ELASTIC MODULUS AND FREE RADICAL DECAY IN IRRADIATED POLYPROPYLENE

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ABSTRACT

Free radical concentration and elastic modulus in irradiated polypropylene were measured in the function of time after the end of irradiation. It is shown that, for samples in contact with air during and after irradiation, peroxy radicals are the main transient species. The dissapearanoe of peroxy radicals with time is accompanied by parallel change of elastic modulus. The change of elastic modulus is related to the molecular degradation caused by complex reaction mechanism involving peroxy radicals.

INTRODUCTION

High energy ionizing radiation produoes free radical species in polymers as primary products[1,2]. These radicals, in subsequent reactions, lead either to crosslinking or degradation. Although the two processes take place simultaneously, usually one of them is predominant , depending on the type of polymer. Besides this, small amounts of gaseous products are formed as well as unsaturated double bonds. Polypropylene is a typical polymer in which irradiation results mainly in degradation and decrease of average molecular weight. As a material widely applied in many radiation processes, polypropylene has been the subject of many investigations[3,4]. Of large practical importance is behaviour when irradiated polypropylene is exposed to the air during and after irradiation. It has been noted that slow postirradiation degradation takes place in the presence of oxygen, resulting in the continuous deterioration of mechanical properties[5]. This process has been ascribed to oxidative chain degradation in which peroxy radicals play important role[3].

In this work an attempt has been made to determine the relative concentration of free radicals in the function of time

after irradiation and to associate this with the measurement of some mechanical property. The elastic modulus has been measured since no relevant data are given in literature.

EXPERIMENTAL

Commercial product, Kastilene, ONIC, isotactic polypropylene was used. All irradiation were done at room temperature, in air, at ^{60}Co gamma source, at absorbed dose rate of about 0.1 Mrad/h. Samples were irradiated with the total absorbed dose of 2.5 Mrad.

ESR spectra of free radicals were determined on X-band, E-line, Varian ESR spectrometer. All measurements were performed at room temperature.

Elastic modulus was determined on samples cut out from 1 mm thick plates to the standard shape of about 0.04 cm^2 cross section. The Zwick, Model 1101, tensile testing machine was used for these measurements. The rate of extension was constant in all measurements: 25 mm/min or about 100%/min.

RESULTS AND DISCUSSION

In Fig. 1.the ESR spectra of free radical species determined one day and six days after irradiation are shown.

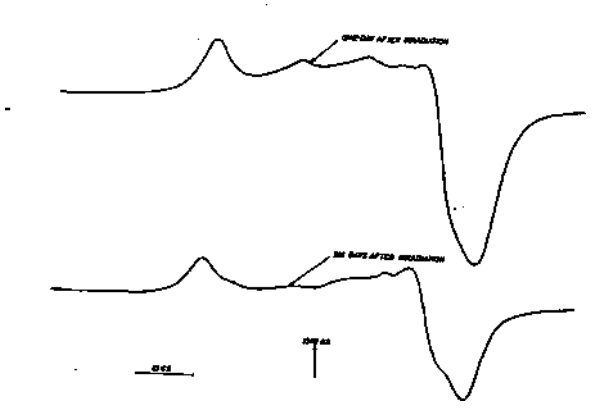

Figure 1.
ESR spectra of free radicals one day and six days after the end of irradiation

It is well established that alkyl free radicals are formed as primary products in irradiated polypropylene [2].:

$$RH \rightsquigarrow \dot{R} + \dot{H}\ (H_2) \qquad (1)$$

In the presence of air the peroxy radicals are formed:

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \qquad (2)$$

The spectra shown on Fig.1. are ascribed to the peroxy radicals. Since the seventeen line spectrum of alkyl radicals was not observed even at the shortes time after irradiation, it is assumed that most of free alkyl radicals are transformed to peroxy radicals by reaction (2) during irradiation and during the time between irradiation and measurement. It is possible that some small amount of unsaturated free allyl and polyenyl radicals are present in the crystalline regions of the samples immediately after irradiation, but these could not be positively identified from the recorded spectra. The decay of free peroxy radicals is given in Fig.2. The relative radical concentration was determined from the height of the main peak of the spectra shown in Fig.1.

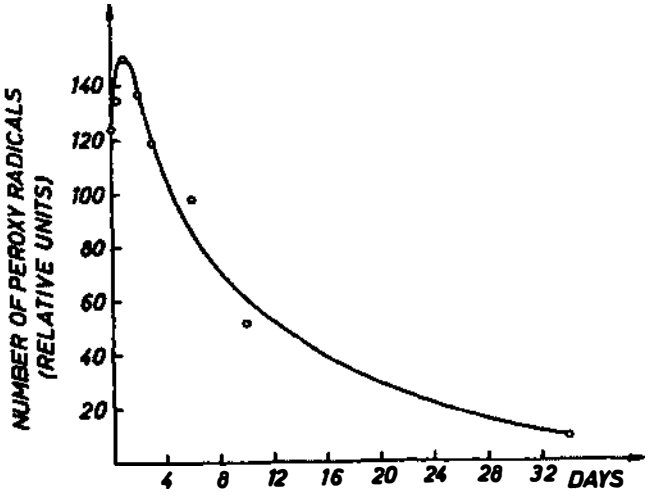

Figure 2.

The decay of peroxy radicals in the function of time after the end of irradiation.

The small initial increase in radical concentration is most probably due to the incomplete peroxidation by reaction (2) during irradiation time and time before succesive measurements.

It is well known that peroxy radicals initiate chain reactions in which propagating step is:

$$R\dot{O}_2 + RH \longrightarrow ROOH + \dot{R} \quad (+ O_2 \quad R\dot{O}_2) \qquad (3)$$

resulting in formation of hydroperoxides, or:

$$R\dot{O}_2 \longrightarrow R_1CHO + R_2\dot{O} \qquad (4)$$

resulting in soission of molecule. The chain is terminated by recombination of two free radicals:

$$R\dot{O}_2 + R\dot{O}_2 \longrightarrow ROOR + O_2 \qquad (5)$$

or

$$R\dot{O} + R\dot{O} \longrightarrow ROOR \qquad (6)$$

giving, as products, higher molecular weight molecules, cross-linked by oxygen bonds.

The degradation and formation of crosslinks, both carbon-carbon and oxygen crosslinks, result in the change of mechanical properties during the period following irradiation. The change of modulus in the function of time is shown in Fig.3. In order to illustrate the correlation with the time dependence of free radical concentration, the reciprocal value of modulus has been plotted in Fig.3. instead of the modulus itself.

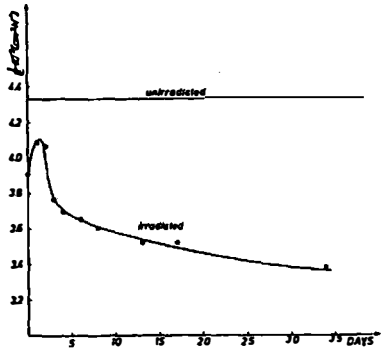

Fig.3.
The change of elastic modulus in the function of time after irradiation

It can be noted that, after small initial increase, the reciprocal modulus decays asymptotically to a constant value. The small initial increase is probably due to the effect of dose rate and the length of irradiation which impose the limiting conditions on the behaviour of the observed system. The continuous decrease of the reciprocal modulus on approximately the same time scale as the decrease of the concentration of the free peroxy radicals indicates the correlation of these two phenomena.It is also shown in Table I in which numerical values of experimental results are given. However, the presence of free radicals cannot be directly associated with the mechanical property or with the modulus because of the small actual concentration of free radicals

Therefore, it can be concluded that chain reactions (3) and (4), as it was suggested earlier[3], produce relatively large number of transformations before termination by reactions (5) or (6). These transformations are manifested, on macroscopical level, by the change of mechanical properties, modulus, etc. The observed change of modulus can be associated with the increasing number of free chain ends and branching induced by degradation and free radical recombination. It can be suggested, therefore, that the measurement of elastic modulus can be a useful indication of the postirradiation effects in polypropylene exposed to air.

A further work is in progress in order to elucidate the correlations and mechanism leading to the change of mechanical properties of irradiated polypropylene.

TABLE I.

Days after irradiation	number of radicals (relative units)	$1/E \cdot 10^{-5} (cm^2/N)$
0	124	3.91
1	150	4.09
2	137	4.06
3	119	3.77
4	-	3.69
6	98	3.66
8	-	3.61
10	52	-
13	-	3.52
17	-	3.53
34	10	3.38
unirradiated	-	4.33

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