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Radiation Physics and Chemistry 75 (2006) 78–86
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Effect of electron-irradiation on cross-link density and crystalline structure of low- and high-density polyethylene

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Received 19 January 2005; accepted 10 May 2005

Abstract

Low- and high-density polyethylenes (LDPE and HDPE) were cross-linked in solid state by electron beam irradiation. Molar mass between cross-link joints, M_c, and cross-link density,v, were calculated using rubber elasticity theory and hot set data. The results showed that the v and creep modulus increased and creep strain and M_c decreased with increasing irradiation dose. As compared to HDPE, the LDPE had higher v and lower M_c values at a similar irradiation dose. X-ray analysis and differential scanning calorimetry investigation of first heating cycle revealed no changes in crystalline structure of the irradiated samples. This was attributed to immobilization of radicals frozen in the crystalline phase. As a result of hindered mobility of the polymeric chains, these radicals were not able to cross-link the chains in the crystalline region. However, after melting of the crystals and during subsequent re-solidification process, different levels of crystallinity were developed depending on the applied irradiation dose. The irradiated samples with higher dose had lower crystallization and melting temperatures with reduced crystallinities. These confined crystallization behaviors, observed after a series of cooling and heating cycles, could be attributed to the decrease in the M_c values. The length of chain segment needed for usual crystallization by chain folding is decreased due to formation of cross-link joints and hence the crystallization process was hindered.

Keywords: Electron-irradiation; Cross-linking; LDPE; HDPE; Cross-link density; Crystalline structure

1. Introduction

Cross-linking is a broadly used method for the modification of polymer properties. This process involves the formation of three-dimensional structures causing substantial changes in material properties. The most common examples of cross-linking application involve the rubbers and thermosetting resins. However, cross-linked polyolefins, especially polyethylene (PE), are of significant interest as well (Rado, 1993; Chodak, 1995; Charlesby, 1952; Charlesby et al., 1987). Cross-linking can be accomplished either by high-energy irradiation or through the use of chemical cross-linking additives (Rado and Zelenak, 1992a; Ota, 1981). PE when irradiated with electron-beam (EB), γ-rays, and other forms of high energy radiation predominantly undergoes cross-linking (Lopez et al., 1994). Cross-linked PE has become widely adapted for a number of industrial applications, which require withstanding high temperature environments. Examples of such

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0969-806X/$ - see front matter
doi:10.1016/j.radphyschem.2005.05.014

applications include wire and cable coating, heat shrinkable materials, hot water tubing and steam resistant food packaging (Morton-Jones and Ellis, 1986; Hoffman, 1991; Rado and Zelenak, 1992b).

Chemical cross-linking is accomplished by incorporating organic peroxides into PE and subsequently activating the peroxide that links the long-chain molecules into a three-dimensional network. This modification is manifested by changes in some properties of PE such as mechanical, physical and chemical properties (Kunert et al., 1981; Kampouris and Andereopoulos, 1987; Khonakdar et al., 2003; Lazar et al., 1990). In the EB process cross-linking is induced by the interaction of high-energy electrons with the polymeric material, resulting in a product with properties that are similar or identical to those obtained by the chemical cross-linking process (Salovey, 1962; Chodak, 1998; Yan et al., 1993). Unlike chemical cross-linking, EB cross-linking occurs quickly, thereby allowing higher throughput. The main advantage of radiation initiation consists of the possibility of generating active intermediates in the solid polymer within a large temperature interval. The sources of radiation for the cross-linking of PE industrially used are betatrones, which allows one to obtain high radiation doses within a short time. The relative ease of process has motivated several researchers to extensively study the EB radiation cross-linking of PE over the time. One main finding reported in most of these studies is the direct proportionality of cross-link density introduced during irradiation to the applied irradiation dose (Delides and Shepherd, 1977). The cross-link density can be estimated by several methods, e.g. stress–strain, modulus or swelling measurements. The equilibrium swelling characteristics are described by Flory and Rehner and subsequently some other theories were also developed such as the Mooney–Rivlin equation (Smedberg et al., 2004). Klein et al. (1986) have studied the structure and properties of oriented irradiated PE by rubber elasticity measurements and tensile creep behavior. They have reported that the apparent molecular weight between network junctions, calculated from the Flory and Mooney–Rivlin theories, depends on irradiation dose. Moreover the contribution of molecular entanglements to the rubber-elastic behavior of electron-irradiated linear PE had been reported by the same authors. (Klein et al., 1987). Lyons (1983) have studied the effect of radiation on the solubility properties of high and linear low-density PEs (LDPEs). Dalai and Wenxiu (2002a, b) investigated the radiation effects on high-density PE/ethylene-vinyl acetate copolymer (HDPE/EVA) and low-density PE/EVA blends.

Radiation-induced crystallinity changes in PE have also been investigated by some researchers. Bhateja (1983) reported that irradiation of a pressure-crystallized ultra high molecular weight PE (UHMWPE) at ambient conditions causes an increase in the degree of crystallinity. Kitamaru et al. (1973) reported that highly transparent irradiated cross-linked linear PE films have very high melting temperatures and a highly ordered stable crystalline phase, but a rather low degree of crystallinity. Ungar and Keller (1980) have studied the effect of radiation on crystals of PE and paraffins. They reported destruction of crystalline structure of PE above certain dose where the radiation temperature approaches the temperature of orthorhombic-hexagonal transition.

In our previous work, we studied a chemically cross-linked HDPE system in which we determined the cross-link density and molecular weight between cross-link junctions (M_c) using hot set data and rubber elasticity theory. We reported a good correlation between mechanical properties and crystallization behavior with cross-link density in the peroxide cross-linked HDPE (Khonakdar et al., 2003). The crystallization of HDPE was significantly affected by degree of network formation. In this work the same methodology is used to determine the cross-link density quantitatively in radiation induced cross-linking systems (HDPE and LDPE) and to study the resulting structural changes on crystallization process. Some interesting observations in crystallization and melting behavior of PE are seen for the radiation-induced cross-linking as compared to the chemical method that are reported here.

2. Experimental

2.1. Materials

LDPE grade LD 00BW, with melt flow index (MFI) of 2.0 (g/10 min) and density of 0.923 (g/cm^3), was obtained from ExxonMobile Co. Germany.

HDPE grade MG7547A, with MFI of 4.0 g/(10 min) and density of 0.954 g/cm^3, was supplied by Borealis group, Denmark.

2.2. Sample preparation

The LDPE and HDPE were compression-molded to flat sheets using Fontune 400 KN (Holland) laboratory hot press at a temperature of 190 °C for 3 min under 10 MPa pressure, then the sheets were cooled by cooling rate of 15 K/min to ambient temperature.

The irradiation of the LDPE and HDPE sheets (dimensions: $120 \times 120 \times 1.5\,mm^3$) was carried out at room temperature using an electron accelerator ELV-2, INP Novosibirsk (Russia) with energy of 1 MeV under various irradiation conditions (doses from 50 to 300 kGy with intervals of 50 kGy) in air.

2.3. Melt flow index

The MFI of the cross-linked LDPE and HDPE samples were measured according to ASTM D-1238 using a Zwick