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Positron annihilation spectroscopic studies of fluorinated ethylene propylene copolymer-*g*-polystyrene

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Abstract

Polystyrene was grafted onto FEP by simultaneous irradiation using a ^{60}Co γ-irradiator. Graft copolymers of different degree of grafting were obtained by varying the irradiation dose. Positron lifetime measurements were carried out on FEP and the grafted samples. A systematic decrease in *o*-Ps lifetime and intensity with grafting is seen indicating a decrease in pore size as well as total free volume fraction. Temperature dependent (95–250 K) *S*-parameter measurements in FEP showed saturation of free volume fraction at temperatures corresponding to the β-relaxation, the onset of which is seen at 150 K. Coincidence Doppler broadening results indicate increase in specific volume in the crystalline region of the polymer. Dynamic mechanical analysis (DMA) showed that tan δ value for β-relaxation of the samples decreased with increasing graft percentage. The results are discussed.

Keywords: Dynamic mechanic analysis; Free volume; Molecular motion

1. Introduction

Radiation induced graft copolymerization of monomers onto fluorine containing polymers has been widely studied to produce membranes for various purposes, such as in separation science and electrochemical applications [1–6]. Grafting of vinyl and acrylic monomers onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films have been studied by several researchers [7–13]. Radiation induced graft copolymerization introduces, structural changes in the starting polymer matrix. This leads to significant changes in the microstructure and morphology of the membranes that affect the overall membrane properties. The incorporation of side chain grafts, represented by the degree of grafting, varies with the reaction parameters, which influences the membrane properties to a large extent. The incorporation of side chain grafts exerts a dilution effect on the grafted film by increasing the amorphous content at the expense of crystallinity of the semi crystalline base fluoropolymers. The structure and the physical properties of the matrix change drastically during the preparative stages. Hence thorough characterization of the membrane in each stage is of paramount importance. The structural changes in the preparative stages of the membrane have been exhaustively studied [14–16]. Gupta et al. [17] have investigated the structural changes on proton exchange membranes, obtained by radiation grafting of styrene onto FEP films and subsequent sulfonation. They have attributed the decrease in the crystallinity of the grafted samples to cumulative effect of the decrease in the crystalline/amorphous ratio due to incorporation of amorphous side chain grafts.

Positron annihilation lifetime spectroscopy (PALS) has found increasing applications in studying molecular arrangement of polymeric materials [18–20]. In polymers a large fraction of positrons form positronium atom (Ps), the bound state of a positron and an electron. The positronium can be either in *para* (spin 0) or *ortho* (spin 1) state. The positron annihilation studies rely on the inherent localization of positron/positronium in defects or free volumes in solids and

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subsequent annihilation with electrons from the surroundings. Both static as well as dynamic free volume holes due to molecular motion can be probed provided the time scale for chain movement is in the order of nanosecond, which is the lifetime of *ortho*-positronium (*o*-Ps). The *o*-Ps lifetime has a strong correlation with the size of the free volume. The annihilation of *o*-Ps in the spherical free volume hole can be described by simple quantum mechanical model of spherical potential well with an electron layer thickness of ΔR. The semi empirical relation between the radius of the free volume hole, R and *o*-Ps lifetime is given by [19]:

$$\frac{1}{\tau_3} = \lambda_3\left(\text{ns}^{-1}\right) = 2\left(1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right) \qquad (1)$$

where $R_0 = R + \Delta R$ and $\Delta R = 1.66$ Å. The product of the hole volume and the *o*-Ps intensity is proportional to the free volume fraction for chemically similar samples.

In the present manuscript PALS is used to characterize FEP and FEP-*g*-PS samples. The results have been correlated with tan δ for β-relaxation of the samples obtained from dynamic mechanical analysis. There seems to be a tangible correlation between the PALS parameters and DMA results. In addition, temperature dependent Doppler broadened annihilation measurements have been carried out from 95–250 K to examine the evolution of free volume across the β-transition in virgin FEP sample.

2. Experimental

Teflon-FEP film (75 μm thickness) was obtained from Du Pont, USA. Styrene (E-Merck) was freshly distilled before use.

2.1. Graft copolymerization

FEP film (5 × 5 cm) with 75 μm thickness was washed with acetone and dried in oven at 50 °C before use. Weighed amount of FEP in varied percentage of monomer (10–35%) in benzene was irradiated for different period at a dose rate of 4.92 kGy/h to obtain grafted films with varied degree of grafting. Irradiation was carried out in a gamma chamber 5000 provided by BRIT, India. The grafted film was freed from homopolymer by Soxhlet extraction with toluene and dried to constant weight. Grafting percent was determined from the weight change between original and grafted films. The virgin sample and representative grafted samples were characterized by XRD technique.

2.2. Dynamic mechanical analysis

Measurement of dynamic mechanical properties for both FEP and FEP-*g*-PS samples was conducted at a frequency of 1 Hz and at a heating rate of 5 °C/min on a Rheometric Scientific DMTA. The temperature range of scanning was from 153 to 423 K.

2.3. Positron annihilation measurements

Positron annihilation lifetime measurements of the membrane samples were performed with a ^{22}Na positron source in sandwich configuration using a fast–fast coincidence spectrometer. A stack of six films was used on either side of the source to ensure complete annihilation of positrons in the sample. The time calibration of MCA was 50 ps/channel. The time resolution of the positron lifetime spectrometer measured for γ-ray of ^{60}Co was 300 ps. The lifetime spectra, typically with 10^6 counts, were analyzed using PATFIT program [21].

For temperature dependent studies on FEP, the sample in sandwich geometry with positron source was mounted on closed cycle helium refrigerator (APD Cryogenics). Simple Doppler broadening spectra were acquired in the range of 70–250 K using 10% HPGe with energy resolution of 2.1 keV at 1333 keV γ-ray of ^{60}Co. The positron lifetime and two-detector coincidence Doppler broadening (CDB) spectra were acquired at few temperatures in the range of 70–250 K. For CDB measurements two HPGe detectors located at an angle of 180° relative to each other were used. The difference in energies of the two annihilation γ-rays i.e., $E_1 - E_2 = \Delta E$, is expressed as cP_L, where P_L is the longitudinal momentum component of the positron–electron and c is the velocity of light. The momentum distribution (ΔE) spectra were obtained by taking the coincidence events between 1022 ± 2.8 keV in the $E_1 + E_2$ axis. The details of the CDB system are described elsewhere [22]. Each CDB spectrum was normalized to unit area and divided by a reference spectrum (silicon) to get the ratio curve.

3. Result and discussion

FEP is a random copolymer of tetrafluorethylene and hexafluoropropylene. It has a structure similar to polytetrafluoroethylene except that a perfluromethyl group replaces an occasional fluorine atom. Fig. 1a shows the effect of total dose on grafting percentage of styrene onto FEP. It is seen that the grafting percentage varies linearly with increasing total dose of exposure. Similar trends in grafting results have been reported earlier [9]. The XRD pattern of virgin and grafted samples are shown in Fig. 1b. The XRD pattern was analyzed by fitting the individual peaks (crystalline and amorphous as the case may be) and the fractional area under the crystalline peak was calculated. The two broad amorphous peaks and the narrow crystalline peak used are indicated in Fig. 1b. The fractional area under the crystalline peak were seen to be 17.6, 17.4 and 18.3% for virgin FEP, 5.2 and 16% grafted samples, respectively. This indicates that there is no significant change in crystallinity upon grafting.

Fig. 2 represents the temperature dependence of tan δ for FEP and FEP-*g*-PS samples. It is seen that FEP has two transitions at 153 and 363 K which may be attributed to β-relaxation and α-relaxation, respectively. Dynamic mechanical analysis of FEP with varying content of hexafluoropropylene has been reported by Sacher [23]. According to Sacher, rise in tan δ at the lowest temperature is an indication of additional peak below