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Photostabilization study of ethylene-butyl acrylate copolymers functionalized in the molten state with hindered amine light stabilizers (HALS)

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Dedicated to Professor Norman S. Allen on the occasion of his 65th birthday.

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ABSTRACT

Hindered Amine Light Stabilizers (HALS), N-methylated and O-alkylhydroxylamine, were successfully anchored onto an ethylene-*co*-butyl acrylate (BA) by a transesterification reaction in the molten state. The content of HALS bonded to the EBA was calculated from the atomic ratio (*N/C*) determined by X-ray Photoelectron Spectroscopy (XPS). After reaction times of 5–30 min in the molten state the content of bonded HALS attained values from 0.17 to 0.63%. The modified EBA with HALS were studied by Chemiluminescence emission and the photostabilization effect was evaluated under accelerated ageing in the presence of pesticides. The antioxidant effect of HALS bonded to EBA was evaluated by determination of Carbonyl Index (CI) and retention of elongation at break as a function of exposure time and pesticide treatment. The stability of the EBA with anchored HALS exhibited higher performance as shown by low CI-values and correlated with the content of bound HALS and the thermal history of the materials. Also, mechanical properties correlated well with the CI results and the photostabilization of bound HALS was effective until 3150 h of exposure time using pesticides.

1. Introduction

Low-density polyethylene (LDPE), ethylene-vinyl acetate copolymers (EVA) and, recently, ethylene-butyl acrylate copolymers (EBA) are the most common plastics materials used for greenhouse cover films. The lifetimes required for these films vary from one agricultural season to several years, depending on the geographical area where they are used, the type of greenhouse, the crop, the use of pesticides, etc. To increase efficiency in long-term applications the polymeric HALS are the most efficient structures but have a high cost disadvantage. The introduction of hindered amine light stabilizers [1] (HALS) has revolutionized the polyolefin industry by providing significantly enhanced UV stabilization over that previously achieved by UV absorbers or excited-state quenchers. This class of chemicals, giving stable free radicals based on piperidine have the capability of generate nitroxide (>NO·) radicals as intermediates that act in the stabilization mechanism trapping radicals and decomposing hydroperoxides produced in the photochemical oxidation [2–4]. These stabilizers are colourless, have ecological acceptability and can have superior light and heat stabilization effects. At the beginning, only low molecular weight HALS structures were available. But for long-term stability of polyolefins high molecular weight or polymeric HALS were developed [5] to avoid disadvantages associated with low molecular mass stabilizers such us high migration rate and low resistance to extraction.

However, many unexpected problems of premature failure can occur during the use of HALS-stabilized polyethylenes in greenhouses due to their interaction with for example, pesticides used in agricultural applications. Both sulphur and chlorine containing pesticides inhibit the functioning of the HALS and can as a result have a detrimental effect on the film-life used in the greenhouse [6,7]. To counteract this effect, the basicity of the hindered piperidines [8], secondary >NH, and tertiary (>NMe) (pK_a = 8.0–9.7) have been lowered by O-alkylhydroxylamine formation (>NOR,

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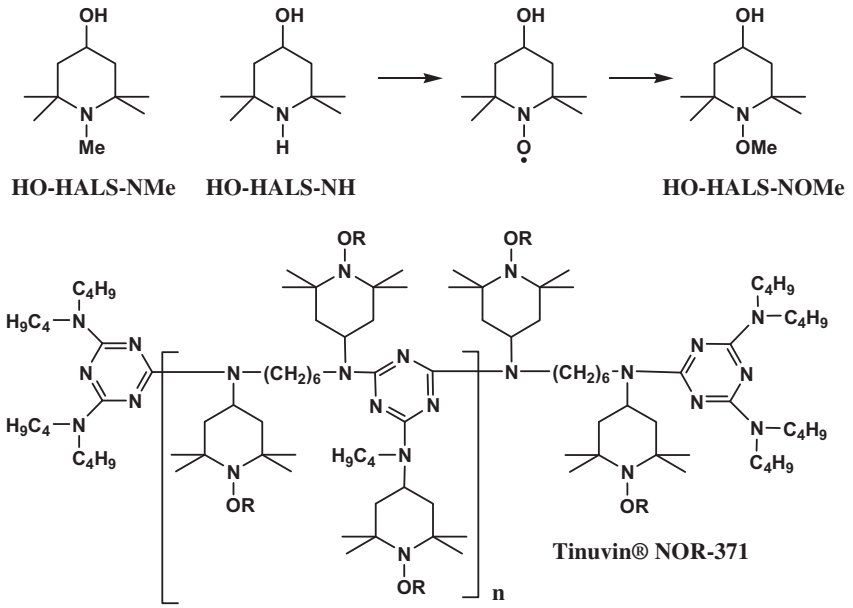

Fig. 1. Commercial structures of *2,2,6,6-tetramethylpiperidin-4-ol* (HO-HALS-NH), 1,2,2,6,6-pentamethylpiperidin-4-ol (HO-HALS-NMe) from Degusa and Tinuvin® NOR-371 from BASF. Synthesis [11,12] of *1-methoxy-2,2,6,6-tetramethylpiperidin-1-oxyl* (HO-HALS-NOMe) form HO-HALS-NH with the corresponding intermediate nitroxide radical (>NO•).

pK_a = ~4.2) thus diminishing the interaction with acidic pesticides and hence their adverse effect on film stabilization.

The increasing demand by the polymer industry for high-performance and cost-effective polymeric materials and the ever-growing concern about the environmental impact of excessive use of solvents, reactions have increasingly been run in solventless polymer melts using typical polymer processing machines, such as batch mixers and screw extruders, as reactors in a so called "reactive processing of polymers" that has become a specialty [9,10] of increasing importance. Due to the melt stability at high temperatures the preferred reaction times are short (less than 10 min) using continuous reactors (i.e. screw extruders) of batch processes (i.e. banbury mixers). This fact makes the effectiveness of the catalysis a crucial key for attaining high conversions in the melt reactions.

In this work we have synthesized polymeric HALS by a transesterification reaction in the molten state of an EBA copolymer (8% of butyl acrylate) using hydroxylated low molecular weight HALS as reactive and an organometallic catalyst of well known activity. As reactive HALS we have synthesized O-methylhydroxylamined based HALS structures due to their improved behaviour in agricultural films. The degree of modification was determined using X-ray Photoelectron Spectroscopy (XPS) by analysing the low content of HALS anchored to the EBA by determining the nitrogen/carbon ratio.

Also, we have studied the photodegradation of EBA copolymers in the presence of pesticides to evaluate the stabilization effect in the modified materials containing HALS (EBA-HALS-NMe and EBA-HALS-NOMe). Fourier Transform Infrared Spectroscopy (FTIR), mechanical properties and Chemiluminescence were used to evaluate the degree of photodegradation and the stabilization effect of the covalently bonded HALS on the materials.

2. Experimental

2.1. Materials

A poly (ethylene-co-butyl acrylate) copolymer (EBA) with an 8% (w/w) content of butyl acrylate (PA-805), was supplied by Repsol company. The base formulation used in this work contained a standard package of process additives stabilizer phenol–phosphite combination. Pesticides Meta-Sodium (sodium methylaminomethanedithioate) and Cypermethrin were supplied by Quimidroga S.A.

For the comparative study of stabilization, Tinuvin® NOR-371 from BASF (MW: 2.8–4.0 × 10^3 g mol^{-1}) was used as reference at a concentration of 0.5% (w/w). Tinuvin® NOR-371 (mp = 91–104 °C) is considered one of the most efficient photostabilisers currently used for polyethylene films under pesticide treatment.

Two commercial hydroxylated HALS with low molecular weight 2,2,6,6-tetramethylpiperidin-4-ol (HO-HALS-NH) and 1,2,2,6,6-pentamethylpiperidin-4-ol (HO-HALS-NMe), were provided by Degussa. Also, 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol (HO-HALS-NOMe) was previously synthesized following the procedure described in the literature [11,12] as shown in Fig. 1 together with the commercial structures.

2.2. Transesterification of EBA in the molten state

The reactions of EBA in the molten state (Fig. 2) were carried out in an internal mixer Haake Rheocord 9000 with a volumetric

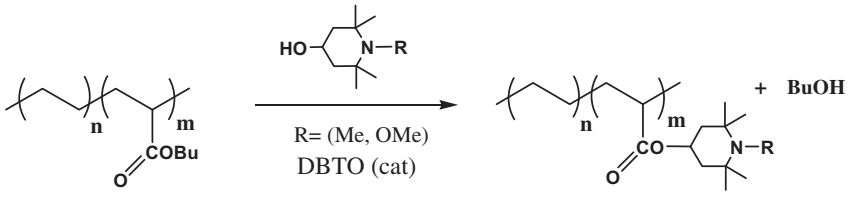

Fig. 2. Chemical modification of EBA (8% BA) by reactive HALS in the molten state.