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### Synthesis, Characterization, and Performance Evaluation of Polymeric HALS in Ethylene-Propylene-Diene Terpolymer (EPDM)

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# Synthesis, Characterization, and Performance Evaluation of Polymeric HALS in Ethylene-Propylene-Diene Terpolymer (EPDM)

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*A polymeric hindered amine light stabilizer (HALS), wherein the hindered amine functionality was attached to the maleic anhydride graft ethylene-propylene-diene terpolymer (EPDM) was synthesized. This involves photoinduced grafting of maleic anhydride groups on unsaturated sites of EPDM, followed by incorporation of amino terminated HALS. The grafting and functionalization reactions were characterized by FTIR and <sup>13</sup>C NMR spectroscopy. The surface changes upon degradation are studied by SEM. The photostabilizing efficiency of this polymeric HALS was studied and compared with conventional HALS under accelerated weathering conditions. The HALS grafted EPDM showed significantly improved photostabilizing efficiency.*

**Keywords** EPDM, light induced grafting, polymeric HALS, photostabilization

## Introduction

Protection of a polymer against thermal and photooxidative degradation is mostly achieved by melt blending the polymer with the appropriate stabilizer (1–3), which ensures that the desirable polymer properties are maintained throughout the entire service life of the polymer. For longer stability of polymers, the permanence of a stabilizer in the polymer matrix with an active form is important. The effectiveness of long time stabilization depends not only on the chemical nature of the stabilization, but also on its physical loss. The rate of additive loss depends on the compatibility of the additive

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with the polymer and is controlled by its volatility, extractability, solubility and diffusion coefficient (4–6). To improve all these properties, the additive should be bound to the polymeric substrate. Hindered amine light stabilizers are one of the most effective photostabilizers and have gained prominence as effective light stabilizers for a variety of polymers (7, 8). However, the conventional low molecular weight stabilizers vaporize easily, have poor extraction resistance, and thus decrease the service life of polymer during its end use (9) therefore; there has been trend towards the use of polymeric HALS (10–14). Ethylene-propylene-diene terpolymer (EPDM) is the fastest growing elastomer in its own class and is widely used in various outdoor applications like coatings, sealants, automotive, etc. (15–17). Since photostability of EPDM elastomer is intrinsically low (18), such material, upon natural or accelerated weathering, results in discoloration, surface cracking, stiffening, crosslinking, and a decrease in the mechanical properties (19). Hence, their stabilization by the appropriate stabilizer bears prime importance. To incorporate HALS, EPDM is necessary to functionalize either by anhydride or epoxide moieties. During the last few years, the possibility of functionalizing EPDM elastomer through the incorporation of anhydride (20, 21) has been investigated. Most of these were accomplished thermally (22, 23), and such high temperature grafting leads to crosslinking, lowering in processibility, and collapse in the molecular weight of the polymer. To overcome this problem and to introduce anhydride moiety on EPDM, we decided to investigate for the first time, the photochemical grafting of MA onto EPDM, performed at a lower temperature in the presence of a suitable photo initiator. In the present article, we report a polymeric HALS based on photoinduced grafting of maleic anhydride onto EPDM, followed by the incorporation of HALS. We have also evaluated the photostabilizing efficiency of given polymeric HALS on EPDM under accelerated weathering conditions.

## Experimental

### Materials

The ethylene-propylene-diene terpolymer (EPDM), with an ethylidene norbornene content of 5%, was kindly supplied by M/s. Sediver, France. EPDM rubbers were purified by dissolving in a toluene solution and precipitating from acetone to remove any stabilizer trace. Maleic anhydride, benzophenone (M/s. S.D Fine Chemicals, India) were recrystallized from chloroform and ethanol, respectively before use. The solvents are purified or dried according to the literature (24). 4-Amino-2,2,6,6-tetramethyl piperidine was obtained from M/s Aldrich Chemicals, USA and used as received. The conventional hindered amine light stabilizer, namely bis (2,2,6,6-tetramethyl-4-piperidiny)l sebacate (Tinuvin-770) was obtained from M/s Ciba-Geigy.

### Photoirradiation

The photo-irradiation experiment was carried out in a accelerated weathering chamber SEPAP 12/24 (M/s Material Physico Chimique, Neuilly/Marne, France) at 60°C. The chamber consists of (4 × 400W) medium pressure mercury vapor lamps supplying radiation ( $\lambda \geq 290$  nm). The instrument is described elsewhere (25).

### **Scanning Electron Microscopy**

Surface changes of irradiated samples were examined by SEM. The stained samples were dried under vacuum for 24 h at 50°C and these gold-coated samples were examined under an electron microscope (Leica Cambridge Stereoscan 440 model).

### **Instrumentation**

FTIR spectra of EPDM, MA-g-EPDM and EPDM with a polymeric light stabilizer were carried out by a Perkin-Elmer 16 PC FT-IR spectrophotometer, equipped with multiple reflectance accessories. Nuclear magnetic resonance (<sup>13</sup>C-NMR) spectra were recorded using a Bruker AC-300 spectrometer using CDCl<sub>3</sub> as a solvent and TMS as an internal standard. For the light induced grafting experiments, a Phillips 150 W, high-pressure mercury lamp was used for photoirradiation, equipped with filters at wavelength longer than 350 nm.

### **Photografting of Maleic Anhydride on EPDM**

The grafting reaction of maleic anhydride onto EPDM was carried out by dissolving 500 mg (0.02 mol) of purified EPDM into 10 mL of toluene in the presence of 200 mg (0.002 mol) of maleic anhydride, by irradiating this mixture with light of wavelength longer than 350 nm, using a pyrex cell of 10 mm thickness, and in the presence of 80 mg (0.0004 mol) benzophenone as photoinitiator, under continuous argon flow for 24 h. The functionalized EPDM prepared above was purified by precipitation in chilled methanol and vacuum dried overnight. The quantitative determination of grafted anhydride groups was performed by infrared spectroscopy, using films deposited onto KBr pellet as previously reported (22) (Scheme 1).

### **Synthesis of Polymeric HALS**

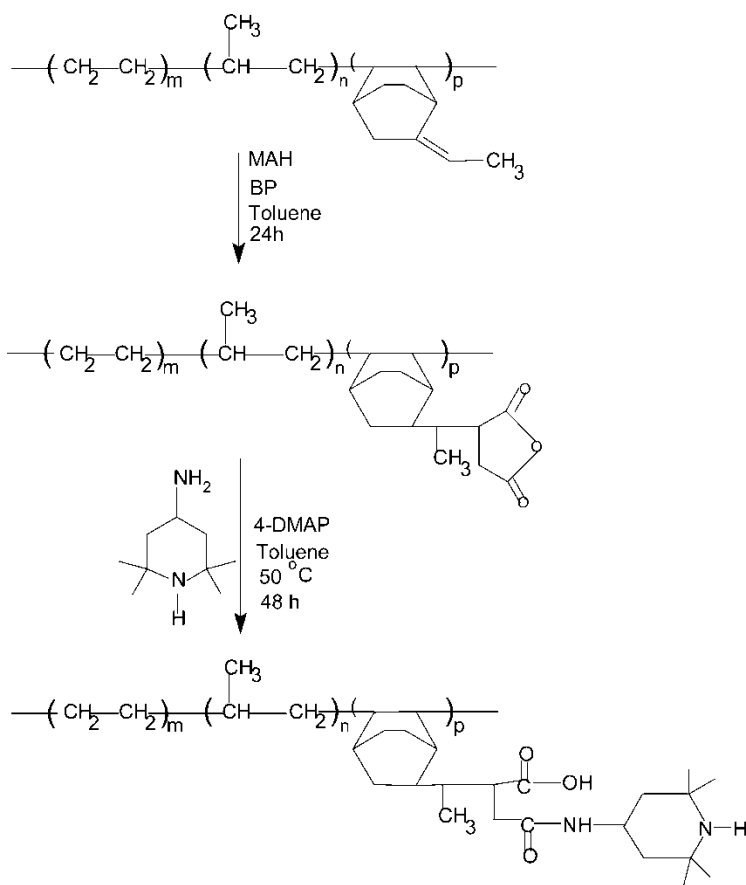
In a 250 mL round bottom flask 75 mL of toluene was introduced, to which 1 gm (0.003 mol) MA-g-EPDM, 4.6 mL (0.02 mol) of 4-amono-2,2,6,6-tetramethyl piperidine and a catalytic amount of 4-DMAP were added. To this reaction mixture, 200 μL of acetic acid was added dropwise for 5 min. The reaction was carried for 48 h at 50°C under inert atmosphere. The reaction mixture was precipitated from methanol, filtered, and dried under reduced pressure for 24 h.

### **Grafting Determination**

The grafting percentage of maleic anhydride and HALS was determined by the Soxhlet extraction method. The MA-g-EPDM and HALS-g-EPDM films were Soxhlet-extracted in methanol for 10 h and then dried in vacuo. The weight percentage of the grafting was calculated as follows:

$$\text{Grafting (wt\%)} = (W_1 - W_0) \times 100/W_0$$

Where,  $W_1$  is the net weight of the grafted films and  $W_0$  is the initial weight of the films.



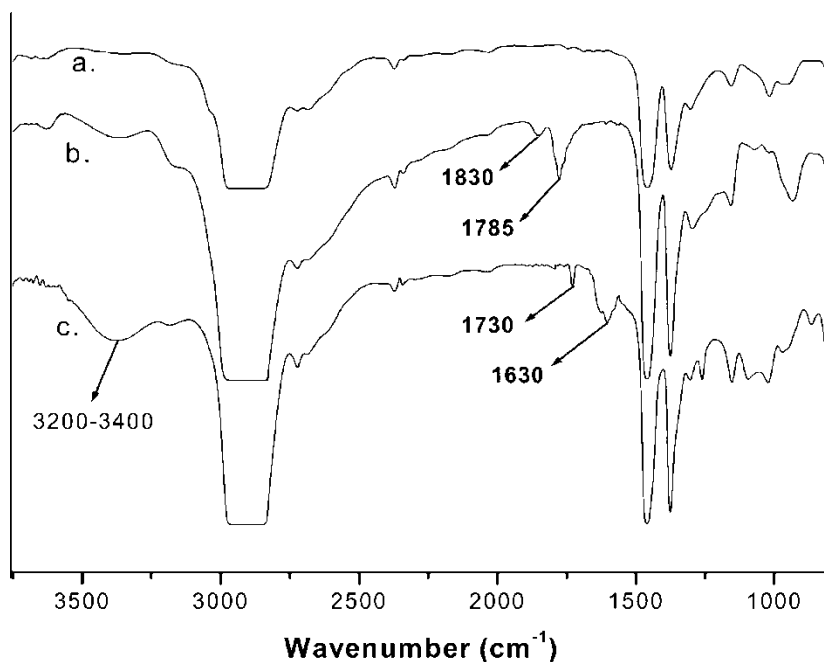
**Scheme 1.** Functionalization of EPDM by maleic anhydride and HALS.

### Measurement of Photostabilizing Efficiency

The photostabilizing efficiency of polymeric HALS on EPDM was monitored by the measurement of the carbonyl and hydroxyl group changes by IR absorption. The EPDM films containing polymeric HALS were prepared by solvent casting from chloroform with  $\approx 100 \mu\text{m}$  thickness. The IR absorption spectral changes of the film upon irradiation with 300 nm UV light were observed for different time intervals. The data obtained were compared with pristine EPDM and EPDM blended with conventional HALS (Tinuvin-770) under similar accelerated conditions.

### Results and Discussion

The synthesized maleic anhydride-g-EPDM and HALS bound EPDM were characterized by FT-IR and  $^{13}\text{C}$  NMR spectroscopy. The FT-IR spectra shown in Figure (1b) clearly reveal the existence of maleic anhydride as two IR bands at 1840 and 1785  $\text{cm}^{-1}$ , attributed to the carbonyl functions of the anhydride groups (10, 11). Singh et al. already reported the HALS bounded to styrenic polymers through anhydride functionality. By considering such a possibility, we successfully synthesized the HALS bounded EPDM.

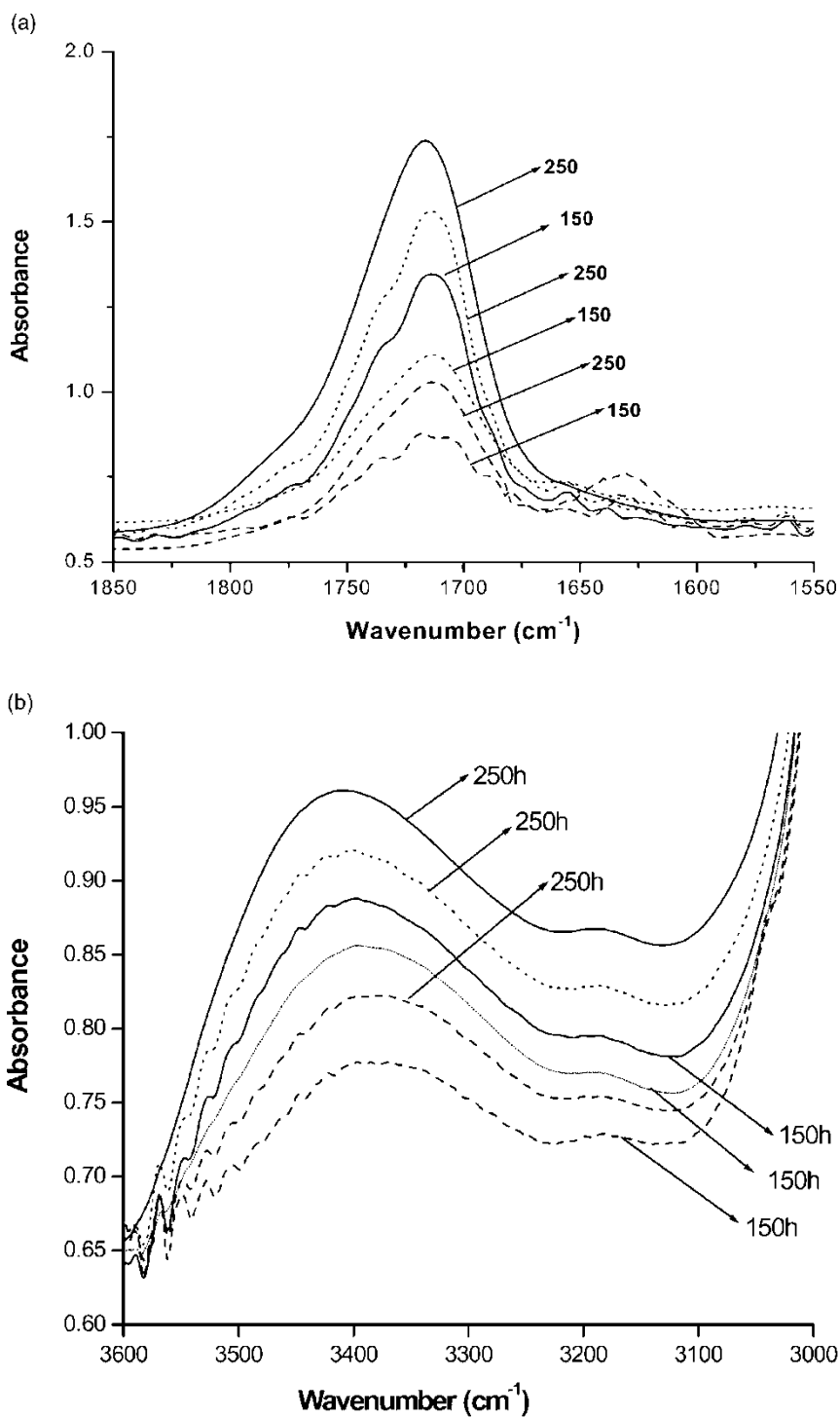


**Figure 1.** FT-IR spectra of (a) Pristine EPDM, (b) MA-g-EPDM, (c) 4-amino-2,2,6,6-tetramethyl piperidine-g-EPDM.

The attachment of HALS groups to EPDM substrate was achieved by treating maleated EPDM with 4-amino-2,2,6,6-tetramethyl piperidine with DMAP as a catalyst (10). The formation of a HALS bearing EPDM elastomer is supported by infrared spectroscopic data, since the spectrum of these substrates showed the bands at  $1630\text{ cm}^{-1}$  (Figure 1c), imide ( $-\text{CONH}-$ ) functionality, band at  $1730\text{ cm}^{-1}$  for acid carbonyl and broadening at  $3400\text{--}3200\text{ cm}^{-1}$  indicates the presence of ( $-\text{NH}-$ ) and hydroxyl stretching, which is attributed to pendant piperidine groups, while the disappearance of band at  $1830$  and  $1785\text{ cm}^{-1}$  also supports opening of the anhydride ring by amino terminated HALS. In the  $^{13}\text{C}$  NMR spectrum of 4-amino-2,2,6,6-tetramethyl piperidine-graft-EPDM, peaks observed at  $177\text{ ppm}$  for amide carbon,  $170\text{ ppm}$  for acid also reveal their existence. The shift in carbonyl frequencies from maximum to a lower side was observed in Figure 2a is due to the existence of lactone, ester, ketone and acid groups at the initial stage of degradation. After longer exposure, all these groups photooxidized to ketones with increasing absorbance at  $1721\text{ cm}^{-1}$ . From gravimetric analysis, grafting percentage of the maleic anhydride and HALS in EPDM films was observed to be  $2\%$  and  $1.1\%$ , respectively.

### **Photostabilizing Efficiency of Polymeric HALS**

The photostabilizing efficiency of polymeric HALS on photooxidation of EPDM was studied from the IR absorption spectral changes and results were compared with that of conventional stabilizer  $1.1\%$  (Tinuvin-770) in EPDM and was plotted in Figure 2(a–b). The efficiency of light stabilizers was measured in terms of the carbonyl index Figure 2a



**Figure 2.** Plot of carbonyl absorbance, (a) and hydroxyl absorbance, (b) vs. wavenumber in Pristine EPDM (—), EPDM + Tinuvin 770 (·····), EPDM + HALS (---) after 150 h and 250 h exposure.

(area under the  $1630\text{--}1850\text{ cm}^{-1}$  peak) and hydroxyl index (area under the peak  $3200\text{--}3700\text{ cm}^{-1}$ ). The carbonyl absorption is maximum at  $1720\text{--}1740\text{ cm}^{-1}$  and the hydroxyl absorption is maximum at  $3420\text{ cm}^{-1}$ . The 1.1-wt% concentration of the light stabilizer showed better performance in EPDM films compared to EPDM, pristine, and with Tinuvin-770. The neat EPDM films showed the maximum carbonyl absorption at both 150 h and 250 h UV exposure followed by EPDM with Tinuvin-770, the HALS bound EPDM show lower carbonyl absorption as compared to above. Figure 2a shows the increase in the carbonyl region with maximum absorbance at  $1720\text{ cm}^{-1}$ . The broadening observed in the peak from  $1780\text{ cm}^{-1}$  to  $1700\text{ cm}^{-1}$  with absorption at  $1712\text{ cm}^{-1}$ ,  $1720\text{--}1740\text{ cm}^{-1}$  and  $1785\text{ cm}^{-1}$ , which can be assigned for carboxylic acid, ketones, esters and lactones, respectively at short-term irradiation, i.e., before 150 h, with increasing time of irradiation, the peak maximum at  $\approx 1720\text{ cm}^{-1}$  was observed. This may be attributed to the formation of long chain fatty acid esters. Thus, the difference in rate of increase in absorbance at this region could be attributed to the photostabilization of polymeric HALS.

The polymeric 4-amino-2,2,6,6-tetramethyl piperidine-graft-EPDM is amorphous in nature and highly compatible with the polymer backbone. It is, therefore, well dispersed in the polymer matrix, and therefore gives better stabilization. The stabilizing efficiency of polymeric HALS is higher than that of conventional additives after given irradiation time. This is probably due to the lower solubility or limited state of dispersion of conventional stabilizer in the host polymer, leaving some part the polymer matrix unprotected.

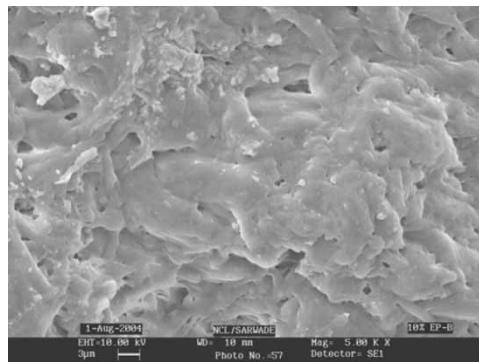
### ***Morphological Changes upon UV Irradiation***

The surface morphology of irradiated EPDM films was studied after 150 h exposure time and is shown in Figure 3(a–c). Figure 3a shows the SEM photograph of pristine EPDM showing maximum micro cavities formation on the surface. The same behavior was observed in EPDM with Tinuvin-770 (Figure 3b), which also shows micro cavities, but less in comparison with pristine material. Figure 3c shows morphological change in EPDM stabilized by polymeric HALS, and shows no micro cracks or cavities on the surface for a given exposure time. This indicates that polymeric HALS is protecting the surface from photo-oxidative degradation. Also, the conventional light stabilizers are comparatively less protecting stabilizers in EPDM systems.

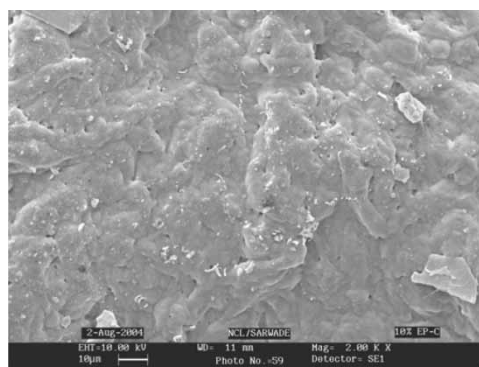
### **Conclusions**

In the present article, we described a procedure to protect the EPDM elastomer against damage derived from photooxidation under accelerated weathering conditions. This method based on two-step functionalization reactions of EPDM, which first implies the photografting of maleic anhydride on to diene part of the terpolymer, followed by the reaction of these functions with amino terminated HALS moieties. This is the first attempt to accomplish functionalization of EPDM by grafting of maleic anhydride using a photochemical method to introduce HALS moiety. This method has a great advantage over the conventional methods as it performed at lower temperature and did not bring out any polymer degradation. The MA-graft-EPDM was successively treated with HALS molecule to open the anhydride ring and to support HALS moieties onto EPDM substrate. Films of HALS bounded EPDM were eventually irra-

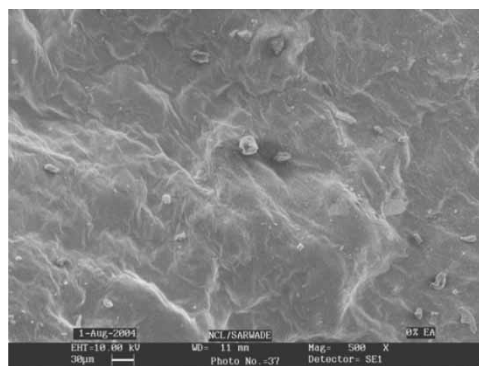




(a)



(b)



(c)

**Figure 3.** SEM photographs of pristine EPDM (a), EPDM with Tinuvin-770, (b), EPDM with polymeric HALS, (c) after 150 h UV exposure.

diated under accelerated photooxidative conditions. The experimental findings strongly indicate that these substrates are considerably more stable towards photooxidation than are the pristine, unmodified material, even in the presence of melt blended conventional HALS.

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