

Settling the Question of Optimum Concentration and Methodology Used for Adding an Antioxidant to PS/PP Polyblend

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Summary: The method of addition of antioxidants to immiscible polymer blends can influence the end use performance of a polyblend artifact. This work is aimed at determining the most suitable procedure for adding antioxidants to a polystyrene (PS)-polypropylene (PP) blend (80/20), and its optimum concentration using three different methodologies. The effects of UV exposure on mechanical properties of the polyblends were examined. Results show that both the method of addition and concentration of the antioxidant do not alter mechanical properties, nevertheless, a concentration of 0.1% w/w is recommended.

Introduction

Blending of polymers is a versatile and economic way to produce new materials that combine the attractive features of the constituent polymers⁽¹⁾, e.g. PS and PP that are currently attracting great interest⁽²⁻⁵⁾.

As with all polymers, polymer blends undergo oxidative degradation during processing and in-service. However, during mixing and melt processing of the polyblend components increased degradation (synergistic effects) may occur as a result of increased shear in a multiphase system of incompatible polymers⁽⁶⁾. Furthermore, products based on polyblend materials are normally subjected to environmental changes, in the presence of oxygen, which limits their useful lifetime

There is a lack of perspectives on the precise methods of addition of antioxidants to immiscible polymer blends, as for example, for PS-PP blend. This work is aimed at determining the optimum amount of an antioxidant and the method to adopt to achieve stabilization of PS/PP polyblend at 80/20 composition by weight.

Experimental

Materials

The polymers used in this study were PS from Estizulia of Venezuela (MFI at 200°C and 5 kg load = 2.3 g/10 min, density = 1.04 g/cm³) and PP from Propilven of Venezuela (MFI at 200°C and 5 kg load = 1,6 g/10min, density = 0,91 g/cm³). The antioxidant Recyclostab 811 was supplied by Ciba-Geigy. Sandozin, a tenside agent, was supplied also by Estizulia.

Preparation

Pellets of PS and PP in a weight ratio of 80/20 were pre-mixed in a blender with different amounts of antioxidants (0.05, 0.075, 0.1, 0.15 and 0.3 w/w %) by following three different methodologies. The pre-mixes were processed in a twin-screw co-rotating Werner & Pfleiderer extruder at 100 rpm. Temperature profiling along the five sections of the extruder (150, 190, 210, 215, 210 °C) were determined previously^(5,7). Thick strands of extrudates were pelletised and test specimens (3mm thick plaques) were prepared, for tensile strength measurements according to an ASTM standard (ASTM D638-77a), by compression moulding (Carver Press, 210oC for 10min, under a load of 35 MPa). Test specimens were exposed to UV radiation in a Xenotest machine and their characteristics measured on an Instron tensile testing machine.

Three methodologies were adopted for the addition of antioxidants to the PS/PP:

Methodology 1: Within a mechanical blender, a certain amount of the tenside agent and a corresponding amount of the antioxidant were added to the PS/PP (80/20) blend, pre-mixed and fed to the extruder. The tenside agent was added in improve adhesion of antioxidant (in powder form) to pellets of the blend components.

Methodology 2: Concentrates of PS and PP with 2.5 % w/w of antioxidant were prepared. The concentrate of each homopolymer was prepared separately according to methodology 1 above. The procedure adopted here would facilitate the dispersion of the antioxidant into homopolymer components.

Methodology 3: This method was similar to method 1, except for the absence of the tenside agent to ascertain its significance.

Results and Discussion

Figure 1 shows that the presence of an antioxidant gives rise to higher values of elongation and stress at break when compared to the corresponding antioxidant-free blend preparation. Furthermore, values for elongation and stress at break obtained by following methodology 1

were higher than those achieved with methodologies 2 and 3, especially for elongation at break.

Neither concentration of antioxidant nor the methodologies used for its addition appeared to affect significant changes in Young's modulus, suggesting that there is no appreciable variation in the rigidity of the formulated blends. It can be inferred from these results, however, that Recyclostab 811 delays effectively both thermo-mechanical and oxidative degradation of PS/PP (80/20) blend, which occurs during extrusion and molding processes.

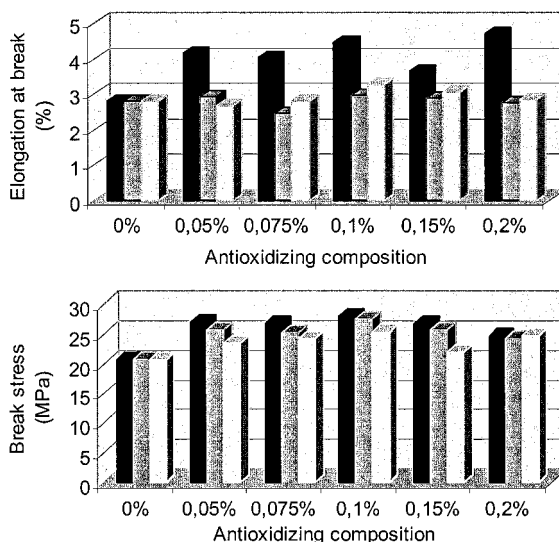


Figure 1. Elongation and stress at break for blends without and with antioxidants.

■ Methodology 1 ▨ Methodology 2 □ Methodology 3

Additionally, it can be seen (Figure 1) that the PS/PP (80/20) polyblend with 0.1% wt of antioxidant reaches the highest values of elongation and stress at break, with no apparent variation in the rigidity of the material, as inferred from Young's modulus values. These results indicate that this is the methodology of choice and that an antioxidant weight percent of 0.1 is an optimum.

On the other hand, considering the UV light irradiation time over samples, it was found that the behaviour of tensile properties appears to be practically independent of the concentration of the antioxidant irrespective of the methodology adopted for its addition, at least, for the exposure time considered in this work (0 to 1000 hrs); see Figure 2 for results obtained by following methodology 1.

It can be seen from Figure 2 (for exposure time = 1000hrs) that the PS/PP (80/20) polyblend shows a decrease in the elongation at break of around 50 % with a slight increase in Young's modulus, independent of antioxidant concentration, which indicates degraded samples⁶⁾.

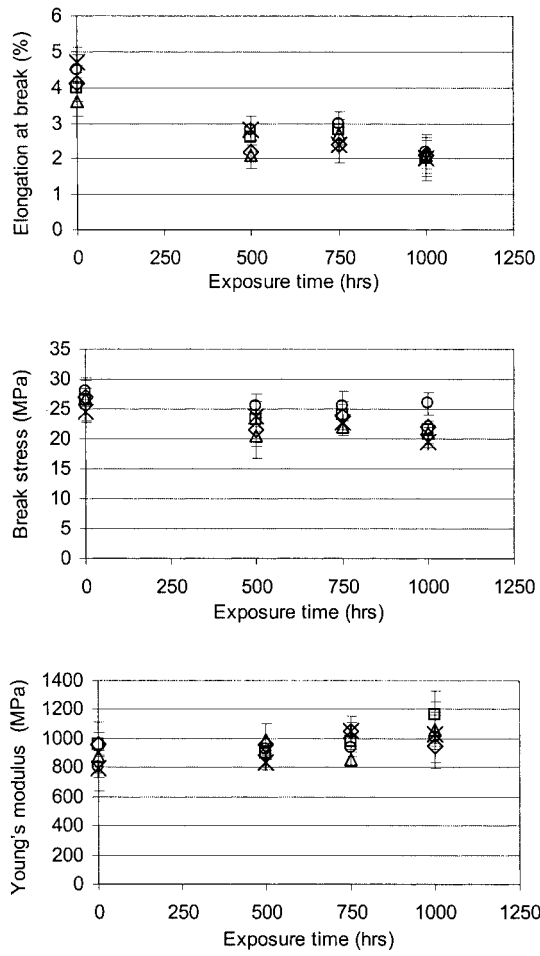


Figure 2. Tensile Properties for proposed methodology 1 of addition.
◇ 0,05% □ 0,075% ○ 0,1% △ 0,15% ✱ 0,2%

Examination of Figure 3 shows that elongation at break is almost independent of the methodology used for adding the antioxidant, except for exposure time = 0h where methodology 1 gives higher value of elongation at break.

Results shown in Figures 2 and 3 indicate that, only during processing and moulding of the polyblend, methodology 1 offers a greater resistance to degradation in such material; in such a case, degradation under UV exposure, is independent of the antioxidant concentration and the methodology of addition.

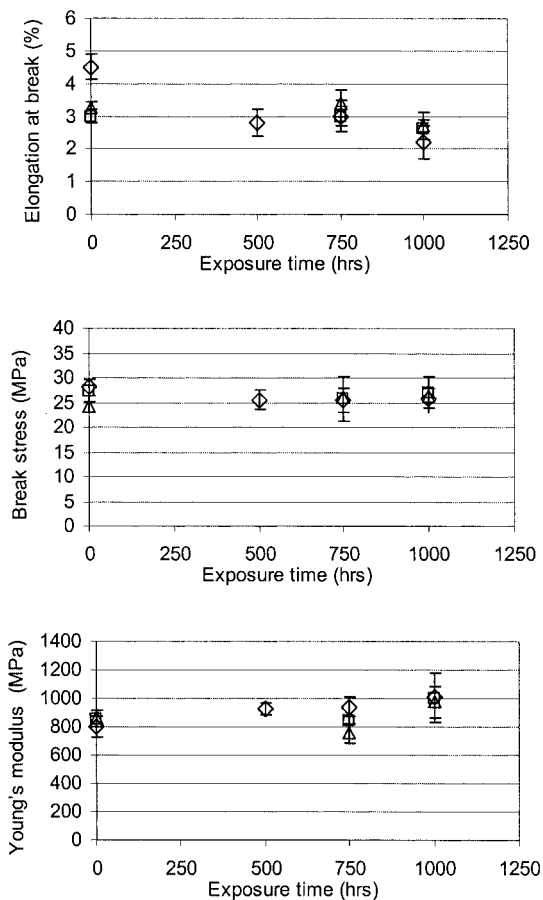


Figure 3. Tensile properties of polyblend PS/PP (80/20), containing 0.1 wt% of an antioxidant, as a function of exposure time and methodology of addition.

◇ Methodology 1 □ Methodology 2 △ Methodology 3

Also, it was found (by IR-spectra analyses and measurements of molecular weights of polymers, previously separated) that degradation in PP during processing and exposure to UV radiation, occurs mainly through chain scission. Zweifel⁽⁶⁾ points out that polypropylene is rapidly degraded by the effect of heat, mechanical shear and radiation with UV light.

On the other hand, IR spectroscopic investigations carried out on the polyblend samples did not show the formation of oxidation products, e.g. ketones, acids, esters, peracids and peresters. Also, sample thickness influences substantially the behaviour of a polyblend with regard to its response to degradation, although a significant drop in molecular weights of PP has been observed⁽⁶⁾ and was attributed to the presence of tertiary carbons in PP. Polymers, with branched alkanes as repeating units, react readily with macro-peroxyl radicals, by intramolecular hydrogen abstraction, giving rise to hydroperoxide sequences⁽⁶⁾ on the macromolecular chains. Chain scissions cause drastic reduction in the average molecular weight and, consequently, loss in mechanical properties.

Conclusion

1. Addition of an antioxidant by Methodology 1, compared with the other two, delays the process of initial degradation, during processing and moulding of the blends. The three proposed methodologies, however, give similar effects with respect to photooxidative degradation.
2. Tensile properties of the PS/PP (80/20) blend samples were practically independent of concentration of the antioxidant, at least, for the exposure time considered in this work (0 to 1000 hrs). It is recommended to use 0.1% wt of antioxidant in the blend as it gave slightly better mechanical properties.
3. The degradation process of the PS/PP (80/20) polyblend carried out initially during processing and moulding, and later by the UV irradiation in a Xenotest, occurs mainly by chain scission of the polymer constituents. This causes a decrease in both the molecular weight and the elongation at break of the polyblends, as well as a slight increase in the rigidity of material, at least, during the exposure time considered under UV light.

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