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Dyed Grafted Poly(tetra fluoro ethylene-perfluoro vinyl ether) copolymer Film with Acrylic Acid for High-Dose Radiation Dosimetry

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Abstract

The grafted films of poly(tetra fluoro ethylene-perfluoro vinyl ether) copolymer film with acrylic acid (PFA-g-PAAc) were prepared by γ-radiation. The films were allowed to react with an ionic dye, namely Brilliant Green (BG). The investigations show that these new dosimeter films of PFABG may be useful for high dose gamma radiation applications. The useful absorbed dose range of the dyed film extends up to about 400 kGy. The radiation-induced colour bleaching has been analyzed with visible spectrophotometery, either at the maximum of absorption band at 633 nm. The effects of relative humidity during irradiation, shelf-life and post-irradiation storage in dark and indirect daylight conditions on dosimeters performance are discussed.

Key word: Brilliant Green/ Poly(tetra fluoro ethylene-perfluoro vinyl ether) copolymer/ Acrylic Acid/ Radiation Dosimetry

Introduction

Radiation-induced graft copolymerization of acrylic acid (AAc) (Hegazy et al., 1981; El-Sawy et al., 1992) and vinyl-soluble monomers onto polymer films is a well-known method for modification of the chemical and physical properties used to produce good quality membranes for modern technologies such as ion-exchange (Burlant and Huffman, 1985) and large-dose radiation dosimetry (Abdel Rehim et al., 1993). The presence of carboxylate groups in the grafted layers lead to the formation of dyed film by a treatment with basic dyes. Several polymeric materials in the form of thin films have been successfully developed and used as dosimeters for routine use in gamma rays as well as electron beam radiation processing. Representative examples are radiochromic plastic films of various types (McLaughlin, 1990; McLaughlin et al., 1988; Abdel-Fattah and Miller, 1996) cellulose triacetate (Abdel-Fattah et al., 1995, 1996) and Gafchromic Dosimetry Media (Abdel-Rehim et al., 1996; Abdel-Rehim and Abdel- Fattah, 2003; ASTM, 2002).

It is aimed, therefore, to prepare films of grafted acrylic acid onto PFA and subjecting them to dyeing by an ionic dye, namely brilliant green (BG). The prepared dyed films by the above mentioned way are then investigated for their eventual application as radiation dosimeters.

Experimental

Graft polymerization

The graft copolymer were prepared by a simultaneous grafting technique strips of PFA films were immersed in aqueous AAc (50/50 wt%) in glass ampoules. Mohr's salt (ammonium ferrous sulphate) (2.5 wt%) was added to the reaction medium to minimize the homopolymerization of AAc during the radiation grafting process (at room temperature). The reactant mixtures in the glass ampoules were dearated by bubbling nitrogen gas for 5-7 minutes, sealed and then subjected to gamma ray irradiation from ^{60}Co at a dose rate of 6.384 Gy/s. The grafted films thus obtained were removed and washed thoroughly with distilled water and then soaked overnight in distilled water to eliminate the residual monomer and homopolymer contained in the films. The films were then dried in an oven for 24 hours at 50-60°C and then weighted. The degree of grafting was calculated as follows:

$$\text{Degree of grafting}(\%) = (W_g - W_o/W_o) \times 100$$

Where, W_o and W_g represent, the weights of the initial and grafted films, respectively.

Synthesis of dyed graft copolymer films

Acrylic acid was thus grafted onto PFA films and the grafting percentage was fixed at about 44% by weight. These graft copolymer PFA-g-PAAc films were then immersed for about one minute in 60°C aqueous solution of (0.2, 0.4, 0.8 g/L) brilliant green (base) to produce PFABG film. These treated films were removed, washed by distilled water, dried and then investigated.

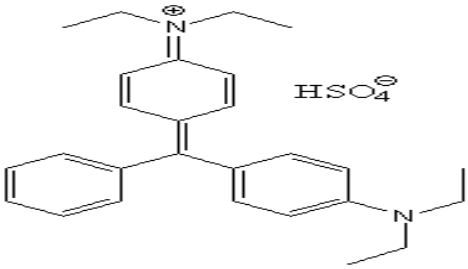
Reaction of dye with polymer

The radiolytic bleaching of aqueous solutions of triphenyl ethan dye (e.g. Brilliant Green) has been shown to have promise for dosimetry in the dose rate of 6.384 kGy/h (Abdel-Ghaffar et al, 2008) . In the present study, brilliant green, $D^+ HSO_4^-$, were reacted in a cationic exchange with PFA-g-PAAc films obtained by the direct reaction grafting method. In light of previous work (McLaughlin 1970), the proposed structure of dye with PFA-g-PAAc can be represented as follows:

$$[D^+]\,HSO_4^- + \underline{[\quad]\ COOH \quad COOH\ \ ]_n} \longrightarrow \underline{[\quad]\ COOD \quad COOD\ ]_n} + H_2SO_4$$

PFA-g-PAAc dyed PFA-g-PAAc

Where $[D^+]$, is the dye cation which have the following structure.



[Brilliant Green]$^+$

$C_{27}H_{33}N_2$

Apparatus

The absorption spectra of unirradiated and irradiated films were measured using UVIKON 860 spectrophotometer. The film thickness was measured using a Digitrix-Mark II thickness gauge (precession ±1µm). Irradiation was carried out with gamma radiation in the ^{60}Co gamma chamber 4000 Å (product of India). The absorbed dose rate in water was measured to be 3.75 kGy/h. The electronic equilibrium condition were maintained during irradiation, through keeping the films between two polystyrene slabs of 3 mm thickness. The dyed grafted PFA films were conditioned in a glove box in air at 33±2% relative humidity and at a temperature of 25±2 ^{o}C before being used. The surface topology of the prepared copolymer, (PVA-g-PAAc) and its modified copolymer with BG, (PVA-g-PAAc-BG) was measured with JEOL JSM-5400, Japan at 20 kv. The surfaces of the samples were sputter-coated with gold for 3 min.

Results and discussion

Absorption spectra

The absorption spectra of PFABG films before and after irradiation are shown in **Fig. (1)**. The absorption spectrum of unirradiated film shows an absorption band in the visible region peaking at 633 nm. The absorption band at 633 nm arise from excitation of an electron from the non-bonding molecular orbitals (NBMO) to the lowest antibonding orbitals, (n $\rightarrow$ π* transition). It obvious that the amplitudes

of all absorption bands in the visible spectrum decrease gradually with the increase of the dose of gamma-ray photons.

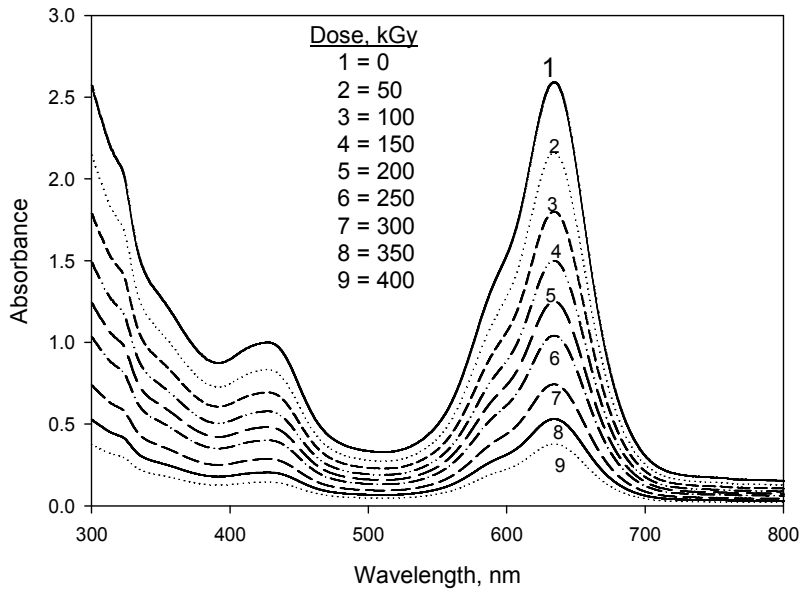


Fig.(1) The absorption spectra of PFABG films unirradiated and irradiated to different absorbed doses

Response curves

Fig. (2) show the change of ($\Delta A/A_o$) values at 633 nm as a function of absorbed dose ($\Delta A = A_o - A_i$, where A_o and A_i are the absorbances of the film before and after irradiation, respectively). The dose response curves of three films containing different concentrations of dye (C_1= 0.2, C_2= 0.4, C_3= 0.8 g/L). Linear relationships were obtained for PFABG film throughout absorbed dose range up to 400 kGy.

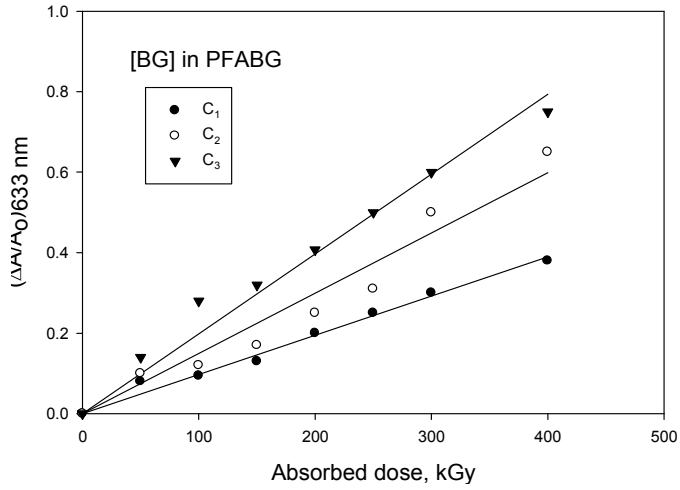


Fig. (2): Change of absorbance at 633 nm as a function of absorbed dose of PFABG films with different concentrations of dye (BG).

Expressions for these three lines may be demonstrated by the following relationships:

$$D = 991.3\ (\Delta A/A_o) \qquad \text{when, } [BG] = C_1$$

$$D = 690.4\ (\Delta A/A_o) \qquad \text{when, } [BG] = C_2$$

$$D = 501.5\ (\Delta A/A_o) \qquad \text{when, } [BG] = C_3$$

Where, D is the absorbed dose in kGy

The above relations help in determination of absorbed dose corresponding to a radiation induced change in absorbance of these films. The use of these three relationships is restricted to the dose range up to 400 kGy.

Humidity during irradiation

To investigate the humidity effects during irradiation of PFABG film, the film was irradiated to a dose of 150 kGy at different relative humidities (RH). These irradiations were made at 25±2°C, while the films were suspended over various saturated salt solutions in an enclosed jar, except for the two extreme values of relative humidities. The 0% RH value was made with films suspended over dried silica gel and 100% RH was made with films suspended over water. **Fig. (3)** shows the variation in response ($\Delta A/A_o$) as a function of percentage RH during irradiation relative to that at 54%. It was found that, for these films

there is no appreciable effect in the range of relative humidity RH (11-54%), although the response show somewhat different sensitivity at both higher and lower humidities.

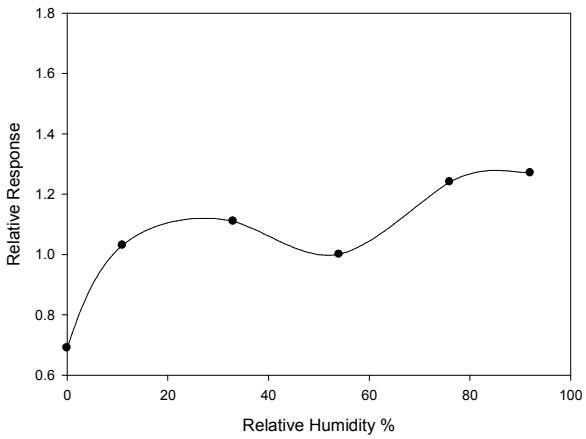


Fig. (3): Variation of relative response of PFABG films (at 633 nm) as a function of relative humidity during irradiation.

Shelf-life

Pre-irradiation stability of films were made by storing films in the dark and under laboratory fluorescent lights at ambient temperature (25˚C). The films were readout spectrophotometrically at different times during the pre-irradiation storage period of 30 days, as shown in **Fig. (4).** It can be seen that the color decreases slightly in the first week and tend to be stable to the end of the storage period.

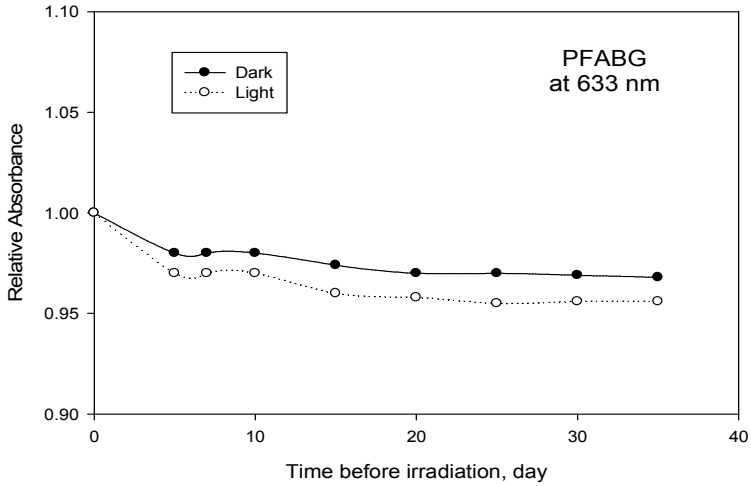


Fig.(4) Pre-irradiation stability of PFABG film stored under different storage conditions

Post-irradiation stability

The post-irradiation stability of PFABG films irradiated to 150 kGy is investigated by storing them in the dark and under laboratory fluorescent light at room temperature. The absorbance of these films was measured at 633 nm at different intervals of time during the post-irradiation storage period of 30 days, as shown in **Fig. (5).** The films show good stability, but we have to left films 7 days for stability requirements. The response of films stored in light decreases gradually with about 10% during the first week and tends to be stable to the end of the storage period. On the other hand, the film stored in dark shows excellent stability overall the storage period.

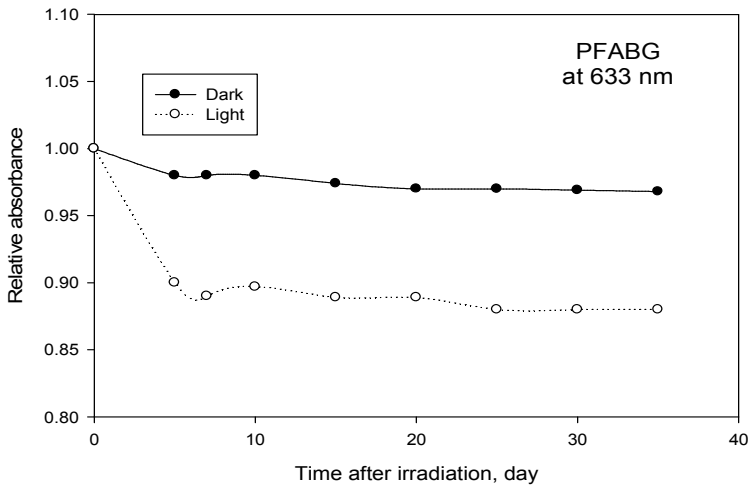
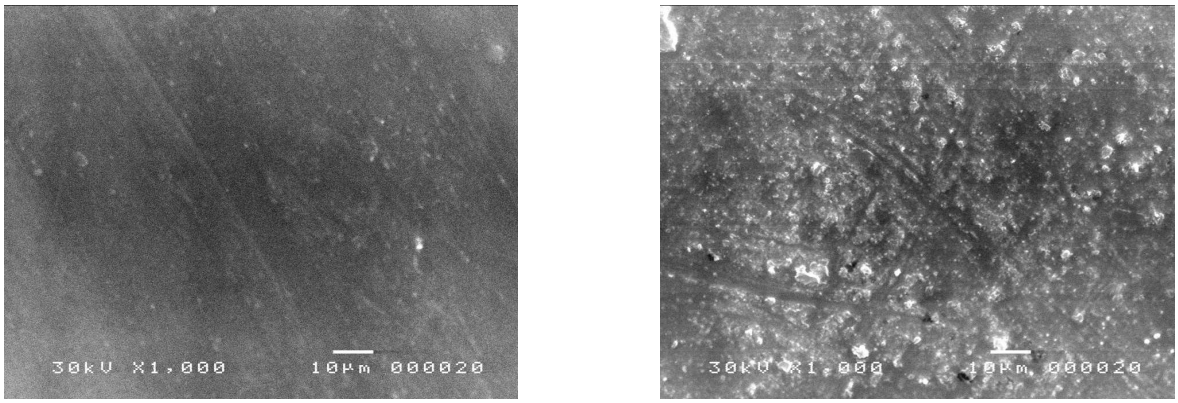


Fig. (5). Post–irradiation stability of TBPE/PVA films stored in dark and light at room temperature.



(a) (b)

Fig. (6). SEM phrlographs of (a) PFA-g-PAAc films and (b) PFA-g-PAAc-BG films

To investigate the effect of dyes on the surface of the grafred films, the morphological features of grafted FPA-g-PAAc films and those adsorbed dye were studied using SEM in **Fig. (6).** In Fig. (6 a) it was found that the surface of the grafted film is smooth, while Fig. (6 b) shows that the surface of the grafted films which reacted dyes became rough. This Roughness is a result of adsorption of (dye) molecules on the surface of the grafted films.

Conclusion

This approach for producing dyed plastic film dosimeters by graft polymerization has proved to be quite successful. The results indicate that the dye (BG) has a fairly uniform distribution within the plastic films. The responses of these films are independent on thickness variations and have linear relations between absorbed dose and the quotient of the change in absorbance and the absorbance before irradiation, $\Delta A/A_o$.

The response of PFABG film have negligible humidity effects in the range of 11%-54% RH. PFABG film has very good post-irradiation stability in dark while in light it gives a decrease in absorbance of about 8% within the first week of storage and tends to be stable to the end of the 30-day storage period.

It is possible for this film to be produced in large quantities and inexpensively which make it suitable for high-dose photon applications as routine dosimeters for radiation processing.

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