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EVALUATION OF MECHANICAL PROPERTIES AND DSC STUDY OF COMMERCIAL MULTILAYER PA/PE FILM TREATED WITH E-BEAM RADIATION

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ABSTRACT

Packaging materials have been widely processed by ionizing radiation in order to improve their chemical and physical properties and also for sterilization purposes. Basically, flexible packaging manufacturers apply specific radiation doses to promote cross-linking and scission of the polymeric chains and thus obtain alterations in certain properties of the material. While enhancing a specific property, significant losses may result in others. In this study, we examined the effects of E-beam radiation on a commercial multilayer PA6/LDPE based film, irradiated with doses up to 127 kGy. Food producers mostly use this structure as a thermoforming bottom web for processed meat products. Two weeks after irradiation, tensile strength and elongation of the film were analyzed. Both mechanical properties were again analyzed 18 months after irradiation took place. Significant changes of mechanical properties were observed specially 18 months after irradiation. Once cross-linking and scission are able to affect the material crystalline arrangement and consequently cause properties changes, a DSC (Differential Scanning Calorimetry) study was carried out for doses up to 130 kGy in order to verify such changes.

1. INTRODUCTION

Ionizing radiation has been used by polymer film manufacturers to modify the chemical and mechanical properties of their final products. When a polymeric material is irradiated, two different reactions occur simultaneously: scission and cross-linking of the polymeric chains[1].

Depending on the type of polymer and the dose applied, one reaction may override the other. Many studies have shown that, if the polymer structure changes, its original light transmittance, mechanical resistance and elongation also change[2,3].

A common packaging structure for sausages, especially frankfurters, is the thermoforming PA/PE multi-layer film. In this structure, PA is responsible for the oxygen barrier, elongation and mechanical resistance during vacuum forming, and PE is responsible for sealability and elongation.

Thermoforming is a manufacturing process for thermoplastic sheet or film. The sheet or film is heated between heaters to its forming temperature. Then it is stretched over or into a temperature-controlled, single-surface metal mold. It is held against the mold surface unit until cooled. There are several categories of thermoforming, including vacuum forming, pressure forming, twin-sheet forming, free blowing, and simple sheet bending. Vacuum forming is a simplified version of thermoforming, whereby a sheet of plastic is heated to a forming temperature, stretched onto or into a single-surface mold, and held against the mold by applying vacuum between the mold surface and the sheet[4]. For this process, both tensile strength and elongation are important mechanical properties to be considered.

The present study is interested in evaluating changes in the PA/PE film maximum tensile strength and elongation at break with increasing radiation dose and also studying changes in the crystallinity of LDPE and PA6 with increasing radiation dose which may be responsible for such mechanical behaviour changes.

2. Experimental

2.1. Material irradiation

For the tensile strength and elongation studies, a 130 μm thick PA/PE film which contained 38,4% PA.6 and 61,9% polyolefin (PE and tie layer) was irradiated in a commercial 300 KeV E-beam irradiator at different doses within the 0–127 kGy range, and the average dose rate was approximately 50 kGy/s. For the DSC study, the same original material was irradiated in an industrial linear E-beam facility, at an energy of 1.5 MeV, at dose range 0-130 kGy (dose rate approx. 11 kGy/s). All the irradiations were performed at room temperature and in the presence of air.

2.2. Material Testing

Tensile strength and elongation

For the non-irradiated material and for each applied dose, five samples of the material were assayed in an Instron 5564. Testing was conducted based on the ASTM D 882-02 Standard for determining packaging tensile strength and elongation at break.

DSC (Differential Scanning Calorimetry) study

For the non-irradiated material and for each applied dose, four samples of the material were assayed in a Shimadzu DSC-50. Testing was conducted under a nitrogen atmosphere and at a temperature rate of 10ºC/min. The DSC tests showed two very distinct dips: one for the melting process of the polyolefin crystalline phase and another for the PA6 crystalline phase melting. The areas of the dips corresponded to the enthalpy change for the melting process

(ΔHm) of each material. The greater the change, the greater the crystalline phase of the component is[5]. Errors and deviations in this study tend to be large, and for this reason, for each dose tested, the results of one of the samples were discarded. The DSC study was carried out 7 months after samples were irradiated .

3. Results and discussion

The results of mechanical properties are shown in Figures 1 and 2. With respect to tensile strength and elongation at break two weeks after treating the film with electrons, it was observed that there were no important changes upon irradiation except at 15 kGy, when these two properties decreased. On the other hand, eighteen months after radiating the film with electrons, a decrease of these properties became more important, except for the dose of 15 kGy once more, when they increased.

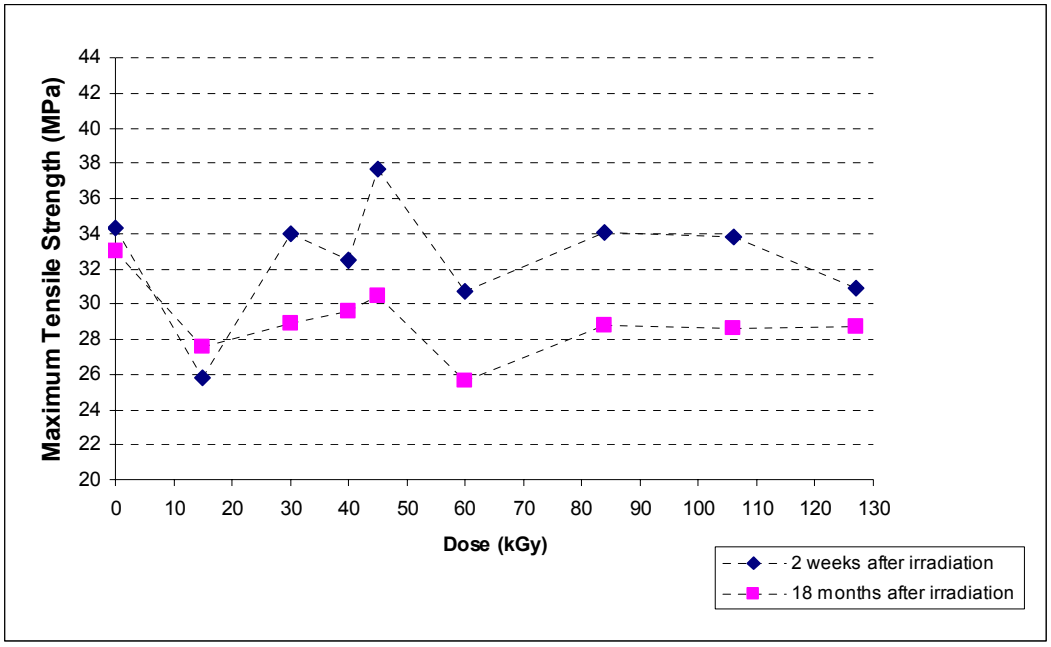

Figure 1. Effect of dose on tensile strength of the PA/PE film two weeks after irradiation and 18 months after irradiation.

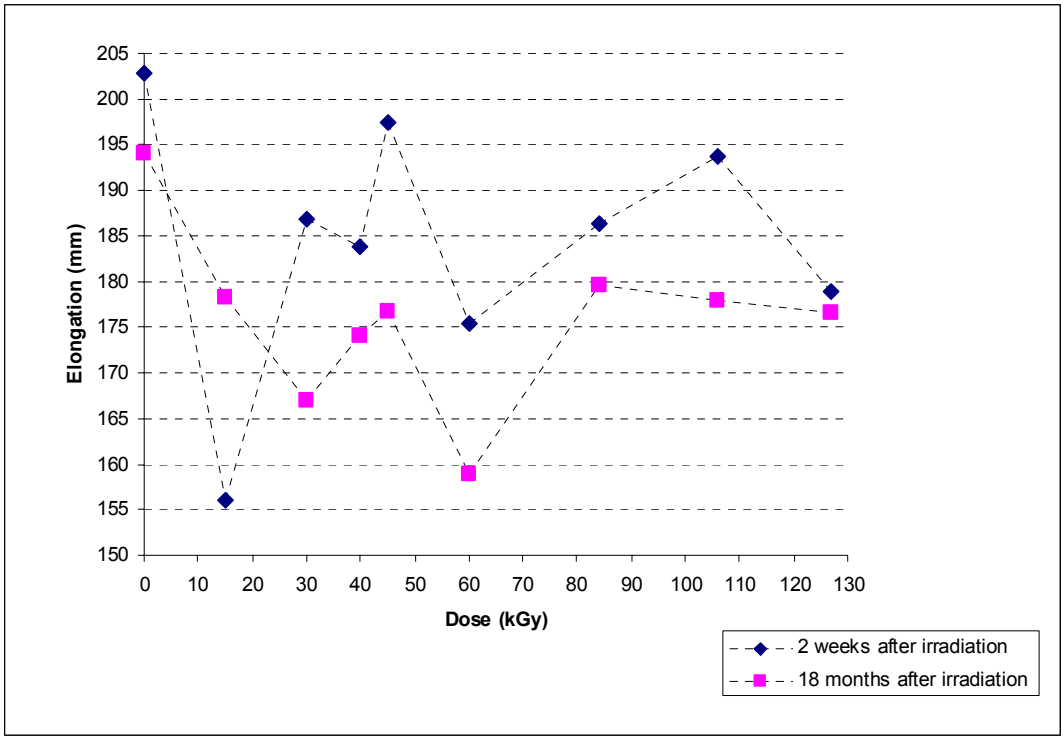

Figure 2. Effect of dose on elongation of the PA/PE film two weeks after irradiation and 18 months after irradiation.

Comparing the mechanical properties for each dose 2 weeks after irradiation and 18 months later (figs.1 and 2), it can be seen that the non-irradiated film lost only 3.8% of its maximum tensile strength and 4.4% of its elongation at break (natural aging) while a loss of 19.2% was reached for tensile strength at the dose of 45 kGy and losses of around 10.5% were reached at 30 and 60 kGy for elongation at break. At 15 kGy there were gains of both tensile strength and elongation. This is a strong sign that the effects of ionizing radiation can be reversible, especially at a dose when the film showed a significant loss of mechanical properties in a period of time right after the irradiation process took place. A summary of the changes in the mechanical properties according to the doses studied can be seen in Table 1.

Table 1. Percent changes in mechanical resistance and elongation when comparing the value of these properties measured 18 months after irradiation to the value obtained two weeks after irradiation.

Dose (kGy)	0	15	30	40	45	60	84	106	127
T. Strength	3.8 %	-6.8%	14.9%	9.2%	19.2%	16.8%	15.5%	15.3%	7.2%
Elongation	4.4 %	-14.3%	10.6%	5.3%	10.5%	9.4%	3.6%	8.2%	1.3%

With respect to the DSC study , figure 3 shows the curve obtained for one of the samples irradiated at 115 kGy. A first dip is seen at a temperature around 118ºC and indicates melting

of the LDPE crystalline phase. The second dip at around 220ºC indicates the PA6 crystalline phase melting.

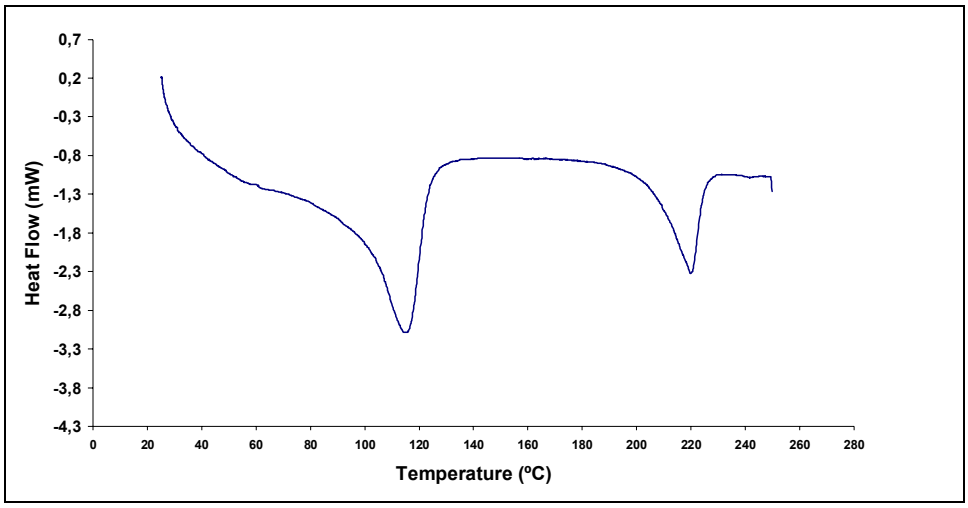

Figure 3. The DSC curve obtained for a sample irradiated at 115 kGy

Other fifty-nine samples were assayed and a summary of the results of the DSC study for the LDPE and PA6 are shown in Figures 4 and 5.

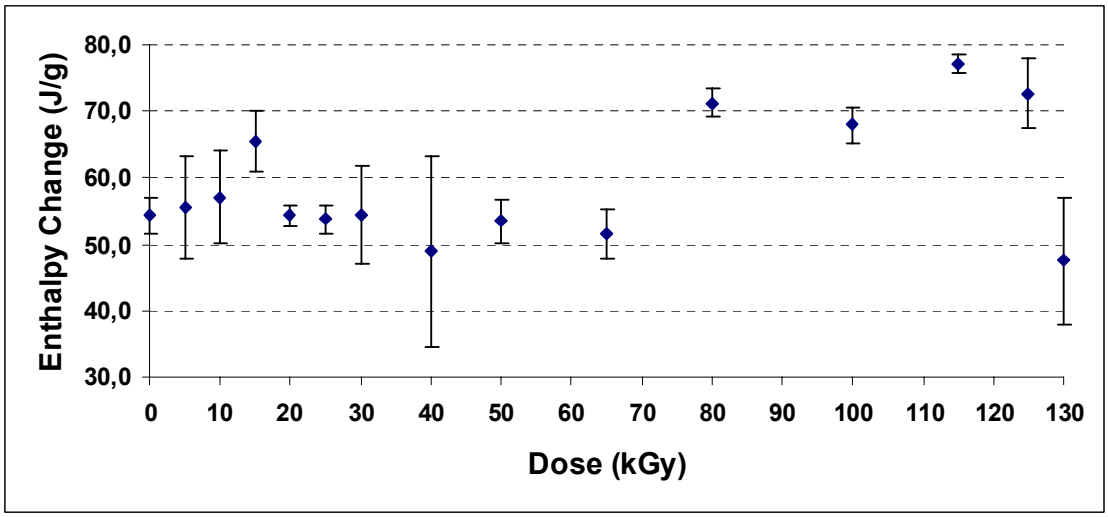

Figure 4. Enthalpy change during crystalline melting of the LDPE upon irradiation dose.

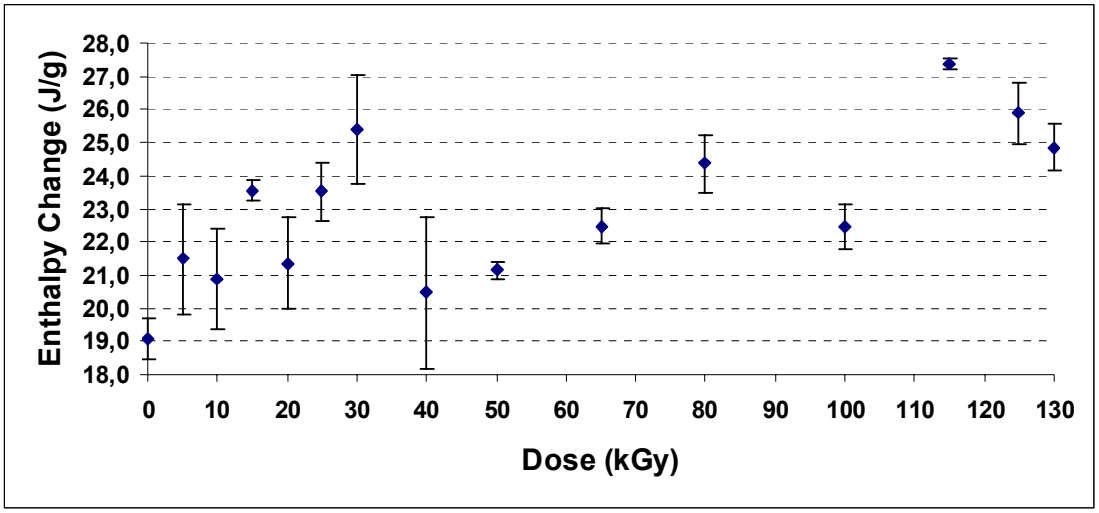

Figure 5. Enthalpy change during crystalline melting of the PA6 upon irradiation dose.

Analyzing the enthalpy change during the melting process (ΔHm) for the LDPE seven months after treating the film with electrons, it can be observed that there were no important changes upon irradiation until the dose of 65 kGy and at the dose of 130 kGy, except at the dose of 15 kGy again. In the range between 80 and 115 kGy differences became far more important. While the non-irradiated LDPE showed an average ΔHm of 54.3 J/g , the ΔHm averages varied from 67.9 to 77.2 J/g in this range of doses.

Analyzing the enthalpy change during the melting process for the PA6 seven months after treating the film with electrons, it can be observed that for all doses applied the ΔHm averages reached higher values when compared to the non-irradiated. While the non-irradiated PA6 showed an average ΔHm of 19,1 J/g , the ΔHm averages varied from 20,5 to 27,4 J/g for the irradiated polyamide .

3. CONCLUSIONS

This study showed that a PE/PA co-extruded film irradiated with electrons does not present important changes of mechanical properties (except at 15 kGy) in the first weeks after being irradiated. Such changes become important 18 months after the film undergoes the ionizing radiation process. While natural aging of the tested film indicated losses of around 4% in the mechanical properties, in the end of 18 months at specific doses, losses of mechanical resistance reached values over 15%. Such results indicate that the irradiation process can accelerate the aging of the film. The DSC study showed that seven months after irradiation, the ΔHm averages for irradiated PA6 were higher than for the non-irradiated polymer. The PA6 is the component responsible for mechanical resistance. In conclusion, the crystalline phase of the polyamide was increased in the irradiated samples and scission overrode the cross-linking effect in this polymer chains. The original chains are broken into smaller sections what explains a higher crystalline arrangement indicated by the DSC study and the loss of mechanical resistance observed as time went by. Such chain scission and subsequent

loss of mechanical properties can be attributed to radiation induced degradation of the polymers. Furthermore, irradiation may lead to the production of low molecular weight volatile or non-volatile radiolysis products, higher formation of unsaturated bonds, polymer chain scission, and molecular weight decrease, causing deterioration of packaging material properties[2,3]. Polymer degradation increases in the presence of air because oxygen is extremely reactive with the free radicals produced by irradiation, as was the case in the present work.

Nevertheless, it is important to point out that this study evaluated and quantified changes of film properties when it underwent ionizing radiation. It does not imply that this film cannot be used for applications in which radiation is involved (e.g. cold pasteurization) since at no dose and at no time the mechanical resistance reached values under the minimum guaranteed by its manufacturer[6].

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