Photodegradation and Stabilization of Styrene–Butadiene–Styrene Rubber

R. P. SINGH, S. M. DESAI, S. S. SOLANKY, P. N. THANKI

Polymer Chemistry Division, National Chemical Laboratory, Pune 411008, India

ABSTRACT: Photooxidative degradation and stabilization of a polystyrene–block–polybutadiene–block–polystyrene thermoplastic elastomer using a polychromatic UV light in air at 60°C has been studied by monitoring the appearance of the hydroxyl and carbonyl groups in Fourier transform infrared spectroscopy. The extent of photooxidative degradation in different samples has been compared. The rate of photooxidation was also estimated in the presence of different concentrations of 2,6-di-*tert*-butyl-4-methylphenol [BHT], 2-(2′-hydroxy-5′-methylphenyl)benzotriazole [Tinuvin P] and tris(nonylphenyl) phosphite [Irgafos TNPP], and 1,2,2,6,6-pentamethyl piperidinyl-4-acrylate was grafted onto the surface of the SBS film. The kinetic evolution of the oxidative reaction was determined. The morphological changes upon irradiation in the solution cast SBS films were studied by scanning electron microscopy. Based on the experimental data a suitable photooxidative degradation mechanism also has been proposed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1103–1114, 2000

Key words: photodegradation; stabilization; UV absorber; SBS; photografting

INTRODUCTION

Natural and synthetic polymers in common use are susceptible to photooxidative degradation on exposure to natural and/or artificial weathering. The deterioration of these polymeric materials is mainly due to the UV portion of sunlight reaching the earth surface.[1,2] The net result of degradation is the loss in the molecular weight and macroscopic physical properties, until ultimately, the polymer becomes useless. The unsaturated synthetic elastomers, being highly sensitive to oxidation, require the addition of stabilizers to provide protection during processing, storage and end-use. Because of the wide spread usage of rubber and plastic materials, considerable efforts have been made to improve their light stability, keeping in mind their low cost. Compatible and mobile stabilizers usually give the best protection, but low molecular weight stabilizers are easily lost from the polymer through evaporation, migration, and extraction. In order to avoid loss, polymer bound and/or polymeric stabilizers have been devised.

In the polystyrene–block–polybutadiene–block–polystyrene [SBS], the central block consists of the rubber-like polymer and the polystyrene segments form the two terminal blocks. This copolymer tends to degrade upon exposure to heat and UV light, causing discoloration and surface embrittlement.[3,4] The process of photooxidative degradation in SBS, a triblock copolymer, is more complex than their homopolymer[5] and SBR-diblock[6] copolymer. In this article we studied the morphological changes upon photooxidation of
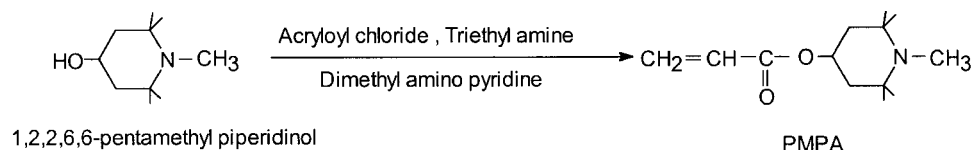
1,2,2,6,6-pentamethyl piperidinol

PMPA

Scheme 1

SBS samples. We have proposed a suitable degradation mechanism based on experimental data. Although various antioxidants have been used to reduce the degradation,[7] the fundamental studies of SBS photodegradation process and its associated phenomenon are seldom reported. Thus, the purpose of this work was to study the performance of various additives on the photooxidative degradation and to estimate the optimum concentration of the best additives.

EXPERIMENTAL

Materials

The SBS thermoplastic elastomer (rubber) used in the present investigations were supplied by M/s ATV projects India Ltd. (Nagothane, India). The unstabilized oil-extended SBS samples are M/s ATV Ltd. products while ENICHEM and SHELL are their competitor's SBS samples. The stabilizers: 2,6-di-*tert*-butyl-4-methylphenol (BHT), 2-(2′-hydroxy-5-methylphenyl)benzotriazole (Tinuvin P) and tris(nonylphenyl) phosphite (Irgafos TNPP) were obtained from M/s Hindustan Ciba-Geigy Ltd. (Bombay). 2,2,6,6,-Tetramethyl-4-piperidinol, 4-dimethyl aminopyridine, benzophenone, and acryloyl chloride were obtained from Aldrich Chemicals. Triethyl amine was obtained from Ranbaxy Laboratories Limited (India). Dichloromethane, obtained from S.D. Fine Chemicals Limited, India, was dried by refluxing over P_2O_5 and distilling twice under nitrogen atmosphere.

Synthesis of 1,2,2,6,6-Pentamethyl piperidinyl-4-acrylate

The model compound was synthesized[8,9] under strictly dry conditions. The starting material, 1,2,2,6,6-pentamethyl-4-piperidinol (PMPO), was synthesized from 2,2,6,6-tetramethyl-4-piperidinol via a simple reaction[10] and recrystalized by sublimation before use. 1,2,2,6,6-pentamethyl-4-piperidinol (1.0 g; 0.0058 M) was taken in a two-

neck round-bottom flask along with 14 mg (0.4 M) 4-dimethylaminopyridine (DMAP), 15 mL dry dichloromethane, 1.2 mL (0.0087 M) triethyl amine (TEA). This reaction mixture was stirred for 10 min followed by the addition of 0.55 mL (0.0069 M) acryloyl chloride with stirring. The reaction mixture was allowed to stir at room temperature for 17 h. The reaction mixture was quenched in ice water, and the product was extracted in dichloromethane and was found to be almost pure. The TLC of the product did not show any spot of starting material or DMAP (catalyst) (Scheme 1).

Sample Preparation

Films of unstabilized oil-extended (ATV-oil), stabilized oil-extended SBS (ATV-prene) ENICHEM and SHELL samples of SBS rubbers were prepared by solution casting. The pellets of the copolymer were dissolved in toluene at room temperature and different concentrations (0.1 and 0.35 wt %) of the stabilizers were incorporated in ATV-oil solution. The solution was homogenized, casted on glass plates to evaporate the solvent, and dried under vacuum to constant weight.

Surface Grafting of PMPA on SBS Film

Thin films of SBS (ATV-oil) were prepared from 1.5 % solution of SBS in dichloromethane. The
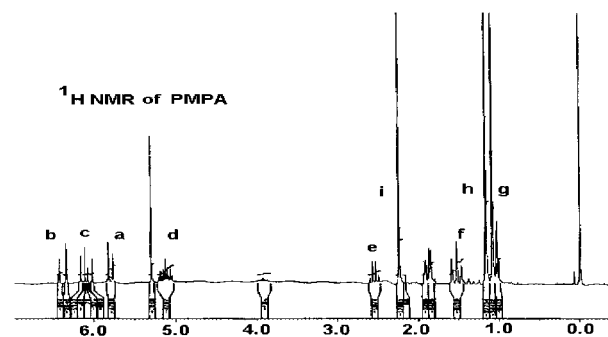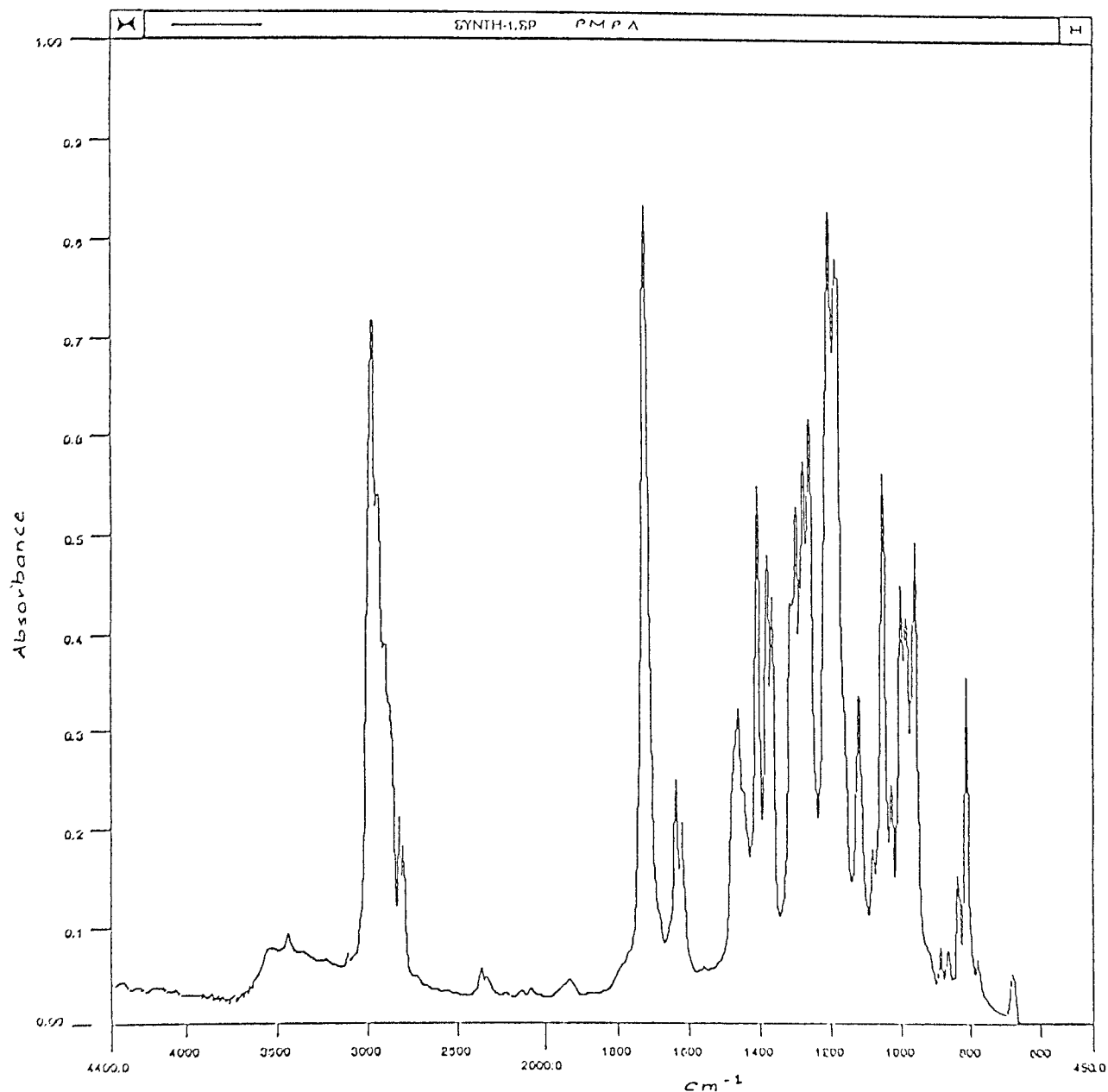

Figure 1 ^{1}H-NMR of 1,2,2,6,6-pentamethyl piperidinyl-4-acrylate.

(a)

Figure 2   (a) FTIR spectrum of 1,2,2,6,6-pentamethyl piperidinyl-4-acrylate. (b) Surface grafting of PMPA on SBS film. (**1**) Neat SBS film; (**2**) photo-irradiated (45 min) SBS film (under the grafting reaction conditions) without PMPA; and (**3**) SBS film grafted with PMPA.

film (thickness = 100 μm) was taken in a specially designed photoreactor, with 30 mL methanol, (0.2 M) benzophenone and 1.12 g (0.166 M) PMPA under nitrogen atmosphere and irradiated ($\lambda \geq 290$ nm) for 45 min at 55 $\pm$ 2°C. The film was soxhlet extracted in methanol for 6 h and then dried under vacuum. The weight of the neat film was 0.23500 g, whereas that of the grafted film was 0.23577 g, which indicated that 0.32 wt % of PMPA was grafted onto the surface of the film.
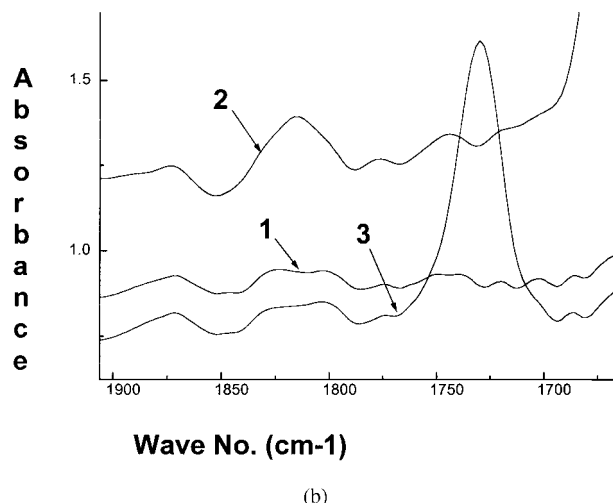
Wave No. (cm-1)

(b)

Figure 2   (*Continued from the previous page*)

The wt % of grafting was calculated using the equation:

$$\% \ WG = \frac{(W_w - W_0)}{W_0} \times 100$$

where W_w is the net weight of the SBS film after grafting and W_0 is the initial weight of the film.

Photo-Irradiation

Films were irradiated in the photo-irradiation chamber (SEPAP 12/24 M/s; Le Materiel Physico Chimique, Neuilly, France) at 60°C. The unit consists of four 400W "medium pressure" mercury sources filtered by a Pyrex envelope supplying radiation longer than 300 nm. These sources were located at the four corners of a square chamber (50 × 50 cm). The equipment is described elsewhere.[11]

Instruments

The structure of PMPA was confirmed from ^{1}H-NMR on Bruker AC 200 FT-NMR instrument at 200 MHz, a Perkin-Elmer 16 PC Fourier transform infrared (FTIR) spectrophotometer, and Perkin-Elmer auto system XL gas chromatograph. The contact angle of water with the surface of neat as well as grafted film was measured using Ramé-Hart Inc. NRL C.A. goniometer (Model No. 100-00-230). ^{1}H- and ^{13}C-NMR spectra were obtained on polymer samples dissolved in $CDCl_3$ at 25°C on a Bruker AC 200 FT-NMR instrument at

200 MHz. The morphological changes on the films were examined under Leica-Cambridge Stereoscan 440 scanning electron microscope. The neat and oxidized films were placed in stoppered bottles containing osmium tetroxide (2% aqueous) and were allowed to stand for 48 h. The films were washed with water and dry ethanol. The stained samples were dried under vacuum for 24 h at 50°C. The gold-coated samples were examined under scanning electron microscope. Moreover, in order to determine the extent of photooxidative degradation, the films were withdrawn and the spectra were recorded after 50, 100, 150, and 200 h of UV irradiation of the sample in SEPAP 12/24 using FTIR spectrophotometer.

Characterization

The structure of PMPA has been confirmed from ^{1}H-NMR (Fig. 1):
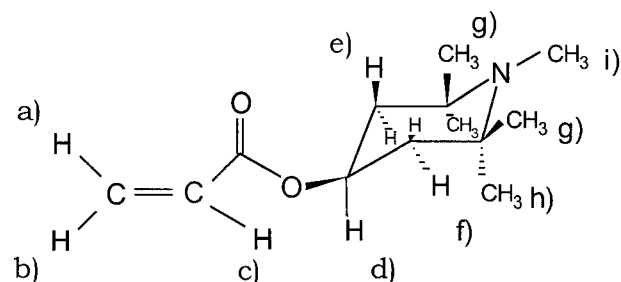
where (a) *cis*-H(1) doublet at δ = 5.75 ppm; (b) *trans*-H(1) doublet obtained at downfield due to coupling with conjugated carbonyl carbon at δ = 6.40 ppm; (c) H(1) quartet at δ = 6.2 ppm (d) H(1) multiplet at δ = 5.15 ppm; (e) H(2) double doublet at δ = 1.8 ppm; (f) H(2) merged doublets at δ = 1.5 ppm; (g) H(6) singlet of both axial CH_3 at δ = 1.1 ppm; (h) H(6) singlet of both equatorial CH_3 at δ = 1.2 ppm; and (i) H(3) singlet indicates N-CH_3 at δ = 2.2 ppm.

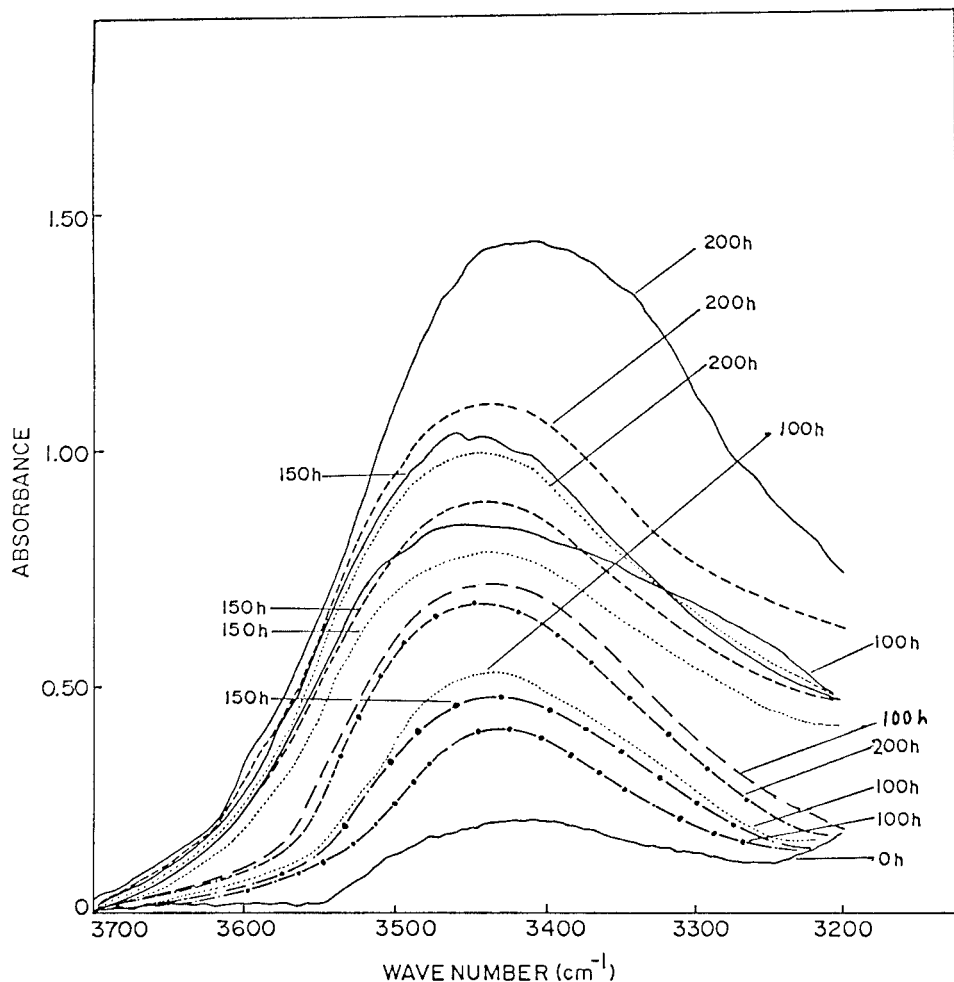**Table I   Polybutadiene Contents in Different Grades of SBS Rubber**

Sample	PB (mol %)	Styrene (mol %)
ATV-prene	77	23
ATV-oil	78	22
ENICHEM	82	18
SHELL	81	19
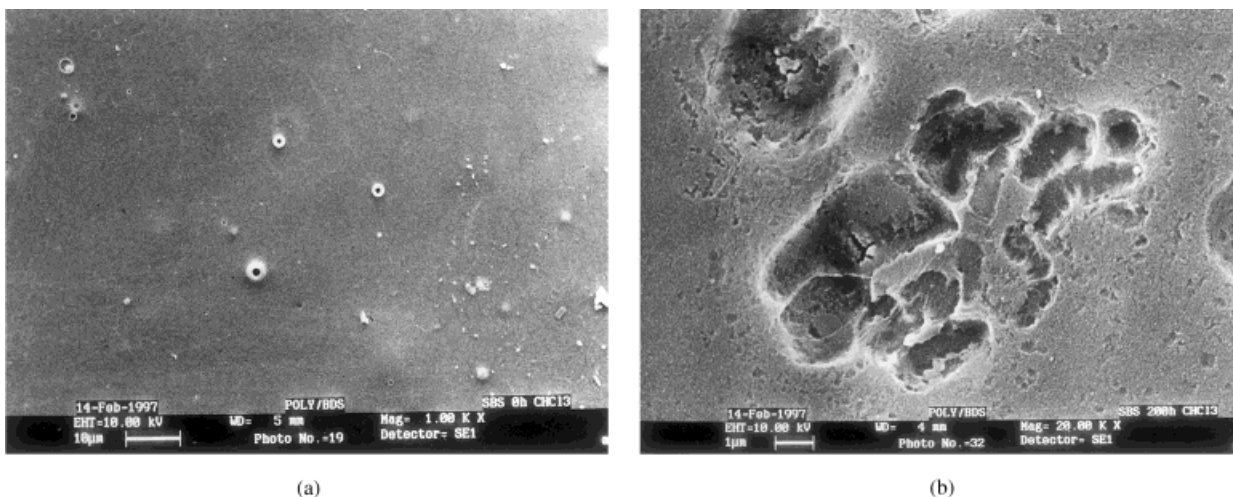
Figure 3   SEM photographs of SBS films casted from CHCl$_3$. (a) Neat film; (b) 200-h UV-exposed film.
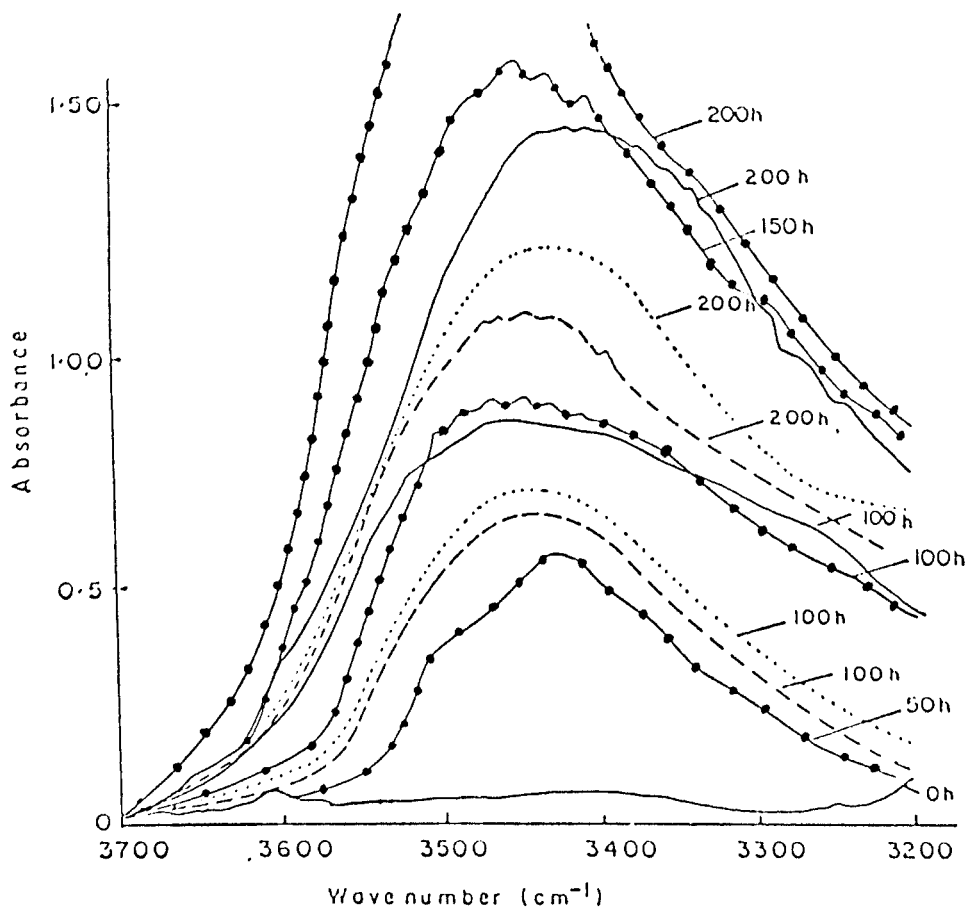
Figure 4   FTIR spectral changes in the hydroxyl region for various hours irradiated ATV-prene (—), ENICHEM (- - -), SHELL (· · · ·), and ATV-oil (—•—) samples.

Figure 5 FTIR spectral changes in the hydroxyl region for various hours irradiated ATV-oil in presence of 0.3 wt % each of BHT (—), Irgafos TNPP (- - -), Tinuvin P (·····), and 0.32 wt % of grafted PMPA (– • – • –).

The FTIR spectrum of PMPA [Fig. 2(a)] shows carbonyl stretching of vinyl ester (unsaturated ester) at 1724 cm^{-1}, C≡C stretching vibration absorption at 1636 cm^{-1}, and vinyl carbon deformation at 984 cm^{-1}. The purity of PMPA obtained from gas chromatography (using BP-1 column) is 98.7%.

The FTIR spectra [Fig. 2(b)] provides substantial evidence for the grafting of PMPA on SBS film. In this spectrum, **1** indicates neat SBS film, **2** indicates the control sample wherein the sample is irradiated in the same reaction condition without PMPA, and **3** shows SBS film grafted with PMPA. Here the peak at 1740 cm^{-1} (C≡O of ester) confirms that the grafting has taken place onto the surface of the film. This figure also summarizes that the generation of carbonyl peak is not as a result of photo-irradiation during the grafting reaction.

The neat film showed a contact angle with water of 105°, while the grafted one exhibited 47°, which also reaffirms the generation of hydrophilic group on the surface of the film.

RESULTS AND DISCUSSION

The polybutadiene content in different grades of SBS rubber have been studied by ^{1}H- and ^{13}C-NMR techniques. The polybutadiene is also characterized by the deformation bands in FTIR spectra at 994, 967, 912, and 729 cm^{-1}. The polybutadiene contents[12,13] are given in Table I.
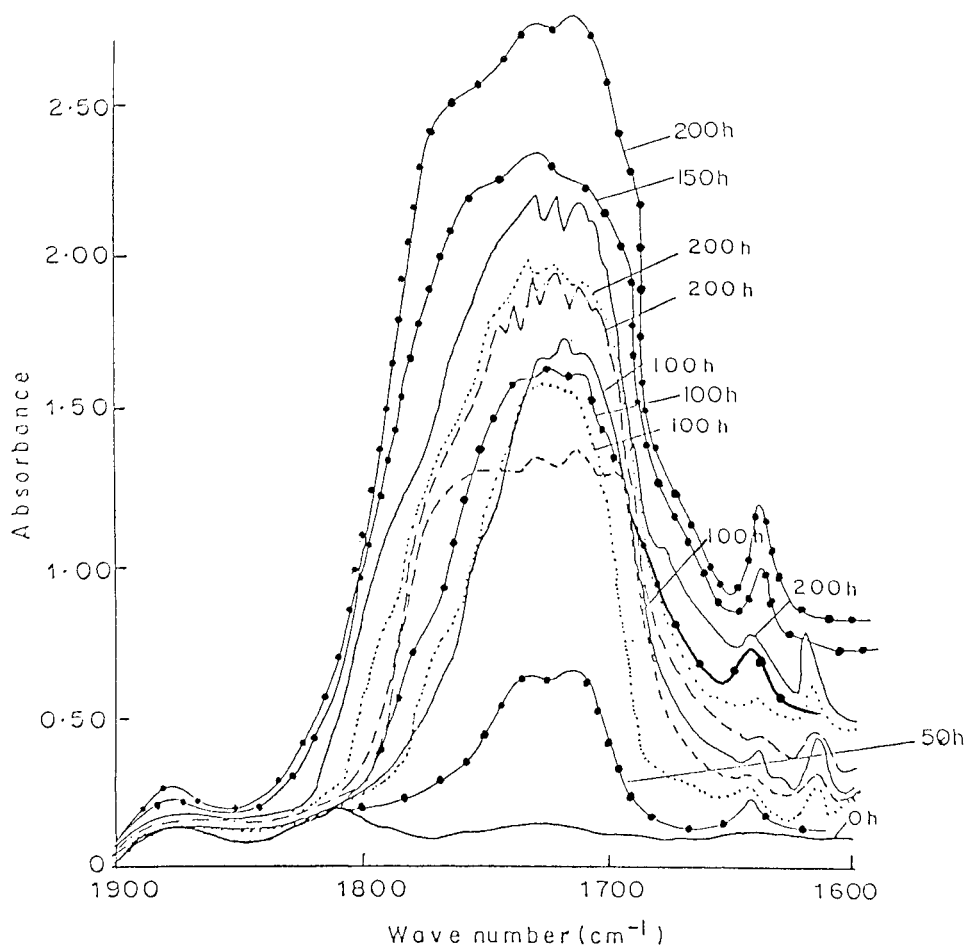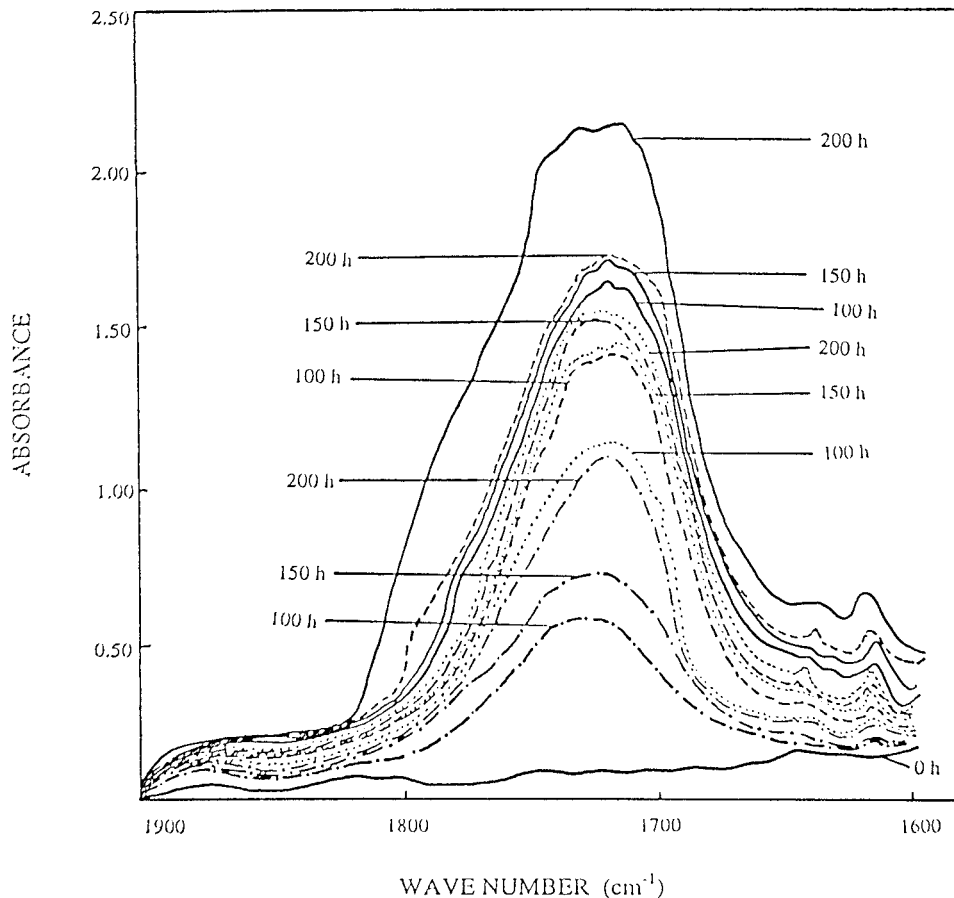
Figure 6 FTIR spectral changes in the carbonyl region for various hours irradiated ATV-prene (—), ENICHEM (- - -), SHELL (· · · ·), and ATV-oil (—•—) samples.

In SBS triblock copolymer, the polybutadiene block is more susceptible to photooxidation. The *cis*-1,4 ($\delta = 27. 3$ ppm), *trans*-1,4 ($\delta = 32.6$ ppm), and *vinyl*-1,2 ($\delta = 114.2$ ppm) were detected in the co-polymers. The photooxidized (100-h irradiation) SBS films showed the appearance of *cis*-epoxides ($\delta = 56.4$ ppm), *trans*-epoxides ($\delta = 58.3$ ppm), and alcohol ($\delta = 71.2$ ppm), but on longer irradiation, the peak intensity was decreased, which is due to decomposition of the epoxides and alcohols to carbonyl end products.

The photooxidized samples showed some surface embrittlement and yellowing but it was exceptionally less in case of Tinuvin P and PMPA-*g*-SBS. In chloroform, the polystyrene and polybutadiene phases are well separated (Fig. 3). Upon irradiation, the microcavities and microcracks were observed on the polymer surface (SHELL). The breaking polymer bonds produce chain fragments upon irradiation, which occupy more volume than original macromolecule, causing strain and stress that is probably responsible for the formation of microcavities and microcracks. The microcavities are irregular in shape, and the internal surface of the cavities is rough in nature. At 100-h exposure, the polystyrene phase also started degradation.

Experiments were carried out both on an unmodified polymer and on the samples containing 0.1–0.35 wt % of different conventional stabilizers and PMPA grafted onto ATV-oil film surface. Irradiation of SBS rubber films to polychromatic light ($\lambda \geq 300$ nm) led to development of IR bands in the hydroxyl and carbonyl regions. A very broad hydroxyl region (3700–3200 cm^{-1}) with a maximum at ~3400 cm^{-1} during photo-irradiation appeared in Figures 4 and 5. This band is due to the neighboring intramolec-

Figure 7   FTIR spectral changes in the carbonyl region for various hours irradiated ATV-oil in presence of 0.3 wt % each of BHT (——), Irgafos TNPP (- - -), Tinuvin P ($\cdots$), and 0.32 wt % of grafted PMPA (– • – • –).

ular hydrogen-bonded hydroperoxides and alcohols. The absorption in the hydroxyl region is more intense in ATV-oil and ATV-prene but minimum in the ENICHEM sample. In the presence of stabilizers in ATV-oil, the minimum hydroxyl region was observed in presence of PMPA (Fig. 5).

The carbonyl region (1900–1600 cm^{-1}) showed several overlapping bands (Figs. 6 and 7). This region is also broad. The absorptions at 1715, 1722, and 1740 cm^{-1} have been assigned[1,2] to carboxylic acid, ketone, and ester, respectively. The carbonyl region increases with increasing irradiation times. An unsaturation at 1640 cm^{-1} is also observed in all the samples. The absorption intensity is more in ATV-oil and ATV-prene but minimum in the ENICHEM sample. Figure 7 shows that PMPA-grafted film give the best stabilization on ATV-oil sample.

The amount of hydroxyl and carboxyl groups were calculated from the FTIR spectra and plotted versus irradiation time in Figures 8 and 9, respectively. The rate of hydroperoxides increases with time of irradiation and is maximum in ATV-oil and ATV-prene. Figure 8 shows that among the used stabilizers, the grafted PMPA is the best for ATV-oil samples. The same behavior was also observed in the amount of carbonyl group formation (Fig. 9). Among the industrial samples, the hydroxyl/carbonyl group formation is minimum in ENICHEM and maximum in ATV-prene and ATV-oil (unstabilized sample), indicating that the ENICHEM weather stabilization is better than that of the ATV-prene and SHELL samples. The minimum hydroxyl/carbonyl group formation was observed upon grafting of PMPA onto the surface, indicating that it is the best stabilizer compared to BHT, Irgafos TNPP, and Tinuvin P to make
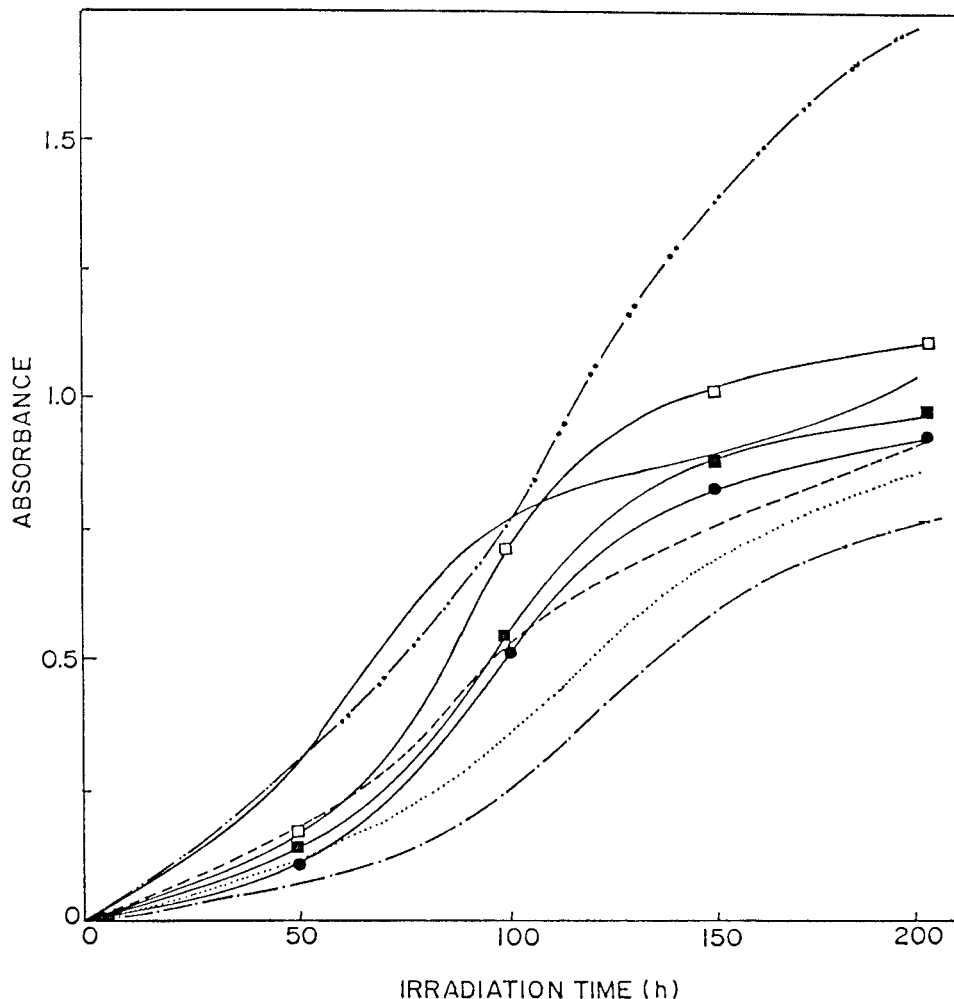
Figure 8 Rate of hydroxyl group formation with irradiation time ATV-prene (—□—), ENICHEM (—●—), SHELL (—■—), and ATV-oil (– ·· –) in presence of 0.3 wt % each of BHT (—), Irgafos TNPP (- - -), Tinuvin P (· · · ·), and 0.32 wt % of grafted PMPA (– · – · –).

ATV-oil film weather-resistant. The 0.3 wt % of the conventional stabilizers is the optimum concentration as a saturation limit in photostabilization of SBS rubber is achieved at this concentration. Figure 10 shows that saturation limit is reached at 0.3 wt % of stabilizer, after which no change in absorbance is observed with a further increase in stabilizer concentration.

Mechanism of Oxidative Degradation and Stabilization

Since SBS rubber contains an unsaturated rubber midblock, the degradation mechanism may resemble to polybutadiene[5,14] and styrene buta-diene rubber[11] to some extent but it is expected more complex as SBS rubber is a triblock copolymer. The degradation of SBS rubber arises from the generation of free radicals by UV light, causing undesirable reaction of double bonds in polybutadiene segment.
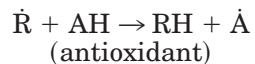
The initial polybutadiene block photooxidation,[15] initiates the rapid degradation of polystyrene segment. The photooxidation of styrene block leads to yellowing. The hydroperoxide, alcohol and hydroxyl groups are observed in the hydroxyl region. The acidic, carboxyl, and ketonic groups are identified in the carbonyl region of FTIR spectra. The ^{13}C-NMR spectrum of the photooxidized SBS rubber[16,17] showed the resonance
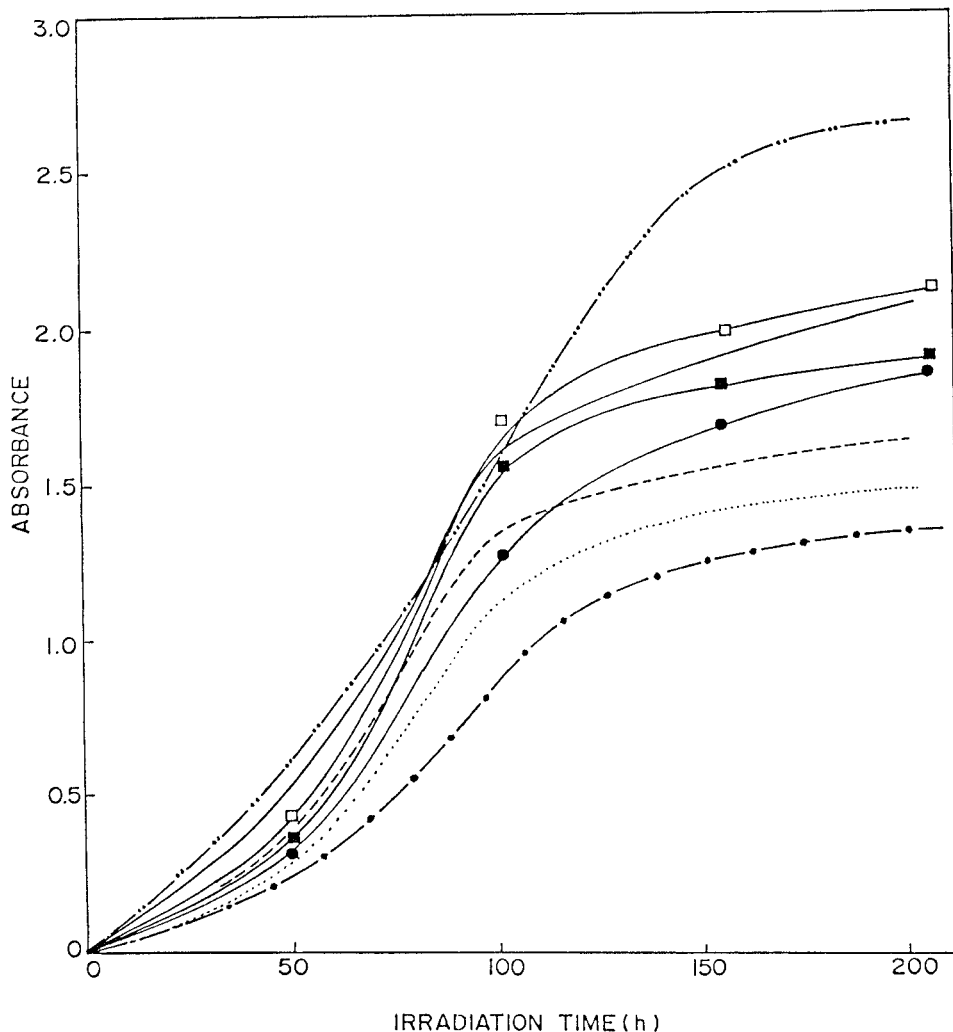
Figure 9 Rate of carbonyl group formation with irradiation time ATV-prene (—□—), ENICHEM (—●—), SHELL (—■—), and ATV-oil (– $\cdot\cdot$ –) in presence of 0.3 wt % each of BHT (—), Irgafos TNPP (- - -), Tinuvin P ($\cdot\cdot\cdot\cdot$), and 0.32 wt % of grafted PMPA (– • – • –).

peaks at 71.2 and 58.5 ppm, which were assigned to alcohol and epoxides, respectively.

The BHT (an antioxidant) reduces the degradation by a conventional method of scavenging the free radicals:

$$\dot{R} + AH \rightarrow RH + \dot{A}$$
(antioxidant)

$$RO\dot{O} + \dot{A} \rightarrow \text{stable products}$$

$$2\dot{A} \rightarrow \text{stable products}$$

Scheme 2

The Irgafos TNPP (a phosphite stabilizer) decomposes the hydroperoxides (Scheme 2). Tinuvin P (hydroxybenzotriazole, a conventional UV absorber) absorbs strongly in UV region and quenches the excited state of the polymer.[18]

Hindered amine light stabilizers (HALS) have gained prominence as effective light stabilizers for a variety of polymers. The stabilization effectiveness of HALS is believed to depend upon their ability to form a stable nitroxyl radical, which then scavenges macro-radicals produced during the oxidative degradation:
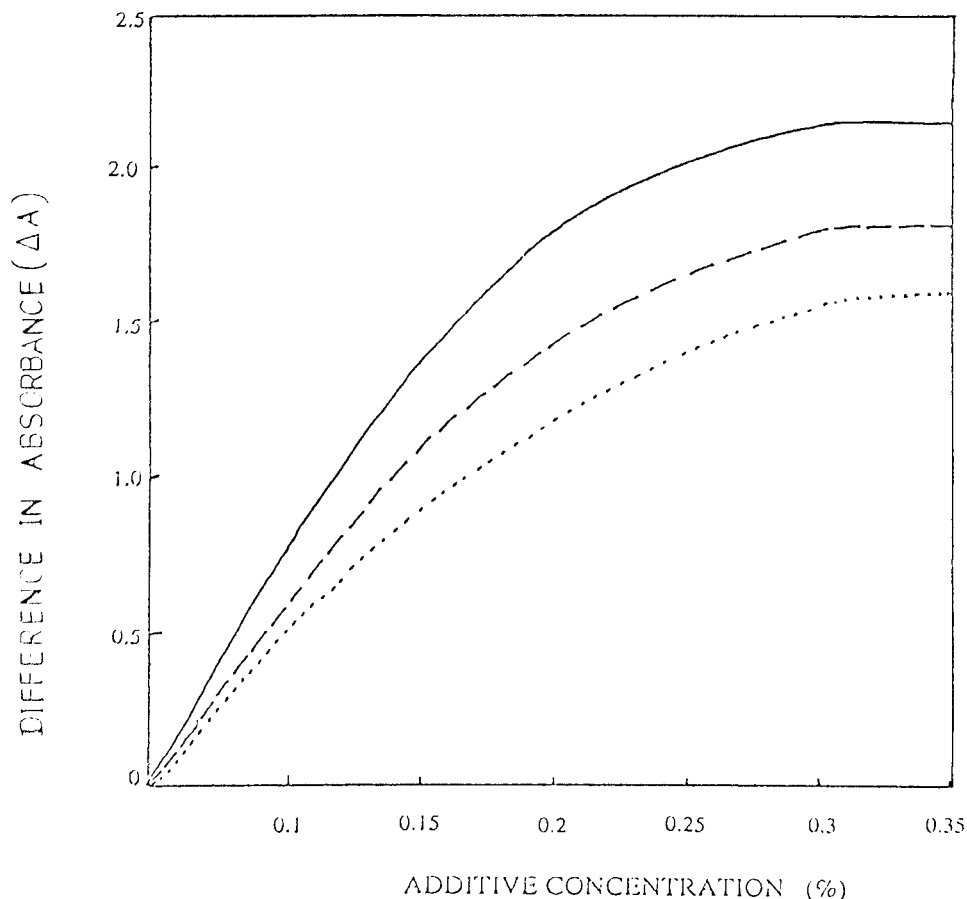
Figure 10 Plot of difference in carbonyl absorbance (ΔA) versus various additive concentration of BHT (—), Irgafos TNPP (- - -), Tinuvin P (····) at 200-h irradiation of ATV-oil sample.
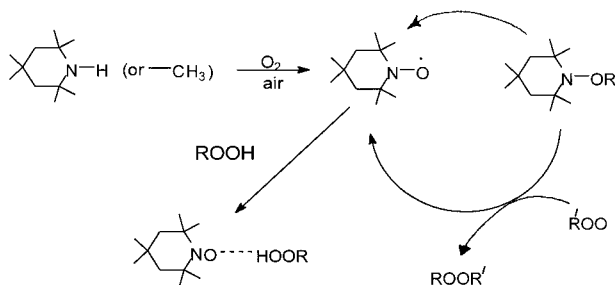
The BHT and Irgafos are processing stabilizers and therefore are not expected to function against UV exposure directly; thus, Tinuvin P is a superior stabilizer compared with BHT and Irgafos TNPP for oil-extended SBR rubber. HALS acts as a free radical scavenger and hydroperoxide decomposer where nitroxyl radicals are generated in the process, and each nitroxyl radical is believed to terminate many free radical chains.

Thus, PMPA shows the best stabilization among the studied stabilizers to the ATV-oil samples. Moreover, surface grafting of PMPA offers permanent attachment to the polymer.

REFERENCES

1. Lemaire, J.; Arnaud, R. In Polymer Photochemistry; Allen, N. S., Ed.; Elsevier, London, Vol. 5, 1984, p 243.

2. Ranby, B.; Rabek, J. F., Eds., Photodegradation, Photo-oxidation and Photostabilization of Polymers, John Wiley & Sons, London, 1975.

3. Jellinek, H. H. G., Ed. Degradation and Stabilization of Polymers, Vol. 1, Elsevier Science Publishers Inc., New York, 1987.

4. Klemchuk, P. P., Ed. Polymer Stabilization and Degradation; ASC Symposium Series 280; American Chemical Society, Washington, DC, 1985.

5. Adam, C.; Lacoste, J.; Dauphin, G. Polym Commn 1991, 32, 317.

6. Singh, R. P. Polym Photochem 1982, 2, 331.

7. Klemchuk, P. P. Ullmann's Encycl. of Industrial Chemistry, 5th Ed., Vol. A3, VCH Publishers, Deerfield Beach, FL, 1985, p 91.

8. Yagi, S. T.; Masaki, N. Y. Adeka Argus Chemical Co. Ltd., Japan Jpn Kokai Tokkyo Koho JP 1988, 63152610.

9. Hofle, G.; Steglien, W.; Vorbriggen, H. Angew Cheimie Int. Ed. 1978, 17, 569.

10. Mani, R.; Sarkar, N.; Singh, R. P.; Sivaram, S. J Macromol Sci Pure Appl Chem A 1996, 33, 1217.

11. Singh, R. P.; Mani, R.; Sivaram, S.; Lacoste, J.; Vaillant, D. J Appl Polym Sci 1993, 50, 1871.

12. Bovey, F. A.; Thiers, G. D. V. J Polym Sci 1959, 38, 73.

13. Sato, H.; Takebayashi, K.; Tanaka, Y. Macromolecules 1987, 20, 2418.

14. Adam, C.; Lacoste, J. Lemaire, J. Polym Degrdn Stab 1989, 26, 269.

15. Singh, R. P.; Raj, R. A.; Vishwa Prasad, A.; Sivaram, S.; Lacoste, J.; Lemaire, J Polym Intern 1995, 36, 309.

16. Gemmer, R. V.; Golub M. A., J Polym Chem Ed 1978, 16, 2985.

17. Brame, E.G., Jr., Ed., Application of Polymer Spectroscopy; Academic Press, New York, 1973, p 73.

18. Chaudet, J. H.; Newland, G. C.; Patten, H. W.; Tamblyn, J. W. SPE Trans 1961, 1, 26.