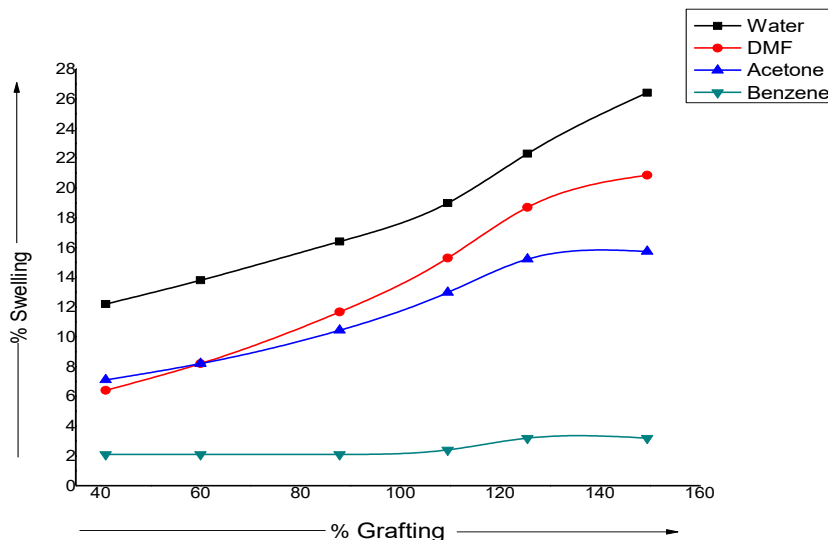


Fig. 6

#### The Effect of Grafting on Swelling of Tefzel-g-Poly(Methacrylate) in Different Solvents

It is seen that the Tefzel film chose not to swell as it is compact in structure, but Tefzel grafted-poly (methacrylate) does show the swelling behavior in all the diluters not including water (lowest swelling) i.e. the solvents may form some kinds of interactions by the side clusters close to the backbone or they might form relations with eth Grafted film swelling occurs at the highest extent in DMF, a polar solvent whereas the possible cause of this phenomena may be the more connections of this solvent with the polar clusters (ester) of the grafted film. The higher swelling from nearly 70% grafting for non-polar solvent such as benzene, demonstrated more solvent interactions with the ethylene segment of the backbone film, compared to that of a polar solvent of acetone which possibly has fewer interactions. Water is the maximum polar solvent among others and shows the least swelling behavior. It could be due to the grafted film apolar loose interactions with the pendant protic groups of water molecules and the non-penetration of the grafted film by water molecules because of the high H-bonding affinity between water molecules themselves which allowed water molecules to interact even penetrate the grafted film Tefzel film surface in dissimilar solvents excluding for water shows percent swelling rise with increase of grafting percentage. The swelling percent of the methacrylate grafted film increases consistently, reaching a steady level at the 120 % of grafting value for benzene and acetone except in DMF where it shows a spike effect. Tefzel-g-poly(methacrylate): DMF (Dimethylformamide) > Benzene > Acetone > Water.

Patterns formed by methacrylation and monomer grafting are identical to what was reported for the radical process invented by Kaur et.al 7.

#### Effect of Total Dose

The outcome of the entire dosage on the proportion of grafting of methacrylate onto Tefzel film has been compared by changing the total dosage variedly and the steady percentage of grafting has been obtained. The result of methacrylate treatment is shown by Fig. 7. Since Tefzel film is



irradiated by photons twice (with a four hour break between two irradiation periods) so we just calculate the sum of two radiation periods. The Fig.7 represents the percent of grafting for methacrylate. The grafting percent has a rising pattern till the total dose of 27 kGy and subsequently it plummets and increases till a maximum of 145.2 percent, at the total dose 33.2 kGy. Moreover, the dosage beyond a certain threshold result in a sharp downside, and afterward, it reverses its direction. The initial slope of the Upper curve of the Pg with the monomer is initial grafting in the amorphous region which can be attributed to the active sites in that region. There is an increase and then a fall of the free radicals amount at the end of the further increase of the total dose which might be due to crystal surface activation which permits the diffusion of the monomer into the amorphous part of the film to the region of grafting also. Other researchers had a similar pattern during the irradiation method and provided different explanations<sup>7</sup>.

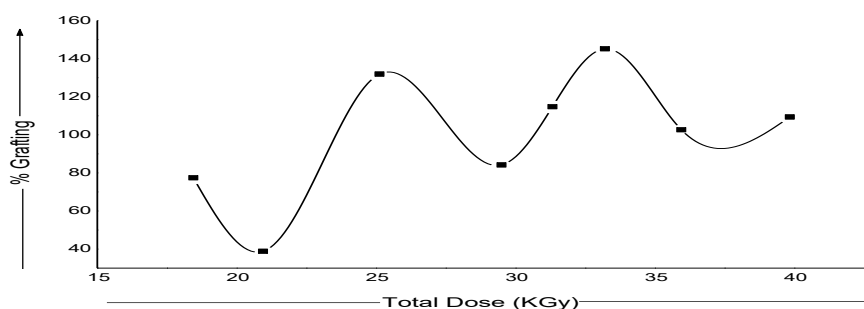
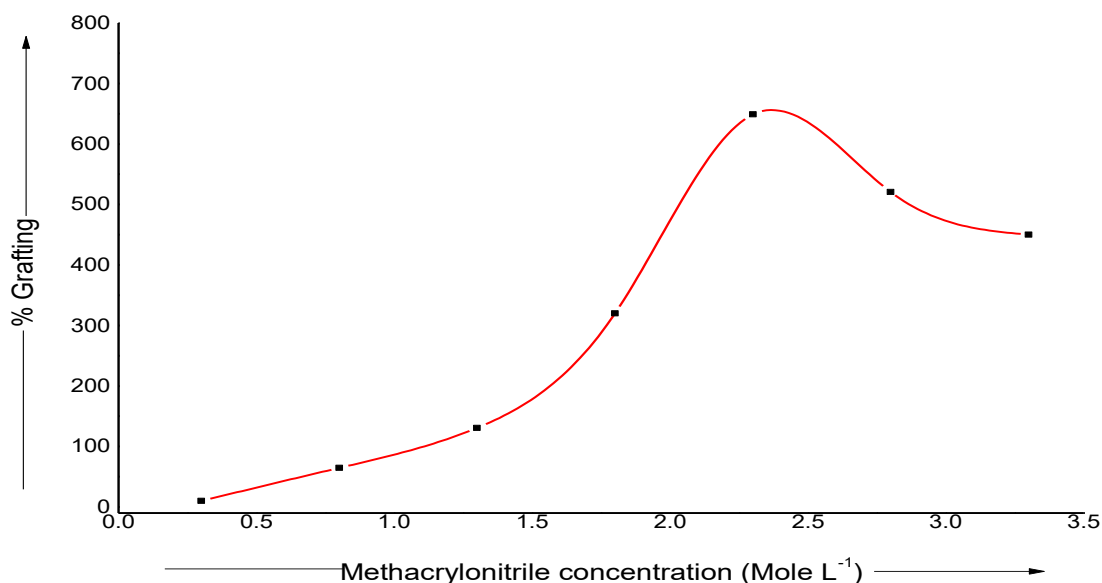


Fig. 7 The Effect of Total Dose on Percentage Grafting of Methacrylate on Tefzel Film

#### Effect of Monomer Concentration

It is this proportion of grafting of methacrylate that has been characterized through variation of monomeric concentrations, and the results it has generated are represented in Fig 8. The current scenario is characterized by methacrylate, which displays a higher sd when the concentration of monomer rises producing a maximum level of 684.9% at methacrylate = 2.30 mol/L beyond which it starts to decrease. This (increasing the number of methyl acrylate) can be reliably explained with a given fact that there exists an equilibrium between vapor and liquid stages in which an amount of methacrylate consequently expresses a tendency to exist in liquid stage (with increasing the number of monomers). (kp), the propagation rate grows too much. This leads to a massive increase in the amount of the monomer available that causes monomer polymerization also in a rapid way. The speed of the methacrylate group amination is also not fast enough to stop the growing chains and so these chains approach the active site so that they perform a grafting.



**Fig. 8 Effect of Amount of Methacrylate on Percent Grafting**

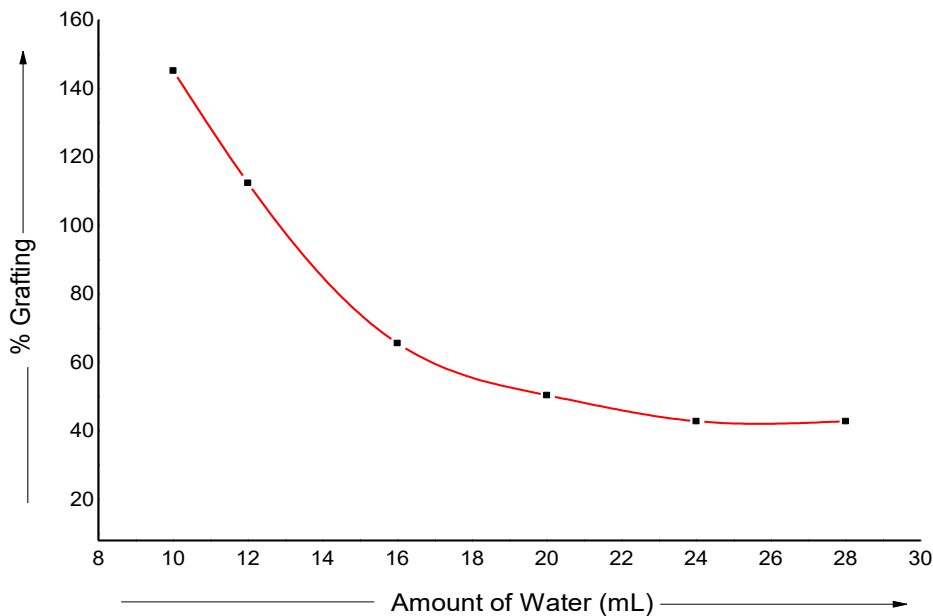
Furthermore, it was also noticed that when grafting methacrylate was carried out in pre irradiated Tefzel film, an oscillatory rise and reduction in P.g was detected, and a reason suggested for this behavior was that the same started in the amorphous region and then followed by the same in the crystalline (Tefzel) area. However, today no distinguished behavior is seen. As for Tefzel film containing two irradiation cycles sitting for a period equal to four hours between them, surface active sites increase evenly because the initial reaction is slowed down eventually. Therefore, an increasing, monomer concentration polydispersity is formed, which directly attacks the active sites which results in higher grafting conversion.

#### Effect of Amount of Water

The impedance of methacrylate, mediated by the medium, was examined in terms of how much reaction medium it drew in. Specifically, the methacrylation used aqueous solvent. The monomer methacrylate graft on Tefzel film has been employed for the medium shown in Fig. 9, its effect on the Pg which stands for grafting percent. It is seen from Fig. 9 that concentration Pg of methacrylate diminishes with the further regular rise in the proportion of water. The water solubility of a monomer is slightly higher and it also possesses comparatively high vapor pressure, whence the concentration of methacrylate monomer lies less in the liquid state which makes the diffusions of monomer with the hydroperoxide groups of the backbone and the steric effects weaker, leading to an eventual lowering of Pg as more water is added to the reaction mixture.

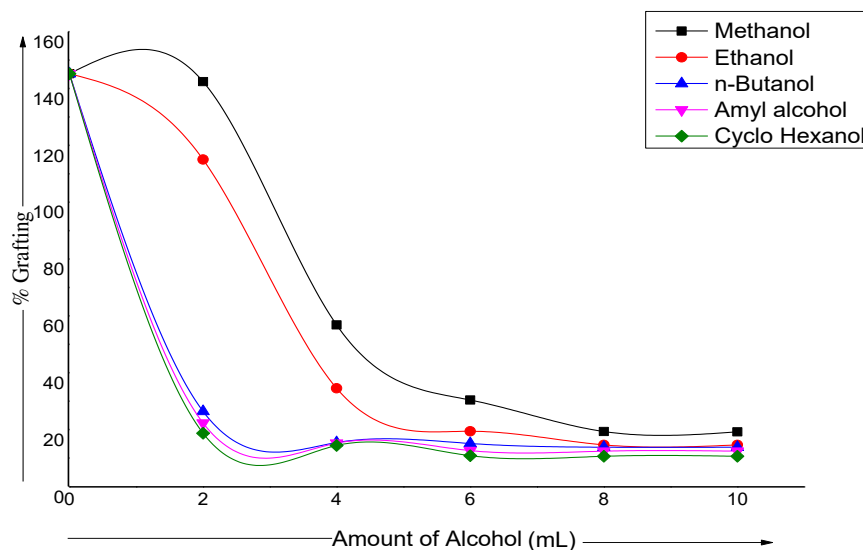
#### Effect of Alcohols

Influence of the type of water: air composition for the blended solvents on Pg for methacrylate on Tefzel film has been examined and the findings are exhibited in Fig.10. Based on the above observations, the yield of the polymer produced in the mixed water–alcohol medium, for instance, 10mL of micellar solution, is a bit lower than that obtained in the aqueous medium alone. is noted saying that for the grafting copolymerization reactions of methacrylate the order of reactivity of various alcohols has been found. From Left to Right, the list progresses as follows– Methanol >Ethanol >n-Butanol >Cyclohexanol >Amyl alcohol.



**Fig. 9 Effect of Amount of Water on Percentage of Grafting of Methacrylate onto Tefzel Film.**

The resulting experiment states that the impact of alcohol on graft polycondensation reaction is inversely proportional to the increasing length of the chain of the alcohol. Alcohols of a higher molecular size (which translates to higher alcohols) have a greater propensity to break the H-bonded water structure as well as the bond linking the alpha carbon of protein and the water molecule. Accordingly, an alcohol-water associated structure forms. The whole process slows down and the mutual disintegration of the shifting reaction medium practically excludes the possibility of the governing polymeric chain reaching the alive site and therefore it makes Pg go down.



**Fig.10 Effect of Amount of Alcohol in (alcohol–water) Binary Mixture on Grafting of Methacrylate onto Tefzel Film.**

## CONCLUSIONS

Pp for methacrylates subjected to double irradiation is higher than Pp for methacrylates subjected to single irradiation at 33.2 kGy constant dose rate. It is probably the matter of the development of the more active backbone's side sites and the diffusion of monomers towards these features. Thus, the monomer of methacrylate is being diffused more onto the open active sites that can get attached to the backbone leading to higher polymer of glycolyl. The rise in Pg and then fall a little later show that grafting in the amorphous region is the first step, and then the monomer migration into the film's bulk where grafting in the crystalline region takes place. Particularly, double irradiation of the film and grafting with polymers exhibited improved resistance to thermal degradation as noted in the TGA data and might be therefore used in the polymer industry. Film made of grafted Tefzel because of its superior thermal stability it will behave very tough towards external attacks and also toward various chemicals which means that it will be almost impossible to destroy and the best life expectation and inconsiderateness to such influences as UV radiations and contamination. It is possible to assemble these films through lamination, metalizing, welding and hot-bonding after blending them with other chemicals. It can be concluded that such films show some sort of swelling behavior in some selected solvents, hence they can be used for different processes of membrane separation. Another thing that is worth mentioning is that this expansion behavior of the film can bring to existence other new grafted membranes that have functions which are needed for specific purposes.

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