2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

PRELIMINARY STUDY OF STYRENE GRAFTING ON POLYETHYLENE FILMS

Gilberto de O. Moraes, Adriana N. Geraldes, Heloísa A. Zen, Duclerc F. Parra, Ademar B. Lugão

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP), Centro de Química e Meio Ambiente (CQMA), Av Professor Lineu Prestes, 2242, 05508-900
São Paulo, SP
gibamaclarenn@hotmail.com

ABSTRACT

Grafting of styrene on polyethylene was carried out as a preliminary study. The experiments covered a range from 5 to 20 kGy and intended to evaluate the absorbed dose that led to the best degree of grafting (DOG) under industrial dose rate. PE films 0,065 mm thick were exposed several times to radiation at room temperature and nitrogen atmosphere. The films were immersed in the solution content styrene/solvent then irradiated (5 to 20 kGy) dose. As an exploratory experiment, styrene grafting was gravimetrically evaluated and characterized by infrared spectroscopy (FTIR).The degree of grafting (DOG) was calculated. Concentrations of methanol/ Styrene at the rate of 80:20 were favorable at low dose of 10 kGy. In presence of acid, best result was achieved at 15 kGy in the range of 5 to 20 kGy.

1. INTRODUCTION

Polyethylene (low and high density) is nowadays a very used semi-crystalline polymer, one of major commodities with large number of applications [1].

A number of techniques can be used to modify a polymer. The radiation-induced technique is known as an efficient and clean one due to absence of undesired by-products, possibility of room temperature processing and faster as well as easier management. Radiation effects on polymer properties present information valuable for investigation of molecular structure and transport process. Data on radiation effects upon properties like density, crystallinity degree and grafting degree are important in this work thanks to the large difference between effects on crystalline and amorphous phases. Such differences are important to the grafting yield [2, 3 and 4].

This work aims to evaluate the patterns of grafting of styrene onto low density polyethylene (LDPE) using gamma radiation from a ^{60}Co source in order to synthesize an ion exchange membrane, using the simultaneous method that consists in radiation of the polymer in presence of the monomer to be grafted (irradiating film + monomer + additive + solvent), with doses and radiation times compatible with industrial procedure.

2. EXPERIMENTAL

2.1 Materials

Braskem Industry supplied of low density polyethylene (LDPE code EB861) films with 0,065 mm thickness. Styrene monomer (Maxepoxi) was provided by Merck.

2.2 Methods

2.2.1 Grafting process: LDPE 0,065mm thickness in samples sliced in 3 x 3 cm^2 were pre-washed in distilled water, dried for 10 minutes in stove and sealed in glass ampoules, three samples each ampoules, with the monomer or a solution monomer/solvent/additive (1:1:1) in the proportion of 1:1. Three ampoules for each dose were used. PE was grafted by simultaneous radiation method under nitrogen atmosphere at room temperature using a ^{60}Co source of gamma rays. PE films were submitted at 1, 5, 15 and 20 kGy dose**.** The solvent chosen was methanol and the addictive was sulphuric acid, both frequently referred to in the literature [5, 6 and 7]. After irradiation, samples were washed in Soxhlet system, dried in stove until constant weight and evaluated through in FTIR soon after. The grafting was achieved in a ^{60}Co source. In spite of papers [5,7] stating low doses rates (0,3 kGy/h and 0.055kGy/h to 5 kGy/h) as the dose of choice if only yield of grafting is the goal, it was applied industrial dose rate of 3kGy/h as the long term purpose is an industrial application.

2.2.2. Infrared spectroscopy

The FTIR analyses were carried on sliced film on MID-FTIR Nexus 670 Thermo Nicolet, after grafting process. The samples were adjusted to the apparatus in order to be exposed directly to infrared beam, without previous preparation of samples, the spectrum was registered.

2.2.3. Degree of gel determination (DOG)

The degree of grafting (DOG) was determined as the following equation (1):

$$\%DOG = [(W_f - W_i)/W_i] \times 100 \qquad (1)$$

where W_i and W_f are the masses of the LDPE samples before and after grafting, respectively.

3. RESULTS AND DISCUSSION

The infrared spectrum of the grafted film (Figure 1) was compared to the infrared spectra of LDPE film. It showed characteristics absorption peaks of the benzene ring at 696 cm^{-1}, of styrene 3080 - 3010 cm^{-1} and 1606 cm^{-1} attributed to the C=C deformation of the aromatic rings. All of these peaks are absent in the pure LDPE spectrum. This means that under radiation condition used the styrene graft onto LDPE was achieved.

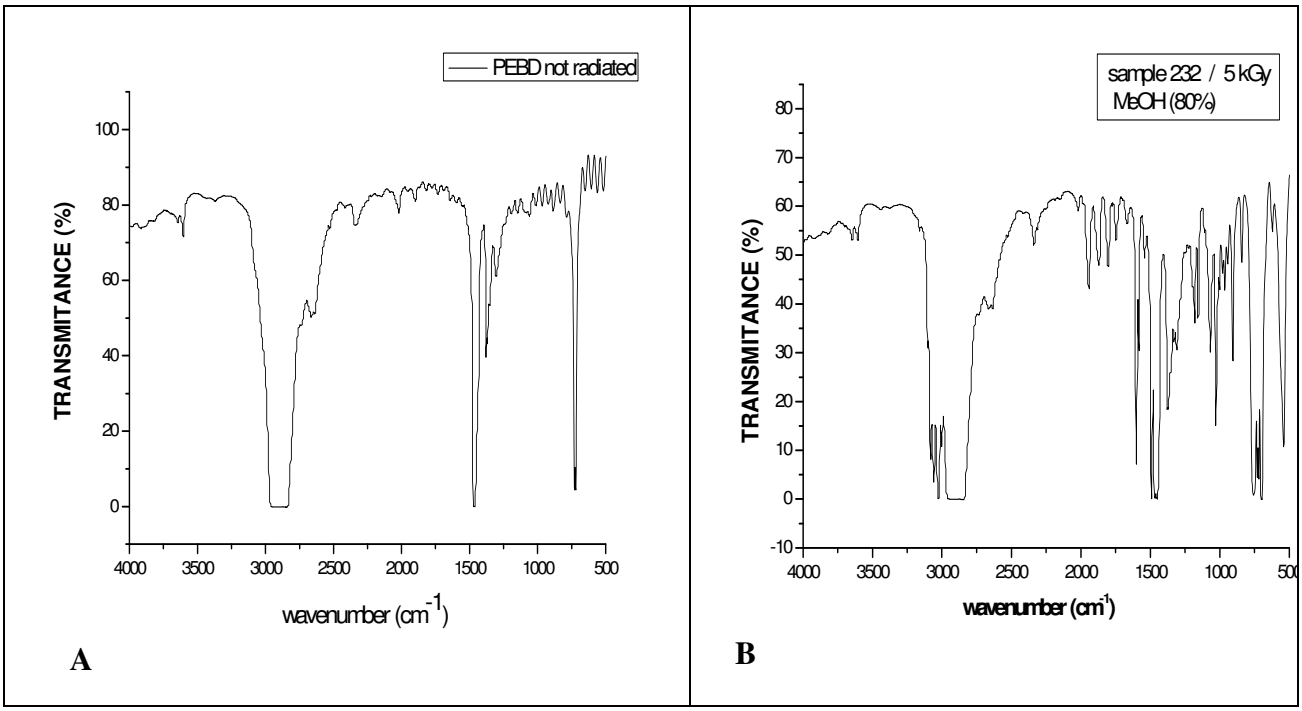

Fig. 1 – Infrared spectra of LDPE (A) and LDPE graft (B) films in the range of 500 - 4000 cm^{-1}.

The samples were analyzed before and after grafting process. Table 1 shows the evaluate DOG for samples prepared in Methanol (70 or 80%), and in methanol with sulphuric acid (0,2M) as additive. The highest grafting level of 121% was achieved in the condition of 10 kGy in solution of methanol.

Table 1. Degree of grafting in the samples for different irradiation dose

LDPE samples number	Dose (kGy)	Sty + methanol (20:80) DOG (%)	Sty + methanol (30:70) DOG (%)	Sty + methanol +H_2SO_4 (1:1:1) DOG (%)
1	5	3		
2	10	121		
3	15	63		
4	20	82		
5	5		11	
6	10		31	
7	15		36	
8	20		31	
9	5			17
10	10			44
11	15			49
12	20			28

In presence of H_2SO_4 as additive, the best result was obtained at 15 kGy but, as a preliminary experience, this result not showed evidence concerning the additive efficiency. Literature reports [5] that solvents associated to additives should increase the yield of DOG. This was not observed in this work until yet. Different rates of solvent/addictives and additives types will be experimented.

Conditions applied in our experiment have shown satisfactory results in the range of dose from 5 to 20 kGy of dose. It was observed that under higher irradiation dose the process results in saturated DOG, probably due to homopolymerization of styrene resulted in consumption of grafting reagent [8].

4. CONCLUSION

Data exposed in this work are exploratory. The range explored is intermediate compared to that observed in literature and the industrial routine. So, there is an uncertainness degree of about 10%. The goal of graft of LDPE samples by radiation-induced through simultaneous process in presence of methanol was achieved. Concentrations of methanol / Styrene at the rate of 80:20 were favorable at low dose of 10 kGy. In presence of acid, best result was achieved at 15 kGy in the range of 5 to 20 kGy. The mix monomer/solvent/addictive at the rate of 1:1:1 did not improve the results observed in the solvent-only process as expected. So far the effect of solvent in promoting grafting was not proved. Different rates should be tried.

ACKNOWLEDGMENTS

This work was supported by CNPq (Conselho Nacional de Pesquisa e Desenvolvimento) processes numbers: 50.7100/2004-2, 50.5205/2004-1. Thanks to Ms Sandra Maria Cunha – CCTM-IPEN and BRASKEM for the LDPE film.

REFERENCES

1. C. Vassile, MO Seymour, et al; " *Handbook of Polyolefins – Synthesis and Propertie*s"

2. B.A.Briskman; "Radiation Effects in Thermal Properties of Polymers. An Analytical Review. Polyethylene" *Nuclear Instruments and Methods in Physics Research* B **185** (2001) 116-122

3. A.B. Lugão ; "Caracterização do Polietileno Reticulado por Radiação" IPEN-PUB-**388**

4. P.R.S.Reddy, G. Agathian, A.Khumar; "Preparation of strong Anion Exchange Membrane Using ^{60}Co Gamma Radiation" Radiation Physics and Chemistry" **74** (2005) 384-390

5. P. Dworjanyn, J.L. Garnett, M.A.Khan, X. Maojun, .Meng-Ping, Y.Nho: "Novell Additives for Accelerating Radiation Grafting and Curing Reactions" *Radiation Physics and Chemistry*, vol. **42**, (1993) 31-40.

6. A.N. Falcão, L.M. Ferreira, M.H. Gil; "Modification of LDPE Molecular Structure by Gamma Irradiation for Bioapplication" *Nuclear Instruments and Methods in Physics Research* B **236** (2005) 513-520

7. A.A.Queiroz "Copolimerização por Enxertia do Polietileno de Baixa Densidade (LDPE) Com estireno Utilizando Radiação Gama" Anais 9º CBECIMAT, Águas de São Pedro, 1990

8. S. Tagawa, Y. Izumi, H. Nagaike, S. Tabuse, Y. Yoshida; "Radiation Grafting of styrene onto Polyethylene" Radiation Physics and Chemistry, **62** (2001).