COMPARING THE GRAFTING OF STYRENE ONTO LINEAR LOW DENSITY POLYETHYLENE AND LOW DENSITY POLYETHYLENE

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ABSTRACT

This work aims to evaluate the best grafting performance between linear low density polyethylene (LLDPE), and low density polyethylene (LDPE) films once synthesized in order to be used as ion exchange membranes.

The simultaneous method was used in the experiment under absorbed dosis covering the range of 5, 10, 15, 20 and 25 kGy, using methanol as solvent and styrene as monomer. The samples were weighted, immersed in ampoules containing the monomer/solvent (30:70) solution, sealed in nitrogen atmosphere and irradiated.

Irradiation process took place at room temperature in a ^{60}Co source. After the irradiation, the samples were washed in Soxhlet system overnight and weighted.

The degree of grafting (DOG) was the criteria used to evaluate the behavior of each type of PE. The samples were characterized also by infrared spectroscopy analyze (FTIR).Results indicated that LDPE behaves better grafting than LLDPE in the ranges of 5, 10, 15 and 20 kGy the best performance was 20 kGy with 100% higher values.

INTRODUCTION

This works aims to compare the performance under irradiation of low density polyethylene (LDPE) and linear high density polyethylene (LHDPE) so that it would be possible to make a choice concerning the best possible backbone in manufacturing a membrane through its modification via radiation induced graft using gamma radiation from a ^{60} Co source.

Polyethylene (PE) is one of the widest commodities, present in large scale in modern industry. The market gives away 5 different types of polyethylene:

- Low density polyethylene (LDPE)
- Linear low density polyethylene (LLDPE)
- Ultra high weight molecular polyethylene (UHMWPE)
- Ultra low density polyethylene (ULDPE)
- High density polyethylene (HDPE)

The applications of PE vary in a wide range such as packaging of food, liquids, pharmaceutical instruments, hospital tools, toys, home utilities, tubes, wires[1], membranes for proton exchange in fuel cells[2, 3] etc.

The IPEN/CQMA aims to modify polyethylene films through grafting with styrene and sulfonation, in order to create a membrane to be applied in proton-exchange membranes. Polyethylene was chosen because of its versatility and low cost. Its low compatibility with other polymers can be overcome by enhancing its polarity through grafting of functional monomers onto polyethylene chains, which can improve its adhesion to other materials without significantly changes its structure[6].Considering all the types of PE available in the market, low density PE is ranked as a better choice due to their cristalinity and low density of branching compared to the other ones. The sulfonation step wasn't be analyzed here.

Low density polyethylene is partially crystalline (50-60%), its melting point around 110 ^{0}C and branched chains[1] and given away to the market as LDPE and LLDPE.

LDPE is known as long chained with very small density of branches, smaller crystallites, and smaller crystallinity compared to LLDPE, which is highly (90%) crystalline, due to its long branches not being well accommodated in the crystalline network[1].

Radiation-induced graft polymerization is now a well-established method for the modification of chemical and physical properties. Grafting of hydrophilic monomers onto hydrophobic substrates via radiation is commercially interesting due to the direct commercial products, once irradiation as a source of has free radicals generates high rate of free radicals capable of inducing the insertion of functional monomer with no chemical initiators, thus, grafts with no by-product[4, 5, 6].

Another factor to improve the yield and facilitate the grafting rate is using low dose rate as many authors have reported [4, 5, 7, 10].

Finally, the process technique is also of importance in the performance of the yield of grafting. There are two techniques; indirect technique (pre-irradiation and peroxidation) and direct technique (simultaneous radiation). The simultaneous method means that the substrate (PE) films are immersed in the monomer then exposed to ionizing radiation. Both the polymer and the monomer are exposed to radiation.

The aim of this study is to modify the substrates (low density polyethylene or LDPE and linear low density polyethylene or LLDPE) under industrial/commercial conditions, which means, under dose rates higher than those observed in scientific papers. The IPEN/CQMA used the EMBRARAD facilities, which irradiates at 10kGy/h each sample at room temperature. It was used a solution of styrene: methanol (monomer: solvent) in a 30:70 proportion and 30% of sulfuric acid as additive. For comparison of yield of grafting of both LDPE and LLDPE it was chosen the simultaneous method, ranging from 5 to 25 kGy as total dose. After irradiation, each sample had its degree of grafting (DOG) evaluated and, then, characterized by infrared spectroscopy analyze (FTIR). Mass increase of the samples were measured to determine the degree of grafting (DOG) according to the Equation (1);

$$DOG\ (\%) = [(wg-wo)/wo)]x100 \qquad (1)$$

EXPERIMENTAL

Prepared films

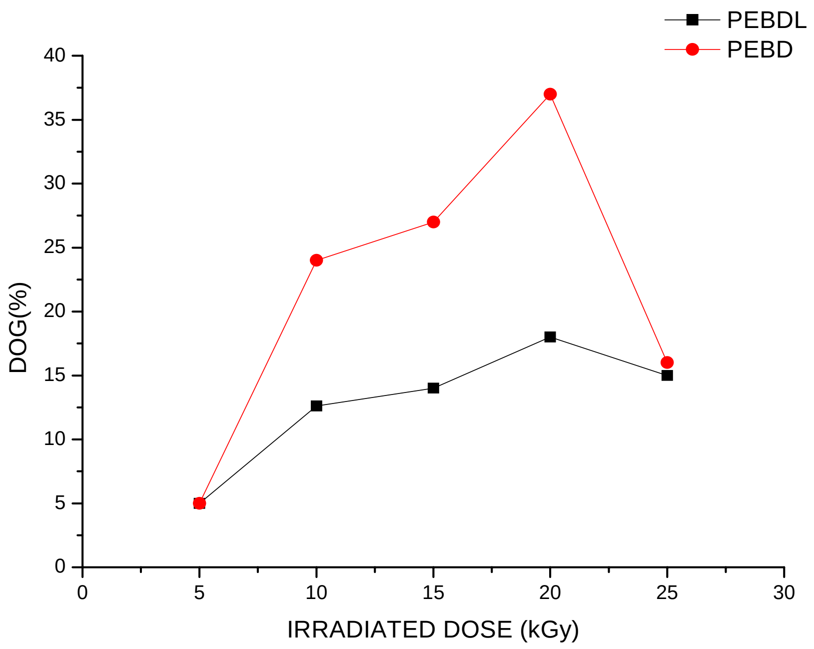
PE films were sliced in 6 x 3 cm, pre-washed in distilled water, weighted and immersed in the solution (30:70 – styrene: methanol or Sty: MeOH) added with 30% H^2SO^4 into glass ampoules, bubbled with N_2 (inert atmosphere) and sealed. Each ampoule had three samples of PE, each dose irradiated three ampoules, so that. Each dose presented in this study is the average result of 9 samples. PE was supplied by BRASKEM PETROQUÍMICA. The monomer was supplied by Air Products and, the nitrogen by White Martins and the additive by Casas Americanas. The irradiation process was carried out in EMBRARAD / CBE facilities.

After processed, the sample was taken off the ampoules, washed in Sohxlet system with acetone for 8 hours. After washing, samples were kept in watch glass, in air overnight to be dried and then weighted again.

The FTIR analyses were performed on Nexus 670 FT-IR Thermo Nicolet. The SEM images were run in a Phillips XL 30 Microscope, providing magnifications up to 40,000 times, with samples analyzed being covered with gold in a Sputter Coater BAL-TEC SCD 050. The images were amplified to 10,000X.

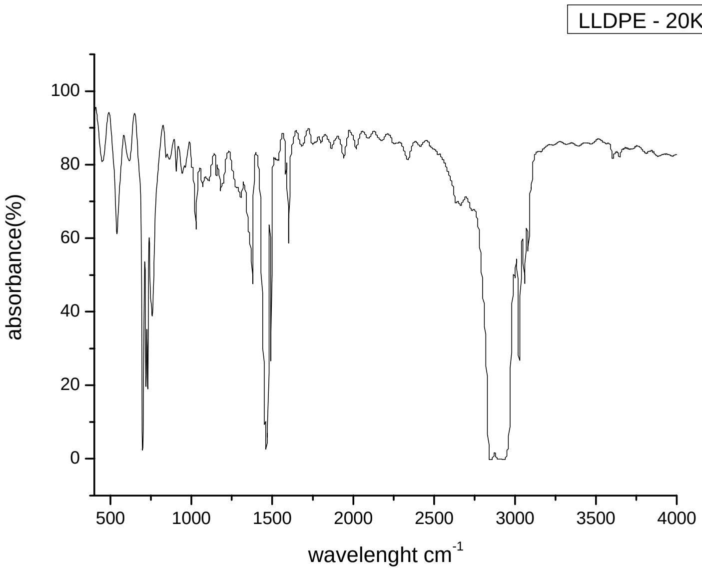
RESULTS AND DISCUSSION

The degree of grafting showed significant difference between the linear and non-linear polyethylene as observed below:

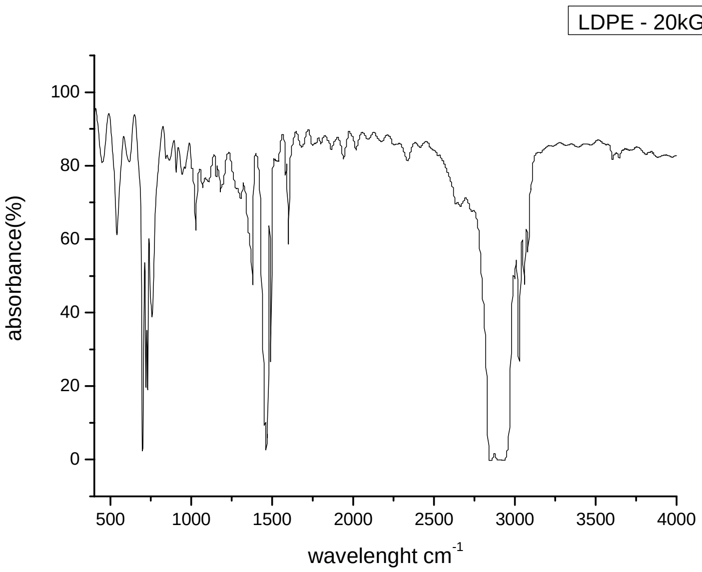


LDPE (red line) yields better than LLDPE in all the range from 5 to 20 kGy, the latest being the best result, yielding twice as much as LDPE.

The films analyzed showed no significant changes in the infrared spectroscopy. Graphics 1 and 2 show the spectrum of 20 kGy for each sample. The spectra are very much alike, taking to the conclusion that there was grafting but in different rates.



Graphic 1



Graphic 2

The absorptions at 698 and 719 cm^{-1} were due to phenyl ring and alkyl chain respectively (11)

CONCLUSION

Radiation inducing grafting of styrene onto LLDPE and LDPE films was investigated using the simultaneous method of irradiation in presence of a solution monomer/ additive/solvent. It was observed that LDPE yields better than LLDPE from 5 to 20 kGy, probably due to higher cristalinity of LLDPE, which makes more difficult to monomer to achieve the amorphous area, so there was poor yield of grafting. The analysis of FTIR proved that there was effective grafting in both types of Polyethylene.

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