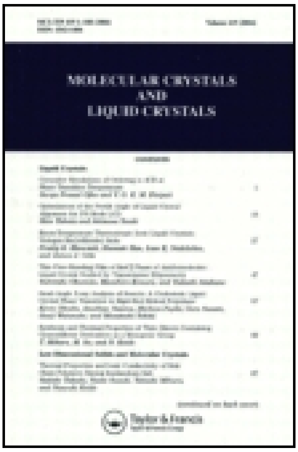

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Surface Modifications on Teflon FEP and Mylar C Induced by a Low Energy Electron Beam: A Raman and FTIR Spectroscopic Study

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Surface Modifications on Teflon FEP and Mylar C Induced by a Low Energy Electron Beam: a Raman and FTIR Spectroscopic Study

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The surface modifications induced on Teflon FEP and Mylar C polymer films by a low energy electron beam are probed using Raman and FTIR spectroscopy. The electron beam, which does not affect the Mylar C surface, may break the copolymer chain into its monomers degrading the Teflon FEP surface. For Mylar C the electron beam decreases the roughness of the polymer surface. This difference in behavior may explain recent results in which the surface modifications investigated by measuring the second crossover energy shift in the electronic emission curve differed for the two polymers (Chinaglia et al [1]). In addition, the Raman data showed no evidence of carbon formation for either polymer samples, which is explained by the fact that only a low energy electron beam is used.

Keywords: ***electron beam irradiation, Raman spectroscopy***

1. INTRODUCTION

Electron beam (EB) irradiation is used to modify polymers in a variety of ways and for several applications [2]. It may induce degradation, crosslinking, grafting, curing and polymerization [3], depending on the polymer chemical structures [4]. Irradiation for such applications is performed with high-energy electron beams, typically 0.5 – 2 MeV, and surface modifications may be assessed by a variety of techniques. Low energy electron beams, e.g. 0-50 keV, have also been employed over the years to electrically charge insulating polymers [5,6]. In such setups, the charging process is monitored by measuring the various currents involved, viz. the incident current, surface emission and the sample currents, in addition to the sample surface potential. This allows investigation into charge storage and transport in the polymer films [7]. Low energy beams have also been found to affect the surface properties of Teflon FEP and Mylar C (PET) [1], which were monitored by measuring the electronic emission curve of a sample exposed to irradiation. The emission curve is a plot of the ratio, σ, between the number of electrons emitted by the surface (secondary and backscattered) and the number of incident electrons versus the energy E of the incident beam. The results in [1] indicated that the emission curve shifted upon prolonged irradiation, but in opposite directions for Teflon FEP and Mylar C. The analysis of shifts in the electronic emission curve, however, cannot provide information on the type of chemical surface modification. In the present work, the fundamental vibrational techniques, infrared and Raman spectroscopies are used to probe structural and functional modifications at the molecular level, in order to investigate the differences in behavior for EB irradiated FEP and Mylar C.

2. EXPERIMENTAL DETAILS

Teflon FEP (25 μm thick) and Mylar C (PET) (23 μm thick), both from Dupont, with no previous surface treatment, were irradiated with electron beam energies of 2.1 keV and 1.2 keV, respectively. The samples were irradiated under vacuum (1×10^{-6} Torr) in a circular area of 3 cm of diameter. The beam current density was 1.43×10^{-8} A/cm^2. Under these conditions, the initially uncharged samples are rapidly negatively charged until the beam energy reaches the second crossover energy [8]. Since the second crossover energy for Teflon FEP is ca. 1850 eV the final sample surface potential is approximately –250 V, and the beam energy was changed to 1850 eV. The sample was continuously irradiated for 6 hours under these conditions. For Mylar C a similar procedure was used, but the second crossover energy is ca. 950 eV, thus leading to a negative sample surface potential of -250 V and a final beam energy of 950 eV. With this final beam energy, the Mylar C sample was irradiated for 8 hours. The inelastic Raman scattering (Stokes) spectra were obtained with a

Renishaw Research Raman Microscope System RM2000. The spectrum is recorded using a Peltier cooled (-70°C) CCD array. The Raman spectra were recorded at room temperature with ca. 4 cm^{-1} resolution. Owing to the high throughput of the instrument, low power lasers can be used at the sample (900 μW for the 633 nm laser line and 65 μW for the 780 nm laser line).

3. RESULTS AND DISCUSSION

The Raman spectra recorded using the 633 nm laser line for both the irradiated and non-irradiated Teflon samples are shown in Figure 1. The molecular structure of Teflon is also given in Figure 1. The center of the Raman bands, the full width at the half maximum (FWHM), the relative intensities calculated using a mixed Gaussian-Lorentz function, and the vibrational assignments of characteristic fundamentals are given in Table 1. The relative intensities of the C-F and C-C-C modes change markedly upon irradiation, which indicates that chemical changes have been induced. Crosslinking can be discarded since FTIR spectra (not shown) did not present any new vibrational band that could be attributed to crosslinking in the irradiated sample, which is consistent with the results by Lee et al [9]. Under identical experimental conditions, the Raman bands and the background signal are stronger for the irradiated Teflon. It is known that the Raman activity is increased with a higher degree of crystallinity in the polymer [10]. However, the FWHM is not smaller as it should be for a more crystalline sample. Besides, it is also known that copolymers are not easily crystallized since they contain two different monomers in the chain. The increase in background signal close to the laser line indicates that the Teflon surface may have its roughness increased due to the electron beam action. Therefore, the EB may be breaking the copolymer chain into its monomers, degrading the Teflon surface and increasing its roughness. We have tried to confirm this by measuring film roughness with atomic force microscopy (AFM). The rms roughness was 3.1 nm both before and after electron-beam irradiation, but an experimental artefact has caused the measurement for the non-irradiated sample to produce a higher roughness than the actual one. This is presently being checked. It is important to point out that different percentages of the laser power were used to ensure that the 633 nm laser line was not changing the sample. This was further confirmed by measuring the

Raman spectra with the 780 nm laser line, using energy densities at the sample even lower than that of 633 nm line (results not shown).

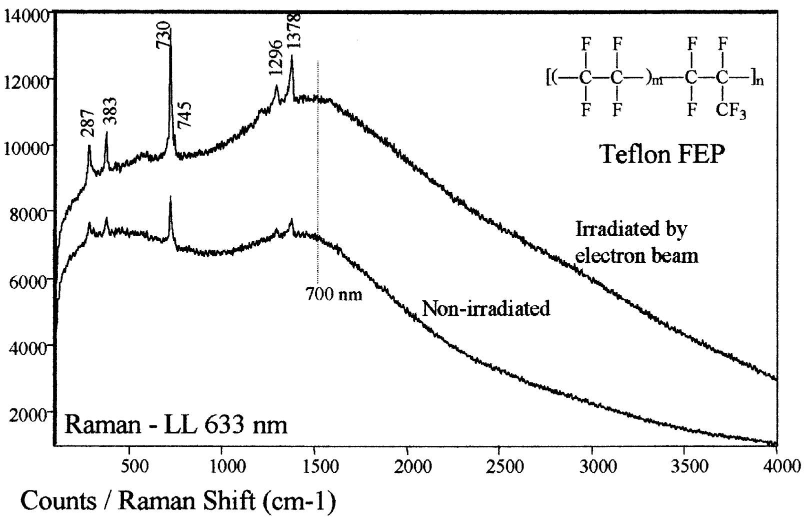

FIGURE 1: Raman spectra recorded with the 633 nm laser line for the irradiated and non-irradiated Teflon films.

Table 1: Center in cm^{-1}, Full Width at the Half Maximum in cm^{-1} (parenthesis), relative intensities (italic) and the assignments for the Raman bands of the Teflon film recorded with the 633 nm laser line.

Non-irradiated Teflon	Irradiated Teflon	Assignment
1376 (19) *42*	1376 (16) *19*	C-F
1297 (22) *18*	1294 (27) *9*	C-F
730 1(9) *50*	730 (8) *100*	C-C-C stret sym
384 (8) *100*	384 (9) *32*	C-C skel bending
291 (24) *89*	291 (16) *27*	C-C skel bending

Figure 2 shows the Raman spectra recorded with the 780 nm laser line for the irradiated and non-irradiated Mylar C samples, in addition to the polymer molecular structure. The Raman bands are similar in relative intensity and FWHM for both samples, suggesting that the electron beam does not induce chemical changes in the polymer chain. However, the background signal is stronger for the non-irradiated Mylar C, pointing to a smoother surface for the irradiated sample. Indeed, subsidiary AFM measurements showed that the rms roughness decreased from 1.7 nm to 1.1 nm after irradiation. These results are consistent with the work by Lee et al [9] who observed that upon electron irradiation Mylar retained the polymer backbone structure and that all polymers investigated by them showed smoother surfaces, except Teflon.

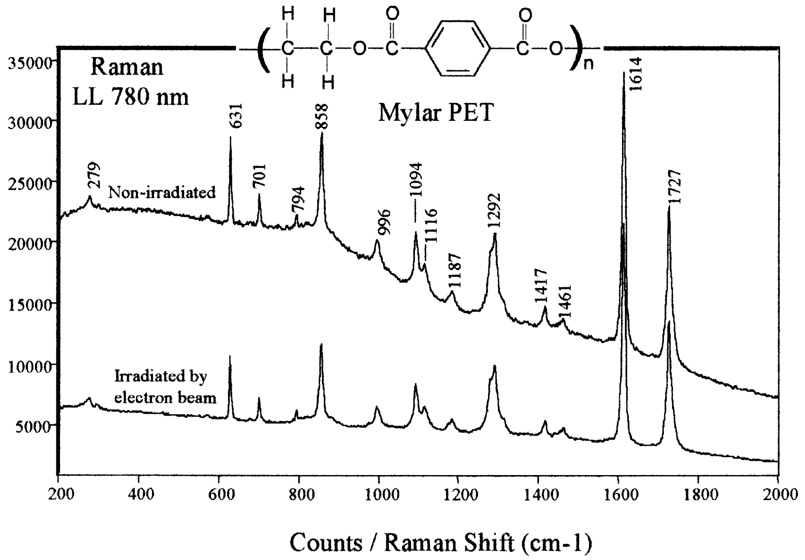

FIGURE 2: Raman spectra recorded with the 780 nm laser line for the irradiated and non-irradiated Mylar films.

Finally, no evidence of burned carbon was found for the irradiated Teflon FEP and Mylar C. That is to say, the electron beam does not produce any "degradation by burning" the polymer, probably because of the low energy of the beam. The burned carbon on the polymer surfaces could be identified by the appearance of a broad band at ca. 1500 cm^{-1} after irradiating the polymers with the electron beam.

CONCLUSIONS

Raman spectroscopy measurements have been used to probe surface modifications of Teflon FEP and Mylar C samples submitted to low-energy EB irradiation. Scissoring is observed in Teflon FEP, which is manifested in changes in the relative intensities of the C-F and C-C-C bands. For Mylar C, EB irradiation does not cause any chemical change in the polymer, but the background in the Raman signal is nevertheless affected because the sample surface becomes smoother, which was confirmed by AFM measurements.

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