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The radiation stability of perfluoroalkoxy resin

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By examining the changes in melting temperature, heat of fusion, tensile strength and ultimate elongation at 150°C, and weight loss, radiation effects on perfluoroalkoxy resins (PFA) were investigated. The results show that at the temperatures used here the predominant effect caused by radiation on PFA is degradation of the molecular weight. The radiation stability is much better than that of polytetrafluoroethylene, however.

Perfluoroalkoxy resins (PFA) are a class of melt-processable fluoroplastics in which perfluoroalkyl side-chains are connected to the carbon–fluorine backbone of the polymer through a flexible oxygen linkage. In a copolymer of tetrafluoroethylene with a few perfluoroalkoxy units, most of the structural units in the polymer are the same as those of polytetrafluoroethylene, which is well-known to be a typical radiation-degradable polymer. Therefore, the introduction of a few perfluoroalkoxy units to the backbone chains of the polymer which lowers the melting point and reduces the crystallinity is expected to affect its radiation stability. In this work radiation-induced changes in melting point, heat of fusion, high-temperature tensile strength and elongation, and weight loss of PFA irradiated at 20 and 230°C were examined. The results reveal that at the temperatures examined in this work the predominant effects caused by high-energy radiation are the scission of polymer chains as shown by the decrease in high-temperature strength and ultimate elongation. In comparison with polytetrafluoroethylene(PTFE), however, the radiation stability of PFA was observed to be greatly improved.

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EXPERIMENTAL

The PFA sample used in this work was a copolymer of tetrafluoroethylene with perfluoro vinyl-propyl ether from the Du Pont Company. Sheet samples were sealed into glass tubes at 0·2 Pa before irradiation.

Irradiation was carried out with a 70 000 Ci ^{60}Co source. The dose rate used was 1 Mrad/h.

Differential scanning calorimetry (DSC) measurements were made on a Perkin–Elmer model DSC-7 differential scanning calorimeter at heating rate of 10°C/min. High-temperature tensile strength and elongation were measured on an Instron-1121 tensile testing machine at strain rate of 50 mm/min and 150°C.

RESULTS AND DISCUSSION

Two irradiation temperatures, 20 and 230°C were selected in this work to examine the effect of radiation on some properties of PFA. The results are shown in Table 1. For samples irradiated at both temperatures, the melting point and heat of fusion are seen to be decreasing functions of the radiation dose. The observed slight increase in melting point, like that observed in polytetrafluoroethylene receiving doses below 5 Mrad[1]

Table 1. The effect of radiation on melting temperature (T_m), heat of fusion (ΔH_f), tensile strength (T_b), ultimate elongation (E_b) and weight loss (WL) of PFA

Irradiation dose (Mrad)	T_m (°C)	ΔH^f (J/g)	T_b^a (MPa)	E_b^a (%)	WL (%)
0	305·4	17·1	19·6(7·1)	750(400)	—
2·1[b]	305·0	22·1	18·6	730	0·081
5·7[b]	305·9	26·3	13·2(8·4)	630(720)	0·155
9·9[b]	306·2	30·3	12·7(9·7)	650(700)	0·293
13·5[b]	306·3	31·8	10·8	500	0·379
15·6[b]	306·2	32·4	9·8(11·2)	400(600)	0·456
2·1[c]	305·9	22·2	14·7	650	0·013
5·7[c]	306·0	24·23	10·3	500	0·021
9·9[c]	306·2	27·0	8·8	420	0·011
13·5[c]	306·8	27·6	7·8	350	0·014
15·6[c]	306·2	28·6	7·8	380	

[a] Testing at 150°C.
[b] Irradiation at 230°C.
[c] Irradiation at 20°C.
The data for perfluoroethylene-propylene copolymer (FEP) irradiated under the same conditions are shown in parentheses.

obviously results from a kinetic effect, i.e. superheating, because of the relatively low dose range examined in this work. The increase in heat of fusion reveals the radiation-induced increase in the crystallinity of irradiated samples, which can be explained as being due to the scission of polymer chains in the amorphous regions which relieves strains or entanglements and permits further crystallization.[2] For a crosslinked polymer the formation of a three-dimensional network structure can greatly improve the high-temperature mechanical properties. Our observations of the decrease in tensile strength and ultimate elongation measured at 150°C for irradiated PFA and a comparison with the values for crosslinked FEP shown in Table 1 indicate that under the radiation conditions of 20 and 230°C in vacuum, the predominant radiation effect on PFA is the degradation of its molecular weight. Under the same conditions, however, PTFE samples which received a 15·6 Mrad dose were observed to be too brittle to measure their mechanical properties.

For samples irradiated at 20°C it can be seen that radiation-induced weight loss is very small and irregular, whereas for irradiation at 230°C the weight loss is seen to increase linearly with increasing dose at the rate of 0·028%/Mrad. Therefore, it can be seen that the introduction of a few flexible perfluoroalkoxy units in the backbone chain of PFA can not only improve its processability, but also its radiation stability.

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