RADIATION EFFECTS ON THE PROPERTIES OF POLYETHYLENE FOAMS CROSSLINKED BY ELECTRON BEAM

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Abstract
Plastics foams referred to as expended or cellular plastics, generally consist of a minimum of two phases, a solid polymer matrix and a gaseous phase derived from a blowing agent. The polyethylene foams are used in different applications in the industry. The methods of production of polyethylene foams are classified in two types, according to the cross-linking type. One of them is the chemical cross-linking, that uses the peroxide as cross-linking agent. The other type is the cross-linking induced by irradiation with electron beam. The polyethylene foams obtained by cross-linking process using irradiation perform excellent appearance in the surface, which is formed basically by closed cells. These foams present, for this reason capacity for thermal insulation and acoustics, as well as of impact absorption. The aim of this work is to present the effect of different radiation doses on the polyethylene of low density, with 5% of Azodicarbonamide (ADCA) as chemical blowing agent, that after irradiation it is thermally expanded for foam production. To certify the effect of the radiation it was studied the mechanical properties, and also, the cell morphology of the foams.

Introduction
Plastic foams are generally made of a minimum of two phases. The polymeric matrix is the solid phase, and, the gaseous phase comes from the blowing agent [1]. Some types of foams have been developed in accordance with specific applications. Due to their unique properties such as light weight, superior insulation, energy absorbing performance, excellent impact protection and comfort features, they are widely used in various fields including furniture, transportation, packing, textiles, toys, shoes, shock and sound-absorbing systems, insulation, flotation, containers for food and drink, among others. The methods of production of polyethylene foams are classified in two types, according to the cross-linking type. 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. A hot thermoplastic polymer with a blowing agent can produce foams when pressure is reduced [2]. The main production process for polymeric foams uses a dispersion gas in a fluid polymer, and there after the stabilization of polymer foam. The polymer foam expansion is due to an increase of cell size, before the stabilization of the polymeric system. Polyethylene is hard, flexible, and resistant to chemical agents and wears action. Polymeric foams made of these keep up their original chemical and physical properties. The study of cross-linked foam by electron beam makes it necessary due to its great consumption and for being a simple process with high productivity. In the EB process, cross-linking is induced by the interaction of high-energy electrons with the polymeric material. Several studies about cross-linked polyolefines, especially polyethylene were carried for diverse authors [3-5].

Experimental
Low density polyethylene (LDPE), supplied by Trocellen with 5% azodicarbonamide (ADCA), as blowing agent, and were used. Plates of this material with 1.91mm thickness were irradiated at the CTR-IPEN, irradiation facilities, using an electron accelerator model JOB 188 (0.5 - 1.5 MeV and 0.1 – 25 mA) at the irradiation dose of 10, 20, 30, 40, 50, 60, 80 and 100 kGy. After irradiation, the cross-linked LDPE plates were thermal expanded to produce foams in an oven at 229ºC, under a forced air stream during 6 minutes in which ADCA decomposition take place. The cross-linking grade of LDPE was evaluated by the gel fraction using technique of xylene extraction at 132ºC for...
24 hrs, according to standard ASTM D2765-95. Compression tests were carried out using an Instron machine, model 5567, with samples thermal degraded at 70°C for 24 hours, according to standard ASTM D3575-77. Determinations of permanent deformation by compression or Compression Set were carried out according to standard ASTM D395-85, method B. In these determinations, LDPE samples with 10 mm thickness were set between two parallel metal plates under a compression of 25% for 24 hours. The morphology of LDPE foams were made by SEM observations on gold metalized samples using JEOL-JXA-6400 equipment.

Results and Discussion

Thermal expansion
In the thermal expansion process, cross-linked LDPE samples with 10, 80 and 100 kGy do not produce foam due to thermal breakdown of the material with low or excess of cross-linking.

Gel fraction
Table 1, present the experimental data of the gel fraction of cross-linked LDPE as function of radiation dose, together with of the material cross-linked with peroxide.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>80</th>
<th>Peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel fraction (%)</td>
<td>23</td>
<td>34</td>
<td>48</td>
<td>59</td>
<td>65</td>
<td>72</td>
<td>79</td>
<td>74</td>
</tr>
</tbody>
</table>

In the Figure 1, data of Table 1 is graphically presented

![Figure 1](image)

Figure 1. Gel fraction of electron beam cross-linked LDPE and with peroxide

It is important to determine the gel fraction of cross-linked polyethylene since an excess of cross-linking limit the foam expansion and insufficiency of cross-linking leads to cell break and therefore a reduction of foam mechanical properties. Ionizing radiation produce free radicals in the irradiated polymer and thereafter the polymeric chains of the macromolecules form cross-linked structures. Cross-linked polyethylene with 30 and 40 kGy produce foams with homogeneous and smooth surfaces, on the other hand, with 20, 50 and 60 kGy foams are produce with wrinkled surfaces and non-uniform cells.
Mechanical properties

In Table 2 are given the results of compression properties of radiation cross-linked samples and those with out thermal aging, under a compression load of 40 and 60%.

**Table 2.** Compression resistance of radiation and peroxide cross-linked PE foams samples and with and without thermal aging.

<table>
<thead>
<tr>
<th>Radiation Dose (kGy)</th>
<th>Compression load – 40% (N)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-aged</td>
<td>Aged</td>
<td>Non-aged</td>
<td>Aged</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>104,9 ± 17,6</td>
<td>76,4 ± 7,5</td>
<td>344,1 ± 51,6</td>
<td>222,4 ± 53,4</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>134,2 ± 12,4</td>
<td>111,1 ± 7,1</td>
<td>390,3 ± 50,1</td>
<td>250,9 ± 43,2</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>179,1 ± 27,4</td>
<td>117,1 ± 24,9</td>
<td>442,8 ± 48,1</td>
<td>231,3 ± 21,1</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>149,7 ± 10,3</td>
<td>-----</td>
<td>376,0 ± 35,6</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>152,1 ± 12,4</td>
<td>108,3 ± 14,5</td>
<td>290,5 ± 31,2</td>
<td>132,7 ± 7,6</td>
<td></td>
</tr>
<tr>
<td>Peroxide</td>
<td>133,5 ± 3,4</td>
<td>125,7 ± 17,3</td>
<td>297,6 ± 45,2</td>
<td>222,1 ± 64,1</td>
<td></td>
</tr>
</tbody>
</table>

Figures 2 and 3 show graphically the compression data of table 2.

![Graph showing compression behavior](image)

**Figure 2.** Compression behavior of cross-linked PE (40%) and with and without thermal aging as function of radiation dose.
From data given in Table 2 and also show in Figures 2 and 3, it was observed that an increase of radiation dose, that correspond to an increase of PE cross-linking, the foam compression resistance, for 40 and 60\% thickness reduction, also increases. Samples with 50 and 60 kGy their compression resistance decreases due to a possible radiation foam degradation. From data on Table 2, it was observed that thermal aging samples had a reduction of the compression resistance. This behavior is due the thermal degradation of samples under heat. The reduction of mechanical properties of thermal aging foams is due to the rupture of closed cell membranes during the initial stage of load applied.

**Test of permanent deformation by compression**

Data of permanent deformation by compression are given in Table 3. The high values in samples with 20 kGy, are due to a low degree of cross-linking. Samples with 30 and 40 kGy show a better performance samples with 60 kGy or more present a high permanent deformation due to the radiation degradation of the material.

**Table 3. Permanent deformation by compression in cross-linked LDPE and peroxide**

<table>
<thead>
<tr>
<th>Radiation Dose (kGy)</th>
<th>Permanent Deformation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>23.70</td>
</tr>
<tr>
<td>30</td>
<td>13.23</td>
</tr>
<tr>
<td>40</td>
<td>9.15</td>
</tr>
<tr>
<td>50</td>
<td>12.38</td>
</tr>
<tr>
<td>60</td>
<td>19.73</td>
</tr>
<tr>
<td>Peroxide</td>
<td>15.26</td>
</tr>
</tbody>
</table>
In Figure 4, the permanent deformation by compression behavior of cross-linked LDPE and with peroxide is presented.

![Figure 4](image.png)

**Figure 4.** Behavior of permanent deformation by compression of cross-linked LDPE by radiation and cross-linked with peroxide

*Scanning electron microscopy (SEM)*

Figures 5, 6, 7 and 8 present the SEM observations of foam cellular structural of cross-linked LDPE at different radiation dose.

![Figure 5](image.png)

**Figure 5.** Foam of cross-linked LDPE with 20 kGy.
Magnification X 15
Figures 5 to 8 showed LDPE foams with closed cell structure due to degree of cross-linking that reduce the cell break during the foam expansion process. Samples with 20 and 60 kGy (Figures 5 and 8) showed heterogeneous and wrinkled surfaces. The grow of foam cells depends on the amount of cross-linked of the LDPE; low cross-linking and high cross-linking can be harmful for the foam cell formation. In both cross-linking conditions thermal breakdown take place.
Conclusions

- The degree of cross-linking in LDPE has a great effect during the foam production, due to its action in cell formation during the decomposition of the expansion agent.
- Cross-linked LDPE with 30 and 40 kGy have produced foams with good mechanical properties.
- Cross-linked LDPE with 20, 50 and 60 kGy produced foams with heterogeneous and wrinkled surfaces, additional, cross-linked LDPE with 10 and 80 kGy has shown, during the expansion process, a thermal breakdown without foam formation due to material degradation.
- Under certain conditions, foams of electron beam cross-linked LDPE have shown smooth and homogeneous surfaces in comparison with those cross-linked with peroxide.
- Compression resistance tests have shown that foams samples produced with 30 kGy had small variation with those made with the same samples under thermal aging.

References