

CHARACTERIZATION OF RADIATION CROSSLINKING DENSITY OF F-40

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ABSTRACT

In this paper, radiation-induced crosslinking mechanism and characterization of the crosslinking density of F-40 and F-4 by X-ray photoelectron spectroscopy (XPS) have been studied. The dose of gelation of F-40 obtained from XPS is 4.1×10^4 Gy. It is found that crosslinking density is the largest in the range of certain dose for F-40 and F-4.

INTRODUCTION

It has been known that the radiation dose of gelation for F-40 and F-4 cannot be obtained with gel content method^[1] since no solvent can be used for them, and thus their crosslinking density can hardly be characterized by this method. We had characterized the radiation crosslinking density of some soluble fluoropolymers by XPS^[2,3]. In this paper, the research work by XPS on crosslinked F-40 (copolymer of tetrafluoroethylene and ethylene) and F-4 (polytetrafluoroethylene), especially on the characterization of radiation crosslinking density with XPS has been investigated.

EXPERIMENTAL

Radiation

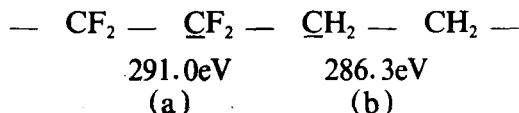
The glasstubes containing F-40 and F-4 samples were evacuated, and sealed under vacuum and irradiated in a ^{60}Co -Source.

Measurement of XPS

The spectra of irradiated samples were recorded on ESCA-650 B spectrometer with PAC-660 Computer Curve Resolver using $\text{MgK}\alpha$ 1,2 X-ray ($E_x = 1253.6\text{eV}$) as radiation source, with chamber pressure of 1.07×10^{-5} Pa and a FWHM of 1.2eV for $\text{Au}_{4f\ 7/2}$, and under the conditions employed in this investigation, the $\text{Au}_{4f\ 7/2}$ level of gold-plated sample was calibrated to that of pure gold, 83.8eV.

RESULTS AND DISCUSSION

Fig. 1 shows the spectra of the C_{1s} level of crosslinked and conventional F-40. From Fig. 1, we can see that there are photoelectron peaks at 291.2eV, 288.5eV, 286.0eV and 284.4eV in the spectra of C_{1s} for crosslinked F-40 and it shows that there are four kinds of carbon group. According to the results calculated by reference (4), we have known the peak position of the following groups:



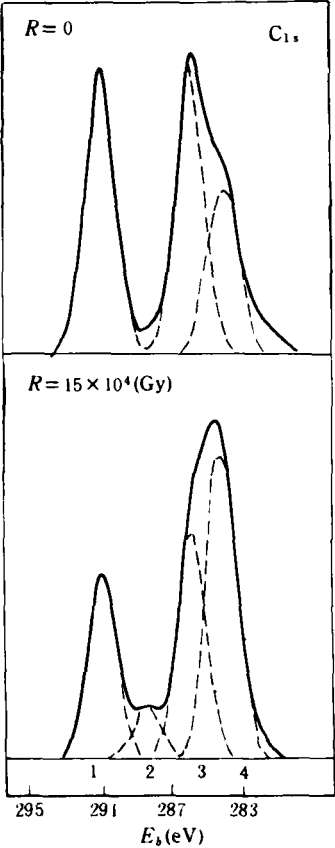
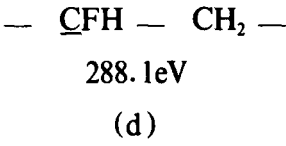
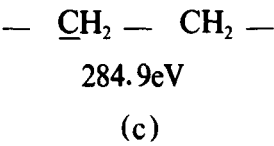


Fig.1 The ESCA spectrum of F-40

It may be considered that peaks 1, 3 and 4 in the spectra of C_{1s} for crosslinked F-40 (Fig.1) belong to a, b and c groups respectively and peak 2 belongs to the crosslinking group —CF—.

Clearly, during crosslinking, the defluorinated reaction occurred, which gives rise to the decrease of F/C (ratio of fluorine to carbon) for crosslinked sample. and therefore it is possible to find the relation between F/C and crosslinking density and to express the crosslinking density of F-40 with F/C. Fig.2 shows the spectra of the C_{1s} level of crosslinked and conventional F-4. From Fig. 2, it can be seen that the relative intensity of the photoelectron peak of the crosslinked F-4 at 292.4eV attributed to —CF₂—CF₂— ground⁴¹ is much lower than that of the conventional one. From this result, it has been shown that crosslinking of F-4 is carried out with defluorinating reaction because F-4 is a perfluoro-type polymer. In other words, the F/C of the sample decreases with the increasing of the crosslinking density.

Table 1 shows that the F/C of F-40 varies with the radiation dose (R).

Table 1 Variation of F/C of F-40 with radiation dose

R (10 ⁴ GY)	F/C
0	0.82
3.30	0.78
5.34	0.81
7.40	0.51
12.1	0.10
15.0	0.54
20.0	0.80
30.0	0.74
54.4	0.72

From Table 1, it can be seen that F/C of F-40 is the smallest, and thus the crosslinking density is the largest in the range of certain dose, and crosslinking density become smaller when the radiation dose is increased continually. This shows that F-40 is not like the other polymers, whose crosslinking density increases with the increasing of radiation dose. We have also found this phenomenon in the radiation crosslinking of polytetrafluoroethylene and the main reason of this phenomenon have not been known yet.

As stated above, F/C of F-40 and F-4 are in relationship with the crosslinking density, and therefore we may express their crosslinking density with F/C .

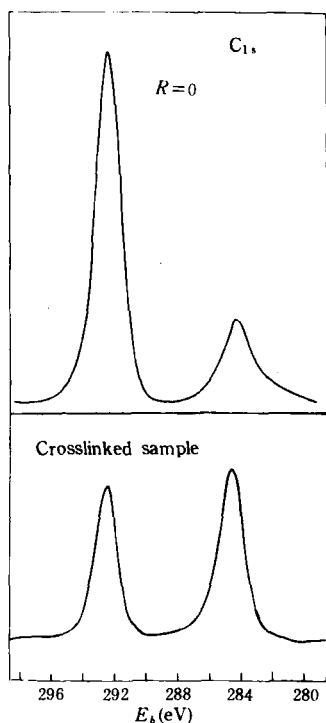


Fig. 2 The ESCA spectrum of F-4.

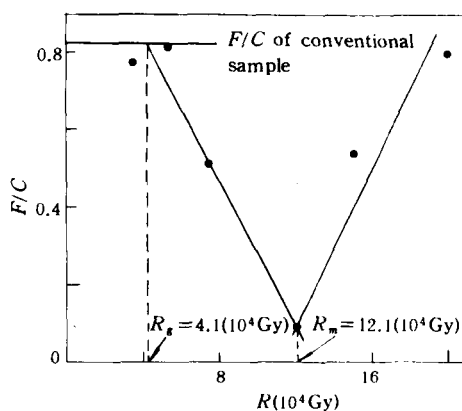


Fig. 3 The relationship between F/C and R of F-40

F/C of crosslinked sample of F-40 was plotted against R and two straight lines were obtained (shown in Fig. 3) and then make a straight line parallel to the R axis using F/C of the conventional sample as the intercept at the F/C ordinate. The radiation dose corresponding to the intercrossing point of this line and the first one of the two lines may be considered as the radiation dose of gelation (R_g), and the radiation dose corresponding to the intercrossing point of the above-mentioned two straight lines may be considered as the dose of the largest crosslinking density (R_m) (Fig. 3). For F-40, R_g and R_m value obtained from XPS are $4.1 \times 10^4 Gy$ and $12.1 \times 10^4 Gy$ respectively.

From Fig. 3, it is known that F/C obviously increases after the dose of the largest crosslinking density. This means that the fracture occurs, and we also found the similar phenomenon in the crosslinking of polytetrafluoroethylene.

Keywords:

XPS; The dose of gelation; F-40 ; F-4; Radiation crosslinking

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