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Synthesis, characterization and performance evaluation of hindered amine light stabilizer end functionalized poly(ethylene-*alt*-propene) copolymer

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A polymeric hindered amine light stabilizer (HALS), wherein the HALS functionality was attached to the terminal chain end of an alternating ethylene–propylene copolymer has been synthesized by terminating the living anionic polymerization of isoprene with 4(2,3-epoxy propoxy)-1,2,2,6,6-pentamethylpiperidine followed by hydrogenation of the resulting polymer using Ziegler type catalyst. The solubility and diffusion coefficient of this polymeric HALS have been studied and compared with conventional low and high molecular weight HALS (Tinuvin 770 and Chimasorb 944). The photo-stabilizing efficiency of this polymeric HALS was also studied and compared with conventional HALS at different concentrations and it was observed that polymeric HALS showed a significantly improved photo-stabilizing efficiency. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: anionic polymerization; alternate ethylene–propylene copolymer; hindered amine light stabilizer)

INTRODUCTION

Protection of polymer against thermal and photo-oxidative degradation is achieved by melt blending the polymer with appropriate stabilizers, which ensures that the desirable polymer properties are maintained through-out the entire service life of the polymer. During the past decade, the chemistry of synthesis of stabilizers and their mechanism of action has been extensively studied[1]. Hindered amine stabilizers (HALS) have gained prominence as effective light stabilizers for a variety of polymers. Compatible and mobile stabilizers usually give the best protection, but low molecular weight stabilizers are easily lost from the polymer through evaporation, migration, or extraction. In order to avoid loss, polymeric stabilizers have been devised. However, the low mobility and poor compatibility of polymeric stabilizers decreases their efficiency[2]. HALS with molecular weights up to 3500 are commercially available, which increase the persistence of stabilizer in the polymer.

To further improve the permanence of the stabilizer in the polymer, a wide range of oligomeric and polymeric stabilizers have been synthesized and evaluated[3]. Polymeric HALS were obtained by either copolymerization or homopolymerization of functional monomers containing hindered amine groups[4–8] or by reacting of functional polymers with a compound containing a sterically hindered amino group[9,10]. For example, 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine was prepared and copolymerized with propylene using a $TiCl_4-MgCl_2/Et_3Al$ catalyst. The copolymer exhibited superior thermal oxidative stability even after exhaustive extraction with boiling heptane[11]. Oligomeric siloxanes with HALS groups were obtained by dehydrocondensation of polyhydridosiloxanes with 1,2,2,6,6-pentamethyl piperidin-4-ol. The stabilizer units in the resulting polymers are SiOC-bound to the siloxane chain[12,13]. Siloxanes with benzotriazole or HALS groups are also proposed as light-stabilizing lubricants for plastics[14–16]. Costanzi *et al.*[17] described the addition of various linear or cyclic oligo(hydrido-siloxanes) to HALS groups. These polymeric HALS show good light stabilizing activity, and are especially suitable for polymers which are exposed to solvent environment.

While choosing a stabilizer, its solubility, compatibility and diffusion rates from the bulk to the surface need to be assessed. While designing a polymeric stabilizer, two apparently contradictory criteria need to be considered. The polymeric stabilizer should have sufficiently high molecular weight, so that it does not easily diffuse out of the polymer (poor mobility). At the same time, it should have high solubility in the polymer (high compatibility), so that the stabilizer can be uniformly dispersed in the polymer. These aspects become particularly relevant for a multiphase polymer system such as heterophasic ethylene–propylene (E–P) copolymer, where the stabilizer can partition between different phases in the system. The actual stabilizer concentration, in either the elastomeric or the thermoplastic phase, may differ very significantly from the average total stabilizer concentration in the polymer. In such systems, knowledge of the phase that is more prone to degradation is essential for proper stabilization.

In this paper we describe a polymeric HALS stabilizer, designed especially for polyolefins. It was anticipated

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that such polymeric HALS may offer the right balance of diffusivity and compatibility of the stabilizer in polyolefins.

EXPERIMENTAL

Materials

Commercial samples of isotactic polypropylene (i-PP, Koylene S 3030 from India Petrochemicals Corporation Limited, Baroda, India) and heterophasic E–P copolymer (EPQ 30R, MI (melt flow index) = 0.6–0.9, 15.1 mol% ethylene from Himont Italia) were used in this study. Polymer samples were purified by using the procedure described elsewhere[18]. Two commercial HALS, Tinuvin 770 (HALS I), ([bis(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate], white crystals, mp 81–83°C, $\bar{M}_n = 480.7$) and Chimassorb 944 (HALS II), (poly{[6-[(1,1,3,3-tetramethylbutyl)-amino]-1,3,5-triazine-2,4-diyl]-[(2,2,6,6-tetramethyl-4-piperidinyl)-imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)-imino], white powder, mp 155–125°C, $\bar{M}_n \cong 3000$) from Ciba-Geigy, Switzerland, were used as references for comparison.

All other reagents were analytical grade obtained either from Fluka AG or Aldrich and used as received, *n*-BuLi (*n*-butyl lithium, Chemetall, Germany, 15% solution in *n*-hexane) was further diluted to 0.46 M solution. Isoprene (Aldrich, USA) was purified by distilling over *n*-BuLi after drying over calcium hydride.

Analysis

Fourier transform infra-red (*FT*i.r. analysis was carried out using Perkin-Elmer 16PC *FT*i.r. instrument. Ultraviolet (u.v.) analysis was performed in a Hewlet-Packard Model 5911-Diode array u.v. Spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were recorded using Bruker AC-200 Spectrometer using TMS as the internal standard. The molecular weight distribution of polymeric HALS was determined by using a Waters GPC-II equipped with a refractive index detector. The measurements were carried out using Waters μ-styragel columns (10^5, 10^4, 10^3, 500 and 100 Å) at ambient temperature (27°C) and THF as eluent at a flow rate of 1.0 ml min^{-1}. Monodisperse PS was used to calibrate the columns. The number average molecular weight ($\bar{M}_n$) was determined using a Knauer Vapor Phase Osmometer in THF at 32°C.

Synthesis of HALS

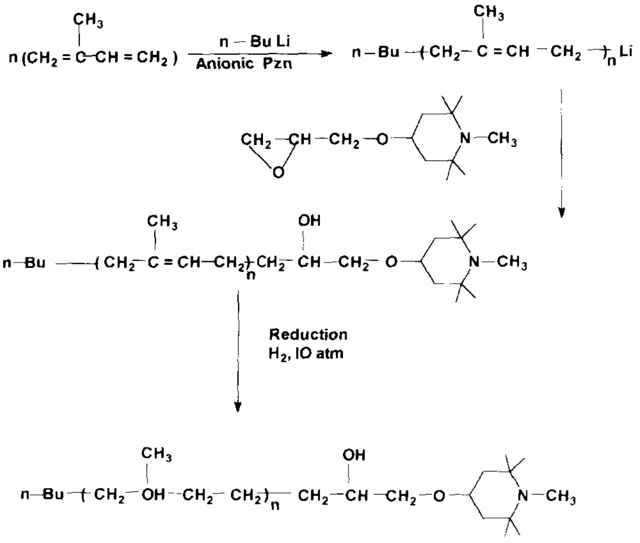
Synthesis of triacetoneamine. Triacetoneamine (2,2,6,6-tetramethyl-4-piperidone) (**1**) was synthesized from the condensation of acetone with ammonia in the presence of calcium chloride using a literature reported procedure[19]. Yield 65%, mp 34–35°C (lit.[19] mp 35–36°C).

Synthesis of 2,2,6,6-tetramethyl-4-piperidinol (**2**). A mixture of triacetoneamine (**1**) (11.635 g, 0.075 mol), sodium borohydride (1.425 g, 0.0375 mol), and 50 ml of 95% ethanol were magnetically stirred in a 200 ml round bottom flask for 6 h in a cold water bath. After removal of the solvent, water (40 ml) was added to the residue and left to stand for 24 h. The water was then removed on the rotary evaporator, and the residue was extracted with *n*-heptane (bp 98°C) in a Soxhlet extractor for 4 h. The crystals which separated from the concentrated extract (*ca* 65 ml) upon cooling were washed with petroleum ether (bp 30–60° C) and dried. Yield 95%, mp 128–129°C (lit.[20] mp 129°C).

Synthesis of 1,2,2,6,6-pentamethyl-4-piperidinol (**3**). 2,2,6,6-Tetramethyl-4-piperidinol (**2**) (3.55 g, 0.02 mol) and a solution of 37% formalin (3.3 ml) and 1 ml of formic acid was heated for 5 h under a reflux condenser on the water bath. To the reaction mixture 10 M potassium hydroxide was added then the product was extracted with ether (3 × 100 ml) and dried over anhydrous sodium sulfate. After evaporation of the solvent the residue was then sublimed at 0.05 mm, bath temperature 88°C. The white sublimate 3.5 g (yield 92%, mp 72–74°C, lit.[20] mp 73–74°C).

Synthesis of 4(2,3-epoxy propoxy)-1,2,2,6,6-pentamethyl piperidine (**4**). 4.28 g (0.025 mol) of 1,2,2,6,6-pentamethyl-4-piperidinol (**3**) in 15 ml of dry THF was added slowly to the reaction flask containing 2 g (0.033 mol) of NaH in 30 ml of dry THF in nitrogen atmosphere. The mixture was refluxed for 1 h. To the cooled mixture excess epichlorohydrin (6 ml) was added and stirred overnight. The mixture was poured into ice water and extracted with ether, dried over Na_2SO_4 and the product was purified by column chromatography (neutral alumina, chloroform/methanol 95 : 5). Yield 65%, bp 115°C at 1 mm Hg. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ: 2.6, 2.8 (*q*, *t*, 2H, epoxy CH_2), 3.1–3.2 (*m*, 1H, epoxy CH), 3.4, 3.55 (two *dd*, 2H, –O–CH–CH<), 3.8–4.0 (*m*, 1H, hindered piperidine ring, C_4, –CH<), 1.4, 1.8 (*t*, *dd*, 4H, C_3, $-CH_2-$), 1.05, 1.2 (two *s*, 12H, CH_3 groups) and 2.25 (*s*, 3H, $>N-CH_3$). Elemental analysis: calculated C = 68.7%; H = 11.0%; N = 6.16%; found C = 68.99%; H = 10.7%; N = 6.26%.

*Synthesis of HALS end functionalized poly(ethylene-*alt*-propene) copolymer.* Alternating E–P copolymer with HALS functionality at the chain-end was synthesized by terminating the living anionic polymerization of isoprene with 4(2,3-epoxy propoxy)-1,2,2,6,6- pentamethyl-piperidine (**4**) followed by hydrogenation of the resulting polymer using a Ziegler type catalyst (*Scheme 1*).



Scheme 1 Synthetic route for obtaining HALS end functionalized poly(ethylene-*alt*-propene) copolymer

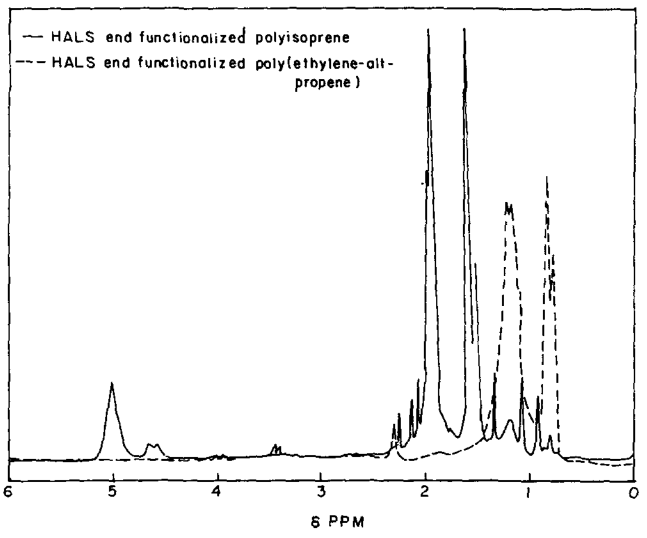


Figure 1 ^{1}H n.m.r. spectra of HALS end functionalized polyisoprene and poly(ethylene-*alt*-propene) copolymer

Synthesis of polyisoprene with HALS functionality by anionic polymerization. To a single necked 250 ml round-bottomed flask containing a Teflon coated magnetic stirring bar and fitted with a septum and nitrogen inlet containing adapter, was added 150 ml of dry toluene (distilled over styryl lithium). This was followed by the addition of isoprene 10.2 g (15 ml). Then 6.2 ml *n*-BuLi (1.13 M) was added to initiate polymerization. A yellow colour indicative of the living species was obtained. After 18 h, a solution of 4(2,3-epoxy propoxy)-1,2,2,6,6-pentamethyl piperidine (1.3 g) in 20 ml of dry toluene was added to the living poly(isoprenylithium) solution using a cannula. The reaction was further stirred for another 18 h and 1 ml of acidic methanol was added to the reaction mixture. Then the polymer solution was washed with distilled water and dried over sodium sulfate and the solvent was removed by rotavapor. The polymer was purified by repeated precipitation in methanol in order to remove unreacted HALS from the polymer. The ^{1}H n.m.r. spectra of HALS end functionalized poly-isoprene and poly(ethylene-*alt*-propene) are shown in *Figure 1*. The conversion to polymer was 99%. $\bar{M}_n$ (v.p.o., vapour pressure osmometer) = 1480, $\bar{M}_n$(calcd) = 1500, $\bar{M}_n$ (gel permeation chromatography, g.p.c.) = 2380, $\bar{M}_w$ (g.p.c.) = 3140, $\bar{M}_w/\bar{M}_n = 1.3$.

Functionality determination[21,22]

A solution of polymer (0.1% by weight in 80/20 mixture of toluene/methanol) was titrated against 0.003 N *p*-toluenesulfonic acid using a pH meter. A plot of pH vs titre value of acid was made. The end point was determined from the curve. Equivalent functionality and functionality were determined from the following equations (1) and (2).

$$\text{Equivalent functionality} = \frac{\text{volume of acid} \times \text{strength of acid}}{\text{weight of polymer} \times 10} \qquad (1)$$

$$\text{Functionality} = \frac{\text{Equivalent functionality} \times \bar{M}_n(\text{v.p.o.})}{100}$$

$$= \frac{0.0665 \times 1480}{100} = 0.985 \qquad (2)$$

Table 1 Concentration of HALS in *i*-PP and heterophasic E–P copolymer samples

Stabilizer	Stabilizer amount (g 1.5 g^{-1} polymer)	Concentration of stabilizer units in the mixture (mol kg^{-1} polymer)
Tinuvin 770	0.003	0.0083
	0.0075	0.0208
	0.015	0.0416
Chimassorb 944	0.00374	0.0083
	0.00936	0.0208
	0.01872	0.0416
Polymeric HALS	0.0185	0.0083
	0.0465	0.0208
	0.093	0.0416

Hydrogenation of polyisoprene having HALS functionality

Into a 300 ml capacity Paar reactor, was added 9 g polymer in 120 ml of dry cyclohexane using a cannula under nitrogen atmosphere. This was followed by the addition of triethylaluminum (1.97×10^{-3} mol, 9.63 ml of 25% solution of triethylaluminum in dry cyclohexane). The reaction temperature was raised to 60°C. Under hydrogen atmosphere, Ni(Oct)$_2$, (2.96×10^{-4} mol, 13.5 ml of 8% solution in dry cyclohexane, [Al]/[Ni] = 6.67) was added to start hydrogenation. The hydrogen pressure was increased to 10 kg cm^{-2}. After the hydrogen consumption had ceased (about 2 h), the hydrogen pressure was released and the polymer was precipitated with 5% acidic methanol. The hydrogenated polymer was purified by repeated (four times) reprecipitation using methanol as non-solvent. The absence of vinyl proton peak in ^{1}H-n.m.r. confirmed 100% hydrogenation.

Mixing of stabilizers

HALS, i.e., low molecular weight HALS (Tinuvin 770), high molecular weight HALS (Chimassorb 944) and polymeric HALS were mixed with additive free isotactic polypropylene and heterophasic E–P copolymer by melt blending. Different concentrations (*Table 1*) of the stabilizers were melt blended with the additive free polymer powder in a Minimax mixer (CSI, CS-183 MMX) at 170°C for 5 min then extruded. Thin films (thickness ~ 80 μm) of the stabilized i-PP and heterophasic E–P copolymer samples were prepared as described elsewhere[18]. All the samples were photo-irradiated in an irradiation chamber, SEPAP 12/24, as described earlier[18].

Diffusion measurement

Diffusion measurements were carried out by using the system described by Roe *et al.*[23]. A stack of 25 additive free (thickness about 60 μm) films of i-PP and E–P copolymer were prepared by heating the stack in hydraulic press at 130°C for 2 min and then this was pressed in a cold condition for 3 min. The stack thus obtained was compact and transparent, without any air bubbles. The additive source were prepared by mixing the stabilizers (Tinuvin 770 and polymeric HALS) by melt blending in a Minimax mixer, and made a thick sheet of thickness about 0.2 mm. For diffusion studies, the film stack was placed with additive source then pressed between two steel plates by the use of a clamp.

Then the whole setup was kept in an oven for a defined time at a particular temperature. Additive concentration in the polymer films was determined by u.v. spectroscopy. During photo-irradiation/melt-blending or mixing, the additive is partly consumed/lost. Therefore its actual concentration after irradiation/mixing is determined definitively by u.v. spectroscopy. Calibration was made in *n*-heptane solution. The film next to the additive source was not included in the calculation, to avoid any errors caused by additive adsorption.

The diffusion coefficient was determined using the method given by Moisan[24]. This method treats the process as a one-dimentional diffusion problem. It is assumed that at the start of the experiment ($t = 0$) the additive concentration is $c = 0$ at any distance from the additive source ($x > 0$) and that during the experiment ($t > 0$) concentration of the additive in the additive source ($x \leq 0$) remains constant and equals the solubility ($c = S$). Concentration at position x and time t is described by equation (3).

$$c(x,t) = S[1 - \mathrm{erf}(x/K)] \qquad (3)$$

where K is determined by the time, and the diffusion coefficient D and can be given by equation (4),

$$K = 2\sqrt{Dt} \qquad (4)$$

For calculation of the parameters D and S from the concentration profile an interactive least-square curve fitting program was used. The solubility is given directly by this calculation.

RESULTS AND DISCUSSION

*Performance evaluation of HALS end functionalized poly(ethylene-*alt*-propene) copolymer (polymeric HALS)*

Diffusion of HALS. *Figure 2* exemplifies the concentration profiles of Tinuvin 770 and P-HALS in a film stack of i-PP and E–P copolymer after 48 h at 60°C and 100 h at 80°C, respectively. As can be seen, there is a very good fit between the experimental data and the theoretical curve obtained from equation (3). Solubilities (S) of the additives in i-PP and E–P copolymer sample were determined from a concentration profile plot by using the equation $C(X,t) = S[1 - \mathrm{erf}(X/K)]$ and a least-square curve fitting programme. Extrapolation of this curve to zero distance ($X = 0$) gives S. Diffusion coefficients (D) calculated from the plots are shown in *Table 2*. The results show that polymeric HALS has a diffusion coefficient of $5.4 \times 10^{-10}\,\mathrm{cm^2\,s^{-1}}$ and 0.03 wt% solubility, which is about five times lower than Tinuvin 770. This is due to the higher molecular weight of the former, which restricts additive diffusion and solubility. Malik *et al.*[25] reported that Chimassorb 944 showed no measurable diffusion even after 10 months (7300 h) at room temperature. The piperidine skeleton in Chimassorb 944 is bound in position 4 through a nitrogen atom. They suggested that the attachment of piperidine through nitrogen gives unmeasurable penetration of this additive into the polymer stack. It was further suggested that the diffusion coefficient (D) and solubility (S) of an additive is reduced with an increase of molecular weight and depends on the difference between the polarity of the polymer molecule and that of the additive.

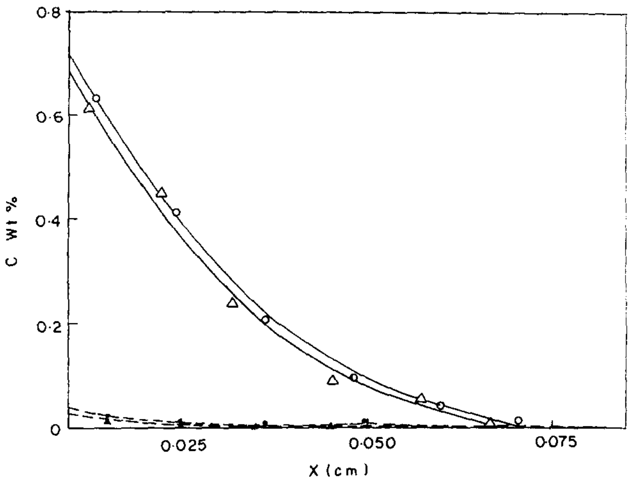


Figure 2 Concentration distribution of Tinuvin 770 in i-PP(△), E–P copolymer(○) and polymeric HALS in i-PP (▲) and E–P copolymer (●) films

Table 2 Diffusion coefficient (D) and solubility (S) of Tinuvin 770 and polymeric HALS in i-PP and E–P copolymer samples

	Tinuvin 770[a]		P-HALS[b]	
Polymer	$D \times 10^{10}$ ($\mathrm{cm^2\,s^{-1}}$)	S (wt%)	$D \times 10^{10}$ ($\mathrm{cm^2\,s^{-1}}$)	S (wt%)
i-PP	24	0.9	5.2	0.03
E–P copolymer	26	1.0	5.4	0.03

[a] Diffusion time 48 h; temperature 60°C
[b] Diffusion time 100 h; temperature 80°C

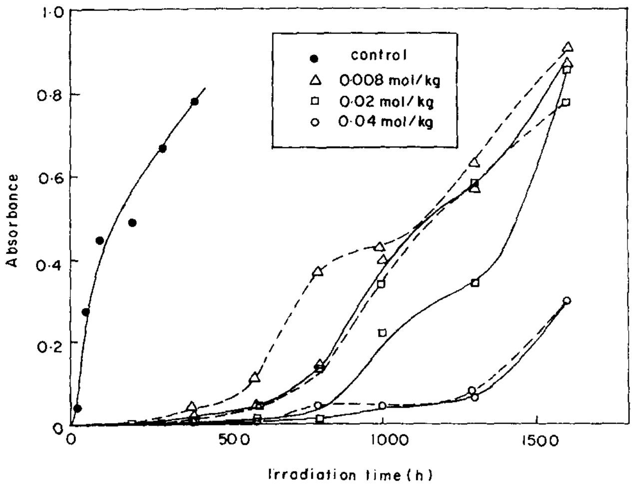


Figure 3 Plot of carbonyl absorbance vs irradiation time in i-PP films (——) and E–P copolymer (– – –) films stabilized with Tinuvin 770 at different concentrations

Photostabilizing efficiency of polymeric HALS. Photostabilizing efficiencies of polymeric HALS in i-PP and E–P copolymer were studied in three different concentrations, and compared with commercial HALS (i.e. Tinuvin 770 and Chimassorb 944), by measuring the carbonyl absorbance at $1720\,\mathrm{cm^{-1}}$. Plots of carbonyl absorbance vs irradiation time in i-PP and E–P copolymer samples stabilized with Tinuvin 770 at three different concentrations are shown in *Figure 3*. At lower concentration level ($0.008\,\mathrm{mol\,kg^{-1}}$), the carbonyl group

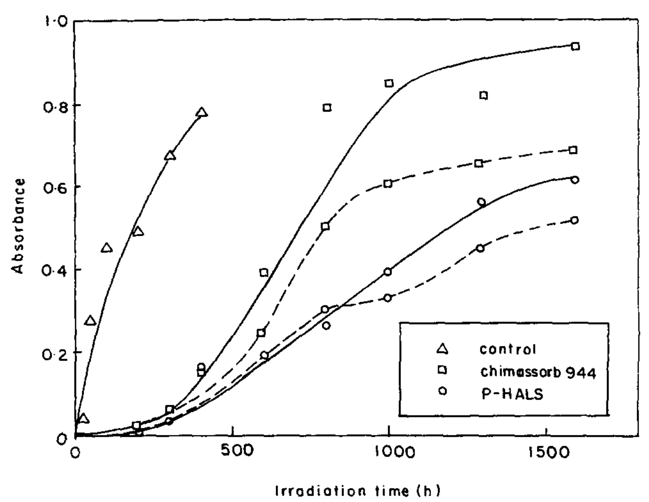


Figure 4 Plot of carbonyl absorbance vs irradiation time in i-PP films (——) and E–P copolymer (– – –) films at stabilizer unit concentration 0.008 mol kg^{-1}

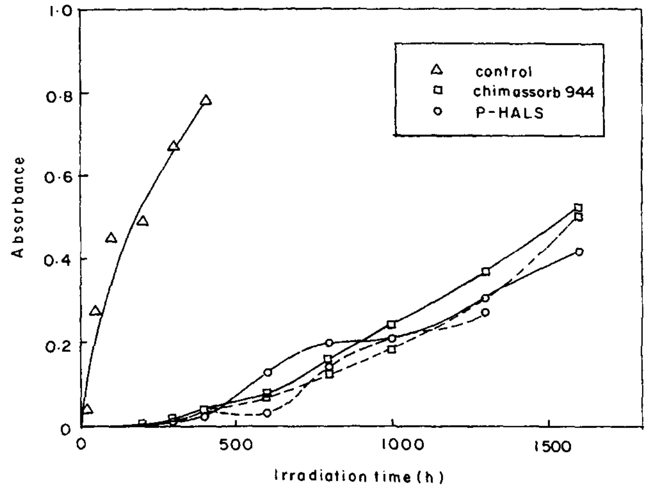


Figure 5 Plot of carbonyl absorbance vs irradiation time in i-PP (——) and E–P copolymer (– – –) films at stabilizer unit concentration 0.02 mol kg^{-1}

formation is more in the case of samples stabilized with Tinuvin 770 compared to polymeric HALS stabilized samples in longer irradiation time. In *Figure 4*, the rate of carbonyl absorbance was plotted against irradiation time at HALS stabilizer (Polymeric HALS and Chimassorb 944) unit concentration of 0.008 mol kg^{-1}. Unprotected i-PP and E–P copolymer films showed a rapid increase in the carbonyl absorbance after only 25 h of irradiation. In the case of stabilized polymer films containing 0.008 mol kg^{-1} of stabilizer, the carbonyl absorbance was observed only after an induction period of 300 h. The increase in carbonyl absorbance is almost linear in polymeric HALS stabilized samples, whereas in the case of Tinuvin 770 and Chimassorb 944 stabilized samples, the increase in carbonyl absorbance is nearly exponential (*Figures 3* and *4*), and reaches an asymptotic value around 1000 h irradiation. This can be understood based on the fact that low molecular weight Tinuvin 770 undergoes migration and surface evaporation at a longer irradiation time, whereas Chimassorb 944 shows negligible diffusion and solubility in polyolefins due to its high molecular weight and the polar nature of the backbone polymer. On the contrary polymeric HALS has significant diffusion compared to Chimassorb 944, and thus remains in the polymer for long enough time to be able to exert its stabilizer behaviour.

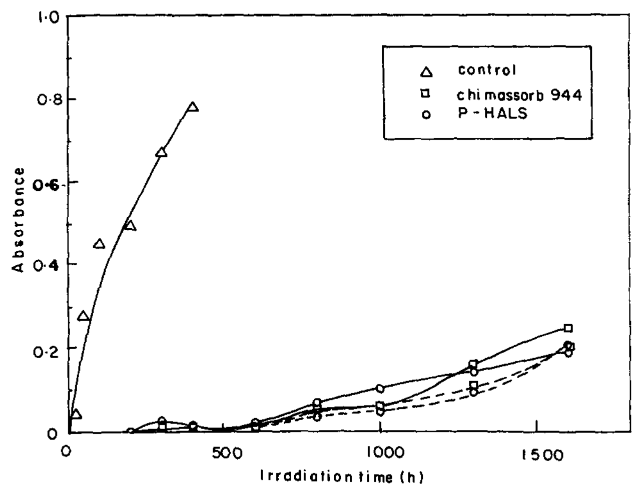


Figure 6 Plot of carbonyl absorbance vs irradiation time in i-PP (——) and E–P copolymer (– – –) films at stabilizer unit concentration 0.04 mol kg^{-1}

Figure 5 shows the carbonyl absorbance with irradiation time in i-PP and E–P copolymer films at higher stabilizer unit concentration of 0.02 mol kg^{-1}. The carbonyl group formation was observed after an induction period of 400 h in all stabilized polymer films. The carbonyl absorbance is almost similar in the case of both polymeric HALS and Chimassorb 944. At even higher concentration levels (stabilizer unit concentration 0.04 mol kg^{-1}), after 500 h only the carbonyl group formation was observed. However there is no significant difference in the photostabilizing efficiency of either polymeric HALS or Chimassorb 944 (*Figure 6*).

The difference in effectiveness between polymeric HALS and Chimassorb 944, as a function of stabilizer concentration, is indicative of the important role played by the ability of polymeric stabilizer to diffuse into the matrix. At a stabilizer concentration of 0.008 mol kg^{-1} of polymer, polymeric HALS shows a superior stabilizer performance compared to Chimassorb 944. Polymeric HALS, with an alternating E–P copolymer in the chain has a higher degree of compatibility with PP and E–P copolymers resulting in higher solubility and greater diffusivity. This enables the polymeric HALS to distribute itself evenly throughout the matrix. On the contrary, Chimassorb 944 has a poor compatibility with the matrix limiting its diffusivity. This leads to a concentration gradient of the stabilizer in the bulk of the polymer matrix. As a consequence its performance is inferior.

At high levels of HALS concentration, the stabilizer will distribute itself throughout the polymer matrix, and factors such as molecular weight, polarity and diffusion are likely to play a lesser role. Therefore polymeric HALS, Tinuvin 770 and Chimassorb 944 show similar effects on photostabilization.

CONCLUSIONS

HALS end functionalized poly(ethylene-*alt*-propene) copolymer (polymeric HALS) show a significantly improved photostabilizing efficiency compared to commercial high molecular weight HALS, Chimassorb 944. At a longer irradiation time, it shows a better performance compared to Tinuvin 770 (low molecular weight) at concentrations typically used for practical applications.

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