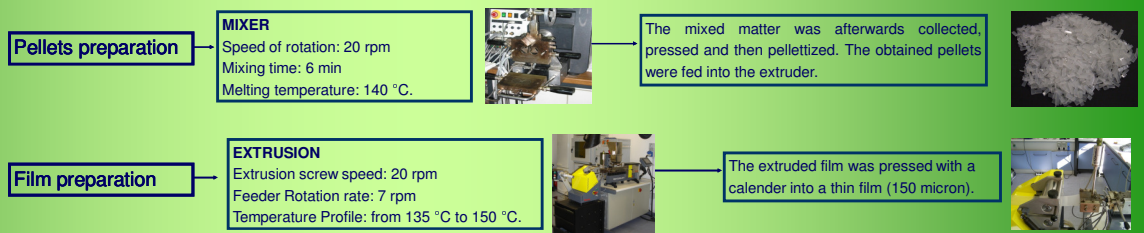


Addition of antioxidants (AO) to polyolefins is a common practice during film's manufacture because they protect the polymers from degradation. For this reason, part of the antioxidant is lost because of its ability to function as a free-radical scavenger. One of the most common synthetic antioxidants is BHT, however, nowadays there is an increased interest in replacing synthetic by natural ones. One of the most interesting is α -tocopherol, which can also be used to protect packaged foods from oxidation during storage. In this work, active films with different α -tocopherol contents were prepared through a two-step process (mixing and extrusion) with the aim of determining the amount of α -tocopherol in the film after processing, in order to optimize its quantity for further use as an antioxidant for the stabilization of food packaged products.

The active films were obtained loading two different antioxidants into an unstabilized LDPE matrix (Polimeri Europa, Italy): the natural α -tocopherol and the synthetic BHT. Three different loading concentrations were chosen: 0.1, 0.5 and 1% w/w. The obtained active films were labeled as LDPE/xTOC, LDPE/yBHT and LDPE/xTOC/yBHT, where xTOC is the content of α -tocopherol and yBHT is the content of BHT, respectively.

Film Preparation



Determination of α -tocopherol in the active films

Different kinds of extraction techniques can be used to extract the antioxidant from the polymer matrix. In this work, the following procedure has been used: 0.5 g of film was extracted with 20 mL of acetonitrile (ACN) for 24 h. Extracts were filtered and injected into an Ultra performance Liquid Chromatograph (UPLC) with diode array detection (DAD). A second extraction was carried out under the same conditions with the same film. A UPLC BEH (5 x 2.1 mm, 1.7 μ m) column was used at 30 °C. A gradient elution method was employed: between 0 min to 1.5 min from 10:90 water/ACN to 100% ACN, followed by isocratic elution of 100% ACN. The total run time of each analysis was 5 min. The flow rate was 0.3 ml/min and the injection volume was 10 μ l. α -tocopherol was detected at 295 nm and BHT at 277nm. Obtained values are reported in Table 1.

Table 1: Concentration of active films in what regards to TOC and BHT

Samples	TOC/BHT Initial amount (ppm)	TOC/BHT Extracted from the film (ppm)
LDPE/1TOC (pellet)	10000/0	415/0
LDPE/0.1TOC	1000/0	73/0
LDPE/0.5TOC	5000/0	888/0
LDPE/1TOC	10000/0	2535/0
LDPE/0.1BHT	0/1000	0/225
LDPE/0.5BHT	0/5000	0/1960
LDPE/1BHT	0/10000	0/4083
LDPE/0.05TOC/0.05BHT	500/500	408/64
LDPE/0.25TOC/0.25BHT	2500/2500	1855/624
LDPE/0.5TOC/0.5BHT	5000/5000	3666/1137

Our results show that a higher concentration of TOC is found in the pellets (just one-step process) than in the films (two-step process). Moreover, it is worth noting that, due to its volatility, films LDPE/xTOC lost a high amount of α -tocopherol during processing. On the contrary, for films prepared with both α -tocopherol and BHT, the loss of natural AO was significantly lower. In fact, the residual amount of α -tocopherol after processing was 81, 74 and 73% of the initial amount in the case of the plastic film with 0.05%, 0.25% and 0.5% TOC+BHT, respectively. This means that BHT protects α -tocopherol from degradation. Indeed the amount of BHT found in the LDPE/yBHT films is higher than the amount found for LDPE/xTOC/yBHT films.

Oxygen Induction Time (OIT)

A Differential scanning calorimetry (DSC) was used to measure the OIT of the investigated films in an oxygen atmosphere with a flow rate of 80 mL/min at 180 °C. OIT is the time interval to onset of exothermic oxidation of the film (Fig.1) and represents the efficiency of the phenolic antioxidant to reduce the oxidative decomposition of the polymer. The OIT values are determined as the intersections between the baseline and the tangent to the curve. The obtained results are reported in Table 2.

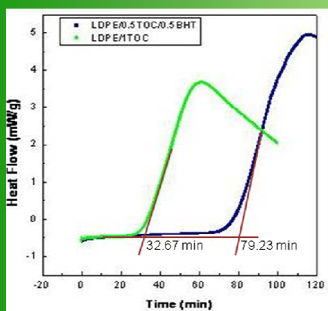


Figure 1. Thermograms of OIT tests of the investigated films obtained by using a DSC Q1000 (TA Instrument)

Table 2

SAMPLES	OIT (min)
LDPE	0.28
LDPE/1TOC (pellet)	91
LDPE/0.1TOC	4
LDPE/0.5TOC	27
LDPE/1TOC	34
LDPE/0.1BHT	4
LDPE/0.5BHT	14
LDPE/1BHT	31
LDPE/0.05TOC/0.05BHT	22
LDPE/0.25TOC/0.25BHT	61
LDPE/0.5TOC/0.5BHT	79

Results show that OIT values of pellets are higher than the value of the corresponding film. This is in accordance with the chromatographic analysis which shows that the amount of natural AO in the pellets is higher than its amount in the film after extrusion process. It is worth noting that α -tocopherol efficiency is higher than that of BHT. In fact, despite the lower α -tocopherol residual content in the film compared to residual BHT content, OIT values of LDPE/xTOC films are similar to those of LDPE/yBHT. This is most likely due to the formation of α -tocopherol oxidation products which also exhibit antioxidant properties. Moreover, the combined effect of TOC and BHT shows a higher efficiency in the film stabilization. As confirmed by the chromatographic results, the use of BHT prevents the degradation of α -tocopherol, thus increasing its residual amount in the film after the two-step process.

Barrier and mechanical properties

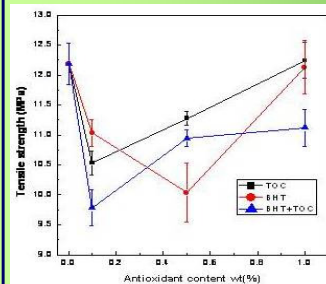


Figure 2. Tensile strength vs Ao content obtained using a dynamometer SANS

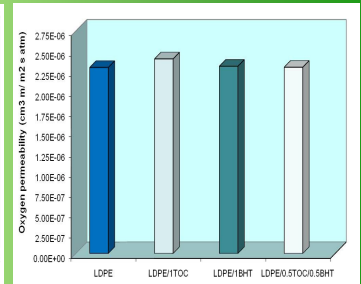


Figure 3. Oxygen permeability of the investigated films obtained by using an OxTran at 23°C and 50% RH

As far as mechanical properties are concerned, both the synthetic and the natural AOs act as plasticizers for the polymeric matrix. However, this effect is reduced as the amount of antioxidant loaded into the film increases. As far as oxygen barrier properties are concerned, no significant differences are observed among the neat LDPE and the active films. This can be related to the similar degree of crystallinity observed for these films. These data provide a positive result since, an increase in the OTR could result in an acceleration in the oxidation of the packaged product and, thus, counteract the positive SL extension effect due to the presence of the antioxidant into the active film.

Conclusions

- A new UPLC method has been tested and used to determine the amount of a synthetic (BHT) and of a natural (α -tocopherol) AO into different active films.
- The influence of the processing steps and conditions on the residual amount of AO into the films has been determined.
- α -tocopherol stabilizes the polymer better than BHT, most likely due to the formation of oxidation products having antioxidant activity
- α -tocopherol residual content into the film after processing is higher when both TOC and BHT are loaded into the polymer. Thus, BHT protects α -tocopherol from degradation.

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