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The effect of gamma radiation on hardness evolution in high density polyethylene at elevated temperatures

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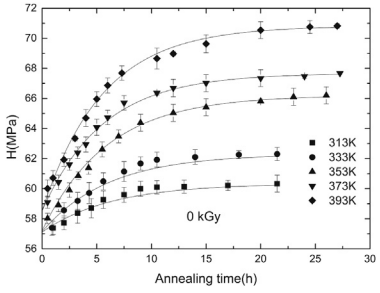
HIGHLIGHTS

- Hardness of HDPE increases with increasing gamma ray dose, annealing time and temperature.
- The hardness change arises from defects in microstructure and molecular structure.
- Defects affecting hardness follow a kinetics of structure relaxation.
- The structure relaxation has a low energy of mixing in crystalline regime.

GRAPHICAL ABSTRACT



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ABSTRACT

This research focuses on characterizing hardness evolution in irradiated high density polyethylene (HDPE) at elevated temperatures. Hardness increases with increasing gamma ray dose, annealing temperature and annealing time. The hardness change is attributed to the variation of defects in microstructure and molecular structure. The kinetics of defects that control the hardness are assumed to follow the first order structure relaxation. The experimental data are in good agreement with the predicted model. The rate constant follows the Arrhenius equation, and the corresponding activation energy decreases with increasing dose. The defects that control hardness in post-annealed HDPE increase with increasing dose and annealing temperature. The structure relaxation of HDPE has a lower energy of mixing in crystalline regions than in amorphous regions. Further, the energy of mixing for defects that influence hardness in HDPE is lower than those observed in polycarbonate (PC), poly(methyl methacrylate) (PMMA) and poly (hydroxyethyl methacrylate) (HEMA). This is due to the fact that polyethylene is a semi-crystalline material, while PC, PMMA and PHEMA are amorphous.

1. Introduction

High density polyethylene (HDPE) is widely used for economic and environmental reasons. HDPEs are often used in medical applications because they exhibit excellent chemical resistance, optimum electrical and mechanical properties, and are easily processed. Polyethylene is a semicrystalline polymer containing amorphous and crystalline phases that are linked by tie molecules [1–3]. In general, mechanical properties of PE vary with both microstructure and molecular structure and depend on many factors such as the percentage of crystallinity, chain entanglement, molecular weight, lamellar size, and cross-link density [4,5]. Internal stresses in the matrix arise from strain incompatibilities between the crystalline and amorphous phases [2,6,7]. These

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internal stresses vary with crystallite size and size distribution, which influence tensile properties, environmental stress crack resistance and microhardness [8–11].

A variety of polyethylene (PE) medical products are sterilized by gamma irradiation. However, the oxidation resulting from gamma sterilization reduces static strength and elongation properties and significantly decreases the resistance of PE bearings to fatigue [12]. Many investigators have studied ionizing radiation effects on the chemical structure and properties of PE [13–15]. When PE is exposed to ionizing radiation it undergoes scission, cross-linking and hydrogen evolution and these events have deleterious effects on many physical and chemical properties [14,15]. Oxidative degradation has also been observed in gamma-irradiated HDPE [16]. The degree of crystallinity in blends of high and low density polyethylene has been shown to decrease with the gamma irradiation dose [17]. Quero et al. studied the influence of gamma radiation on the morphology, thermal, and mechanical properties of HDPE/LDPE blends [18]. In this study, they found no significant changes in the degree of crystallinity in blends exposed to radiation doses below 150 kGy. However, when irradiated samples were tested after aging, the degree of crystallinity continued to change with annealing time. Free radicals and unstable radiolysis products have been shown to react for long periods after exposure to radiation [19]. When irradiated ultra-high molecular weight PE (UHMWPE) undergoes environmental aging before, during and after irradiation, physical properties evolve with time [20]. Molecular weight, sample size, mechanical history and additives all influence the aging effects. In fact, effects observed at higher doses and shorter annealing times are similar to those observed at lower doses and with longer annealing times. Lednicky et al. [21] exposed HDPE samples to gamma radiation and measured microhardness comparing three variables: no aging after irradiation, post irradiation annealing at 120 °C for 10 min and remelting after irradiation for 10 min at 150 °C. Thermally untreated samples exhibited microhardness values and melting points that increase with radiation dose. Samples with post radiation annealing exhibited this trend as well, but to a lesser extent that the thermally untreated samples. However, the melted samples exhibited decreases in T_m that are more pronounced with dose. Microhardness values are lower than those with no aging and with annealing but increases with radiation dose. The authors attribute this to crosslinking that increases with radiation dose.

Of course, annealing induces changes in mechanical properties in non-irradiated polymers, so it is important to record the thermal history of samples prior to any irradiation testing. For example, Solukhin et al. [22] demonstrated that the elastic modulus and hardness of polycarbonate increase in a stepwise manner during aging at room temperature. Zhou et al. [23] reported the hardening of PE as a function of annealing temperature. They observed a sudden decrease in hardness near the melting temperature due to recrystallization. Annealing polymers, in general, increases the modulus and tensile strength and reduces the ultimate elongation [24–26].

In metallic alloys, mechanical properties are usually explained as they relate to microstructures [27]. Similar to metallic alloys, the mechanical and physical properties of polymers can also be interpreted using microstructure models along with concerns for the specific molecular structure. Our laboratory is currently conducting a series of studies on the physical and mechanical properties of gamma-irradiated polymers explained by defect models. Microhardness evolution in poly(methyl methacrylate), hydroxyethyl methacrylate copolymer, and polycarbonate at elevated temperatures was found to exhibit the first order defect kinetics [28–30]. Color centers were used to explain the UV–vis spectra of gamma-irradiated polymers [31,32]. Permanent and annealable (free radical) color centers are created simultaneously during gamma ray radiation. Free radicals were characterized via the EPR spectra of gamma-irradiated polymers [33,34]. This paper focuses on microhardness as it relates to unstable defects induced in HDPE by gamma ray irradiation. Importantly, this study characterizes the effect of dose, post irradiation annealing time and temperature on microhardness.

2. Experimental

High density polyethylene (HDPE) sheets, 300 mm × 300 mm × 6.35 mm, with weight average molecular weight of 36,864 and polydispersity index of 2.14 were obtained from Alfa Aesar Company (Ward Hill, MA, USA). Specimens of 30 mm × 6 mm × 3 mm were cut from the sheets, ground with 180, 400, 800, 1200, 2500, and 4000 grit carbimet paper, and then polished with 1.03 μm alumina slurries. In order to minimize residual stresses from machining and molding, specimens were annealed at 363 K in air for 24 h and furnace cooled. Samples were sealed in glass tubes in air and then irradiated by a gamma ray source in Institute of Nuclear Energy Research at a dose rate of 5 kGy h^{-1}. The accumulated doses were 200, 400, 600, and 800 kGy. The specimens were quickly taken out from glass tubes and annealed at 313, 333, 353, 373 and 393 K in atmosphere.

Microhardness was measured via an Akashi HVK-E tester (Mitutojo Corporation, Minato-Ku, Tokyo, Japan). The load was 50 g with a dwell time of 30 s. The samples were removed from the furnace, tested at room temperature as soon as possible, and then returned immediately to the furnace. The mechanical data for irradiated samples and control samples (not exposed to gamma rays) were recorded as a function of annealing time. The experimental data are the average of three samples under the same conditions.

X-ray diffraction data was recorded on a Shimadzu XRD6000 (Nakagyo-ku, Kyoto, Japan). The X-ray source on this instrument is a Cu 2 kW X-ray tube; the current is 20 mA and voltage is 30 kV. Samples were scanned from 5° to 80° at a rate of 2° min^{-1}.

Differential Scanning Calorimetry, DSC, was carried out on a DSC 200F3 (Netzsch, Germany). The specimens (5 mg) were placed aluminum crucibles under a nitrogen purge and scanned from room temperature to 180 °C at a ramp rate of 10 °C min^{-1}. The densities of the control PE and irradiated PE were obtained via an Ohaus Density Determination Kit P/N 77402-00, Cambridge, England. The test liquid was ethanol which has a density of 0.78097 g cc^{-1} at 30 °C.

3. Results and discussion

Fig. 1(a) and (b) are plots of microhardness versus annealing time at five temperatures for non-irradiated sample and sample irradiated at dose 200 kGy, respectively. Similar curves of hardness versus annealing time at the same temperature range for doses 400, 600, and 800 kGy were also obtained (not shown). Control (unannealed samples) is included as well. It is seen from Fig. 1 that for a given dose and temperature, the hardness increases with annealing time. For a given annealing time, the hardness increases with dose and annealing temperature. The control samples exhibit the lowest hardness values. The data shown herein agree with the experimental findings of Lednicky [21] mentioned above for samples that did not undergo post irradiation heat treatment or aging, hardness increased with radiation dose. Samples that were heat treated at 393 K after irradiation also exhibited an increase in hardness with dose, but the effect was less pronounced in the heat treated samples. The authors attribute this to melting of some of the lamella that occurred during the 10 min exposure to 393 K. The PE hardness data reported herein is similar to that observed by our laboratory in