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MODIFICATION OF TRACK ETCHED FLUORINATED FILMS BY RADIATION INDUCED GRAFT COPOLYMERIZATION

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Abstract. With the aim of improving the basic characteristics of Track Etched Membranes (TEMs), functionalization by graft copolymerization has been attempted in the present work. Thin films (25 μm) of poly(vinyl fluoride) (PVF) (Tedlar) were irradiated by swift heavy ions (110 MeV Si⁸⁺). The irradiated films were chemically etched to form latent tracks. Atomic Force Microscopy (AFM) was used to ascertain the formation of latent tracks. Irradiation effects were studied using UV-visible spectroscopic techniques. The tracks were functionalized by gamma radiation induced grafting with 4-vinyl pyridine (4-VP). In order to anticipate the best grafting conditions, percentage of grafting was studied as a function of various reaction conditions such as (i) total dose, (ii) monomer concentration and (iii) amount of water. Maximum percentage of grafting (13.66 %) was obtained at a total dose of 57.024 kGy using 2 ml of 4-VP in 10 ml of water. The grafted films were characterized by FTIR technique.

Key words: poly(vinyl fluoride), swift heavy ions, track etched membranes, radiation grafting; γ rays.

1. Introduction

Polymeric films are extensively used in the field of biotechnology, medicines and purification [1, 2]. However, the application of polymeric films in commerce and industry has been limited owing to the fact that conventional membranes rupture under operational conditions and have a limited chemical and thermal stability and short life-time. Therefore, there is a strong demand to develop special membranes which can meet specific requirements.

One of the methods for special membranes manufacture is to prepare Track Etched Membranes (TEMS). When polymer film is bombarded with high-

energy radiation, it results in the formation of damaged areas in the film. These damaged areas are known as tracks. These tracks are subsequently etched to form discrete pores with a defined pore size. The membranes having the etched tracks are known as track etched membranes (TEMs) [3, 4].

The formation of latent tracks during SHI irradiation in polymeric materials using suitable combination of projectile and target has emerged as an exciting field of research and development having diverse applications in the field of biotechnology, medicine, ecology, *etc.* [5]. Fabrication of porous membranes by track etching for their industrial applications as filters, collimators, channel plates, and templates of nano- and microwires is also studied by different authors [4-8].

TEMs resist the filtering media of other type due to their advanced features [6-9].

Much effort was made to develop TEMs from fluoropolymers. The best results were obtained with poly(vinylidene fluoride) (PVDF) that exhibits good chemical and mechanical properties. Samples of PVDF track membranes were produced and tested in several laboratories [10, 11]. However the TEMs have certain disadvantages such as low water flow rate due to hydrophobic nature of their polymeric surface [12]. Functionalization of these track etched membranes may highly improve the properties required for many of the specific applications of TEMs.

Among the variety of techniques employed for improving the basic characteristics of TEMs, functionalization by graft copolymerization offers a versatile method for incorporating new molecular functionalities into the existing polymer in a well controlled manner. Modification of such a membrane by grafting it with different monomers extends the possibility of their application [13, 14].

Graft copolymerization can be initiated either by high energy irradiation (gamma ray, electron beam, swift heavy ions) or by chemical methods. Among the various methods radiation grafting has gained popularity among the researchers because its main advantage is to avoid the use of polymerization additives since initiation is induced through the formation of free radicals in the bulk as a result of ionizing radiation/polymer interaction. The swift heavy ion induced grafting of acrylic acid onto poly(vinylidene fluoride) was reported by Betz *et al.* [15]. The polymer was irradiated with different ionizing radiation: swift heavy ions or electrons. Sulfonate and sulfonamide groups were introduced into phenyl rings belonging to styrene residues, which are radiation grafted (using swift heavy ion and gamma radiation), into PVDF and also into poly(vinylidene fluoride/hexafluoropropylene) [P(VDF-HFP)] by Porte-Durrieu *et al.* [16]. It was found that in contrast to gamma radiation, which leads to a homogeneous modification, the advantage of swift heavy ion grafting is that only small regions are modified; thus the surface may present hydrophilic (corresponding to the modified areas) and hydrophobic (corresponding to the unmodified areas) microdomains of different sizes, depending on the absorbed dose and grafting yield. Graft polymerization into the latent tracks of some perfluoropolymer films irradiated by heavy ions was carried out by Shirkova *et al.* [17]. R. Mazzei *et al.* [18] carried out swift heavy ion induced graft polymerization in track etched membranes submicroscopic pores. Cl or Pb irradiated foils of PVDF were chemically etched to produce nuclear track membranes (NTM) with submicroscopic pores. The NTM were grafted with styrene using the remaining active sites produced by the heavy ion beams. Scherer and co-authors [19] have reported the use of post-irradiation grafting of styrene onto ETFE for the preparation of ion-exchange membranes.

Gamma radiation grafting onto TEMs made of poly(ethylene terephthalate) (PET) and polypropylene (PP) films was performed by N. Shtanko *et al.* [20].

Recently, attempts are being made to prepare “smart” or “intelligent membranes” through modification of TEMs. Intelligent membranes have the peculiarity to respond to the external environmental conditions. Many investigations were devoted to obtaining of the membranes capable of opening and closing the pores in response to an external stimulus such as temperature [20-22], pH [23] and ionic strength [24].

The aim of this work was to produce track membranes using swift heavy ions modified by gamma radiation-induced grafting of 4-vinylpyridine, which have qualitatively new properties allowing essential extension of the TEM application fields.

We have attempted to prepare TEMs using PVF-TEDLAR films as substrate. It is well-known that PVF has excellent properties, such as resistance to outdoor weathering exposures, high degree of physical toughness, chemical

inertness, transparency, and retention of its properties at both low and elevated temperatures in the film form [25]. PVF has wide applications in aviation, architectural decoration, agriculture, food packing, and is an excellent engineering plastic that is indispensable in industry [26].

4-VP was chosen as the preferred monomer because the polymer films grafted with 4-vinyl pyridine have shown the capability of separating the chloride ions from saline water in the work carried out in our lab [27]. To our knowledge, this is the first report on gamma rays induced grafting of 4-VP onto TEMs prepared from PVF TEDLAR using SHIs.

2. Experimental

2.1. Materials

The PVF (Tedlar) films (25 μm) were generously supplied by E.I. Dupont India Ltd. and was used as received. 4-VP acetone (analytical reagent grade) were purchased from Sigma-Aldrich were used as received.

2.2. Irradiation with Swift Heavy Ions to Produce TEMs

Tedlar films were irradiated in vacuum ($1.5 \cdot 10^{-5}$ Torr) at room temperature using 15UD Pelletron accelerator (GPSC) at IUAC, New Delhi. The 110 MeV Si^{8+} ion beams in the fluence range of $6 \cdot 10^5$ – 110^6 ions/cm² were used for irradiation. The ion beam current was about 0.5-1 particle nA. The films were subjected to oxidative etching at 373 K to produce track etched membranes (TEMs) [28].

2.3. Gamma-Radiation Induced Grafting

There are essentially three methods for radiation grafting [29]. The Tedlar TEMs were grafted with 4-VP by peroxidation method [29] using ^{60}Co gamma ray source at Himachal Pradesh University, Shimla, India. The test tubes containing Tedlar TEMs were subjected to gamma rays from ^{60}Co source in air at room temperature at a dose rate of 2.59 kGy/h. The preirradiated films were placed in a standard joint two-necked flask fitted with a condenser and thermometer. A definite amount of water was added to the reaction flask followed by the addition of the monomer. The flask was placed in an oil bath for 2 h and the contents of the flask were refluxed at the boiling point of the solvent. The grafted films were washed with 1:1 acetone:water mixture and soaked overnight to extract the residual monomer and the homo polymer occluded in the films. The films were dried in vacuum oven at 773 K and weighed. The grafted yield was determined as:

$$\% \text{Grafting} = \frac{W_2 - W_1}{W_1} \cdot 100$$

where W_2 and W_1 are the weights of the grafted and ungrafted Tedlar TEMs, respectively.

In order to anticipate the best grafting conditions, percentage of grafting was studied as a function of various reaction conditions such as (i) total dose, (ii) monomer concentration and (iii) amount of water

2.4. Characterization

The Tedlar TEMs were characterized by AFM, UV-vis spectroscopic studies. The grafted films were characterized by FTIR spectroscopic studies.

Fourier transform infrared (FTIR) spectra were recorded on a Thermo 5700 FTIR spectrophotometer. The ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-vis spectrometer (400–190 nm). AFM studies were performed at IUAC, New Delhi. The surface morphology of these samples was studied with a Veeco Digital Nanoscope IIIa SPM at NSC. Since the polymers are soft materials, tapping mode was used with RTESP tips and a low force constant.

3. Results and Discussion

3.1. UV-vis Spectroscopy Analysis

Irradiation of polymers typically generates both rapidly decaying as well as relatively stable radiolysis products. The more stable products have conjugated structures that absorb both in UV and especially in the visible region [30]. In Tedlar irradiated with SHIs appearance of new bands in the UV spectrum (Fig. 1) close to 284, 288, and 292 confirms the formation of dienes and trienes. Makuuchi *et al.* observed the similar effects after irradiation of fluorinated polymers with bands at around 230 and 270 nm assigned to diene and triene [31].

3.2. AFM Studies

Very few studies on polymer TEMs have been by means of scanning probe microscopy [32]. Ambuj *et al.* [33] analyzed the modifications induced by ion beams in polymer using conducting AFM technique. AFM was used to get information about the surface structure and porosity of the TEM. The AFM images of Tedlar irradiated with Si in the fluence $1 \cdot 10^6$ are shown. The formation of latent tracks is clearly visible in Fig. 2a. Fig. 2b shows the enlarged view of one of the tracks.

3.3. Gamma Radiation Induced Grafting Parameters

The polymer is exposed to ionizing radiation in the presence of air or oxygen. This produces either peroxy radicals or hydroperoxy groups on the polymer substrate

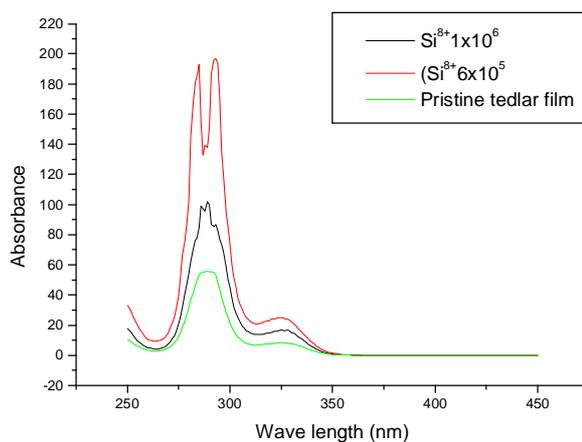


Fig. 1. UV-visible absorption spectra of Tedlar irradiated with Si ions

which, when heated in the presence of monomer, will decompose and grafting may be initiated.

Fluoropolymers generally undergo net chain scission on radiolysis at ambient temperature and the stable radicals formed are predominantly chain-end and main-chain radicals. The chain-end radicals are formed by cleavage of main chain carbon–carbon bonds and the radicals formed within the chains arise from cleavage of carbon–fluorine bonds. At ambient temperature the radicals are believed to be principally located in the crystalline-amorphous interphase regions in the fluoropolymers [34].

Effect of various parameters on percentage of grafting by peroxidation method has been discussed below:
Effect of Total Dose

Fig. 3 describes the effect of total dose on grafting of 4VP onto Tedlar TEM. It is observed from Fig. 3 that grafting of 4 VP onto Tedlar increases with increasing total dose and reaches a maximum value at a total dose of 57.024 kGy, beyond which it decreases slowly. Increase in percentage of grafting is due to the fact that with increasing total dose various initiation steps leading to the generation of active sites on Tedlar backbone are accelerated. Decrease in percentage of grafting at higher dose beyond 57.024 kGy may be explained by the fact that at higher doses energy transfer processes occur in the irradiated mixture causing the intramolecular scission of the grafted branches. The growing grafted chains which still have active sites may attack the neighboring grafted branches thus bringing in chain scission and chain termination simultaneously [35]. As a consequence of back biting by the growing grafted chains, the length of the grafted branches is considerably reduced thus decreasing the overall weight of the grafted polymer and hence decrease in the grafting is observed. Similar results for fluoro polymers were also obtained by Chapiro *et al.* [36] and Cardona *et al.* [37].

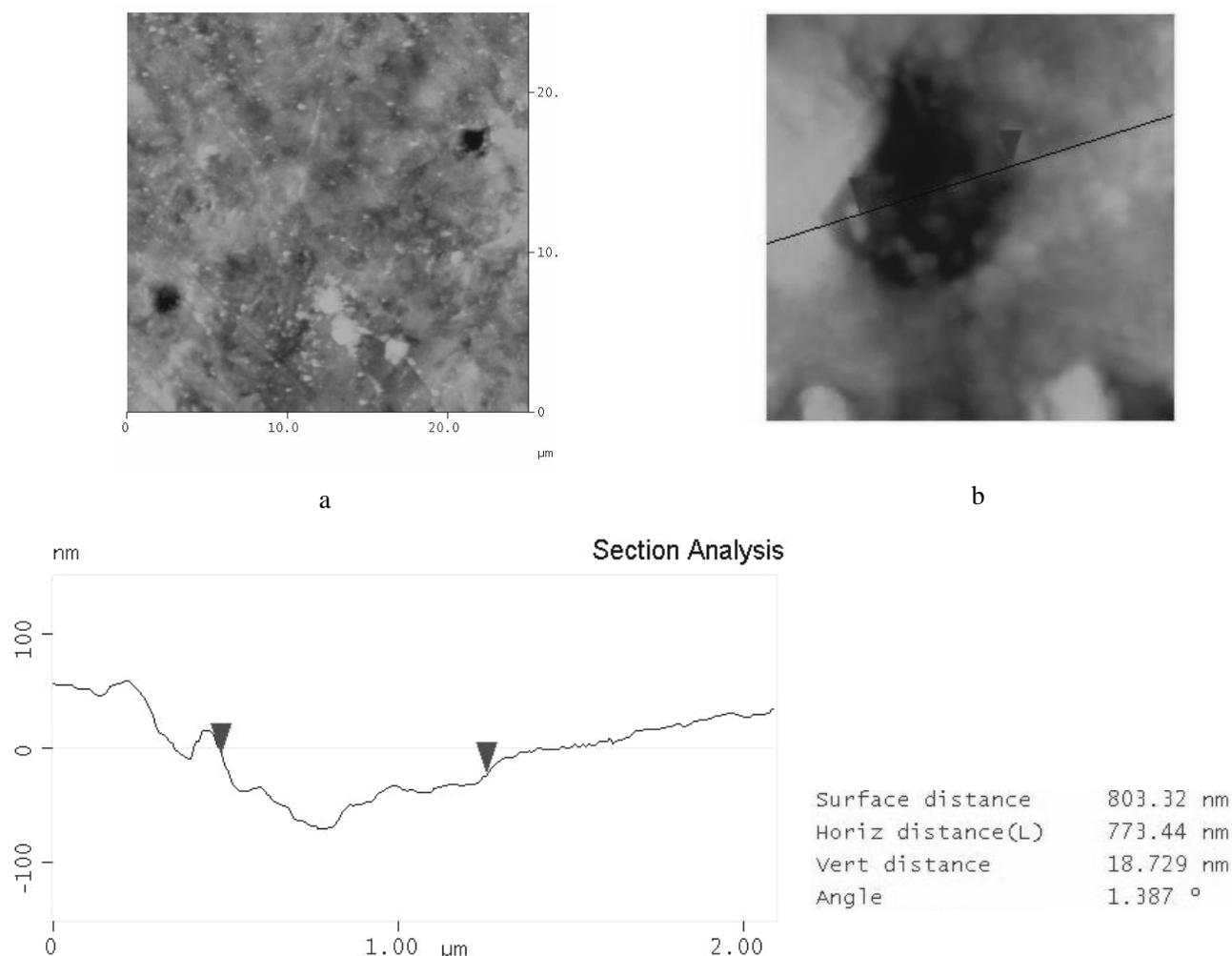


Fig. 2. AFM images of Tedlar irradiated with Si ion at fluence 1410^6

Effect of Monomer Concentration

The effect of concentration of 4-VP on percentage of grafting onto Tedlar film is presented in Fig. 4. The percentage of grafting increases sharply with monomer concentration initially, thereafter it tends to decrease. The initial increase in percentage of grafting may be explained as follows: in preirradiation grafting the formation of homopolymer at low concentration of monomer is minimum and the rates of propagation and initiation increase with the increase of monomer concentration. At higher monomer concentrations, the homopolymerization increases preferentially resulting in hindered monomer diffusion into grafting sites and hence the grafting percent decreases. Also, 4-VP is wasted in the side chain reactions because of its high monomer-transfer value ($CM = 7 \pm 2 \cdot 10^{-4}$), thereby decreasing percentage of grafting [38]. Similar observations have also been reported by M. Nasef *et al.* while grafting styrene onto fluorinated polymers [39].

Effect of Amount of Water

The addition of solvent to a monomer/substrate combination can enhance the yield in the radiation-induced grafting and determine the specific nature of the graft copolymer [40].

The presence of water in a reaction medium in the grafting reactions has been found to have a very important effect on percentage of grafting of vinyl monomers onto polymers. In order to study the effect of amount of water during grafting of 4-VP onto Tedlar, grafting has been carried out as a function of amount of water and the results are presented in Fig. 5. It is observed from the figure that initially percentage of grafting increases with increasing amount of water up to 10 ml of water, beyond which it decreases. Initial increase in percentage of grafting can be attributed to the fact that in presence of water hydroperoxide groups of the irradiated films are hydrogen bounded and are more exposed to grafting leading to an increase in grafting. Decrease in percentage of grafting

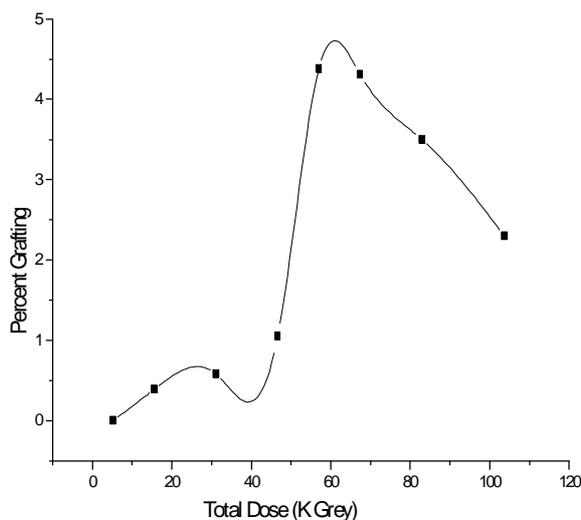


Fig. 3. Effect of total dose on percentage of grafting of 4-VP on Tedlar track membrane. Dose rate is 2.59 kGy, amount of water is 10 ml, 4-VP – 1 ml

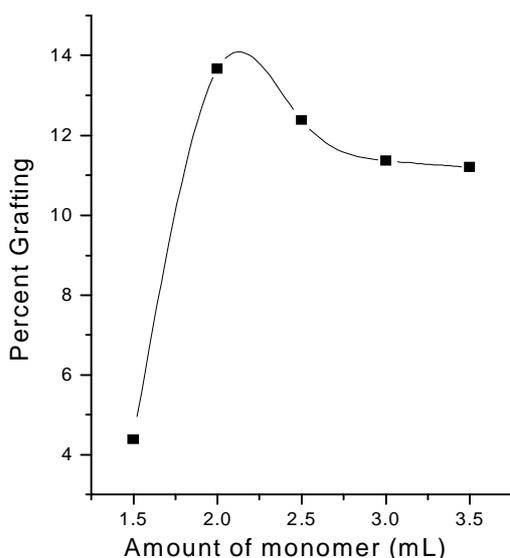


Fig. 4. Effect of 4-VP on percentage of grafting on Tedlar track membranes. Dose rate is 2.592 kGy/Hr, total dose is 57.024 kGy, amount of water is 10 ml

beyond 10 ml of water can be explained by the dilution of the monomer in the reaction medium with increasing amount of water. The homopolymer, poly(4-VP) being soluble in water raises the viscosity of the medium which inhibits the movement of the growing polymeric chains to the active sites leading to decrease in grafting. Further, since 4-VP forms hydrogen bonds with water molecules, the presence of excess water may entrap the monomer thereby reducing the accessibility of the monomer to the active sites of polymer backbone [27].

The grafted membranes are characterized by FTIR spectroscopy. FTIR of Tedlar showed peaks at 2933.3 cm^{-1} and 2857.4 cm^{-1} (CH_2 str.). The CF/CC str. absorptions appear around 1100 cm^{-1} [41]. The Tedlar-g-poly (4-VP) show additional peaks at 1575 cm^{-1} due to C=N str and 3402 cm^{-1} (NH_2 str.).

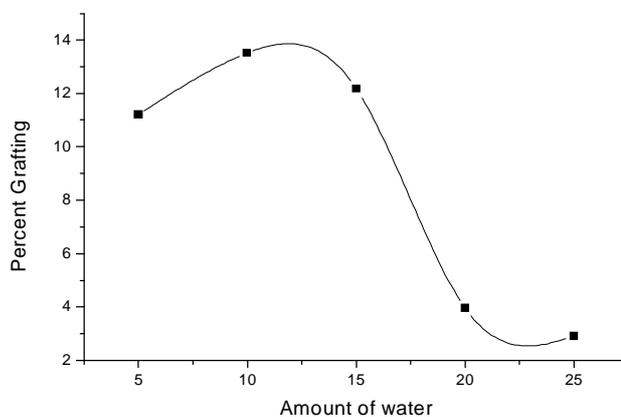


Fig. 5. Effect of amount of water on percentage grafting. Total dose is 57.024 kGy; amount of 4-VP is 2 ml

4. Conclusions

Despite the stability of fluoropolymers, TEMs prepared from them can be readily modified by radiation-induced graft copolymerization. Maximum percentage of grafting (13.66 %) in Tedlar TEMs was obtained at a total dose of 57.024 kGy using 2 ml of 4-VP in 10 ml of water. This concept could be further explored for the creation of multi-purpose membranes that can separate a variety of mixtures as a function of different external conditions (such as temperature, pH, *etc.*) during the filtration process. The prepared membranes are being investigated for their use in membrane technology.

However, recently the focus of the research has been broadened and studies of the potential for the use of grafted fluoropolymers as substrates for solid phase organic chemistry (SPOC) are being done. As these applications are further developed and new applications are found, interest in the grafting of fluoropolymers is certain to grow tremendously.

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МОДИФІКАЦІЯ ФЛҮОРВИТРАВЛЕНИХ ПЛІВОК РАДІАЦІЙНО ІНДУКОВАНОЮ ПРИЩЕПЛЕНОЮ КОПОЛІМЕРИЗАЦІЄЮ

Анотація. В роботі вивчена можливість покращення основних характеристик ТЕМ-мембран функціоналізацією внаслідок прищепленої кополімеризації. Тонкі плівки (25 нм) полівінілфториду (ПВФ) були опромінені швидкими важкими йонами (110 MeV Si⁸⁺). Опромінені плівки хімічно витравлювали до утворення латентних слідів. Для підтвердження утворення латентного сліду використано атомну силову мікроскопію. Вплив опромінення вивчали за допомогою УФ-спектроскопії. Для створення найкращих умов прищеплення вивчали відсоток прищеплення як функцію різних чинників реакції, таких як загальна доза, концентрація мономерів і кількість води. Показано, що максимальний відсоток прищеплення (13.66 %) досягається при загальній дозі 57.024 кГу з використанням 2 мл 4-вінілпіридину в 10 мл води. Прищеплені плівки охарактеризовано за допомогою Фур'є-спектроскопії.

Ключові слова: полівінілфторид, швидкі важкі йони, ТЕМ-мембрани, радіаційне прищеплення, гама-опромінення.