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Physicomechanical properties and crystallinity of γ-irradiated low density polyethylene

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Abstract

Differential thermal analysis (DTA) and mechanical testing have been used to study the effects of γ-irradiation on the degree of crystallinity and physicomechanical properties of low density polyethylene (LDPE). The crystallinity was found to change with irradiation dose as well as the elastic modulus, ultimate tensile strength and ductility. These changes in mechanical properties correlated with the crystallinity produced by the accumulation of stable radiation defects. The effects of strain rate on the tensile properties of LDPE samples moulded at different die temperatures have also been investigated. The fracture stress and ductility increased initially with strain rate; then constant values were obtained at higher strain rates. These effects were more pronounced at lower die temperatures.

INTRODUCTION

Polymers are known as viscoelastic because, phenomenologically, their deformation behaviour lies between that of a classical elastic solid (Hookean) and a classical viscous liquid (Newtonian). This complex deformation behaviour has precipitated one of the basic problems in rheology. The relationship between stress, strain and time in deformation of a viscoelastic material was described by Han [1]. Polyethylene molecules are folded to form a lamellar configuration, the interlamellar spacing being of the order of 100 Å. At the surface of lamellae the mobility of the chain segments is different from that inside the lamellae [2]. The transition corresponding to the motion of the surface groups of the lamellae (transition) will increase crystallinity. It is well known that the elastic modulus and tensile strength of polymers can be improved either by the addition of small particles (fillers) or by irradiation or by both [3–7].

Since polymers have properties that vary substantially with changes in deformation rate, the effects of strain rate on the tensile properties of

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LDPE were examined. Furthermore the influence of γ-irradiation on both tensile and thermal properties was investigated.

EXPERIMENTAL

The material used in the present investigation was low density polyethylene (LDPE) grade F8 3003 produced by QAPCO, Qatar. The material has the following properties: melt index, 0.24–0.30 g; density (23 °C), 0.921–0.923 g/cm^3; crystalline melting point, 115 °C; softening point, 97 °C.

Samples were fabricated into standard tensile specimens having gauge length of 60 mm, width 12.7 mm and thickness 3.2 mm using an injection moulding machine. The injection conditions for all samples were, melt temperature 200 °C and pressure 10 MPa. In order to examine the effect of die temperature on the tensile properties of LDPE, three groups of samples were produced at die temperatures of 25°C, 50°C and 100 °C. Tensile properties were measured with a universal testing machine at different ram velocities between 0.5 mm min^{-1} and 300 mm min^{-1}. The load and extension were measured using a load cell and a displacement transducer, respectively, while the load–extension diagram was recorded on a chart recorder. Fabricated samples were γ-irradiated in air at room temperature using a Co 60 gamma cell manufactured by Atomic Energy of Canada Co. Ltd. Samples were irradiated to different doses up to 255 MRad at a dose rate of 1 MRad min^{-1}. These samples were used to examine the influence of γ-irradiation on the physical and mechanical properties of LDPE. The specific heat, C_p, the enthalpy change ΔH and the crystallinity, C, of as-fabricated and γ-irradiated polyethylene were measured using a Shimadzu DSC TA300 thermal analyser. The methods of measurement have been described elsewhere [8]. The specific heats (C_p) of the as-fabricated and irradiated samples were also determined.

RESULTS AND DISCUSSION

Typical DSC curves obtained for as-fabricated and irradiated LPDE samples are shown in Fig. 1. With increasing the irradiation dose, differences in the magnitude of the enthalpy H as well as in the position and width of the endotherm were found. The crystallite melting temperature was taken as the temperature corresponding to the intersection of the linear portion of the curve with the base line. The change in enthalpy increased from 8.28 to 19.09 J g^{-1} at an irradiation dose of 255 MRad. It is observed also that the entropy change, ΔS, increased as irradiation dose increased (Fig. 2). The estimated value of crystallinity and the specific heat at the crystallite melting temperature are given in Table 1, for different irradiation doses.

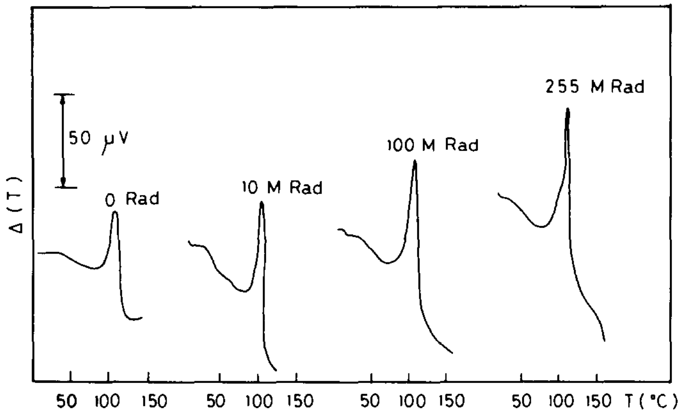

Fig. 1. Typical DTA tracings with DSC cell for LDPE with different irradiation doses.

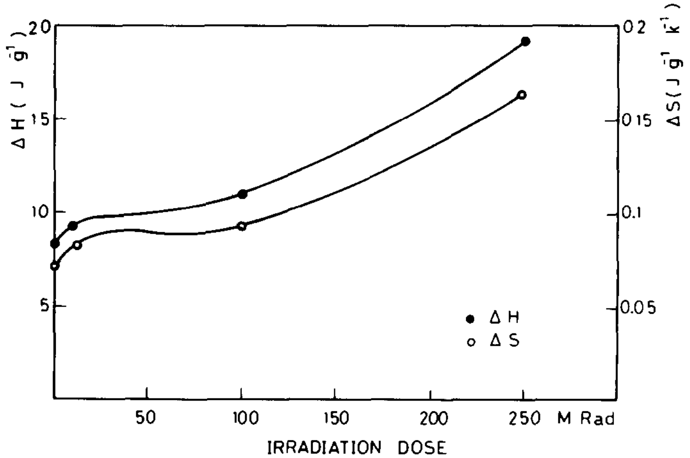

Fig. 2. Effects of irradiation dose on enthalpy change and entropy of LDPE.

TABLE 1

Variation of specific heat, crystallinity and crystallite melting temperature with radiation dose

	Dose (MRad)			
	0	10	100	255
C_p ($J\,g^{-1}\,K^{-1}$)	17.10	14.46	10.86	20.11
C (%)	2.85	3.19	3.56	6.58
T_m (°C)	107	107	108	112

It is clear that the crystallinity increases with irradiation dose while the specific heat decreased up to an irradiation dose of 100 MRad and then increased at 255 MRad. The crystallite melting temperature did not change up to 10 MRad and tends to increase at higher irradiation dose.

This behaviour can be interpreted as being due to the folding of polyethylene from its lamellar configuration [9]. Furthermore, the influence of irradiation was determined by the decrease in chain mobility as the result of radiochemical crosslinking and by the corresponding increase in the extent of structure traps [10]. In the case of cross linking by irradiation of the LDPE, the chains are linked by direct chemical bonding. The crosslinking reaction is interpreted as being a result of recombination of such chain radicals to form a crosslinked network. The crystallite melting temperature is shifted as the motion of the segments is hindered by the crosslinks.

Although crosslinking and decrease in the degree of crystallinity of PE upon irradiation have been described in many works [11,12], the present results agree with more recently published work [13–15] in which the fact that the degree of crystallinity of PE increases with increasing irradiation dose (at relatively small doses) in the open air was discussed.

Typical stress–strain diagrams of LDPE samples produced under identical injection conditions and tested at different ram velocities, are shown in Fig. 3. All curves start with an elastic linear portion up to an apparent yield stress of approximately 1.2 MPa; beyond yielding the stress continues to rise until fracture. The yield strength and yield strain of LDPE appear to be insensitive to the rate of deformation. However, the yield strength of other types of polymers as well as yield strain were found to vary linearly with the logarithm of strain rate [16].

The effect of ram velocity on the ultimate tensile strength measured by the fracture stress of LDPE samples produced at different die tempera-

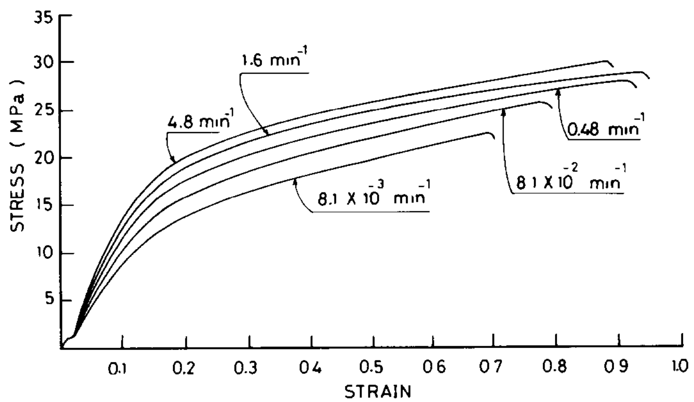

Fig. 3. Stress–strain diagrams of LDPE at different strain rates.

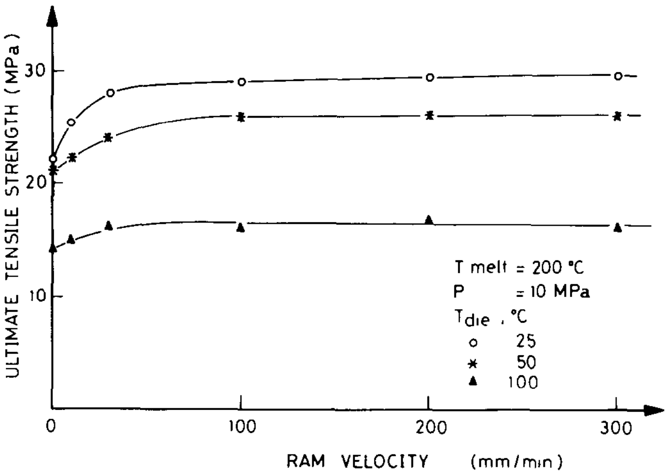

Fig. 4. Effect of extension rate on ultimate tensile strength of polyethylene produced at different die temperatures.

tures is shown in Fig. 4. The fracture stress increases with ram velocity up to approximately 80 mm min^{-1} and higher velocities have no apparent effect on the fracture stress. The influence of ram velocity is more pronounced at the lower die temperatures. Furthermore, it is clear that the die temperature has a great influence on the fracture strength of LDPE produced under identical conditions.

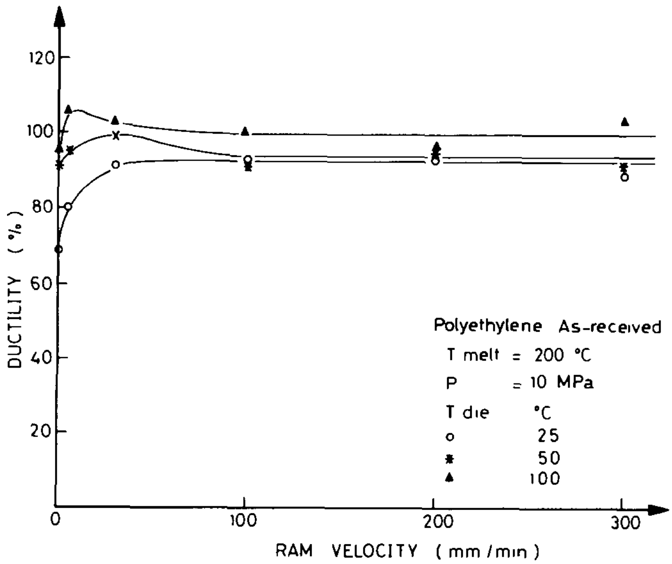

Fig. 5. Effect of ram velocity on ductility of polyethylene produced at different die temperatures.

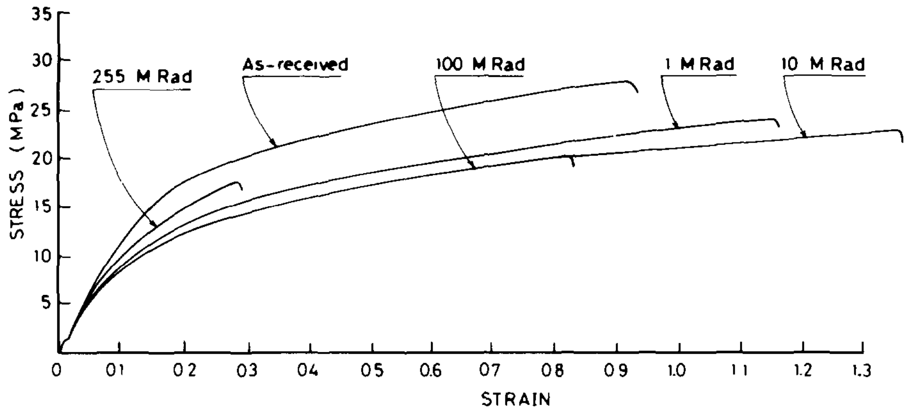

Fig. 6. Influence of irradiation dose on the stress–strain diagrams of LDPE ($T_{melt} = 200\,°C$, $T_{die} = 50\,°C$, pressure = 10 MPa).

The ductility of LDPE expressed as percentage fracture strain was found to increase with ram velocity until a steady state is reached at a velocity between 60 and 80 mm min^{-1}, depending on die temperature. It is also noticeable that ductility increases with die temperature. These results are shown in Fig. 5.

Typical stress–strain diagrams for LDPE subjected to different doses of γ-irradiation after injection moulding are shown in Fig. 6. The shape of the

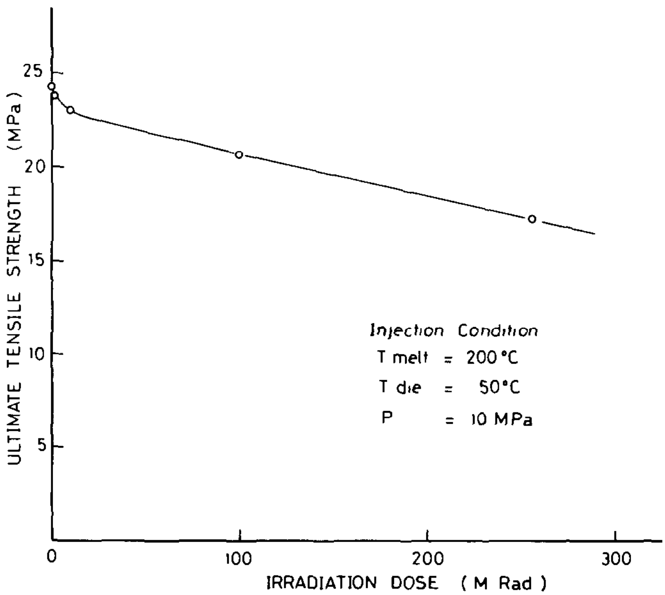

Fig. 7. Effect of irradiation dose on the ultimate tensile strength of low density polyethylene.

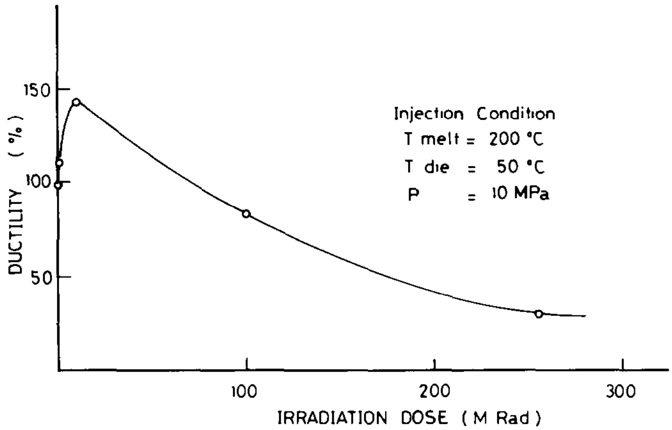

Fig. 8. Effect of irradiation dose on the ductility of low density polyethylene.

stress–strain curve changes with irradiation dose. The ultimate tensile strength of the material calculated at fracture, decreased steadily with irradiation dose, as shown in Fig. 7. In contrast ductility increased up to an irradiation dose of 10 MRad then decreased steadily (Fig. 8). Similarly, the modulus of elasticity decreased initially up to the same value then tended to increase as shown in Fig. 9.

CONCLUSIONS

(1) The enthalpy and entropy of LDPE were found to increase with γ-irradiation dose.

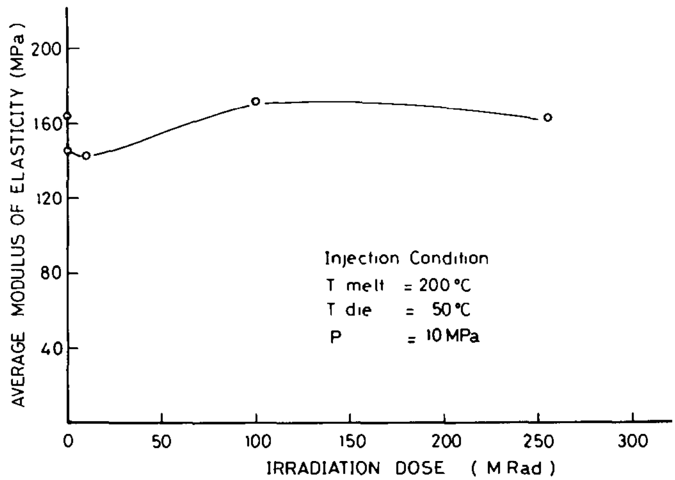

Fig. 9. Variation of modulus of elasticity with irradiation dose for LDPE.

(2) The ultimate tensile strength of LDPE was found to increase with ram velocity until a steady state is reached at approximately 80 mm min^{-1}, and it decreased with increasing die temperature.

(3) Similarly, ductility increased initially with ram velocity; then a steady state is reached. Higher die temperature caused an increase in ductility.

(4) Irradiation lowered the ultimate tensile strength of LDPE over the entire range examined, while ductility increased initially with irradiation until a peak value is reached at 5 MRad; then it decreased to much lower values at higher irradiation doses.

(5) The elastic modulus decreased initially with irradiation dose until a minimum value is reached (at 5 MRad) then tended to increase at higher irradiation doses.

REFERENCES

1 C.D. Han, Rheology in Polymer Processing, Academic Press, New York, 1976.
2 A. Peterlin, J. Polym. Sci., 9 (1965) 61.
3 A.J. Podrou, Z. Rubinzation and M.A. Colmenares, Eur. Polym. J., 23 (1987) 429.
4 F.P. La Mantia, A. Valanza and D. Acierno, Eur. Polym. J., 22 (1986) 647.
5 A.M. El-Khatib, M. Kassem and A.A. Ezzat, J. Polymer Mater., 7 (1990) 21.
6 W.K. Busfield and Buchnan Morely, Eur. Polym. J., 19 (1983) 1131.
7 I. Diaconu, S. Dumitresan and C.R. Simionesan, Eur. Polym. J., 16 (1980) 511.
8 M.E. Kassem, N.G. Gomaa, A.M. El-Khatib and S.H. Kandil, Phys. Status Solidi A, 117 (1990) 119.
9 A. Peterlin, J. Polym. Sci., 9 (1965) 61.
10 O.V. Prokopev, A.G. Rozno and V.V. Gromov, Zh. Fiz. Khim., 62(3) (1988) 821.
11 G.N. Patel and A. Keller, J. Polym. Sci., Polym. Phys. Edn., 13 (1975) 323.
12 S.R. Ahmad and A. Charlesby, Int. Radiat. Phys. Chem., 8 (1976) 585.
13 S.K. Bhateja, Polymer, 23 (1982) 654.
14 J. Pabiot and J. Verdu, Polym. Eng. Sci., 21 (1981) 32.
15 V.M. Aslanian, V.I. Vardanian, M.H. Avetisian, S.S. Felekian and S.R. Ayvasian, Polymer, 28 (1987) 755.
16 J.A. Roetling, Polymer, 6 (1965) 615.