Spectroscopic and thermal degradation studies of polystyrene grafting onto poly(tetrafluoroethylene-co-hexafluoropropylene) films via electron-beam irradiation

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1. Introduction

Graft polymerization by high-energy irradiation such as electron beam (E-beam), gamma ray (γ-ray) or swift heavy ion irradiation is an effective method for incorporating desirable functionalities into an inert polymeric substrate [1–6]. Among these methods, E-beam radiation is a low-cost process due to its high production rate and high power efficiency. Moreover the E-beam method can be used to diversify the properties of a polymer via a grafting process with controlled dosages and usage of functional monomers [7].

Over the past few decades E-beam irradiation graft polymerization has received increasing attention as a method for producing high-performance chemically active polymer materials for adsorption and separation processes. Previous studies have examined a range of commercial polymers available in different forms such as films, fibers, resins, textiles, and powders [5,6]. Various approaches have been developed to prepare polymeric absorbent materials using E-beam irradiation: (1) direct graft polymerization of vinyl monomers containing desirable chemically active functional groups, (2) graft copolymerization of different monomers onto a polymer backbone, and (3) chemical modification of a grafted polymer after grafting of vinyl monomers onto a polymeric substrate [2–4,8–10]. Because of the limited number of vinyl monomers with functional groups available, the latter two approaches can be considered the most promising [11].

Fluorinated polymers are widely used as E-beam irradiated graft polymerization substrates because of their advantageous properties, which include good mechanical properties, high thermal stability, excellent chemical resistance, and a low friction coefficient [12]. In addition, because these polymers are sensitive to radiation, E-beam irradiation can be used to graft functional vinyl monomers onto their main chains. Several types of fluorinated polymer, including poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) [13–15], poly(tetrafluoroethylene) (PTFE) [16,17], and poly(ethylene-co-tetrathylene) (ETFE) [18] have been investigated using FTIR-ATR spectroscopy, Raman Spectroscopy and TGA. Our results indicated that PS graft formation involved the removal of HF after C–C main chain scission, leading to the formation of an unsaturated structure. When heated, the PS-grafted FEP films underwent two-step thermal degradation, independent of the degree of grafting. The two degradation steps were assigned to the degradation of the PS grafts and the FEP matrix. Sulfonation of the PS-grafted FEP films was found to give rise to para-disubstituted sulfonic acid groups. The PSS-grafted FEP films were found to undergo a three-step thermal degradation, independent of the degree of sulfonation. The three degradation steps were assigned to removal of water molecules hydrogen bonded to the sulfonic acid groups, and the degradation of the PSS grafts and FEP matrix.

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investigated as substrates for E-beam irradiation graft polymerization. Among the fluorinated polymers studied to date, FEP exhibits good radiation stability, and E-beam irradiation grafting of monomers onto FEP films has been used to manufacture several kinds of membranes for applications such as cation-exchange membranes, ion-exchange membranes and polymer electrolyte membranes.

E-beam irradiation induces radical formation in the surface layer of fluorinated polymer samples. Many research groups have attempted to understand the mechanism of radical formation in, and grafting onto, fluorinated polymer substrates [13–18]. The E-beam irradiation induced grafting of styrene monomers onto fluorinated polymer films has been reported [13–18]. However, data on the physical and chemical properties of polystyrene (PS) grafted onto fluorinated polymer substrates are scarce, and little is known regarding the dependence of these properties on the degree of grafting and sulfonation [19]. Thus, studies are needed to elucidate the mechanism of E-beam irradiation induced grafting onto, and the chemical modification of, fluorinated polymer films, as well as the physical properties of the resulting materials.

In the present study, we therefore examined the E-beam irradiation grafting polymerization of styrene monomers onto a film of the fluorinated polymer FEP. We used FTIR-ATR spectroscopy and TGA to investigate the grafting of PS and sulfonated PS onto FEP films (see Scheme 1) via E-beam irradiation grafting polymerization. In particular, we sought to understand the grafting mechanism and the dependence of the thermal properties on the degrees of grafting and sulfonation.

2. Experimental

2.1. Materials

FEP film with a thickness of 125 μm was purchased from Dupont Co., and styrene monomer of reagent grade (Aldrich Co.) was used without further purification. The chlorosulfonic acid and dichloromethane used for sulfonation were also of reagent grade (Kanto Chemical), and were used without further purification.

2.2. Grafting of styrene monomers onto FEP film

The FEP film was cut into a piece of dimensions 15 mm × 40 mm and cleaned by immersion in acetone for 24 h, after which it was dried at 80 °C for several hours. The cleaned FEP film was then placed in a glass reactor filled with styrene monomer to a depth of less than 2 mm, where a 2 mm depth of styrene is approximately equal to the effective penetration depth for 0.7 MeV energy [20,21]. The electron beam was irradiated onto both the styrene and the FEP film, and styrene was grafted onto the FEP film in a dry oven at 60 °C. The electron beam accelerator used has a maximum beam energy of 0.7 MeV and a maximum beam current of 35 mA [ELV-0.5, Budker Institute of Nuclear Physics (BINP), Russia]. The grafted FEP film was boiled in toluene solution for 2 h to remove ungrafted polystyrene, after which it was washed several times in cold toluene, and finally dried at 80 °C for 8 h. The degree of grafting was estimated by measuring the difference in weight between the samples before and after grafting:

\[
\text{Degree of grafting(\%) = } \left( \frac{W_g - W_o}{W_o} \right) \times 100
\]

where \(W_g\) and \(W_o\) are the weights of the grafted film and the virgin film, respectively.

2.3. Sulfonation of the grafted FEP film

The polystyrene grafted FEP films were sulfonated by boiling the film with 0.2 M chlorosulfonic acid diluted in dichloromethane at 60 °C for 8 h in a glass flask with a condenser. After sulfonation was completed, the film was hydrated by washing several times with distilled water, and then it was stored in deionized water. The degree of sulfonation was estimated by measuring the difference in weight between the samples before and after sulfonation:

\[
\text{Degree of sulfonation (\%) = } \left( \frac{W_s - W_g}{W_g} \right) \times 100
\]

where \(W_s\) and \(W_g\) are the weights of the grafted and sulfonated films, respectively.

2.4. Measurements

FTIR spectroscopic measurements were carried out on a BOMEM DA8 FTIR spectrometer equipped with a Diamond ATR system (Harrick Scientific). IR spectra were recorded at 4 cm\(^{-1}\) resolution with a liquid nitrogen cooled mercury cadmium telluride detector under vacuum. Raman spectra were collected using a Renishaw Raman microscope consisting of an air-cooled charge-coupled device (CCD) detector, and an argon ion laser operating at 514 nm. Thermal degradation behavior was investigated with a ramping rate of 10.0 K/min under a nitrogen atmosphere using a thermal analyzer (Model TG/DTA-6300, Seiko, Japan).

3. Results and discussion

3.1. Grafted films

Styrene-grafted FEP films with various degrees of grafting were prepared by the simultaneous E-beam irradiation method. The degree of grafting could be controlled by varying the E-beam energy dose at 60 °C. Estimated degrees of grafting were 20, 50, and 70%, respectively, depending on the E-beam irradiation dose.

Fig. 1 shows the FTIR spectra of the virgin film and grafted FEP films. The band at 982 cm\(^{-1}\) derives from the C–F stretching vibration of the CF\(_2\) group [22,23]. The C–F stretching vibration of the CF\(_2\) group appears in the region 1300–1100 cm\(^{-1}\), as shown in Fig. 1(a) [24,25]. After irradiation, bands characteristic of PS were observed, indicating that PS grafts had formed. The asymmetric and symmetric CH\(_2\) stretching vibrations in the PS groups were...
detected at 2924 and 2850 cm\(^{-1}\), respectively. The pairs of bands at 1602 and 1583 cm\(^{-1}\) and at 1492 and 1452 cm\(^{-1}\) are due to the quadrant stretching vibration and semicircular stretching vibration of the phenyl ring in the PS groups, respectively [26]. In addition, a new band is observed at 1630 cm\(^{-1}\), which is assigned to the C–C stretching vibration. This result indicates the formation of carbon double bonds in the PS-grafted FEP films. However, the spectra contained no features indicating the formation of C–C sp\(^{3}\) stretches.
groups in the films [32]. However, the second and third breaking of hydrogen bonds between water molecules and PSS showed three-step thermal degradation behavior in which the PS grafts underwent thermal degradation first, followed by degradation of the FEP film; this behavior was independent of the degree of grafting.

Fig. 4. FTIR spectra of sulfonated PS-grafted FEP films with various degrees of sulfonation: (a) 19.38%, (b) 49.92%, and (c) 69.49%.

Sulfonation of the PS-grafted FEP films gave rise to para-disubstituted sulfonic acid. The sulfonated PS-grafted FEP films showed three-step thermal degradation behavior in which water hydrogen bonded to the sulfonic acid groups was removed first, followed by degradation of the PSS groups and then of the FEP matrix; this behavior was independent of the degree of sulfonation.

4. Conclusions

We have prepared PS-grafted FEP films with different degrees of grafting and sulfonated PS-grafted FEP films using an E-beam irradiation method. We used FTIR-ATR spectroscopy, Raman spectroscopy and TGA to investigate the chemical formation of PS grafts on the FEP films after E-beam irradiation and the thermal properties of the grafted and ungrafted films. In addition, we determined the positions at which sulfonic acid groups were substituted in sulfonated PS-grafted FEP films and the thermal properties of these films by using FTIR-ATR spectroscopy and TGA. Our findings showed that the degree of grafting depended on the E-beam irradiation dose.

In the grafting of PS onto FEP films, the styrene grafting reaction on the E-beam irradiated FEP films involves a dehydrofluorination reaction in which HF is removed after C–C main chain scission, which leads to the formation of an unsaturated structure. When the PS-grafted FEP films were heated, they exhibited two-step thermal degradation behavior in which the PS grafts underwent thermal degradation first, followed by degradation of the FEP film; this behavior was independent of the degree of grafting.

Fig. 5. TGA thermograms of sulfonated PS-grafted FEP films with various degrees of sulfonation: (a) 19.38%, (b) 49.92%, and (c) 69.49%.

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