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STERILIZED PP/HMSPP CUSHION FOAMS FOR MEDICAL AND FOOD PACKAGING APPLICATIONS

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ABSTRACT

Treatment with gamma radiation is becoming a common process for the sterilization of packages, mostly made of natural or synthetic plastics, used in aseptic processing of foods and pharmaceuticals. Packaging materials may be irradiated either prior or after filling; the irradiation prior to filling is usually chosen for dairy products, processed food, beverages, pharmaceuticals and medical devices. Cushion foams are used to help protect fragile items during moving transport. Shock, vibration and damage are avoided by the cushioning effect and chances of product damage are reduced. It is easy to use and perforated for easy tearing. Cushion foams are employed to wrap glasses, plates, crockery, lamps, electronics and other breakable items. This paper presents special cushion foams to be used for medical and food packaging applications; so, these foams will be gamma irradiated before getting in contact with these special articles. Foams were previously produced from a 50% blending Polypropylene homopolymer / High Melt Strength Polypropylene (HMSPP) thereof, that presented following results for properties assessed: melt flow index, 230^{o} C – 3.67 g/10 minutes; crystallinity = 47%; melt strength, at 200^{o} C = 7.3 cN. This admixture was further fed into the barrel of a single-screw extruder, Rheomex 332 p, equipped with 3:1,33 d screw and 19/33 special screw for foaming, with standard controller and monitored panel, temperature controller (2 channels), melt temperature (2 channels) and melt pressure (4 channels). By using a 175/200/210/220/165/25 (^{o}C) profile temperature, and after attaining a homogeneous melting, a given amount of physical blowing agent (nitrogen) was injected and mixed with the polymer melt stream to produce the foam. Foamed extrudate was subjected to sterilization radiation doses: 25, 50, 75 and 100 kGy and further evaluated as per: appearance (whiteness / yellowness) and temperature dependent oxidative-induction time (TOIT) tests, by comparing results obtained, prior and pos-gamma irradiation. (Usually 25 kGy has been set as sterilization dose, depending on the bio burden and microorganism, radiation dose for sterilization can be lower or higher). Samples which showed themselves clear and radiation tolerant will be considered effective cushion foam for medical and food packaging applications.

1. INTRODUCTION

There is a strong and growing demand for **extruded polypropylene (PP) foam** in a market which has been traditionally served by materials such as polyurethane, polystyrene and polyethylene. PP brings additional benefits to this market area, such as:

- high heat resistance,
- excellent chemical resistance,
- insulation properties.

Polypropylene-based foams include, basically:

- thermoformed, foamed trays for packaging meat, sausages, cheese and other foods,
- high speed, direct extrusion for extrusion coating,
- insulation materials in building construction,
- material for car interiors and protecting goods during transport;
- syringe barrels, culture dishes, tissue culture bottles, intravenous catheters and tubing, bottles, surgical probes, suture material and other goods.

Due to its limited low melt strength and low extensibility, traditional PP does not allow for controlling cell growth nor preventing the cell wall from breaking during the foaming process. So, the traditional and linear PP was modified to High Melt Strength Polypropylene (HMSPP), by using gamma radiation at 12.5 kGy, in acetylene environment and followed by thermal recombination [1-4]. In the present work it was employed a PP/HMSPP 50% mixture, which showed satisfactory when subjected to the physical foaming process, injecting nitrogen as the physical blowing agent in polymer melt stream being extrudate.

A crucial step in pharmaceutical production is sterilization. In pharmaceutical production line it is very important to have reduced initial contamination in order to avoid pyrogenic reaction besides that, it would be possible to reduce the sterilization radiation dose. There are many sterilization methods to choose from, such as steam, sterile filtration, ethylene oxide gas (EtO), electron beam (E-beam) and gamma radiation. Each technique has aspects that make it suitable or unsuitable for the sterilization of a particular product [5].

For example, EtO, while being a highly effective method, leaves behind potentially hazardous residuals and cannot reach products in airtight packages. E-beam, while being one of the fastest methods of sterilization, cannot penetrate well into dense product or bulk packaging of some products. In addition, the product complexities of heterogeneous components often require extensive product qualification. Gamma radiation can cause certain product and package materials to degrade [6].

Polypropylene is an excellent material for use in a variety of applications, particularly medical and food packaging applications. Polypropylene is shatter resistant, resistant to most chemical agents, inexpensive, easily formed, easily handled and may be incinerated or recycled. Currently available polypropylene is subject to certain limitations, however. For example, polypropylene materials tend to be somewhat cloudy or translucent rather than clear. Also, typical polypropylene tends to soften and deform when sterilized at high temperature by steam or turn yellow and/or become brittle when treated with high energy radiation, particularly gamma radiation [6].

Conventionally stabilized polypropylenes are not suitable for sterilization by high-energy radiation because of the severe embrittlement and discoloration that occur immediately in the plastic after sterilization. Whereas the embrittlement of the plastic after irradiation is an inherent property of the polymer, the discoloration is caused by reaction products of the phenolic antioxidants normally included in standard polypropylenes. Early radiation-tolerant polypropylenes were homopolymers stabilized with small quantities of phenolic antioxidants

and large quantities of sulfide-diester secondary antioxidants. These materials did discolor slightly after irradiation. The modern resins that are most successful in withstanding irradiation exhibit reduced crystallinity and narrow molecular-weight distribution, are formulated with hindered amine light stabilizers (HALS), and contain no discoloring phenolic antioxidants; ,therefore, when HALS are used in a polypropylene formulation, the phenolic antioxidants must be scrupulously avoided [7].

Gamma radiation does have some significant advantages over other methods of producing sterile product. These benefits include:

- Better assurance of product sterility than filtration and aseptic processing.
- No residue like EtO leaves behind.
- More penetrating than E-beam.
- Low-temperature process (lesser than 50^{o} C) [8].

25, 50, 75 and 100 kGy radiation doses [6] were applied to foamed extrudates, which were further assessed for appearance (whiteness/yellowness) and temperature dependent oxidative-induction time (TOIT) test [9]; results obtained allowed establishing the minimum and maximum sterilization radiation dose for packaging aimed to medical and food applications.

2. EXPERIMENTAL

Polypropylene homopolymer (linear PP) and polypropylene thereof modified via gamma irradiation, with 12.5 kGy dose, in acetylene environment and further thermally treated for recombination (HMSPP). In this study, it was used PP/HMSPP 50% (w/w) blend, in pellets.
Major properties of PP/HMSPP 50% blend, were assessed and results obtained are listed in Table 1.

Table 1. PP and HMSPP thereof characteristic properties used within 50% proportion for foams production

Material	Commercial Name	MI (*) (g/10 min)	MT (^{o} C)	Crystallinity (**) (%)	Melt Strength (***) (cN)	Gel (****) (%)
PP	Braskem H503	3.5	168.3	45	4.5	Zero
HMSPP	Modified from H503	3.7	165.9	46	12.1	Zero
PP/HMSPP, 50%		3.6	168.8	46	7.3	Zero

MI: Melt Index; MT: Melting Temperature
(*): 230^o C, 2.16 kg, in10 min.
(**) Crystallinity: error = ± 5%
(***): Melt Strength, at 200^o C.
(****):Xylene extraction, within 24 hours

2.1. Sample Preparation

Polypropylene resin (H-503) was supplied by Braskem, 3.5 g/10 min Melt Index at 230^o C, 2.16 kg. Aliquots of this material were inserted into plastic bags, kept in acetylene and sent to be gamma irradiated in Embrarad, 60Co source, 12.5 kGy dose, dosimetry performed by using Harwell Red Perspex 4034 [8], in order to get HMSPP – High Melt Strength Polypropylene.

Irradiated PP (HMSPP) was further subject to thermal treatment, one hour in an oven at 120^o C, for molecules recombination.

A 50% PP/HMSPP (w/w) pellets blending was prepared from these materials and used in the present study. PP, HMSPP and 50% PP/HMSPP blend were subject to a foaming physical method, by using a single-screw extruder, Rheomex 332 p, equipped with 3:1.33 d screw and 19/33 special screw for foaming, having nitrogen as the blowing agent [10].

2.2. Melt Index

According to ASTM D1238 [11], samples were evaluated in a Ceast Modular Melt Flow plastometer, at 230^{o} C, 2.16 kg load.

2.3 Thermal analyses - Temperature dependent Oxidative-Induction Time (TOIT)

Thermal analyses were accomplished in a Mettler Toledo Differential Scanning Calorimeter, by using a 50 – 280^{o} C, 10^{o} C/min program, flow rate equal to 50 ml/min for both nitrogen and oxygen, open aluminum standard 40 μL pan, for specimens weighing approximately 10 mg.

Under OIT (Oxidative-Induction Time) standard conditions, the initial breakdown of antioxidant protection is accompanied by a release of energy, causing an upward deflection of the curve above the baseline. The period of time during which there is no oxidation is commonly referred to as the "induction time". This induction time is either a measure of the amount of antioxidant present in the polymer or the effectiveness of the particular antioxidant used.

OIT classical methodology, when applied to pure polyolefin samples, irradiated and non-irradiated ones, yield fractional results, always showing very poor response to the polymer sample history and without any repeatability and reproducibility.

In order to cope with the limitations of the traditional OIT method, it was developed a more useful method applicable to a much broader set of resins. A new procedure for determining OIT, in non-stabilized and stabilized, irradiated and non-irradiated polypropylene was presented by Lugão et al [9]. This procedure is based on two main features: (1) starting the oxidation on melted samples, at temperatures as low as possible; (2) oxidation under slow heating conditions. So, each sample has a set of two values for both time and temperature, as the new method is not isothermal any longer, and named TOIT: temperature oxidative-induction time.

TOIT results are reported according to a pair of temperature (^{o}C) and time (min.) values. For example, a TOIT pair of 199.07/26.37 values means that a resin oxidative degradation occurred at 199.07 ^{o}C, after an elapsed time of 26.37 min, from oxygen injection.

PP, HMSPP and foamed extrudate from PP/HMSPP 50% gamma irradiated with 25, 50, 75 and 100 kGy were TOIT evaluated according to DSC programming in Table 2.

Table 2. DSC TOIT programming, starting from 25° C.

Rate (° C/min)	Hold. Temp. (° C)	Hold time (min)	Comments
20	190	5	Heating in N_2 to melt to erase previous history
-10	150	10	Cooling below melting point, with the sample still not crystallized
2	200		Slow heating in N_2/O_2 atmosphere

2.4 Melt Strength

Required tensile drawdown force of extruded sample was assessed in function of its stretching. PP, HMSPP and PP/HMSPP 50% were extruded in a Haake rheometer, assembled to a 71.97 Rheotens, from Göttfert, at 200° C.

Temperature profile used in Haake Rheometer was: 175/200/210/220 (°C).

2.5 Gel Fraction

Gel fraction was accomplished in 0.3 g of pellets sample, previously wrapped in a stainless steel 120 mesh, immersed in 150 mL of xylene. According to ASTM D2765 [12], this system remained for 12 hours in reflux (heating the round bottom flask, in a heating mantle, 135° C). Non-reticulated fraction remains in the solvent and reticulated fraction is kept in the stainless steel mesh, being this assembling dried in an oven at 150° C, for one hour, and after cooling at room temperature, was weighed again and so gel-fraction was calculated as per a conventional gravimetric test.

2.6 Extrudate samples

Foamed extrudates from PP/HMSPP 50% (w/w) blend were sent to be gamma irradiated in Embrarad, ^{60}Co source, with: 25, 50, 75 and 100 kGy radiation doses.

2.7 Appearance for Whiteness/Yellowness (Visual)

Foamed extrudates were previously and visually investigated for their appearance: whiteness/yellowness. After gamma irradiated at selected doses, foamed extrudates were again visually inspected.

3. RESULTS and DISCUSSION

Melt indexes results obtained for modified PP (HMSPP) showed a slight variation when compared to PP linear homopolymer. Once system degradation was modeled using melt flow index (MFI) as a control variable [13], that is, the higher MFI the higher increase in chain scission, it just occurred aimed the branching buildup.

Zero results obtained for gel fraction analyses confirm branching formation. It is known [14] that the primary effect of radiation on thermoplastic polymers is creation of macroradicals and ions after scission of bonds. Built radicals lead to further changes in molecular structure through chemical reactions, and degradation, branching and crosslinking of the polymer chain are the final consequences. These processes are in competition and which one predominates depends on the type of the polymer, as well as the applied dose, dose rate, type of radiation and temperature.

Gamma irradiated foamed samples in Embrarad, at 25, 50, 75 and 100 kGy, shown in Fig. 1, did not present color alterations, neither in whiteness nor in yellowness.

Figure 1. Appearance of gamma irradiated samples at 25, 50, 75 and 100 kGy.

In OIT classical methodology, the isothermal test temperature is typically selected to produce OIT (Oxidative Induction Time) values between 15 and 100 minutes, for typical isothermal test temperatures ranging within 150 and 210^{o} C; the higher the test temperature, the lower the OIT value. If the material is strongly stabilized, as in case of both PP and HMSPP, OIT values can be quite long.

Temperature dependent oxidative-induction time (TOIT) run in 6 samples are shown in Fig. 2.

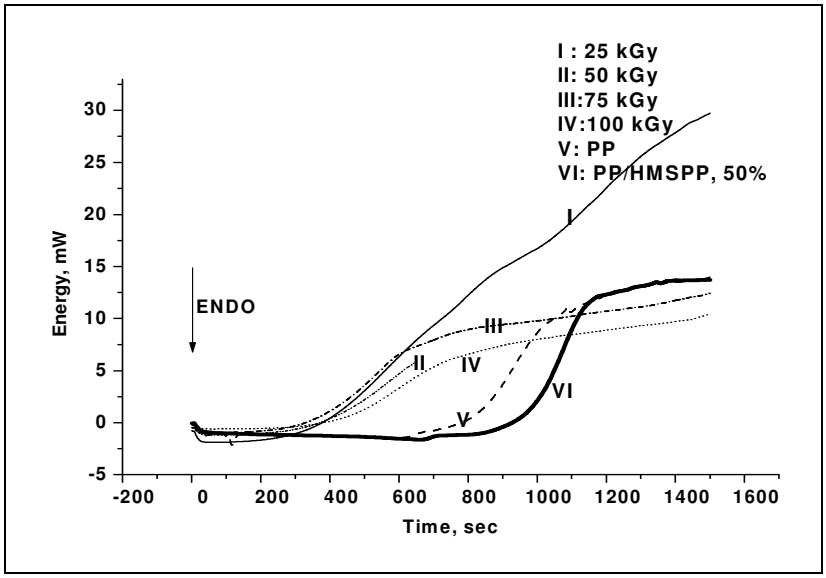

Figure 2. TOIT, as a function of time

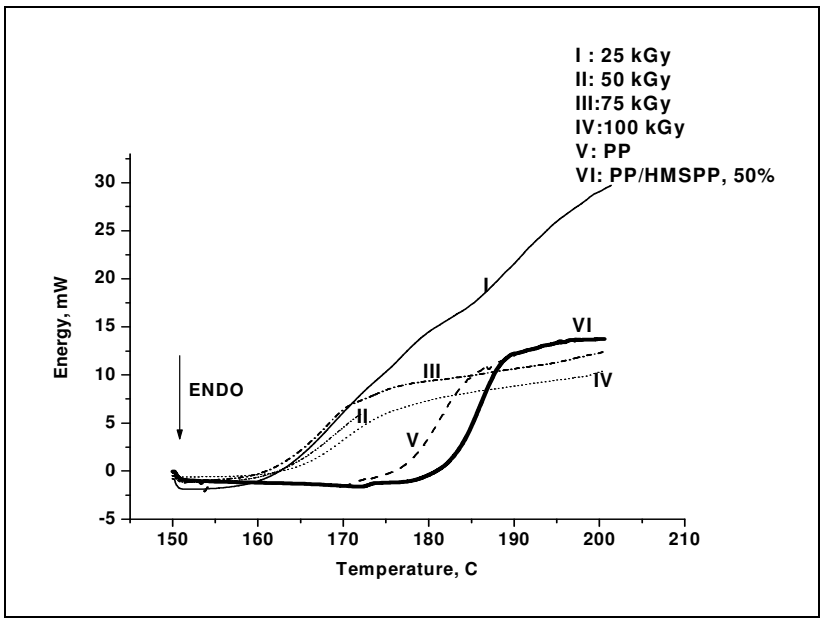

Figure 3. TOIT, as a function of temperature

The interaction between Figs. 2 and 3 will give the pair TOIT, Temperature/time, displayed in Table 3.

Table 3. Pair TOIT for samples analyzed.

Material	Temperature (C)	Time (min)
HMSPP	180	16.0
PP	174	12.0
PP/HMSPP, 50%, 25 kGy	158	4.2
PP/HMSPP, 50%, 50 kGy	156	3.2
PP/HMSPP, 50%, 75 kGy	155	3.0
PP/HMSPP, 50%, 100 kGy	157	2.5

4. CONCLUSIONS

Foamed samples, comprising homopolymer PP/HMSPP thereof, in a 50% mixture (w/w), did visually not show any variation in color, i.e., whiteness/yellowness, after gamma irradiated with 25, 50, 75 and 100 kGy radiation doses; so, within this doses interval, foamed samples were not affected by gamma irradiation and are able to be used in sterilization of packages to be sterilized, intended for foods and pharmaceuticals products.

Pair TOIT: temperature/time, which evaluates the degradation induced by oxygen, showed very close results for gamma irradiated samples, either for temperature or the induced oxygen time, indicating that all the samples were equally affected by gamma irradiation.

High values for TOIT pair in PP and HMSPP were expected, since they were not subjected to gamma irradiation; so, it should be emphasized that assessed PP/HMSPP, 50% (w/w) foamed samples proved to be radiant tolerant, once all of them kept the original appearance and did not present deep yellow colors after irradiation.

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