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A Novel Photoadditive for Polyolefin Photostabilization: Hindered Amine Light Stabilizer

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SUMMARY: Hindered-amine light stabilizers were surface anchored to polyethylene and polypropylene thin films by: i) direct photo-grafting of 1,2,2,6,6-pentamethyl piperidinyl-4-acrylate onto the surface and ii) by reacting of 1,2,2,6,6-pentamethyl-4-piperidinol with succinic anhydride functionalized polyolefin surface. The samples were exposed to UV irradiation in air and the oxidative-degradation of the polymers was studied with FT-IR spectroscopy. The photo-stability of surface anchored Hindered-amine stabilizers (HAS) was compared with films stabilized with commercial HAS by melt blending. The results of the study evince superiority of surface anchored HAS over that of melt blended polyolefins.

INTRODUCTION

Most of the polymers are susceptible to degradation by oxygen under an additional influence of UV light or heat[1]. This consequent oxidative-degradation can be partially prevented by introducing stabilizers into the polymeric system. It was presumed that the stability of polymer against thermal and photo-oxidative degradation can be achieved by melt blending the polymer with appropriate stabilizers. Compatible and mobile stabilizers usually give the best stabilization, but those of low molecular weight are easily lost from the polymer through evaporation, migration and extraction. Efforts have been made to overcome this loss by incorporation of polymeric stabilizers. However, the low mobility and poor compatibility of polymeric stabilizers decrease their efficiency[2]. Since the degradation of a polymer commences from the surface and slowly proceeds into the bulk of the polymeric substrate[3,4], the stabilizers are therefore expected to be most potent if they are concentrated at the surface. But, when situated at the surface, they are easily lost. To prevent this loss they should be anchored chemically to the polymer surface.

Photochemical grafting has been reported as an efficient and emerging method of attaching a stabilizer to the surface of the polymer in a permanent manner[5,6]. This technique is classified into i) the monomeric stabilizer is directly grafted onto the surface of the substrate and ii) the monomer with a reactive group is first grafted and the resultant reactive group is then used as a site for further functionalization. In particular, this approach has been used to control the leaching of stabilizer

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from the polymers. A high level of grafting of a hindered-amine light stabilizers (HAS)-type of stabilizer onto polyolefins surface using reactive process techniques has already been reported[7].

The photostabilizers used in our study have been synthesized in our laboratory. The synthesis of 1,2,2,6,6-pentamethyl piperidinyl-4-acrylate (PMPA) is described elsewhere[8]. We have also developed a simple photochemical technique for surface functionalization of polyolefins whereby, the succinic anhydride group is introduced onto the polymer surface and 1,2,2,6,6-pentamethyl-4-piperidinol (PMPO) is thus anchored to the surface of the polyolefins through the succinic anhydride moiety (Scheme 1). This technique is efficient and provides high degree of chemo- and topological selectivity. The objective of the present study was, therefore to study the UV stability of such surface-modified polymers.

EXPERIMENTAL PART

Materials

Commercial samples of isotactic polypropylene (i-PP, Koylene S30330), low density polyethylene (ldPE, Indothene 16MA400) were obtained from Indian Petrochemicals Corp. Baroda, India. 2,2, 6,6-tetramethyl-4-piperidinol (TMPO), was obtained from M/s Aldrich Chemicals, USA and used as received. Maleic anhydride (E. Merck, India) was recrystalized from chloroform and benzophenone (Aldrich) was recrystalized from ethanol. All the solvents obtained from S. D. Fine Chemicals Ltd., Baroda, India, were of A.R. grade. 0.2 wt% of 2,2,6,6-tetrametyl-4-piperidinol was melt blended with *i*-PP and ldPE for the study. The photo-irradiation of the polyolefin thin films (~100μm thickness) was carried out in an accelerated weathering chamber SEPAP 12/24 at 60° C. The chamber consists of (4 x 400W) UV lamps supplying radiation longer than 300 nm. The details of the equipment are described elsewhere[8].

a) Preparation of Polyolefin Surface Bearing Succinic Anhydride Groups

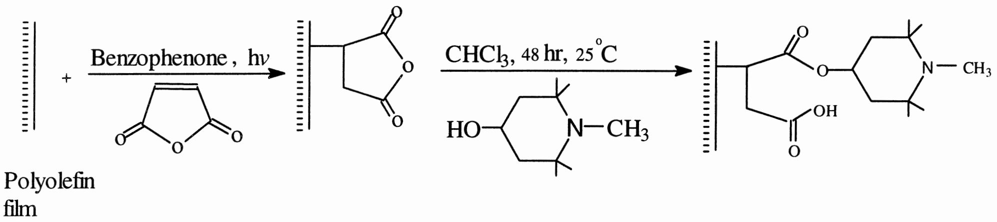
The ldPE and i-PP films were taken in a photo-reactor (pyrex glass) with 25 ml dry acetone, (2.0 M) pure maleic anhydride, (0.29 M) benzophenone at 65°C reaction temperature under UV irradiation ($\lambda \geq 290$ nm) for 2 hrs using 400 W medium pressure mercury vapor lamp. The reaction was carried out under nitrogen atmosphere. After the completion of reaction, these films were soxhlet extracted at reflux temperature with acetone for 8 hrs in order to remove physically adhered / homopolymerized maleic anhydride. The films were dried at room temperature under vacuum till constant weight was obtained.

A control experiment was carried out to prove that the generation of characteristic peak is due to grafting and not due to the photo-degradation caused by the UV irradiation used for the photo-grafting. The same procedure was followed in case of i-PP films also.

b) Preparation of Polyolefin-bound HAS

Surface modified ldPE films (3 x 1 cm^2) bearing succinic anhydride (SA) group was reacted with (0.016M) PMPO in dry chloroform for 48 hrs at room temperature with occasional stirring. FTIR spectroscopy was used to monitor the completion of reaction. The film was soxhlet extracted with chloroform for 5 hrs to remove any unreacted HAS.

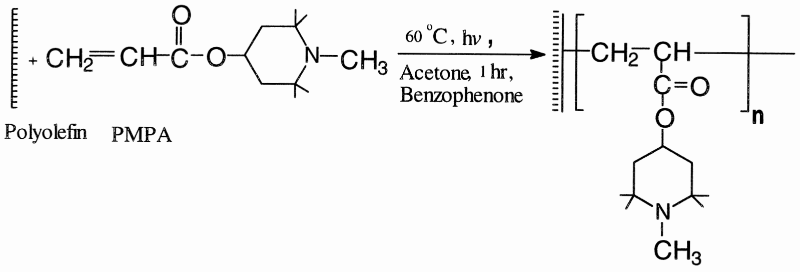
Scheme 1. Synthesis route for obtaining polymer-bound hindered amine light stabilizer.



c) Surface photo-grafting of PMPA onto polyolefin films

1,2,2,6,6-pentamethyl-4-piperidinol (PMPO) was synthesized from 2,2,6,6-tetramethyl-4-piperidinol (TMPO) via reductive-amination[9]. The synthesis of 1,2,2,6,6-pentamethyl piperidinyl-4 -acrylate (PMPA) from PMPO is previously reported by us.[8]

The films of ldPE and i-PP were taken in a specially designed photo-reactor with 42 ml of acetone, 0.4M benzophenone and allowed to stand under nitrogen atmosphere for 1½ h, added 0.27 M PMPA with 7 ml of acetone and thoroughly de-areated with nitrogen for 10 min. The films were UV irradiated for 1 h at 60 ± 2 °C under nitrogen atmosphere and soxhlet extracted in methanol for 6 h, then dried under vacuum at room temperature till constant weight was obtained.



Analysis

Polymers were purified to remove the processing additives / stabilizers and film samples were prepared by melt pressing. The methods of purification and sample preparation (~100 µm thick film) have been described elsewhere[9]. The weatherability of all the samples was carried in an accelerated weathering chamber SEPAP 12/24. FT-IR measurements were carried out with a Perkin-Elmer 16 PC Spectrometer (supplied with ATR accessory). The water contact angle was measured with *RAME'-HART Inc. NRL C.A. GONIOMETER* Model No *100-00*-230.

Analysis of surface modification

Surface modification of polymer can be substantiated from the results of water contact angle, surface concentration of HAS and from the ATR-FTIR spectroscopy data.

a) **Gravimetry:** Gravimetric analysis was used to calculate the amount of HAS onto the polyolefins surface. The moles of HAS present/cm^2 on the surface of the film was calculated from the increase in the weight of the polyolefins film after the HAS incorporation.

b) **Spectroscopy:** ATR-FTIR spectroscopy (Figure 1) was used as a tool to confirm the surface grafting of HAS onto the surface of ldPE and i-PP films.

Moreover, the decrease in water contact angle of ldPE from 96° to 78° for ldPE-g-PMPA / 72° for ldPE-g-SA-PMPO and that of i-PP from 98° to 81° for i-PP-g-PMPA/ 70° for i-PP-g-SA-PMPO reaffirms the fact that grafting of HAS have taken place onto the surface of the polyolefin films.

RESULTS AND DISCUSSION

The polyolefin surface modification was characterized using ATR-FTIR spectroscopy. In the IR overlay spectra (Figure 1), the unmodified ldPE film is denoted by **A**, where as a sharp peak at 1735 cm^{-1} in film **B** is due to the carbonyl group (ester) of the grafted PMPA. The characteristic peaks at 1868 and 1789 cm^{-1} in the film **C** are due to the grafting of succinic anhydride. The complete disappearance of peaks at 1868 and 1789 cm^{-1} in **D** confirms that the succinic anhydride groups present on the films were completely reacted with PMPO. The presence of some carboxylic acid and carboxylate anion on the surface and the appearance of later as bands at 1500 cm^{-1} and 1600 cm^{-1} in the FT-IR spectrum is probably due to the ring opening of succinic anhydride molecules grafted on the surface. (Scheme 1)

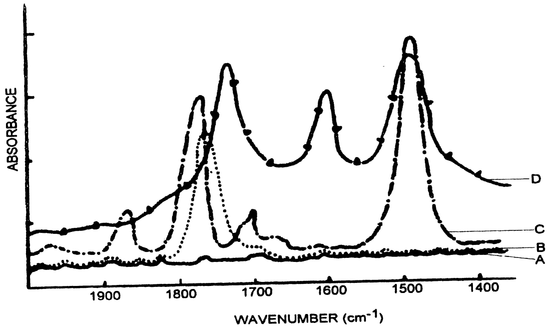


Fig. 1 Confirmation of grafting onto the surface of ldPE film, here: **A** is neat ldPE film, **B** represents ldPE-g-PMPA, **C** indicates ldPE-g-Succinic anhydride and **D** indicates ldPE-g-SA-PMPO.

The concentration of different HAS onto the surface of ldPE and *i*-PP films determined by gravimetric analysis are given in (Table 1). It is clear from the table that the concentration of HAS on the polymer surface is significantly high when PMPA is grafted on the polyolefins.

Table 1. Concentration of HAS on the polyolefin film surface.

Sample	Conc. in μmol/cm^2
ldPE-g-PMPA	1.11
ldPE-g-SA-PMPO	0.98
i-PP-g-PMPA	0.74
i-PP-g-SA-PMPO	0.66

Photo-stabilization efficiency of surface anchored HAS in polyolefins

Since it is almost impossible to control degree of grafting, the studies are carried out with closest possible concentration of stabilizer. The photo-stabilization efficiencies of PMPA, SA-PMPO in i-PP and ldPE were studied from carbonyl group formation at 1740 cm^{-1} (Figure 2). The rate of carbonyl index (C.I.) formation was plotted against irradiation time (Figure 3) and their performance was compared with those prepared by melt blending. The Figure 3 shows that the unprotected polyethylene developed a drastic increase in carbonyl absorbance just within the initial hours of irradiation. The ldPE-g-PMPA and ldPE-g-SA-PMPO films showed a remarkable photo-stability compared to the polymer stabilized with melt blended TMPO. Since the stabilizer is not homogeneously dispersed into the system in case of melt blending, it offers a poor stability to the substrate as compared to the surface anchored HAS.

Moreover, it is also reported[10] that when the NH group of 2,2,6,6-tetramethyl piperidine is not fully hindered, its photostabilizing efficiency is considerably reduced. As the nitroxyl radicals corresponding to such amines are not stable, this result was taken as a confirmation for the prime role of nitroxyl radicals. Ranby et al.[11] have demonstrated an effective stability of i-PP against UV-initiated degradation by grafting the i-PP surface with glycidyl methacrylate followed by chemical attachment of HAS to the oxirane group.

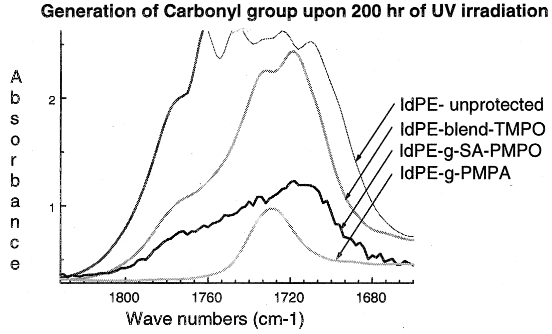
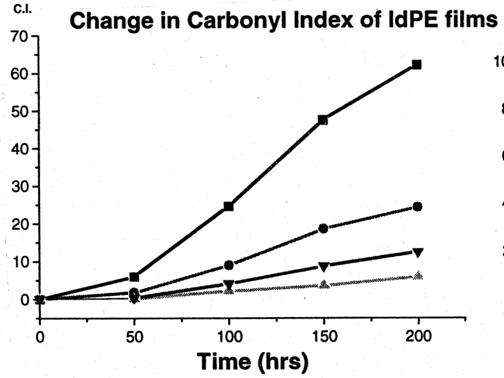


Fig. 2 Generation of carbonyl peak in ldPE films with increasing irradiation times.



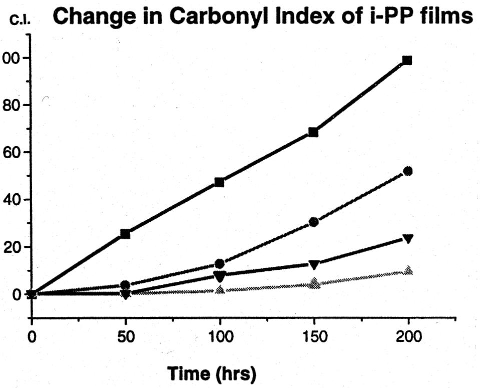


Fig. 3 Photostabilizing efficiency of surface-grafted HAS in ldPE films.

Fig. 4 Photostabilizing efficiency of surface - grafted HAS in i-PP films.

In both the figures (-▲-) indicates polymer-g-PMPA, (-▼-) indicates polymer-g-SA-PMPO, (-●-) indicates polymer-blend TMPO and (-■-) denotes the unprotected polymer film .The carbonyl index (C.I) was measured using the following equation.[12]

$$\text{Carbonyl Index (C.I.)} = \frac{\text{Absorbance at 1740 wave numbers}}{\text{Absorbance at 2820 wave numbers}}$$

Where, the peak at 1740 cm^{-1} in the FT-IR spectrum was found to change and the peak at 2820 cm^{-1} remain unchanged throughout the study.

It can be clearly noticed from Fig. 2, 3 and 4 that the photo-stability offered by PMPA is maximum. It is assumed that in case of polymer grafted with SA-PMPO the free carbonyl group of (- COOH) acts as a chromophore and sensitizes the degradation thus decreasing the efficiency of the stabilizer which is not so in case of PMPA. A similar trend was observed when the change in the hydroxyl peak intensity in the FT- IR spectrum was measured with the irradiation time. The fact is well established that the degradation of a polymer commences from its surface and proceeds to the bulk of the substrate. When the availability of the photo-stabilizer is extended to the degradation site, the rate of degradation is minimized. Being a monomeric HAS, it can directly be attached to the surface of the polymer without any pre-grafting by a functional monomer. This is the reason why PMPA outperforms all other photo-stabilizers.

CONCLUSION

The hindered amine stabilizer end functionalized polyolefins shows significantly improved photo-stabilizing efficiency as compared to the melt blended commercial HAS. However, when the HAS is directly anchored to the polymer surface, it demonstrates the best stabilizing property. Moreover, when directly anchored to the polymer surface, the concentration of HAS is higher than that obtained by secondary functionalization.

ACKNOWLEDGEMENT

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