THERMAL DEGRADATION OF FOAMS POLYETHYLENE CROSSLINKED BY ELECTRON BEAM AND PEROXIDE

Djalma B. Dias and Leonardo G. de Andrade e Silva

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP) Av. Professor Lineu Prestes 2242 05508-000 São Paulo, SP <u>dbdias@ipen.br</u> lgasilva@ipen.br

ABSTRACT

The mechanical properties of low-density polyethylene (LDPE) depend on the irradiation dose, temperature and aging. In this work, low density polyethylene plates, having 5% of expander agent, azodicarbonamide (ADCA), for foams obtainment, were irradiated with electron beam by irradiation doses of 20, 30, 40 and 50 kGy. The samples of foam of polyethylene cross-linked by irradiation and peroxide were submitted to accelerated thermal aging at the temperatures of 70°C during 24 hours in an oven under hot air circulation. The samples of aged material were analyzed by thermogravimetric analysis (TGA) and permanent deformation by compression (compression set). They were compared to non-aged samples. The results of TGA showed that the thermal degradation were modified with the aging, resulting in a material lower decomposition temperatures. In the tests of permanent deformation by compression it was observed an increase on the deformation in relation to the non-thermal aging sample. Such behavior can be attributed to the chain scission in function of the aging time.

1. INTRODUCTION

The plastic foams generally consist of a minimum of two phases, a solid polymeric matrix, and a gaseous phase, derived from a blowing agent [1]. Some types polyethylene foam can be cross-linked, other are not.

The polyethylene foams are classified in two types, according to the method of cross-linking. In the first method, intermolecular chains are formed by decomposition of chemical agents, such as peroxides. In the other method, the cross-linking is induced by electron beam radiation. In this method, a three-dimensional structure is formed by the irradiation [2]. The interaction of the ionizing radiation with polymeric materials transfers energy to the materials, inducing mainly the excitement and the ionization of molecules, generating reactions that can produce permanent modifications in the chemistry-physic structure of polymers [3].

The induced modifications can result in the degradation of the polymeric material or in the improvement of its properties. The accelerated aging can produce other modifications. Due to great polymer use in the most diverse applications, including the outdoors use, the study covers its resistance to weathering, not only for aesthetic aspects as discoloration or loss of brightness, but also for changes in its thermo mechanical properties.

The study of the aging it is of great importance for the development of more resistant materials and additives that enhances the useful life to polymers [4].

The thermal stability of a polymer, mainly of polyethylene foams, is an important parameter for evaluation of its performance in severe conditions. In this work, the results of the study of the thermal aging of polyethylene foam and its effect on the mechanical and thermal properties are presented.

The objective of this study was to verify the foam performance got from polyethylene crosslinked by radiation and by the chemical processes, being peroxide used as cross-linking agent. For this, LDPE foam had been submitted to the compression tests at 70°C in an oven during 24 hours. The properties of aged and non-aged foams had not been compared to verify the behavior of foam got from the two-cross-linked methods.

2. EXPERIMENTAL PROCEDURE

Trocellen Company supplied the samples with dimensions 50 x 50 x 1.91 mm. Were produced using 5 wt% Azodicarbonamide (ADCA) blowing agent and plasticizing agent. Polyethylene sheets (dimensions: 200 x 200 x 1.91 mm) were irradiated in the electron accelerator, 188 model JOB with energies ranging from 0.5 to 1.5 MeV and currents from 0.1 to 25 mA, at different radiation doses (20, 30, 40 and 50 kGy). After irradiation, the samples were placed into the oven at 200 to 229°C under air circulation for 240 to 360 seconds to obtain foams of uniform surface. The foam samples were cut into rectangular shape bars (dimensions: 30 x 20 x 10 mm) and placed between two metallic parallel plates and submitted to a 25% compression at 70°C in an oven during a 24-hour period, to verify the thermal degradation of the foam. The determination of the permanent deformation by compression, known as compression set, according to the standard ASTM D 395-85, method B. The thermogravimetry analysis (TGA), were performed on TGA-50 of Shimadzu with samples of about 2 mg, in platinum pans under nitrogen atmosphere in a temperature range between 30 and 600°C at a heating rate of 10°C/min to verify the decomposition temperature of the LDPE foams cross-linked by radiation and by peroxide in aged and non-aged samples.

3. RESULTS AND DISCUSSION

3.1. Assays of Resistance to the Permanent Deformation by Compression

The values for the permanent deformation by compression are presented in Table 1, where it was observed high values for 20 kGy doses, due to the low degree of cross-linking. With the increase of the dose and increase of the cross-linking, the foams with doses of 30, 40 and 50 kGy had presented an improvement in its performance, compared to the foams that use peroxide as cross-linked agent. After the thermal aging, the foams presented higher permanent deformation, characterizing the degradation of the LDPE, caused by the temperature. In foam processed with peroxide as cross-linked agent, the generated by-products during the decomposition of peroxide can have exerted a deleterious effect in the mechanical performance of the material.

Table 1. Permanent deformation by compression of cross-linked LDPE foam, aged and
non-aged, as function of irradiation dose and peroxide

	Non-Aged Foams-	Aged Foams-
Irradiation Dose	Permanent Deformation by	Permanent Deformation by
(kGy)	Compression	Compression
	(%)	(%)
20	23.70	32.65
30	13.23	18.67
40	9.15	22.02
50	12.38	24.50
Peroxide	15.26	29.15

3.2. Thermal Analysis

The TGA experiments had been performed to determine the temperature of degradation in samples thermal aged and non-aged of cross-linked LDPE foam by radiation and by peroxide.

The results are shown in Table 2.

Table 2. Decomposition temperature of cross-linked LDPE foams aged and non-aged as function of irradiation dose and peroxide

Samples	Non-aged (°C)	Aged (°C)
Peroxide	434	427
20 kGy	445	436
30 kGy	446	443
40 kGy	443	440
50 kGy	440	438

The aged foam samples presented reduction in the degradation temperature, indicating the degradation of the material due to the thermal aging process.

3. CONCLUSIONS

The heat aging study showed that:

The non-aged LDPE foam cross-linked by radiation with doses of 30, 40 and 50 kGy had presented a higher resistance to the permanent deformation for compression when compared with that processed with peroxide as cross-link agent.

The aged LDPE foam cross-linked by radiation with dose of 30 kGy presented lower permanent deformation.

In TGA analysis, the samples with 30, 40 and 50 kGy presented higher thermal resistance in the non-aged samples, when compared with the samples processed with peroxide and the samples irradiated with 20 kGy.

ACKNOWLEDGEMENTS

The authors would like to tank CNPQ and FAPESP for the financial support.

REFERENCES

- 1. D. Klempner, and K. C. Frisch, "*Handbook of Polymeric Foams and Foam Technology*," Hanser Publishers, New York (1991).
- 2. A. Charlesby, "Crosslinking of polyethylene by pile radiation," *Proc. R. Soc.*, pp.187 (1952).
- 3. P. J. Corishi, "Radiation effects on polymers radiation process," *Polymer Processing & Applications*, Pergamon, New York (1992).
- 4. P. Gijsman, J. Hennekens and K. Janssen, Am. Chem. Soc., p. 622 (1996).