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Studies on polyethylene pellets modified by low dose radiation prior to part formation

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Abstract

When it is combined with other processing steps, radiation modification of polyethylene pellets prior to conversion into end products (formed parts) has brought about significant improvement of various properties of the polymers and products made from them despite the low cross-linking degree. The physical and chemical changes of the polymers after the radiation modification by electron beam (EB) and gamma ray at low dose levels are studied using various characterizations. Fourier Transform Infrared Spectroscopy (FTIR) showed the formation of carbonyl groups and changes of unsaturated bonds. Gel permeation chromatography (GPC) results indicated broadening of the molecular weight distribution. Rheological analysis in linear visco-elasticity regime showed increased dynamic viscosity and large amplitude oscillatory shear (LAOS) analysis showed increased hysteresis. It is proposed that the radiation at low dose levels and under ambient conditions induces various reactions on the polymer chains including long chain branching, oxidation and changes of unsaturated bonds.

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1. Introduction

It has been well known for many years that irradiating parts formed from PE leads to cross-linking of the polymer and hence improvements of mechanical properties and thermal stability, etc., of the parts. Generally, a high degree of cross-linking (e.g. 60–75% gel content) is imparted by such modification and the radiation doses required for such processes are typically in the range of 50–150 kGy. However, there has been

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significantly less research and development on radiation modification of polyethylenes prior to part formation in the forms of pellets and powders, etc. High levels of cross-linking would drastically decrease the melt flow of the polymers and high gel contents would make it very difficult or impossible to process the polymers and convert them into parts.

A family of polyethylene pellets and powders were modified by radiation prior to part formation at lower doses (<25 kGy) and under ambient conditions. The modified resins have low gel content (<3%). The processibility of the polymers is maintained with the low dose modification while significant improvements of practical properties are achieved [1,2].

Ionizing irradiation of PE polymers may induce various reactions such as cross-linking, chain scission, chain branching, oxidation and gas formation. The radiochemical yield of each event depends on, among other things, the radiation conditions (type and energy of the irradiator, atmosphere, temperature, dose and dose rate, etc.) and the chemical nature and morphology of the polymer. In order to better understand the physical and chemical changes in the polymers after the radiation modification, studies were carried out on some of the irradiated PE polymers with comparison to un-irradiated ones. This paper reports the results of some of the studies on an HDPE polymer.

2. Experimental

2.1. Materials

An HDPE homopolymer in white pellet form with a narrow molecular weigh distribution (DMDA-8007 from Dow) was used. It has a melt flow index (MFI) of about 8.0 g/10 min measured at 190 °C and under a load of 2.16 kg, and a density of 0.963 g/cm^3 or higher. The resin was used as received.

2.2. Irradiation

For electron beam (EB) irradiation, the HDPE resin was irradiated using an EB accelerator under ambient atmosphere and temperature. The EB accelerator's beam energy was 12 MeV and the beam power was 8 kW. The surface dose was targeted at 8, 16 and 24 kGy. Dose mapping was carried out using Far-West radiochromic film dosimeters and the actual average absorbed doses were determined to be 8.8, 17.6 and 26.4 kGy, respectively, with a dose uniformity ratio (max/min ratio) of 1.3. The target surface doses will be used in this paper to refer to "the EB radiation doses" unless otherwise specified. For gamma irradiation, the HDPE resin was irradiated with a gamma irradiator under ambient atmosphere and temperature. The source activity was 2.2 MCi. The minimum irradiation dose was targeted at 16 kGy. Dose mapping was carried out using Far-West radiochromic film dosimeters and the actual average absorbed dose was determined to be 21.4 kGy. The minimum absorbed dose will be used in this paper to refer to "the gamma radiation dose" unless otherwise specified.

2.3. Characterizations

2.3.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were performed in transmission on polymer films with a Fourier Transform Spectrometer, Perkin–Elmer FT-IR 2000. The resolution was 4 cm^{-1} or 1 cm^{-1} and 10 scans were signal averaged. Films of polymers (about 30 cm^2) were prepared by molding them on a press using heated plates at 200 °C for 30 s with a pressure of 10 ton. The molten sample was rapidly quenched in water. The film thickness was between 50 and 100 μm. Spectra are normalized on 1368 cm^{-1} (absorbance = 0.1).

2.3.2. Gel permeation chromatography (GPC)

The molecular weight distributions (MWD) for the resin samples were determined using a GPC 2000 V Waters chromatograph instrument with a set of three columns (HT6E, HT6E, HT2). The analysis temperature was 135 °C in trichlorobenzene (TCB) and the injection volume was 215.5 μL. The universal calibration was performed with PS standards. The MWD was verified with PE NBS 1475 standard.