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DBAR and DSC Study on UV Irradiated PTFE

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Abstract. Polytetrafluoroethylene (PTFE) films were irradiated with ultra-violet (UV) radiation (254 nm) and studied with respect to UV exposure time using Doppler Broadening of Annihilation Radiation (DBAR) and Differential Scanning Calorimetry (DSC). There is degradation of PTFE when exposed to UV radiation, and this affects the microstructure of the sample. The analysis of DBAR spectra of UV irradiated PTFE yields S and W parameters, which show significant variation with UV exposure time when compared to DSC data. The results are discussed in this paper.

Introduction

Polytetrafluoroethylene (PTFE) is a semi-crystalline polymer which is commercially known as teflon. It is a long chain symmetric linear polymer which can fit into a structure with a high degree of crystallinity which, however, depends on the thermal history of the sample. Although PTFE has inert chemical nature, a wide working range of temperature (-100^0C to 300^0C) and good thermal stability, it undergoes degradation when subjected to irradiation with ionizing radiation as well as ultra violet (UV) radiation. The heterogeneous micro-structure (i.e., existence of crystalline and amorphous domains) results in localized degradation of PTFE. It depends on the parameters like degree of crystallinity and the average size of crystallites (lamellar thickness of the crystalline regions). UV irradiation of PTFE results in chemical modifications of the surface due to molecular chain scission caused by the absorption of incident energy and results in chemical functionalization of the surface, which could lead to applications [1]. This modification converts the chemically inert sample (PTFE) into one wherein the surface is amenable to chemical modification. However, a survey of literature reveals that there is carbonization of randomly distributed regions of the sample due to multiple reflections of the ultra violet light, the crystalline lamellae acting as mirrors, thereby increasing the path length of radiation in the sample and consequently improving the probability of C-F and C-C chain scission, followed by carbonization takes place; these regions absorb UV light strongly leading to further degradation of the sample [2].

Doppler Broadening of Annihilation Radiation (DBAR) is one of the techniques of Positron Annihilation Spectroscopy (PAS) which enables a study of micro structure of the polymeric material, provided it is complemented by other techniques like Differential Scanning Calorimetry (DSC). DSC is a quantitative technique of thermal analysis which enables the determination of degree of crystallinity and the transition temperatures of the sample at different UV irradiation exposure times.

Experimental

PTFE films were irradiated under UV light (254 nm), with exposure time varying from 30 minutes up to 612 minutes. These irradiated films were then used to obtain DSC scans, with a heating rate of 10^0C/min in nitrogen atmosphere; the melting temperature and the heat of fusion were determined by DSC (TA instruments Q20 V24.10 Build 122; 1mg to 3mg of the PTFE samples were taken in Al pans to record the spectra from temperature 40^0C to 400^0C. For the study of DBAR, a high resolution hyper pure germanium detector (HPGe) was used to record the energy spectrum of annihilation gamma rays from sample [3]. Sodium-22 (Na^{22}) of activity 300kBq was used as the positron source, which after deposition on thin kapton foil was stacked between the PTFE films (1mm) thickness. This source-sample sandwich assembly was kept at 7cm away from the beryllium window of HPGe detector. The line parameters namely S and W parameter were extracted from the energy spectrum using a self- designed program.

Results and Discussion

DSC scans of the PTFE samples are shown in figure (1), for different UV exposure time. The modifications in micro-structure of PTFE due to UV irradiation are reflected in variation of DBAR parameter, as shown in

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figure (2). The results extracted from the DSC spectra of UV irradiated PTFE are summarized in table (1). The DBAR spectrum was analyzed using line shape parameters , namely, S-parameter which can be defined as the ratio of area around 511 kilo-electron volt peak normalized over the total area and the W-parameter which can be defined as the normalized area under the tails.

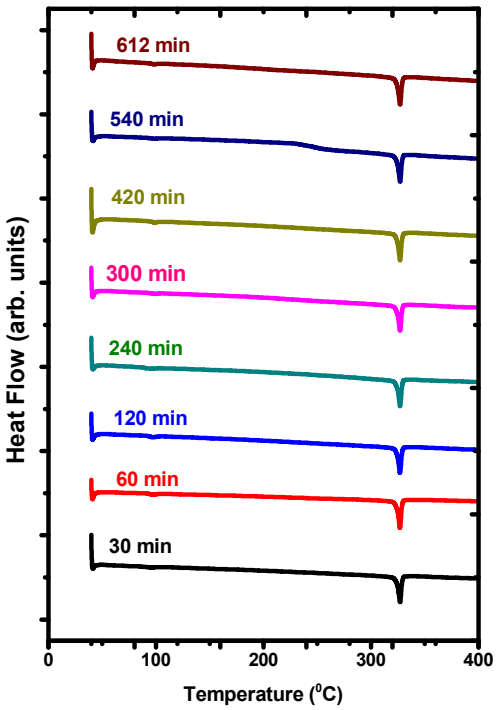

Fig. 1: DSC scans of PTFE irradiated with UV (254 nm) light for different exposure times.

From the DBAR results shown in figure (2), it can be noted that, with an increase in the UV exposure from 30 minutes to 612 minutes, the S-parameter initially increases significantly, followed by saturation. The reverse trend observed in W-parameter, as expected, since it corresponds to the longitudinal component of high momentum electrons with which the thermalized positrons annihilate in the PTFE sample.

It has been shown by work done earlier [2] that UV irradiation of semi-crystalline PTFE results in formation of localized regions of degradation leading to carbonization. The fact that it results in change in S-parameter implies that the UV irradiation at 254 nm affects the bulk of the sample, not just the surface. The DSC scans of UV irradiated PTFE also show undulations, which is interpreted as due to formation of chain fragments due to action of UV radiation (chain scission) on polymeric molecules of PTFE. However, there is not much change in the degree of crystallinity and melting temperature of the sample at different irradiation exposure times. This implies that DBAR is more sensitive than DSC in reflecting micro-structural changes in the sample.

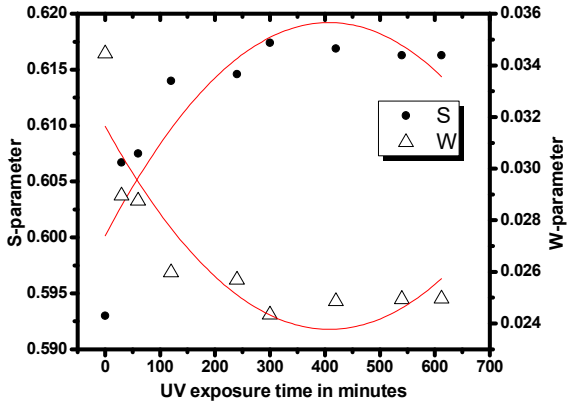

Fig. 2: S-parameter v/s UV exposure time for UV irradiated PTFE. The line drawn is to guide the eye.

Table 1. Results of DSC studies on UV irradiated PTFE.

UV exposure time (min)	Heat of Fusion $(\Delta H_f)_s$ (J/g)	Crystallinity (χ_c) (%)	Melting point (T_m) (°C)
30	14.35	36	326.96
60	15.78	40	327.00
120	13.9	35	326.99
240	14.92	38	327.08
300	14.03	35	327.06
420	14.71	38	327.03
540	14.54	37	327.10
612	15.32	39	327.08

Conclusion

UV exposed PTFE films were studied experimentally using DBAR and DSC. The analysis of DBAR spectra yielded the line shape parameters; S-parameter shows a increasing trend with increase in UV irradiation time at lower exposure times, indicating enhanced annihilation of positrons with low momentum electrons.

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