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INVESTIGATION OF THE EFFECTS OF DEGRADATION OF HIGH DENSITY POLYETHYLENE BY ^{13}C NMR SPECTROSCOPY AND ^{1}H RELAXOMETRY

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ABSTRACT. The structural and dynamic changes occurring in high-density polyethylene exposed to gamma-, X-radiation and extreme temperature have been investigated by high-resolution solid state CP/MAS ^{13}C NMR and ^{1}H NMR relaxometry. The ^{13}C CP/MAS NMR spectra show that the gamma and X-radiation can induce the formation of Y-type branches in HDPE. The Laplace distribution of transverse T_2 and longitudinal T_1 relaxation times are used first to identify dynamics and morphological components of HDPE samples and then to characterize the degradation effects of these samples subjected to external aging factors. The small amplitude of the fourth component from T_2 Laplace spectra confirms the connection of free ends of polymer chains to form Y-branches HDPE subjected to X-radiation. The T_1 spectra Laplace show that the cooling at nitrogen temperature will affect mostly the crystallinity of HDPE.

Keywords: *High Density Polyethylene (HDPE), gamma and X-ray irradiation, ^{13}C CP/MAS NMR, ^{1}H NMR, T_1, T_2, Laplace distributions.*

INTRODUCTION

High density polyethylene consists of quasi-linear molecules with less than one branching point per 200 carbon atoms in the backbone. Therefore HDPE is characterized by high degrees of crystallinity, highest modulus and lowest permeability of all the classes of polyethylene. These properties make HDPE suitable for certain daily-use liquid holders and chemical storage tanks [1]. For such storage bottles, it is important to maintain unaltered their physicochemical properties therefore, the effects of degradation under the action of various ageing factors like high or low temperature or high energy

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irradiation, must be know. Such agents can produce modification at the level of chemical structure or polymer chain.

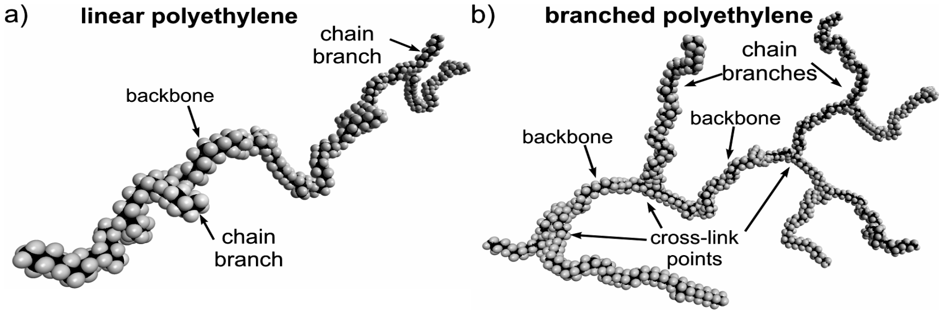

Figure 1. Schematic representation of a) liner b) branched polyethylene.

For example, the exposure of PE to high-energy radiation leads to backbone and branch scission, formation of new cross-links and formation of unsaturated and oxidized groups. Moreover, aging factors can produce changes in the melting behavior and crystallinity with direct effect on the elastic modulus [2]. The changes in the crystalline and amorphous phases, the formation and nature of the new cross-link points in gamma-irradiated HDPE were extensively studied [2, 3]. The branching analysis of polyethylene has been a subject of considerable interest in the past two decades due to the importance of branching type and distribution (see Figure 1) in such materials. The use of various solid-state NMR pulse sequences allows identifying the characteristic resonance peaks associated to crystalline and amorphous phases in semi-crystalline polymers (see Figure 2). The ^{13}C NMR technique is the primary method that is commonly used for such analysis [2-6]. In the last decade, ^{1}H relaxation times or Laplace distributions of transverse relaxation times were used for investigating the effects of aging under factors like temperature and UV-radiation [7, 8].

The aim of this paper is to investigate the effects on the structure and morphology of different aging agents like gamma and X-ray and extreme temperatures. The modifications at the level of functional groups are investigated by ^{13}C CP/MAS NMR spectroscopy, while the modifications in the HDPE polymer chain segmental dynamics are monitored via the changes in the Laplace distribution of transverse T_2 relaxation times. This is possible due to the fact that the peaks from T_2 distributions can be associated with rigid, mobile, loose loops and free ends polymer chain segments. The longitudinal T_1 relaxation time edits different characteristics than T_2 therefore the T_1 distributions are used to observe the effects of aging factors at the level of HDPE crystalline and amorphous phases.

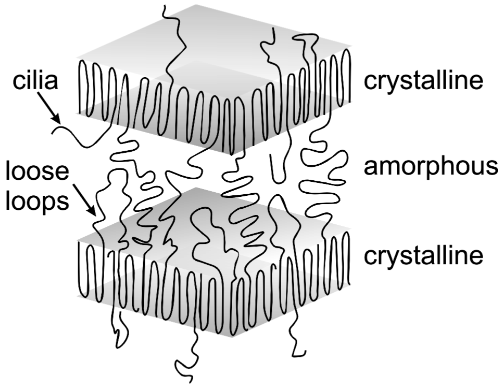

Figure 2. Schematic representation of high density polyethylene morphology.

RESULTS AND DISCUSSION

Figure 4 presents the CP/MAS ^{13}C NMR spectra of un-irradiated and gamma and X-ray irradiated high density polyethylene. In the spectra of the un-irradiated sample one can identify a high and narrow peak at 32 ppm and a broad peak at 31 ppm (Figure 4a). The narrow peak located at 32 ppm is associated to the methylene functional group from crystalline components and the peak from 31 ppm is associated to the amorphous phase [2]. In the spectrum of gamma irradiated sample an additional peak appears at 34 ppm (Figure 4b). This can be associated to the carbon-carbon bonds from cross-linking points in polyethylene [3, 5]. According to the interpretation of Horii et al. and Randall, these cross-link points are most likely the origin of Y-branches than H-branches [3, and references therein]. This means that the effect of gamma irradiation is connected with a higher probability a polymer chain-end to another backbone than to connect to backbones. Similar appearances of a peak located at 34 ppm and associated to the carbon-carbon bonds in crystalline phase of high density polyethylene are observed in the X-ray irradiated sample (Figure 4c). The relative intensity of the cross-link peak observed in the CP/MAS ^{13}C NMR spectra of HDPE irradiated with X-rays is higher than the relative intensity of the same peak observed in the case of HDPE irradiated with gamma rays. Taking into account also the fact that the irradiation dose was approximately 25 times smallest in the case of X-rays, one can conclude that this type of radiation produces significant higher degradation of HDPE than gamma radiation.

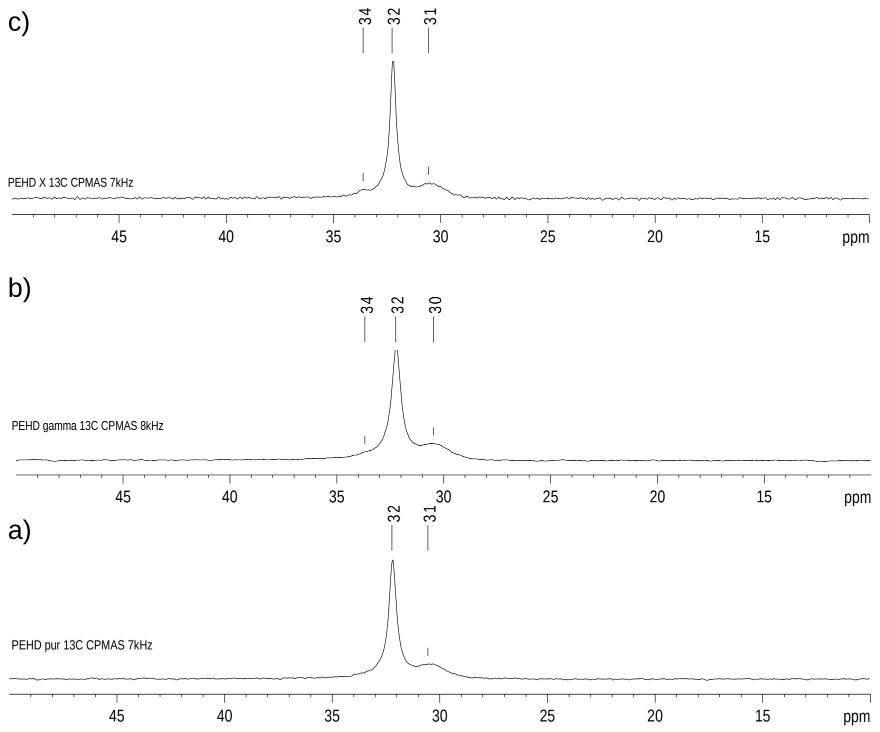

Figure 4. CP/MAS ^{13}C NMR spectra of a) pure; b) gamma irradiated and c) X-ray irradiated high-density polyethylene.

The degradation effects on high-density polyethylene morphology of X-ray irradiation are compared with those produced by extreme temperature. For that, a series of CPMG curves are recorded and presented in Figure 5a together with the curve corresponding to pure HDPE. Small differences can be observed among these decays. The CPMG curve (open gray stars) decay slowest than the pure HDPE (filled circles) while the curves corresponding to HDPE degraded (open squares) in liquid nitrogen and melted (open gray triangles) decay faster. A better analysis of these CPMG curves can be obtained from the corresponding T_2 distributions which are presented in Figure 5b. All distribution from the Laplace spectra presents four peaks. The main peak is located at the lowest T_2 values, around 200 μs, therefore characterized by a reduced mobility, and can be associated with the crystalline phase of HDPE (see Figure 2). The second peak located between 1–2 ms, is characterized by a mobility characteristic to linked polymer chains therefore can be associated to the amorphous phase of HDPE. With one order of magnitude higher one can find a peak associated to the more mobile chain segments like the loose loops from the amorphous phase, while with two orders of magnitude one can find peaks which can be associated with the extremely mobile polymer chain segments like the end chains or cilia (see Figure 2).

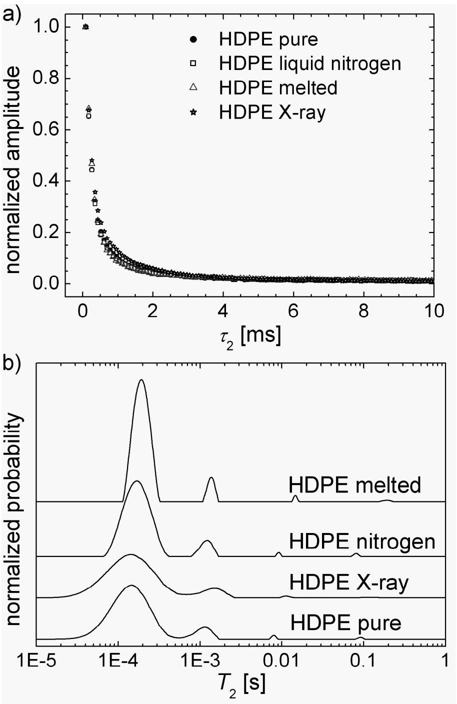

Figure 5. a) The CPMG echoes decays; b) the corresponding T_2 distributions for the pure and aged in liquid nitrogen, melted and X-ray irradiated HDPE.

The distributions of pure and X-ray irradiated sample are almost similar with two exceptions: i) the HDPE chain segments from amorphous phase become more mobile, observed from increased values of T_2, and ii) the peak corresponding to end segments almost disappear then can be associated with the formation of Y – branches observed also from ^{13}C CP/ MAS NMR spectra. The positions of peaks in the T_2 distributions for HDPE aged in liquid nitrogen correspond with the peaks of pure HDPE. Nevertheless, the effect of 5 min cure in liquid nitrogen leads to a more organized chain distribution into the crystalline and amorphous phases, as can be observed from the corresponding narrowed peaks. The highest homogeneity is produced by melting the HDPE sample. This treatment will increase also the mobility of loose loops and cilia from amorphous phase.

The melting cure lead to significant changes also into the saturation recovery build-up curve of the same pure and aged HDPE samples (see

Figure 6a). Only three components (see Figure 6b) can be identified in the T_1 distributions and these can be associated from right to left (decreasing T_1 values) with the crystalline, interface and amorphous phase of HDPE [1]. The discrepancy between T_2 and T_1 distributions arises from different NMR sensitivity of these two parameters for describing multiphase in polyethylene [2]. In contrast to the thermal treatment, irradiation with X-rays leads to a small ordering of HDPE network. The melting cure destroys a significant part of amorphous and crystalline phase and increase the interfacial high density polyethylene network.

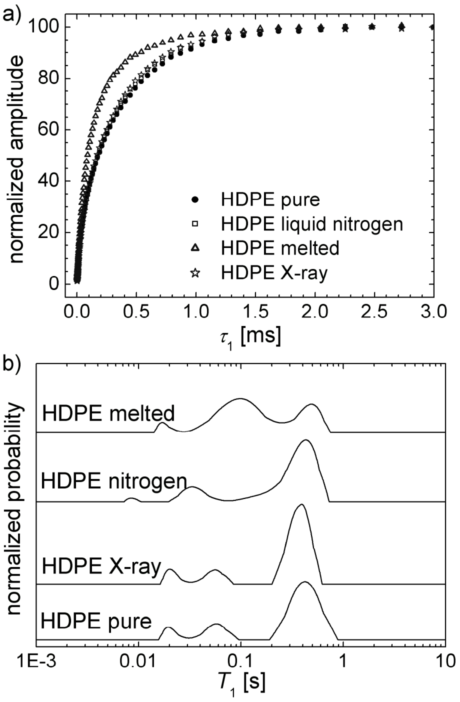

Figure 6. a) The saturation recovery and b) the corresponding T_1 distributions for the pure and aged in liquid nitrogen, melted and X-ray irradiated HDPE.

CONCLUSIONS

The resonance peaks due to direct cross-links and forming Y-branches have been detected in the ^{13}C of gamma- and X-irradiated HDPE. The T_2 Laplace spectra consisting in four well resolved peaks, associated to rigid, mobile, loose loops and free ends, after irradiation with X-rays or cured at extreme temperatures reveals changes in the HDPE polymer chain dynamics. The T_1 Laplace distributions edit a three-phase: crystalline, amorphous and interface, morphology of HDPE. The major degradation effect was observed in the crystalline phase of melted HDPE sample. The ^{1}H NMR Laplace distributions was proved to be a valuable tool to investigate the high density polyethylene degradation.

EXPERIMENTAL SECTION

The ^{13}C CP/MAS NMR spectra were recorded with 500 MHz DSX Bruker spectrometer and a 4 mm probe-head. The rotor frequency was 7 kHz for the pure and X-ray irradiated HDPE and 8 kHz for the gamma-irradiated HDPE sample. The pulse program is presented in figure 3a. The recycle delay was 5 s and the scan numbers was set to 4. The spectra were recorded at a temperature of 28.5 ^{0}C.

The ^{1}H NMR data were recorded using the Bruker Minispec spectrometer with the 10 mm probe-head working at 19.688 MHz ^{1}H Larmor frequency. The tipping pulse was 8.4 μs and the refocusing pulse 16.8 μs. In order to ensure a good signal to noise ratio 256 scans were recorded for the 1000 CPMG echoes with an echo time of 70 μs (see Figure 3b) and a recycle delay of 3 s.

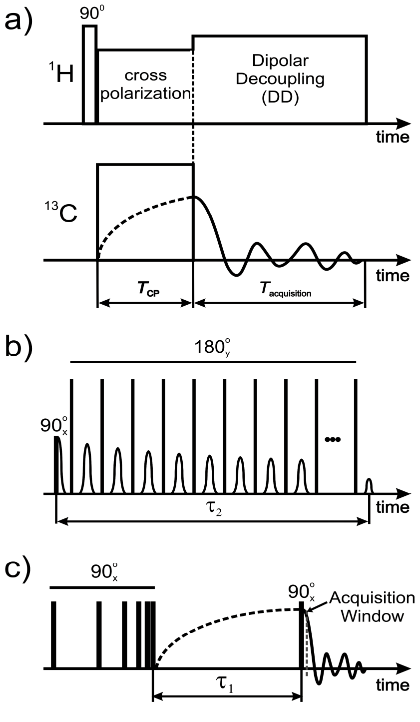

Figure 3. a) ^{1}H -^{13}C cross-polarization; b) CPMG and c) saturation recovery pulse sequences.

For the saturation recovery (see Figure 3c) the number of saturating pulses was 10 while the scans number was reduced at 64 [9]. The recovery time, τ_1 was increased from 1 ms with a ratio of 1.1 in unevenly 85 steps up to 3 s. In all measurements the temperature was set to 35 ^oC. Finally, in order to find the transverse T_2 and longitudinal T_1 relaxation times distributions, the CPMG decays and saturation- recovery build-up curves were analyzed using the well know UPIN algorithm, which perform a Laplace inversion of the measured data [10]. The HDPE samples were aged using various agents and different conditions: i) the dose of irradiation with gamma ray was 8989 Gy accumulated during 1696 h at a 5,3 Gy/h; ii) the accumulated dose of irradiation with X-ray was 358 Gy during 12 days; iii) HDPE was melted at a temperature of 256 ^oC during 24 h and then cooled at a room temperature; iv) HDPE was sinked into liquid nitrogen at -196 ^oC for 5 min and then heated at room temperature.

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