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SURFACE-ANCHORED HINDERED-AMINE LIGHT STABILIZERS FOR IMPROVED UV STABILITY OF POLYOLEFINS

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ABSTRACT

Hindered-amine light stabilizers (HALS) were surface anchored to polyolefin films by reacting the HALS, namely, 1,2,2,6,6-pentamethyl-4-piperidinol and 1,2,2,6,6-pentamethyl-4-aminopiperidine, with succinic anhydride functionalized polyolefin surfaces. The photostability of polyolefin films with surface-anchored HALS were compared with films stabilized with commercial HALS (Tinuvin 770) by melt blending. It is shown that the photostabilizing efficiency of surface-anchored HALS is superior that of melt-blended polyolefins.

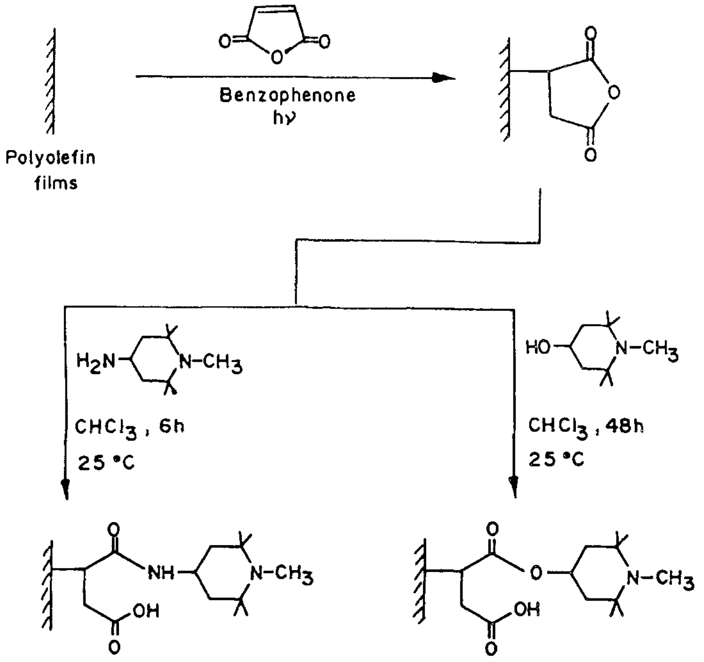
INTRODUCTION

Polymers are susceptible to degradation by oxygen in combination with UV light or heat. The oxidative degradation can be partially prevented by introducing suitable stabilizers into the polymer by melt blending. Compatible and mobile stabilizers usually give the best protection, but low molecular weight stabilizers are easily lost from the polymer through migration, evaporation, or extraction. To avoid such loss, polymeric stabilizers have been introduced, but the low mobility and poor compatibility of polymeric stabilizers decreases their efficiency [1]. The oxidation and degradation of a polypropylene film starts from the surface and slowly proceeds into the interior of the polymer [2, 3]. Stabilizers are therefore expected to be most effective if they are concentrated at the surface, where the oxidation takes place.

However, when situated at the surface they are easily lost through evaporation or extraction. To prevent such loss they should preferably be anchored chemically to the polymer surface.

Surface grafting of stabilizers has been reported as a convenient technique for attaching a stabilizer to the polymer in a permanent manner [4–6]]. Recently, there has been great interest in the use of polymer-bound stabilizers to control the location of the stabilizers in polymer systems [7–9]. Acrylic coating have been developed employing a bound hindered-amine light stabilizer. These coatings exhibit superior weatherability over similar acrylic coatings using free HALS [10–13]. In particular, this approach has been used to control the leaching of stabilizers from polymers, and it is particularly useful in coating systems. Recently, Al-Malaika et al. achieved a high level of grafting of a HALS-type stabilizer onto polyolefins using reactive processing techniques [14–16].

In our laboratory we have discovered a mild photochemical technique for surface functionalization of polyolefins whereby the succinic anhydride group could be introduced onto the polymer surface [17]. The technique is clean and proceeds with a high degree of chemo- and topological selectivity. Succinic anhydride is a reactive functional group to which a number of other functionalities can be attached through simple chemical reactions. The objective of the present work was, therefore, to anchor a HALS to the surface of a polyolefin through the succinic anhydride moiety (Scheme 1) and to examine the UV stability of such surface-modified polymers. The HALS used were 1,2,2,6,6-pentamethyl-4-piperidinol (HALS-1) and 1,2,2,6,6-pentamethyl-4-aminopiperidine (HALS-2).



SCHEME 1. Synthetic route for obtaining polymer-bound hindered-amine light stabilizers.

EXPERIMENTAL

Materials

Commercial samples of isotactic polypropylene (i-PP, Koylene S3030), low density polyethylene (LDPE, Indothene 16MA400) from Indian Petrochemicals Corp., Baroda, India, and heterophasic ethylene–propylene copolymer (EPQ 30R, MI = 0.6–0.9, 15.1 mol% ethylene) from Himont, Italy were used in this study. Commercial hindered-amine light stabilizer (HALS), Tinuvin 770 [bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate, white crystals, mp 81–83°C, $\overline{M}_n = 480.7$] from Ciba-Geigy, Switzerland, was used as reference for comparison. Maleic anhydride (E. Merck, India) was recrystallized from chloroform and stored under desiccation. Benzophenone (Aldrich) was recrystallized from ethanol.

Analysis

FT-IR measurements were carried out with a Perkin-Elmer 16PC Spectrometer, and UV analyses were carried out from chloroform solutions with an HP 8452A Diode Array Spectrophotometer. Polymers were purified to be free of additives and stabilizers, and film samples were prepared by melt pressing. The methods of purification and sample preparation (80 μm thick film) have been described elsewhere [18]. These films were used as controls for the measurement of the carbonyl index. All solvents used were purified by literature procedures [19].

Synthesis of Hindered-Amine Light Stabilizers (HALS)

Triacetonamine (2,2,6,6-tetramethyl-4-piperidone) was synthesized from the condensation of acetone with ammonia in the presence of calcium chloride as per a literature procedure [20].

1,2,2,6,6-Tetramethyl-4-piperidinol was prepared by a reported procedure [21]. Yield 92%, mp 72–74°C (Lit. [20] mp 73–74°C).

Synthesis of 1,2,2,6,6-Pentamethyl-4-aminopiperidine [22]

1,2,2,6,6-Pentamethyl-4-piperidone oxime was prepared by reacting 1,2,2,6,6-pentamethyl-4-piperidone with hydroxylamine hydrochloride according to a reported procedure [21]. The oxime (9.2 g, 0.05 mol) was dissolved in 80 mL methanol and hydrogenated using ammonium hydroxide (5 mL) and Raney nickel (1.5 g) at atmospheric pressure and room temperature for 4 hours. The catalyst was filtered and washed with dichloromethane. The filtrate was dried with sodium sulfate, and the product was distilled under vacuum at 15 mm, bp 97–99°C (Lit. [21] bp 85–86°C at 10 mmHg).

Preparation of Polyolefin Surfaces Bearing Succinic Anhydride Groups

A film of polyethylene (thickness 80 μm) was suspended in a small glass reactor using a Teflon thread. The glass reactor was cylindrical in shape with dimensions of 12 cm diameter and 13 cm height with a two-way lid. A beaker containing a

25-mL solution of maleic anhydride (7.35 g) and benzophenone (1.35 g) in dry acetone was placed inside the reactor at a distance of 3 cm from the film. The reactor was purged with nitrogen for 20 minutes to remove any oxygen present. The reactor was placed in a UV chamber equipped with an electrical heating arrangement, and the temperature of the reactor was raised to 60°C by external heating. The film was irradiated for 2 hours using a 400-W high-pressure mercury vapor lamp which emitted light in the near-UV region ($\lambda > 290$ nm). The distance between the reactor and the UV lamp was 18 cm. The reaction was presumed to occur equally on both sides of the free-standing film since the monomer and sensitizer were in the vapor phase surrounding the film. The modified polyethylene film thus produced was Soxhlet extracted with acetone for 8 hours dried under vacuum at 30°C, and stored under N_2 atmosphere.

Preparation of Polyethylene Polymer-Bound HALS-1 (PB-HALS-1)

Surface-modified polyethylene film (3×1 cm^2) bearing the succinic anhydride group was reacted with 1,2,2,6,6-pentamethyl-4-piperidinol (0.016 M) in dry chloroform for 48 hours at 25°C with occasional stirring. Completion of the reaction was monitored by FT-IR. The film was Soxhlet extracted with chloroform for 5 hours to remove any unreacted HALS.

Preparation of Polyethylene Polymer-Bound HALS-2 (PB-HALS-2)

Surface-modified polyethylene film (3×1 cm^2) bearing the succinic anhydride group was reacted with 1,2,2,6,6-pentamethyl-4-aminopiperidine (0.016 M) in dry chloroform for 6 hours at 25°C with occasional stirring. Completion of the reaction was monitored by FT-IR. The film was Soxhlet extracted with chloroform for 5 hours to remove any unreacted HALS.

The same procedure was followed in the cases of polypropylene and heterophasic ethylene-propylene copolymers. A sample of unmodified polyethylene film bearing no succinic anhydride group was treated with HALS-1 and HALS-2 under similar reaction conditions. It was confirmed by UV spectroscopy that there was no HALS, either occluded or adsorbed, in the films. This indicates that in the absence of a reactive succinic anhydride functionality, no additive was anchored onto the polyolefin film. Film samples containing commercial HALS (Tinuvin 770, 0.3 wt%) were prepared by melt blending for a comparative study.

Analysis of Surface Concentration

UV-VIS Spectroscopy

Polyolefin film bearing succinic anhydride groups (1×3 cm^2) was immersed in 5 mL of 0.016 M 1,2,2,6,6-pentamethyl-4-piperidinol solution in chloroform. The film was allowed to react with HALS at 25°C for 48 hours with occasional stirring. A blank experiment was conducted with untreated polyolefin film under identical conditions. The concentration of the HALS in solution after reaction with the surface anhydride groups of the film was determined by UV-Vis spectroscopy. A calibration curve was prepared from UV absorptions of HALS solution of known concentration at 276 nm. The depletion of HALS concentration in the solution gave a measure of the surface concentration of HALS.

Gravimetry

Gravimetric analysis was used to calculate the amount of HALS on the polyethylene surface. From the increase in weight after HALS incorporation, the moles of HALS present/cm^2 was calculated (Table 1).

RESULTS AND DISCUSSION

The polyolefin surface bearing the succinic anhydride group was characterized by FT-IR spectroscopy. The IR spectrum of the succinic anhydride modified polyolefin film shows two sharp peaks at 1868 and 1789 cm^{-1}, characteristic of the cyclic anhydride group (Fig. 1, Curve a). Maleic anhydride undergoes graft polymerization onto polyolefins, typically at a temperature above 120°C, in the melt phase and in the presence of a hydrogen donor solvent (acetone), it is unlikely that surface grafting of poly(maleic anhydride) occurs to any significant extent [17]. The succinic anhydride functionalized polyolefin films were reacted with 1,2,2,6,6,-pentamethyl-4-piperidinol (PB-HALS-1) and 1,2,2,6,6-pentamethyl-4-amino piperidine (PB-HALS-2). The FT-IR of these films shows the complete disappearance of the peaks at 1868 and 1789 cm^{-1} (Fig. 1, Curves b and c). This confirms that the succinic anhydride groups present in the films were completely reacted with HALS (Scheme 1). The IR spectrum of PB-HALS-1 shows a broad band at the carbonyl region due to ester linkage (1736 cm^{-1}) and acid groups (1720 cm^{-1}) (Fig. 1, Curve b) whereas the IR spectrum of PB-HALS-2 shows peaks at 1669 and 1720 cm^{-1} for amide and acid groups, respectively (Fig. 1, Curve c).

The concentration of HALS present on the polymer surface was determined by UV-Vis spectroscopy and gravimetry. The results are shown in Table 1. The concentrations of the functional group are very high and are indicative of substantial penetration of the functional group beyond a monolayer coverage. The maximum concentration for monolayer coverage on one side of the film is 3.3×10^{-9} mol/cm^2 [23]. Angle-dependent x-ray photoelectron spectroscopy (XPS) studies of

TABLE 1. Concentration of Polymer-Bound HALS-2 Present in Polyolefin Films

	Concentration, $\mu mol \cdot cm^{-2}$	
Sample	By UV	By gravimetry
PE	0.92	0.9
PP	0.42	0.4
E-P	1.08	1.0

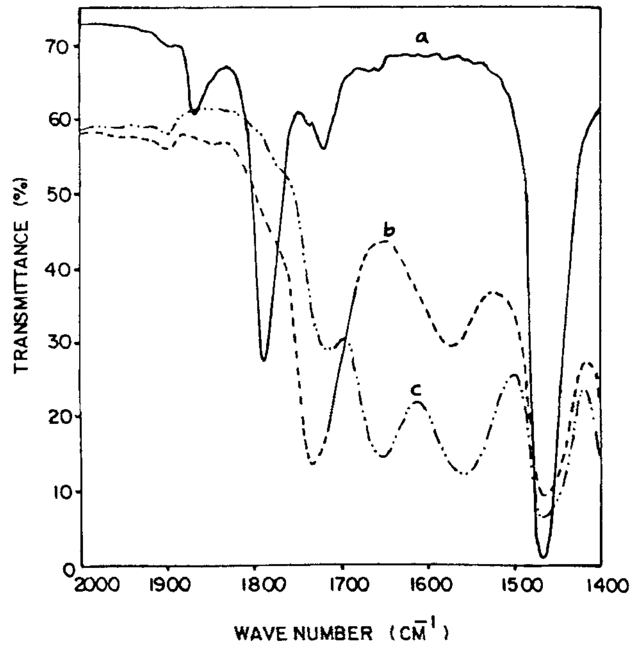


FIG. 1. FT-IR spectra of polyethylene film. (a) Succinic anhydride modified, (b) PB-HALS-1, (c) PB-HALS-2.

such surface-modified polyethylenes indicate a penetration depth greater than 40–50 Å [24].

Photostabilizing Efficiency of Polymer-Bound HALS (PB-HALS-1 and PB-HALS-2) in Polyolefins

The photoirradiation was carried out in a SEPAP 12/24 photoirradiation chamber at 60°C. This unit has a UV source supplying radiation longer than 300 nm. The details of the equipment are described elsewhere [18].

The photostabilizing efficiencies of PB-HALS-1 and PB-HALS-2 in polyethylene, polypropylene, and heterophasic ethylene–propylene copolymer were studied from carbonyl group formation at 1710 cm^{-1} and normalized for a 100-μm film thickness (carbonyl index) with irradiation time, and their performances were compared with polymers prepared by melt blending. The carbonyl group formation in surface-modified polyethylene upon photoirradiation is shown in Fig. 2. The rate of carbonyl index formation was plotted against irradiation time. Unprotected polyethylene showed a rapid increase in carbonyl absorbance only after 25 hours of irradiation. PB-HALS-1 and PB-HALS-2 show remarkable photostability compared to the polymer stabilized with melt-blended Tinuvin 770. In the case of melt-blended HALS, a carbonyl absorbance value of 0.1 was reached within 100 hours of irradiation time whereas in the case of polymer-bound HALS there was no significant carbonyl group absorbance up to 600 hours, and upon longer irradiation time a slow increase in the carbonyl index was observed. Carbonyl group formation

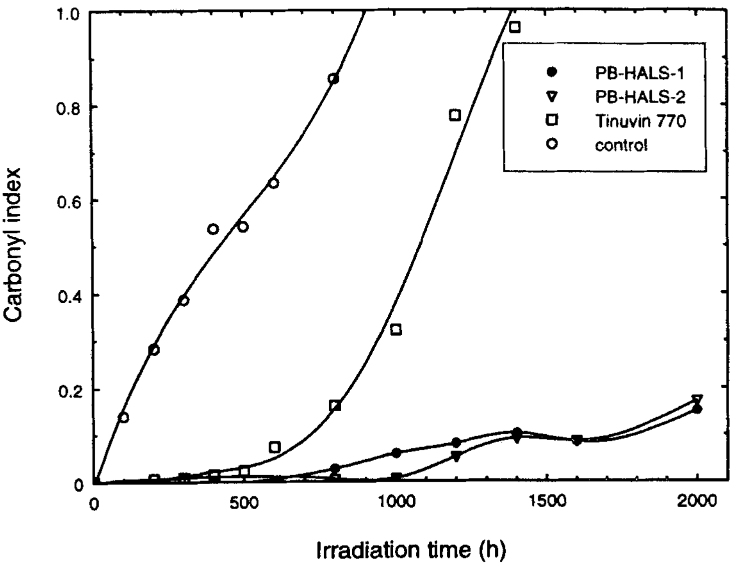


FIG. 2. Photostabilizing efficiency of polymer-bound HALS and Tinuvin 770 in polyethylene films.

upon irradiation of a surface-modified polypropylene and a heterophasic E–P copolymer is shown in Figs. 3 and 4, respectively. A remarkable photo-stabilizing efficiency was also observed in the case of HALS surface anchored to polyolefins.

PB-HALS-1 shows a better effect on photostability compared to PB-HALS-2 in all cases. Shlyapinthok [25] reported that, if the NH group is not fully hindered as in the 2,2,6,6-tetramethylpiperidine derivatives, the photostabilizing efficiency is considerably reduced. Since the nitroxyl radicals corresponding to such amines are not stable, this result was taken as confirmation for the prime role of nitroxyl radicals. Since nitroxyl radicals are known as efficient traps for alkyl radicals, it was postulated that they are the main active species in stabilization. However, both PB-HALS-1 and PB-HALS-2 show remarkable photostability. Ranby et al. [26] reported that polypropylene is effectively protected against UV-initiated degradation by grafting the PP surface with glycidyl methacrylate in thin surface layers followed by chemical attachment of HALS to the oxirane group. The same authors reported that similar surface grafting led to no significant effect in the case of polyethylene. However, no explanation for this observation was provided. Similarly, Mingbo and Xingzhou [5] reported that polypropylene film photografted on the surface with 2,2,6,6-tetramethyl-4-piperidinyl methacrylate showed a high degree of photostabilization. PB-HALS-1 showed a better effectiveness compared to the other reported [5, 26] polymer-bound HALS. The increase in carbonyl group was observed only after an induction period of 600 hours whereas it was 200 hours in the case of polypropylene grafted with 2,2,6,6-tetramethyl-4-piperidyl-methacrylate [5] and 100 hours for polypropylene grafted with aminotetramethylpiperidine [26].

It is generally believed that for any appreciable stabilizing action, the stabilizer should be present in a sufficient concentration and up to a reasonable depth. Carls-

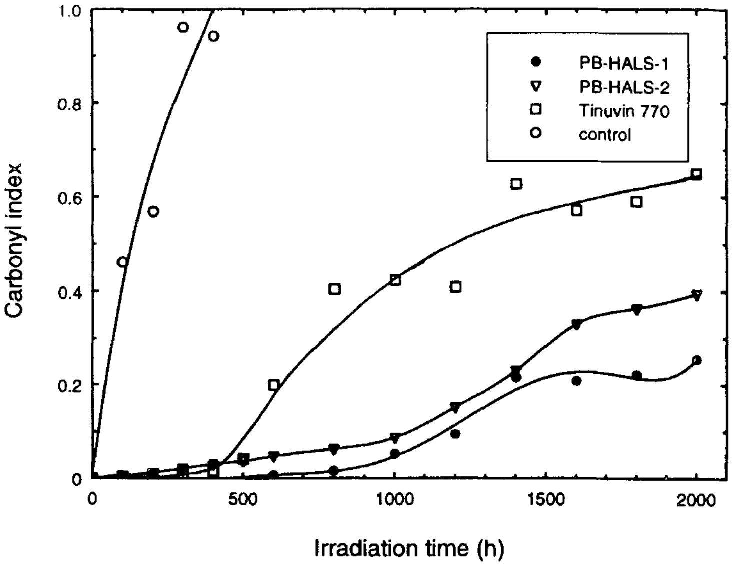


FIG. 3. Photostabilizing efficiency of polymer-bound HALS and Tinuvin 770 in polypropylene films.

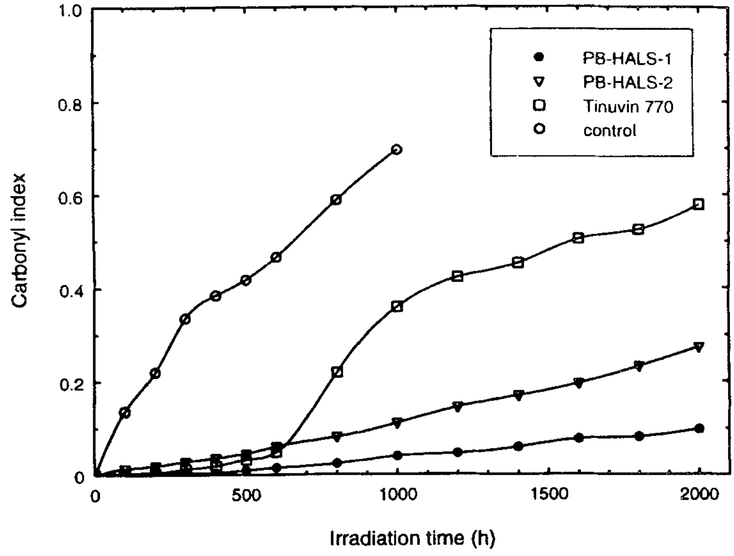


FIG. 4. Photostabilizing efficiency of polymer-bound HALS and Tinuvin 770 in E-P copolymer films.

son and Wiles [2, 3, 27] used attenuated total reflectance FT-IR spectroscopy to show that the oxidation of unstabilized polypropylene was confined to within 10 μm (100,000 Å) depth. This is because oxygen diffusion decreases rapidly as one proceeds from the surface toward the core, and maximum damage due to photooxidation occurs in regions where the dissolved oxygen concentration is very high. A similar observation was also made in the case of polyethylene [28]. Although we lack information on the precise depths up to which the stabilizers are incorporated in the present case, the results indicate that an adequate concentration of HALS is present in sufficient depth for effective photostabilization.

CONCLUSIONS

Polyethylene, polypropylene, and heterophasic E-P copolymer films were effectively protected against photoirradiation by anchoring HALS onto the succinic anhydride modified polymer surfaces. The improved photostability of such materials must be attributed to chemical bonding between the additive and the polymer surface, and hence to its permanence.

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