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Crosslinking rate dependence on the thickness of high-density polyethylene sheets after gamma-ray irradiation in the presence of air

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Structural changes and dynamic mechanical properties of istotropic high-density polyethylene (HDPE) for both virgin and gamma-ray irradiated samples of different thickness, have been studied. The structural changes due to irradiation in the presence of air were studied by using infra-red spectroscopy. The radiation induced radicals were not post-irradiation annealed. The effects of these changes on the mechanical behaviour were investigated by using a modified dynamic resonance technique. It was found that the polymer chain crosslinking rate, as a result of irradiation by gamma-ray doses up to 200 kGy, depends on the sample thickness. However, for irradiation doses above 600 kGy, polymer chain scission is the most dominant phenomenon and is independent of the sample thickness.

(Keywords: gamma irradiation; dynamic mechanical properties; HDPE)

INTRODUCTION

Engineering polymers are progressively replacing metals and other conventional materials in many engineering applications. Physical, mechanical and chemical properties of the polymeric materials are crucial in assessing their fields of applicability. For example, many of the properties of polyethylene have been thoroughly investigated, and to mention just a few, the thermal expansion, heat capacity, electrical and thermal conductivities and mechanical properties[1–4] of polyethylene have been rigorously studied with the aim of relating these properties to the internal structure of the polymer.

The effect of ionization radiation on polymers is known to be one of the major sources for altering their internal structure, thus leading to a wide range of interrelated changes in their properties. Such treatment may result in crosslinking of the molecular chains, or degradation and destruction of the macromolecules, i.e. formation of molecules with smaller chain lengths and possibly a change in the number and nature of the polymer double bonds[5–7]. For polyethylene, irradiation leads to the elimination of hydrogen and increases the degree of unsaturation in the molecule. The radiation crosslinking of polyethylene gives a material which is insoluble in organic solvents, has increased thermal stability, and which also possesses a number of other valuable properties. For a small number of crosslinks, the resulting polyethylene will be soft and flexible. Increasing the network density, and the number of crosslinks, increases the stiffness of the polymeric material. A very large number of crosslinks gives a very hard material[8,9]. Radiation crosslinking of polyethylene has been utilized for the commercial production of films which combine the properties typical of polyethylene with a thermal stability up to 200°C and a significant increase in the tensile strength[8,9].

The aim of this present work is to investigate the effect of the radiation dose on the internal friction of the polyethylene and the stiffness of the samples. In addition, the effect of sample thickness on the density of radiation crosslinking and polymer degradation is also highlighted.

EXPERIMENTAL

Sample preparation

Linear polyethylene (Marlex 6006), with a density of 960 kg m^{-3}, was heated to 150°C and compressed three times under a pressure of 276 MPa. The temperature was then raised to 180°C and the material again compressed three times; the heater was then switched off and the pressure kept at 6.9 MPa for 24 h allowing the samples to cool slowly, resulting in polycrystalline sheets. The samples were then cut to the shape of narrow long strips of a width of less than 2 mm.

Sample irradiation

The prepared samples with different thicknesses were irradiated by a ^{60}Co γ-ray source at room temperature in air. Doses of up to 1 MGy were used at a dose rate of 4.72 kGy h^{-1}.

Measurement of mechanical properties

The mechanical behaviour of the γ-irradiated HDPE

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samples of different thickness, together with unirradiated control samples, was examined by using a modified vibrational technique which is shown schematically in *Figure 1*. Plotting the amplitude of the vibration against the frequency, around the resonance frequency f_0, gives a resonance curve which characterizes the mechanical response of the sample. Typical resonance curves of irradiated samples are shown in *Figure 2*.

From the resonance curve, the internal friction Q^{-1} of the samples can be obtained by using the following equation[10–12]:

$$Q^{-1} = 0.5773\Delta f/f_0 \quad (1)$$

where Δf is FWHM of the resonance peak. At the resonance condition, the stiffness or the fixural rigidity can be determined from the following relationship:

$$\text{Stiffness} = 4\pi^2 A\rho L^4 f_0^2/Z^4 \quad (2)$$

where L is the sample length, ρ is the density, and A is the sample cross-sectional area; the Z factor depends upon the mode of resonance, which is equal to 1.8751 for the fundamental mode[13–15].

Measurement of infra-red spectra

A Perkin–Elmer 1430 ratio recording infra-red spectrophotometer was used to examine the HDPE γ-ray irradiated samples, with spectra being obtained in the scanning range from 2.5–50 μm.

RESULTS AND DISCUSSION

Typical resonance curves obtained for 200 and 1000 kGy γ-irradiated HDPE samples of 0.2 mm thickness are given in *Figure 2*; these show distinct peaks at 24.3 and 11.4 Hz for the 200 and 1000 kGy irradiation samples, respectively.

Figure 3 shows the variation of the internal friction with γ-ray irradiation dose. It is clear from this figure that the internal friction of samples with different thicknesses varies with irradiation dose up to 200 kGy, while samples irradiated at 500 kGy and 1 MGy have almost identical internal friction values. It is also observed that, in general, irradiation in atmospheric oxygen decreases the samples' internal friction, i.e. improves the internal friction property. This improvement is seen for irradiation doses up to 200 kGy, while after that a continuous increase of the internal friction

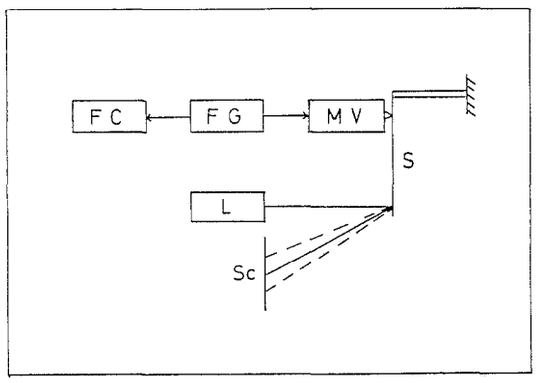

Figure 1 Schematic diagram of the dynamic resonance measuring system: FG, function generator; FC, frequency counter; L, low-power laser source; MV, electromagnetic mechanical vibrator; S, sample; Sc, screen

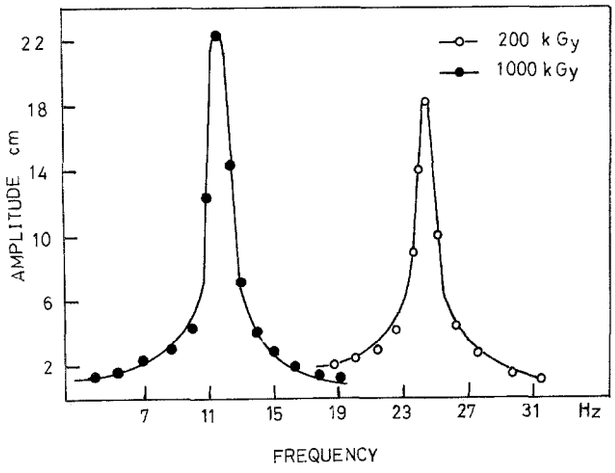

Figure 2 Typical resonance curves of HDPE, irradiated in air, samples with different γ-ray doses

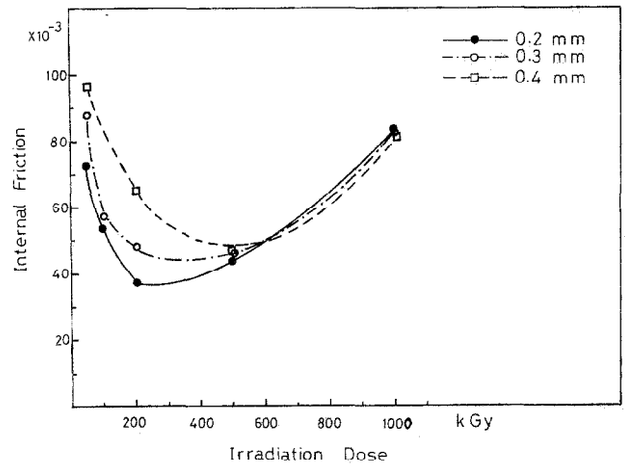

Figure 3 Internal friction *versus* irradiation dose for HDPE samples of different thickness

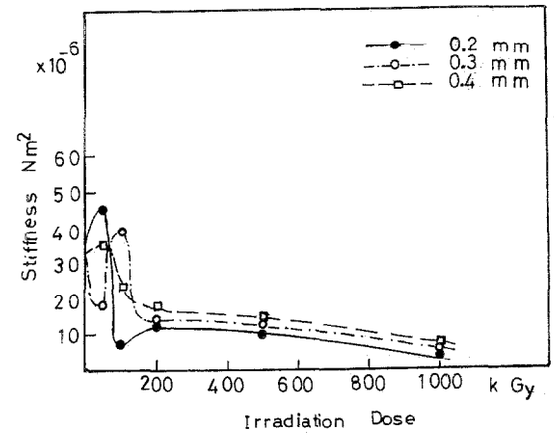

Figure 4 Stiffness modulus *versus* irradiation dose for HDPE samples of different thickness

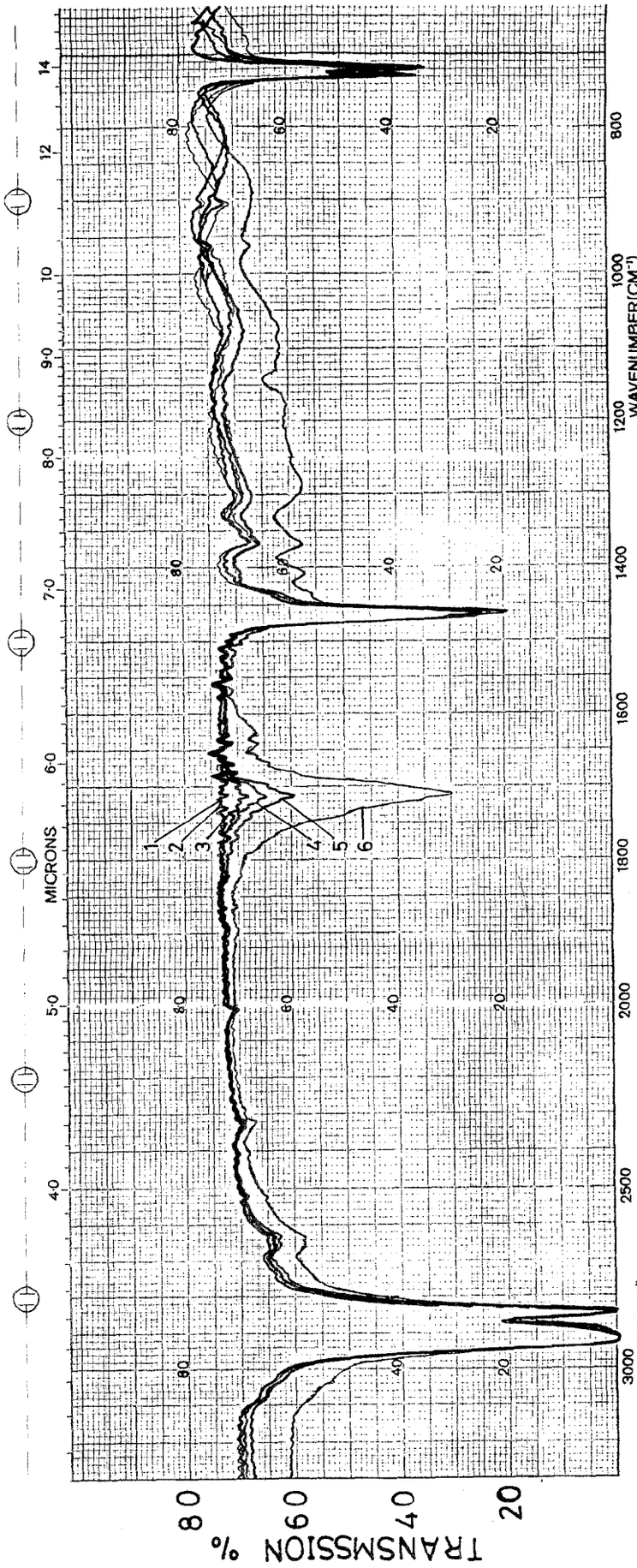

Figure 5 Infra-red spectra of HDPE samples shown for different γ-irradiation doses: (1) 50 kGy; (2) 100 kGy; (3) 200 kGy; (4) 350 kGy; (5) 500 kGy; (6) 1 MGy

with γ-ray doses up to 1 MGy was observed. This can be attributed to oxygen diffusing into the samples, with the thinner the sample then the greater the effect of oxygen, thus causing a greater number of chain scissions and hence a lower internal friction.

The variation of the stiffness for HDPE samples of different thicknesses with γ-irradiation dose is given in *Figure 4*. The stiffness of the 0.2 mm thick sample shows a maximum value at 50 kGy, followed by a sharp decrease to a minimum value at a dose of 100 kGy and then, after a slight rise, a continuous decrease over the range from 200 to 1000 kGy. The sample of 0.4 mm thickness shows a similar behaviour in that the slow continuous decrease for the range from 200 kGy to 1 MGy dose has values which are almost identical to that of the thinner sample. The sample of 0.3 mm thickness shows a different stiffness response from the other samples for irradiation doses below 200 kGy, but has the same behaviour again as the other samples in the range from 200 kGy up to 1 MGy. This can again be attributed to oxygen diffusion into the samples, with a higher diffusion oxygen into thinner films causing greater oxidative degradation, thus reducing the sample's stiffness.

Figure 5 shows the infra-red spectra of HDPE samples irradiated with various doses at room temperature. It is clear from this figure that the band at 1725 cm^{-1} shows the formation of carboxylic groups which arise from interaction of oxygen with the radicals. The increase in this growth for doses above 200 kGy causes polymer degradation, with no detectable amount of formation of this group being seen for irradiation doses below 100 kGy; i.e. the concentration of such groups is too small to be detected.

The influence of γ-irradiation on HDPE is to allow the polymer to undergo crosslinking reactions at low irradiation doses. The polymer undergoes crosslinking as well as oxidative degradation at doses of up to 600 kGy, while at higher levels of irradiation degradation is the dominant process.

Crosslinking by irradiation takes place when chains are linked by direct chemical bonding, which can be interpreted as being a result of recombination of the chain radicals to form a crosslinked network. Many researchers have described HDPE crosslinking and oxidative degradation as a result of formation of peroxy radicals and peroxide bridging intermediates upon irradiation[16–20].

The infra-red spectra of the irradiated HPDE samples clearly indicate that polymer degradation is the dominant process operating at doses above 200 kGy, with crosslinking of the polymer being likely to take place at dosage levels below 100 kGy.

The internal friction, as well as the stiffness of samples studied, depends strongly on their thickness when they are irradiated, in atmospheric oxygen, in the dose range below 200 kGy. Under these conditions, crosslinking is the dominant process, with the rate of crosslinking in an irradiated sample being thickness dependent. For doses below 200 kGy, oxygen diffusion into the sample and sample thickness are both important criteria. Degradation is the dominant process above 200 kGy, as observed in *Figure 5*. Variation of the internal friction and sample stiffness with irradiation doses above 200 kGy shows these parameters to be independent of sample thickness, and hence degradation of the samples is independent of thickness, i.e. the effect of oxidative degradation on the mechanical properties is reduced at dosage levels of 600 kGy and above.

CONCLUSIONS

From the foregoing analysis the effect of γ-irradiation on HDPE may be envisaged as a three-stage process. For doses up to 100 kGy, the effect of radiation crosslinking is overridden by that of a perturbation process. Crosslinking and degradation are the predominating phenomena between 100 and 200 kGy. For higher doses, oxidative degradation prevails, depending on the diffusion of oxygen into the samples.

The internal friction of HDPE shows minima for samples irradiated at 200 kGy, and is strongly dependent on the sample thickness over the dose range up to 200 kGy. This indicates that the crosslinking rate depends on the sample thickness of HDPE in this range, due to the thickness parameter controlling the oxygen diffusion process.

Enhancement of the stiffness, as well as the internal friction of the HDPE samples, is detectable only over the crosslinking region of irradiation.

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