

CHAR FORMATION IN POLYETHYLENE: EFFECT OF THE MACROMOLECULAR ARCHITECTURE

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INTRODUCTION

Organic polymers ignite following a very complex mechanism, which involves the occurrence of several physical and chemical events [1,2]. From a general point of view, the typical involvement of polymers in fires occurs through their chemical degradation taking place in three steps: ignition, combustion, and smouldering. The ignition process is bound to be kinetically controlled because it involves a heterophasic reaction between oxygen of air and the solid or liquid polymer material [2]. The degree of kinetic control and therefore the dependence of ignition on irradiation is related to the polymer chemical reactivity with oxygen and oxygen diffusion rate into the polymer phase. In this work, the charring ability of polyethylenes (PEs) having different macromolecular architectures, in terms of molecular weight and presence of short- or long-branching structures, is thoroughly investigated.

EXPERIMENTAL

Materials

Different grades of commercial LDPEs and HDPEs were studied namely HDPE_HV (Lupolen 5021DX), HDPE_LV (Eraclene MP90U), LDPE_HV (Lupolen 2420F) and LDPE_LV (Alcudia PE02).

Characterization

FTIR-ATR measurements were performed both on the pristine and degraded materials in order to have a chemical characterization of the materials. Differential Scanning Calorimetry (DSC) characterization was performed in order to evaluate the crystallization temperature (T_c), crystallization enthalpy (ΔH_c), melting temperature (T_m), and melting enthalpy (ΔH_m). Rheological analyses were carried out using a parallel plate-plate instrument to evaluate the complex viscosity as a function of frequency. The obtained experimental data were fitted using the Cross model. The thermal and thermoxidative behavior of the materials were assessed using Thermogravimetric analysis both in dynamic heating and isothermal conditions. Finally the time to ignition (TTI) of the polymers were evaluated through cone calorimetry tests and the temperatures involved before combustion were recorded using thermocouples in contact with the upper surface of the specimens.

RESULTS AND DISCUSSION

Preliminary spectroscopic, thermal and rheological characterizations were carried out on the different PEs in order to determine their physico-chemical behavior. The results of TGA performed in oxidative atmosphere have highlighted different behaviours between the samples, in terms of both thermo-oxidative stability and degradation temperatures. In Figure 1 the isothermal TG curves are reported in which is possible to see different residual weight after 60 min of treatment in oxidative atmosphere at 320°C. This phenomena was connected to the different char formation on the surface of the samples and FTIR-ATR spectroscopy confirmed the presence in large amount of C=C aromatic stretching for HDPE_HV. The chemical/physical modifications occurring in the PEs preignition step were studied on the samples exposed to 20 kW/m² in the Cone Calorimeter also monitoring the temperature on the surface of the samples. The TTI was correlated with the char stability and for the HDPE_HV was 240s instead 170-180s that was found for the other samples.

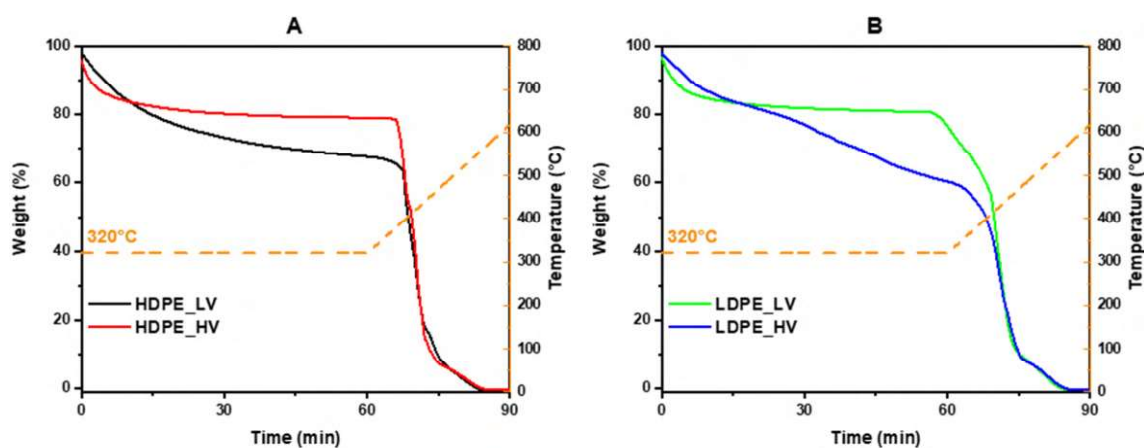


Fig. 1 Isothermal TG curves for 60 min at 320°C, then heated to 650°C (10°C/min) for HDPEs (A) and LDPEs (B) samples.

The mechanism of char formation in polyethylene proceeds through oxidative dehydrogenation reactions resulting in conjugated polyenes, which further undergo crosslinking, until the formation of char. Therefore, the kinetics of the charring mechanism and the stability of the formed char are strongly affected by the promptness of the polymer macromolecules in interacting with the surrounding chains to form crosslinked structures, representing the precursors of the carbonaceous residue. Aiming at verifying the possible different tendency of the chains of the different PE samples in establishing polymer-polymer interactions when subjected at high-temperature treatments, time sweep tests were performed on all the investigated materials.

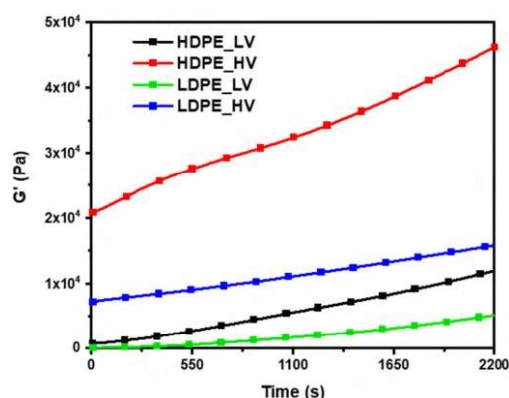


Fig. 2 Storage modulus (G') as a function of time for all investigated materials.

These tests (Figure 2) have been demonstrated that the linear chain structure of HDPE (especially in the case of high molecular weight polymers) leads to the establishment of strong interactions between the macromolecules (due to their close proximity), enabling the formation of a well-developed crosslinking network, which is likely able to further evolve into a stable char. Conversely, the presence of long-chain branched structures increases the distance between the polymer backbones, making more difficult the establishment of strong and durable interactions, notwithstanding the formation of a highly entangled structure. This issue might compromise the formation of a stable char for long-chain branched LDPE, which, indeed, showed a lower charring ability [3].

References

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