



# Effect of electron-induced reactive processing on morphology and structural properties of high-density polyethylene



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## ABSTRACT

High-density polyethylene (HD-PE) irradiated in the solid state is compared with HD-PE modified by electron-induced reactive processing (EIREP) which combines in a unique set-up the modification of polymers with high energy electrons and melt mixing processes. The effect of these different processes on the morphology and structural properties of HD-PE was investigated with X-ray analysis, differential scanning calorimetry, optical light microscopy combined with a hot stage and transmission electron microscopy as function of applied dose. The increased molecular mass was measured by using gel permeation chromatography and confirmed with rheological measurements. Even though the crystallinity and melting temperatures are constant within the studied range of dose significant differences have been observed in the morphology as well as in the crystallization behaviour. Electron treatment in the solid state causes a shift of crystallization temperature to lower temperatures due to branching and degradation whereas the irradiation under the dynamic conditions of melt mixing leads to higher crystallization temperatures with increased doses due to in-situ self-nucleation. The morphology and crystalline structure of HD-PE is not influenced by an electron treatment in the solid state, but by EIREP. Spatial and thermal stable heterogeneities have been generated only in HD-PE modified with high energy electrons under the dynamic conditions of melt mixing.

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## 1. Introduction

Modification of polymers with high energy electrons is well investigated and used to modify the properties by crosslinking, degradation, grafting and curing [1–6]. During interaction of high energy electrons with polymeric material excited atoms or molecules as well as ions and secondary electrons are generated leading to subsequent changes of polymer molecules via radical induced chemical reactions. These electron-induced chemical reactions depend on polymer structure, absorbed dose, temperature, aggregate state as well as chemical environment [7–9].

For industrial applications like heat shrinkable films, tubes or thermostable pipes, polyethylene is usually irradiated at room temperature in the solid state where chemical reactions will occur mainly in the amorphous phase and at the lamellar surfaces due to limited mobility of polymer chains in the crystalline phase. The number of radicals is controlled by the applied dose defined as

absorbed energy per unit of mass. In contrast to the state of the art technology at stationary conditions, the electron-induced reactive processing (EIREP) induces chemical reactions by spatial and temporal precise energy input via high energy electrons under the dynamic conditions of melt mixing [10–16]. The penetration depth of high energy electrons is limited to a part of the polymer melt in the mixing volume and can be controlled by the electron energy. However, the electron energy does not only influence the penetration depth, but also the ratio of treatment volume (reaction zone) to the total volume (mixing volume) in the mixing chamber. Due to the melt mixing process during irradiation the polymer melt is changed within the treatment zone and thereby the whole volume of polymer melt is modified.

In the present study, high-density polyethylene (HD-PE) was modified by state of the art technology as well as by EIREP in order to investigate the effect of these different procedures on the morphology and structural properties of HD-PE as function of absorbed dose.

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## 2. Experimental

### 2.1. Material

High density polyethylene (DOW™ HDPE 25055E, density: 0.953 g/cm<sup>3</sup>; MFI: 25 g/10 min at 190 °C and 2.16 kg) was purchased from DOW, Germany.

### 2.2. Preparation

The irradiation was carried out using an electron accelerator ELV-2 (Budker Institute of Nuclear Physics, Novosibirsk, Russia). The electron treatments in the solid state were performed at room temperature using tensile test specimens of HD-PE which were injection moulded using a BOY 22A HV (Dr. Boy GmbH & Co. KG, Neustadt-Fernthal, Germany). Electron treatments during melt mixing have been applied in an internal mixer with a chamber volume of 50 cm<sup>3</sup>. The EIReP samples have been processed by mixing polyethylene for 10 min at 165 °C with a rotor speed of 60 rpm and a friction ratio of 1.5. After electron treatment the experiment was stopped and the polymer was removed from the chamber for cooling. It has to be noted that the cooling rate of the EIReP samples are different from the cooling rate of injection moulded samples. All samples were irradiated under nitrogen atmosphere to avoid oxidative degradation. The electron energy was kept constant at 1.0 MeV while the dose values varied from 5, 10, and 20 to 40 kGy. Furthermore, 80 kGy and 160 kGy have been applied to tensile test specimens modified in the solid state.

### 2.3. Characterization

#### 2.3.1. Gel content

Sol-Gel analysis was carried out to determine the fraction of insoluble HD-PE (gel). Approximately 200 mg of the sample in form of flakes were extracted for 16 h in boiling p-xylene at 144 °C to remove the soluble part of HD-PE. After the extraction the samples were vacuum dried to a constant mass. The gel content was calculated in percent according to the following equation:

$$X_c = (m_1/m_0) \times 100\% \quad (1)$$

where  $X_c$  is the gel content,  $m_1$  is the final mass after extraction and  $m_0$  is the initial mass of the sample.

#### 2.3.2. Gel permeation chromatography (GPC)

The molecular masses were determined by using a PL-GPC220 (Polymer Laboratories Ltd., Shropshire, UK) at 150 °C. The instrument contains two columns (PLgel-Olexis, 300 mm × 7.5 mm) coupled with a refractive-index detector and a MALLS detector (DAWN Heleos-II, Wyatt Technology Corporation, Santa Barbara, USA). As eluent 1,2,4-trichlorobenzene has been used. The flow rate amounted to 1.0 ml/min.

#### 2.3.3. Rheological measurements

The melt rheological behaviour was analysed using an ARES rheometer (Rheometrics Scientific, New Castle, USA) with parallel-plate geometry. The tests were carried out in a frequency sweep mode under nitrogen atmosphere at 190 °C. The frequency was increased logarithmically at constant strain amplitude of 10%.

#### 2.3.4. Differential scanning calorimetry (DSC)

DSC was performed in order to evaluate the crystallinity  $\alpha$  (DSC) as well as the temperature of melting and crystallization using a Q2000 (TA instruments, New castle, USA). Approximately 5 mg of the samples were measured under nitrogen in a heating-cooling-

heating cycle in a temperature range between –80 °C and 180 °C with a scan rate of 10 K/min. For calculation of crystallinity  $\alpha$  (DSC) the melting enthalpy of the first heating run was divided by the melting enthalpy of HD-PE with 100% crystallinity (288 J/g) [17].

#### 2.3.5. X-ray analysis

XRD investigations have been applied for calculation of crystallinity  $\alpha$  (WAXS), evaluation of size of crystallites and for estimation of long period of the crystalline lamellae. Wide angle X-ray (WAXS) diffractograms were recorded using a 2-circle diffractometer (XRD 3003  $\theta/\theta$ , Seifert-FPM, Germany) with a Cu-K $\alpha$  X-ray source. To prevent orientation effects, the samples were cut into small pieces and irregularly distributed between two aluminium foils. The scanning angle varied from 5° to 40° at 40 kV and 30 mA with a step size of 0.05° and a scanning rate of 4°/min. Small angle X-Ray (SAXS) measurements were performed on a 3fold pinhole system (self-construction of Leibniz Institute of Polymer Research) with a RIGAKU rotating anode using 40 kV and 100 mA.

#### 2.3.6. Optical light microscopy (OLM)

The characterization of morphologically properties was performed by several microscopic techniques. An optical transmission light microscope equipped with polarization filter and a hot stage was used for investigations of size and formation of spherulites as well as for studies of melt and crystallization behaviour. Prior to the OLM investigations, the samples were precisely cut at - 60 °C into thin sections of a uniform thickness of 10  $\mu$ m using a cryo-microtome (Leica RM2265, Germany). The OLM investigations were performed using a microscope Axioimager. A1m (Zeiss, Germany) combined with a camera (AxioCam ICc3) and the software AxioVs 4.8.1.0 for capturing the images. Characterization of melt and crystallization behaviour have been carried out using a hot stage LTS420 (Linkam Scientific Instruments Ltd., Tadworth, UK) with the control unit Linksys32 and a water cooling system.

#### 2.3.7. Transmission electron microscopy (TEM)

Transmission electron microscopy was used for characterization of formation and thickness of lamellae. In order to enhance the contrast cryo-sectioned surfaces have been stained in vapour of RuO<sub>4</sub> for 24 h. Afterwards ultrathin sections with a thickness of 50 nm were cut from the stained samples with a diamond knife (DIATOME, Switzerland) at - 180 °C using a cryo-Ultramicrotome UC7 (Leica, Austria). TEM images were recorded on a Libra200 MS (Carl Zeiss GmbH, Germany) and the lamella thickness was measured on at least 200 lamellae per sample using the software Digital Micrograph.

#### 2.3.8. Mechanical testing

Tensile tests were performed on injection moulded dumb-bell shaped tensile test specimens according to ISO 527-2/1BA/20 using a universal tensile testing machine Zwick (Ulm, Germany). In each case five samples have been tested at room temperature with a constant cross-head speed of 1 mm/min.

## 3. Results & discussion

### 3.1. Gel content

HD-PE is a semi-crystalline thermoplastic containing crystalline domains distributed within the amorphous phase. Due to hindered mobility of polymer radicals within the crystalline regions, crosslinking will occur preferentially in the amorphous phase or in the fold surface. At temperatures above the melting temperature, there are no crystalline domains and the efficiency of electron induced crosslinking increases. Therefore, the generation of a three-

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