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Polyethylene Obtained by Plasma Polymerization of Hexene

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Summary: This work presents the synthesis by plasma of polyhexene (PHe) as an alternative to produce thin films of polyethylene (PE) without catalysts or other chemical compounds. PHe was obtained using 1-Hexene in glow discharges at 13.5 MHz, 10^{-1} mBar and power between 40 and 120 W. The results showed that plasma PHe had the typical C—C and C—H bonds of PE with other bonds, as C=C and C=O, that indicate unsaturation and oxidation in the polymers. The thermal degradation of PHe starts at 250 °C, 100 °C lower than in PE. However, at $T > 500$ °C, PHe has more residual mass than PE. In the interval of 20–100 °C, the electrical conductivity of PHe was calculated between 10^{-11} and 10^{-8} S/cm. These results suggest that the structures of PHe and PE are similar and that the plasma polymerization of 1-hexene is an alternative route to obtain oxidized and unsaturated varieties of PE as thin films on different surfaces.

Keywords: plasma; polyethylene; polyhexene; polymerization

Introduction

The applications of PE are based on its simple structure which results in high chemical passivity, low electrical conductivity and a hydrophobic behavior in the polymer. PE is used as an electric insulator and as protective films in coating treatments and packaging material. The biomedical applications of PE are increasing constantly based on its biochemical passivity.[1–3] These characteristics reduce its degradation, but on the other hand complicate its possibilities to combine with other materials with different physicochemical properties like metals.

PE is produced generally from ethylene in gas-phase polymerizations using different catalysts of Ti, V, Cr or Mg.[4–6] However, in order to obtain PE without catalysts, initiators, solvents or other chemical reagents that could contaminate the polymers, different syntheses have to be considered. Polymerizations with these conditions can be developed by plasma, where the electrical field applied to the synthesis produces ions and excited molecules that make the function of initiators and catalysts.

Plasma polymerizations have been used to obtain polymers with a semi-controlled purity, hydrophobicity and electric conductivity. This technique has also been used in the superficial modifications of solids to enhance the electrical properties for microelectronic or optical devices[7] and in the growing of cells in biomedical applications.[8] In this work, we study the plasma polymerization of 1-hexene to produce thin films of PE in chemical reactions without catalyst or other chemical reagents that could be harmful in biomedical applications.

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Experimental Part

The synthesis uses the plasma excitation of 1-hexene (Aldrich, 99%) in a tubular glass reactor with volume around 1300 cm^3. 1-Hexene is formed with a short chain of hydrocarbons and with it, the polymerization would propagate in steps of 6 carbons. 1-Hexene is liquid at room conditions with a high vapor pressure, thus although its plasma polymerizations are in gas-phase, the monomers can be handled in liquid-phase.

The reactor has a diameter of 9 cm and 26 cm of length with stainless steel flanges in its extremes. Each flange has three access ports. In the central access, two stainless steel electrodes of 7 cm diameter and 6 cm of separation between them were collocated. The monomer container, a Pirani gauge and a vacuum pump were connected to the other ports, see Figure 1. The electrodes were connected to a RFX-600 Advanced Energy radiofrequency power source in order to generate glow discharges at 13.5 MHz. The power was between 20 and 120 W, pressure was in the 10^{-1} mbar range and the polymerization time was 180 min.

The polymers were synthesized as consecutive thin compact films on the inner surface of the reactor. After the synthesis, the polymers were washed and swelled with the monomer and acetone, and separated from the surfaces of the reactor with a thin spatula. The polymers were named polyhexenes (PHe) to differentiate from the traditional PE and to preserve the name of the monomer in the polymer. Some of the analyses were compared with PE in order to study the differences or coincidences with the plasma polyhexenes.

The thickness of the films was obtained with a Mitutoyo Micrometer with resolution of 1 μm. The micrographs were taken with a Jeol JSM-5900LV scanning electron microscope. The structural analysis was made with an infrared (IR) spectrophotometer Perkin Elmer spectrum 2000 GX-FTIR System using 32 scans. The IR spectrum was taken directly from the films without a substrate or any other support. The thermogravimetric studies were made in a TA Instruments 51 Thermal analyzer. The heating ramp was 10 °C/min in a nitrogen atmosphere, from room temperature to 800 °C. The electrical conductivity was calculated through the resistance measured with a two-Cu parallel electrodes arrangement with the sample in the middle.

Results and Discussion

Morphology

PHe films synthesized at different power are shown in Figure 2. There are layers with different thickness, from approximately 2 μm to 10 μm. This layered structure may be consequence of slight fluctuations in the synthesis conditions, pressure and power, during the polymerizations; however, the total average thickness was 14 μm. In general, all the polymers show smooth surfaces with compact layers. This smooth morphology is similar to that of PE.

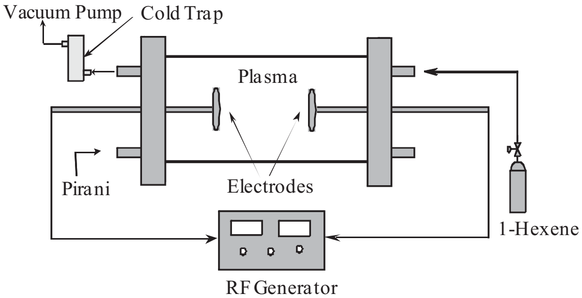
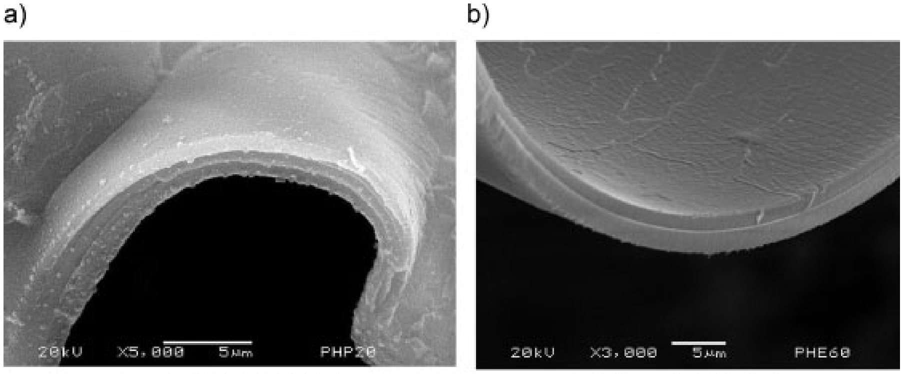
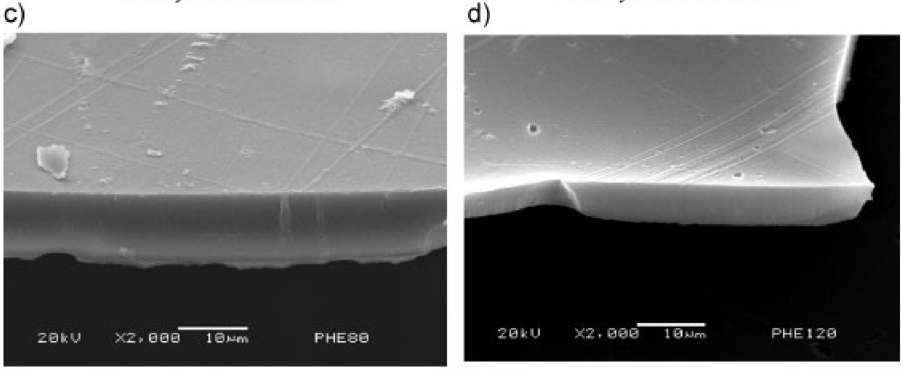


Figure 1.
Set up of the reactor.



PHe synthesized at 20 W.

PHe synthesized at 60 W.



PHe 80 W

PHe 120 W

Figure 2.
Morphology of plasma PHe.

Infrared Spectroscopy

Figure 3 shows the IR spectra of PE and PHe synthesized between 20 and 120 W. From a global point of view, PHe has the principal peaks of PE. The main absorption can be observed between 3000 and 2830 cm^{-1} that corresponds to the C–H bonds, typical in the PE structure. The

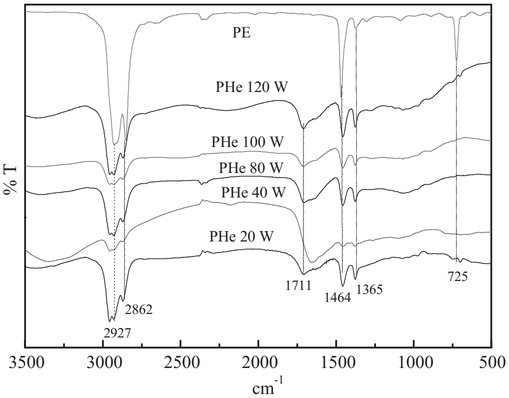
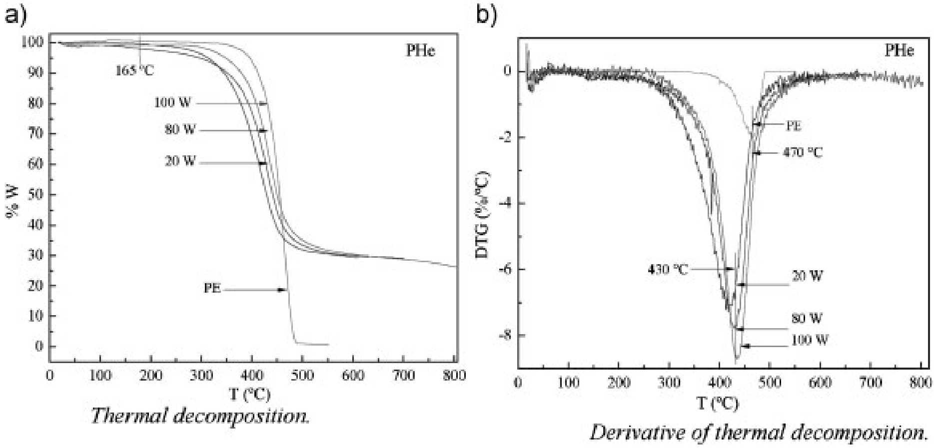


Figure 3.
IR spectra of PHe.



Thermal decomposition.

Derivative of thermal decomposition.

Figure 4.
Thermal descomposition of PHe.

bands centered at 1464 and 1365 cm^{-1} also belong to the C–H groups.

Another important region in PHe, not shown in PE, is between 1780 and 1600 cm^{-1}, which corresponds to C=C and C=O bonds. The first groups can be remnants of the 1-hexene; however, as there are no other chemical reagents during the polymerization, the oxidated bonds can be originated in the long-life radicals produced in the plasma, that neutralize with the atmospheric oxygen at the end of the polymerization. The C=C and C=O groups are the main difference with PE, which only has saturated carbons. This is also reflected in the absence of the peak centered at 725 cm^{-1}, which can be associated with the absorption of C–C, and appears in PHe as C=C bonds (1711 cm^{-1}).

Thermogravimetric Analysis

Figure 4 shows the thermal decomposition of PHe synthesized at different power. The first point to highlight is that PHe, as PE, does not present a significant absorption of water. The main decomposition starts at approximately 250 C and ends at around 500 C, with a residual mass of 30%. The center of the decomposition is located around 430 C. The same points can be

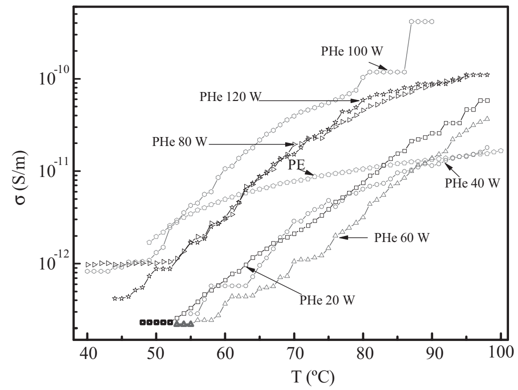


Figure 5.
Electrical conductivity of PHe.

found in PE at different values, where the main decomposition starts at approximately 350 C and ends at 480 C, centered at 470 C, in a narrower interval of decomposition. In general, the behavior of all PHe films is similar, with more resistance to temperature than PE at T > 450 C. At 800 C, PHe still preserves approximately 30% of its mass, while PE loses almost all mass at 500 C. The wider interval of decomposition suggests a polydisperse molecular weight in PHe.

Electrical Conductivity

The conductivity was calculated with the resistance of the polymers measured between 10 and 250 V and temperature was from 20 to 100 C. Figure 5 shows the conductivity of PHe and PE as a function of temperature. The general tendency indicates that the conductivity of PHe increases with temperature and the power of synthesis, from 10^{-13} to 10^{-10} S/m. This increase with temperature is typical in semiconductors or insulators.

At low power and temperature, conductivity of PE is higher than that of PHe, however, at high power and temperature the conductivity of PHe is more than one order of magnitude higher. This can be because of the influence of unsaturated bonds and the polarizability of the oxygenated sites in PHe.

Conclusions

The synthesis by plasma of polyhexene using 1-hexene was studied in order to obtain thin films of polyethylene without using other chemical reagents different from the main monomer. The results indicate that the infrared spectra of polyhexenes show similar structure to PE with the main C–C and C–H groups in PHe. However, unsaturated C=C bonds coming from the monomer were also found in PHe. Other oxidated groups as C=O appeared in the polymer, probably as a result of the neutralization of long-life radicals created during the high-energy collisions in the plasma. No other chemical groups, different from those of PE, were found.

The initial point of thermal degradation of PHe was at approximately 250 °C, 100 °C lower than in PE, 350 °C. However, the residual mass of PHe was more stable at temperatures higher than 450 °C, where PE loses almost all of its mass, while PHe preserves up to 30%. The wide interval of decomposition in PHe, in which the smaller chains volatilize at low temperature and the longest decompose at high temperature, was considered as an indicative of polydispersity in the polymers. The electrical conductivity of PHe also has similar tendencies, with lower conductivity than PE at low temperature and power of synthesis. However, this tendency reverts at high temperature and power.

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