Protection of styrene–butadiene copolymer film with bound synergistic stabilizers against ferric stearate — catalysed photo-oxidative degradation at elevated temperature

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The thermal and photo-oxidative stability at 90°C against 365 nm light in air of commercial styrene–butadiene copolymer (SBR) film in the absence and presence of ferric stearate as an oxidation accelerator was compared with that of SBR in which a synergistic mixture of an antioxidant 3,5-di-*t*-butyl-4-hydroxybenzylmercaptan (BHBM) in combination with a stabilizer, 1,1,5-triphenyl-2-s-(3',5'-di-*t*-butyl-4'-hydroxy) benzyl-iso-4-thiobiuret (PBHBT) bounded with the polymer. The chain-scission and crosslinking reactions were followed by measurement of molecular weight, degree of degradation, gel fraction, elongation-to-break, density, hydroperoxide, carbonyl and hydroxyl groups contents. The newly developed metal-deactivator and photostabilizer PBHBT, has been found to possess a very high efficiency in SBR. It is also shown that the bound PBHBT in combination with BHBM results in improved physical, mechanical and chemical properties of SBR even in the presence of ferric stearate.

Keywords Styrene–butadiene copolymer; bound synergistic stabilizers; 3,5-di-*t*-butyl-4-hydroxybenzyl mercaptan; 1,1,5-triphenyl-2-S-(3',5'-di-*t*-butyl-4'-hydroxy) benzyl-iso-4-thiobiuret; ferric stearate; photo-oxidative degradation

INTRODUCTION

Styrene–butadiene copolymer (SBR) is an excellent commercial engineering material but its outdoor performance is very poor especially with the presence of metal ion impurities. The effect of metal ions is generally explained by their ability to catalyse the radical-forming decomposition of hydroperoxides generated during ageing, thus supplying new radicals to the radical-type ageing process. To do this, metal deactivators have been added to provide protection during processing and end-use. Even highly efficient oxidation inhibitors including the phenolics acting as electron-transfer antioxidants and sulphur-containing compounds operating as peroxide decomposers, alone are not able to suppress the catalytic influence of the metal ions during processing and photo-oxidative degradation. In particular, a combination of these two types of stabilizers in the bound state often show remarkable synergistic effects[1], as unbound stabilizers are not resistant to leaching and chemical extraction in polymeric materials during their service-life. Therefore, the incorporation of the synergistic antidegradants in the macromolecular chains appears to be a better way of adding the stabilizers into the polymer simply by dilution of the polymer, as these antidegradants give thermal and photo-oxidative stabilizing effects that cannot be achieved by stabilizers added in a conventional way. Most of the available literature is generally concerned with the metal deactivation and photo-stabilization of homopolymer polyolefins, and especially of polypropylene[2–5]. Unfortunately, very little systematic investigation has been concerned with metal deactivation and photo-oxidative stabilization of commercial SBR copolymer at elevated temperatures.

Here, an attempt has been made to improve the thermal and photo-oxidative performance of SBR films in the presence and absence of ferric stearate using a synergistic mixture of 3,5-di-*t*-butyl-4-hydroxybenzylmercaptan (BHBM) and 1,1,5-triphenyl-2-S-(3',5'-di-*t*-butyl-4'-hydroxy) benzyl-iso-4-thiobiuret (PBHBT).

(BHBM) (PBHBT)
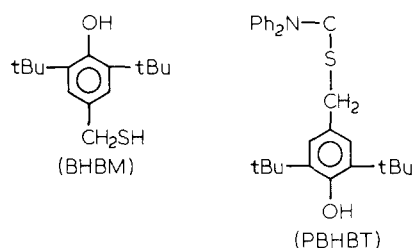
The antioxidant BHBM in combination with an effective photostabilizer as well as a metal deactivator (PBHBT) have been bound onto SBR in the latex phase and the changes in physical, chemical and mechanical properties due to degradation were determined.

EXPERIMENTAL

Materials

The styrene–butadiene copolymer (SBR) used in the present study was obtained by coagulating from a sample of Synaprene 1500 supplied by M/s Synthetics and Chemicals Ltd., Bareilly, India. The percentage composition of the sample was 75% butadiene and 25% styrene. Inhibitors and other possible impurities from the sample were removed by repeatedly extracting the sample

with acetone and methanol. It was further purified by precipitation twice from 2% solution in benzene with methanol. The precipitate was repeatedly washed with methanol, dried under vacuum (10^{-2} mm Hg) and stored under nitrogen atmosphere. The PBHBT stabilizer was prepared according to the published procedure[6].

Grafting procedure

In the grafting procedure, the emulsions of the various concentrations of BHBM and PBHBT were prepared in aqueous suspension under high turbulence and brought into contact with the stripped latex of SBR. In the grafting reaction, a redox system was operated at 60°C. The emulsions were purged with N_2 before being added to the SBR latex which had previously been purged with N_2. The pure cumene hydroperoxide initiator was added in aliquots within the first half the reaction which was completed within 6 h. At the end of the reaction, the SBR was coagulated using dilute acid and dried under vacuum at 50°C.

Extraction method

The ungrafted BHBM/PBHBT was removed by continuous extraction of the crumbs with hot hexane using a Soxhlet apparatus. An extraction period of 60 h was found to be sufficient to remove all unbound materials. After extraction the polymer sample was dried under vacuum.

Quantitative determination of the stabilizers

The procedure used was based on that developed by Metcalf and Tomlinson[7].

An aliquot consisting of a suitable volume of extract was evaporated to dryness on a rotary evaporator. The extract was then mixed in a 5 ml toluene/ethanol mixture (25/75 v/v); 0.5 ml dipyridyl solution and 1.0 ml $FeSt_3$/EtOH were then added. The mixture was shaken vigorously and transferred into a 10 ml volumetric flask. The aliquot vessel was washed out 3 times with a toluene/EtOH mixture and the washing transferred to the volumetric flask, which was then made up to the volume with the toluene/EtOH mixture. The flask was then allowed to stand in a bath thermostatically controlled at 30°C for 3 h. The absorbance was measured at 520 nm. The concentration of the antioxidant in the solution was obtained from a calibration curve constructed using BHBM and PBHBT solutions of known concentrations. It was found that up to 85% of the added stabilizers were bound to the polymer.

Processing

SBR with and without bound stabilizers was mixed with 0.05 wt.% ferric stearate in the RAPRA torque rheometer model MK3 for 5 min at 170°C at high speed and at a ram pressure of 40 psi. The samples were processed with closed chambers. The hot melt was quickly removed from the chamber and rapidly cooled in cold water. Normal SBR was also mixed with 0.05 wt.% ferric stearate and processed under similar conditions.

Pressing of films

The specimens (each 0.4 g) were placed between the glazing plates between cellophane paper. They were preheated in the press at 170°C for 2 min without pressure. They were then pressed at 60 psi pressure for another 2

min. This gave the required thin films of thickness $\sim 2.5 \times 10^{-3}$ inches.

Irradiation procedure

Photo-oxidative degradation was carried out in air with a Hanovia chromatolite low pressure mercury lamp. The films were irradiated with monochromatic light (365 nm) for various periods at 90°C and 60% relative humidity. The temperature of the system was controlled to within ± 0.1°C. By using potassium ferri-oxalate actinometry[8] the light intensity flux of the 365 nm light from the lamp at the polymer film has been determined as 1.78×10^{-11} einstein s^{-1} cm^{-2}.

Determination of molecular weight and degree of degradation

The kinetics of the photo-oxidative degradation were followed by changes of weight-average molecular weight ($\bar{M}_w$) of the polymer specimens determined by light scattering. Zimm plots have been employed to estimate $\bar{M}_w$ as a function of time. The method for the calculation of degree of degradation (α) from light scattering data was described previously[9].

Determination of gel fraction in SBR films

0.3 g samples of irradiated SBR film were treated, with 25 ml dichloromethane in centrifuge tubes (50 ml). The tubes were capped to prevent spillage or volatilization and centrifuged for 30 mins at 56 000 r.p.m. using an ultra-centrifuge. The solutions were removed by pipetting. Approximately 0.5 ml was left containing the gel and this was allowed to evaporate slowly at ambient temperature for 24 h before adding a further 25 ml dichloromethane and the phase separation was repeated. The remaining gel was dried for up to 72 h at ambient temperature, then removed and weighed.

Measurement of mechanical properties

The elongation-to-break test, according to ASTM D 412, was made using an Instron tensile tester, model TTCM, at an elongation speed of 50 cm min^{-1}. Density measurements were carried out using a methanol–water mixture.

Hydroperoxides

The kinetics of hydroperoxide groups (–OOH) formation was measured by a modified iodometric method for the analysis of hydroperoxide group concentrations[10].

Measurement of carbonyl and hydroxyl products by i.r. spectroscopy

The i.r. absorbance of the photo-oxidative degraded SBR film in a 1% solution in dichloromethane was determined using a compensated spectrum. A path length of 2 mm was used. Small adjustments to the path length were made on the cell containing the unexposed sample in the reference beam.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of weight-average molecular weight ($\bar{M}_w$) upon 365 nm irradiation with time at 90°C in air for unstabilized and stabilized SBR in the absence and presence of 0.05 wt.% ferric stearate. The
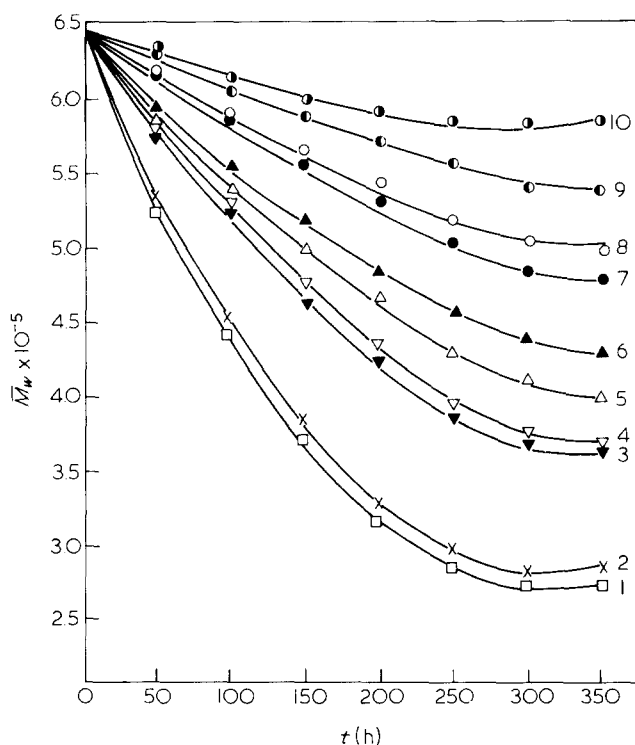
Figure 1 Effect of various concentrations of PBHBT with and without the combination of BHBM on the $\bar{M}_W$ of 365 nm photo-oxidative degraded SBR films at 90°C in the absence and presence of 0.05 wt % FeSt$_3$

change in $\bar{M}_w$ may be the result of two processes which can occur simultaneously: chain scission and/or change in the hydrodynamic shape of the macromolecules due to crosslinking. The plots show a rapid initial decrease in $\bar{M}_w$ which then slows down suggesting that the initial rapid drop is due to random chain scission of bonds at various links. After a prolonged irradiation, there is saturation limit due to crosslinking and macrogel formation by fragments of the polymer molecules. After evaporation of solvent from the prolonged irradiated SBR film solution, especially for normal copolymer with 0.05 wt.% FeSt$_3$, an insoluble gel is formed. The soluble part in dichloromethane gives reproducible $\bar{M}_w$ values which change with time indicating random chain scission processes. For the gel formation process it should be pointed out that the higher molecular weight fractions of the polymer have a higher probability of forming an infinite network structure than the low molecular weight fractions. Therefore, extraction of the resultant gel is expected to give a soluble low molecular weight fraction. The values of $\bar{M}_w$ are higher with antidegradants BHBM/PBHBT and lower with FeSt$_3$ as compared with corresponding values for neat SBR.

Figure 2 shows that the plots of degree of degradation (α) as a function of time are linear initially, proving that at the beginning of irradiation random scission dominates and there is breaking of one type of bond. This is true at low degrees of degradation, but then there was a significant deviation from linearity. Similar relationships have been found in cases where crosslinking (branching) competes with chain scission reactions at higher degrees of degradation.

Figures 1 and *2* also show the dependence of $\bar{M}_w$ and α on exposure time for various concentrations of BHBM and PBHBT in the absence and presence of 0.05 wt.%

FeSt$_3$. It was found that both $\bar{M}_w$ and α are concentration dependent. Increased concentrations of the bound stabilizers offer greater protection to the polymer. At about 0.5 wt.% BHBM and 1.0 wt.% PBHBT with and without 0.05 wt.% FeSt$_3$, it appears that autoretardation sets it. In other words, grafting of the antidegradants onto SBR make the polymer resistant to thermal and environmental degradation because these antidegradants cannot be extracted or leached. It was also found, from a measurement of torque against time, that BHBM and PBHBT had the effect of increasing the ease of processing of SBR.

Perhaps the most interesting and the most technologically useful aspect of the work of this nature is finding suitable combinations of the antioxidant BHBM and the metal deactivator PBHBT which will give rise to synergism. In this work three ratios of BHBM/PBHBT have been mixed, and each case gave rise to synergism. It can be seen in each case of the various combinations studied that the performance of the protected SBR is far superior to the neat SBR with and without FeSt$_3$. This is also demonstrated in *Figures 1* and *2*, where SBR containing a mixture of 0.5 wt.% BHBM and 1.0 wt.% PBHBT has been compared with SBR containing the same levels of BHBM and PBHBT added individually. It can be seen that for SBR containing synergistic mixtures of BHBM/PBHBT, the rate of change in slope is very small compared with other plots. The slow rate of change in slope can be interpreted to mean a higher degree of protection of the polymer by the antidegradants. A low value of degree of degradation suggests a low rate of
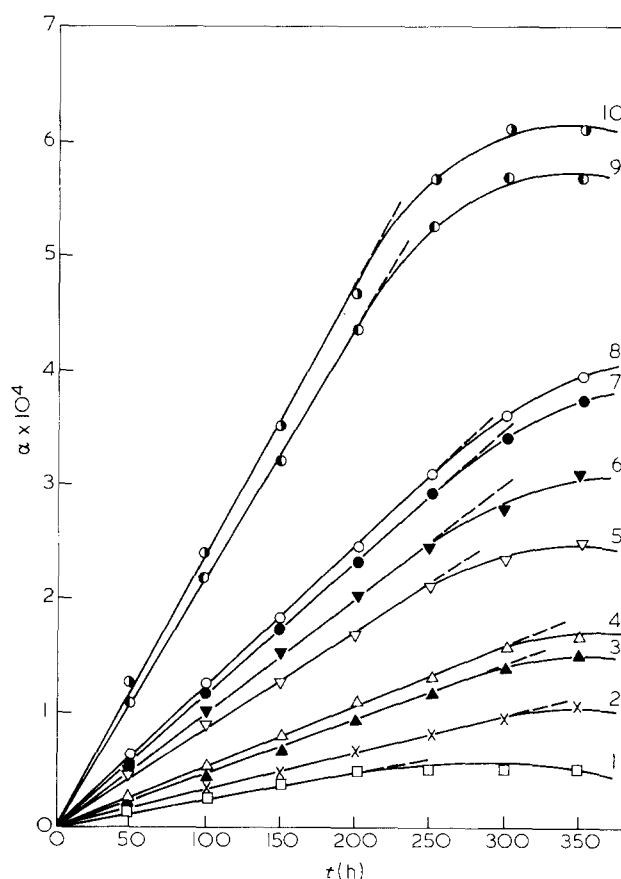

Figure 2 Effect of various concentrations of PBHBT with and without the combination of BHBM on the degree of degradation (α) at 365 nm photo-oxidative degraded SBR films at 90°C in the absence and presence of 0.05 wt% FeSt$_3$
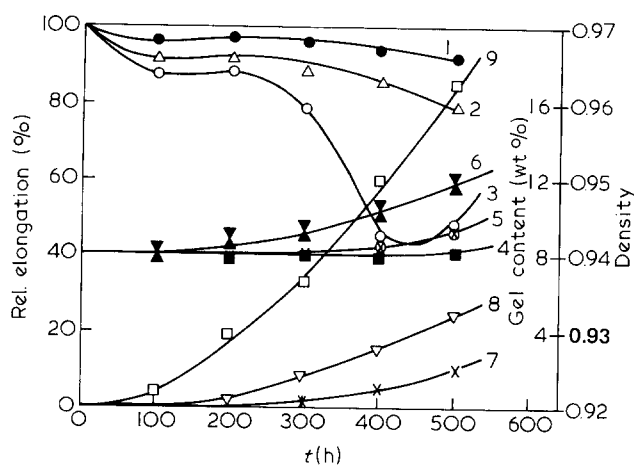
Figure 3 Effect of PBHBT in combination with BHBM on the relative elongation to-break, gel content and density at 365 nm photo-oxidative degraded SBR films at 90°C in the absence and presence at 0.05 wt% FeSt₃

removal or destruction of the synergistic mixtures by light and heat. A comparison of the curves (*Figures 1* and *2*) obtained for the sample without FeSt₃ and without BHBM/PBHBT with the curve of the identically stabilized sample in contact with FeSt₃ also exemplifies the enormous catalytic influence of FeSt₃.

Determination of dichloromethane insoluble gel formation as a function of irradiation time offers a simple method for the evaluation of the degree of crosslinking of the irradiated SBR samples. The curves in *Figure 3* show that normal SBR, with and without 0.05 wt.% FeSt₃, has a relatively strong tendency for crosslinking. The samples containing the synergistic mixtures are, however, appreciably more resistant to this process both in the presence and absence of FeSt₃. It appears that the mixtures of BHBM and PBHBT partially screen the u.v. light so causing some delay in crosslinking. Noting the relatively slower increase of gel fraction following exposure, a light-screening effect which suppresses the polymer ageing processes is proposed. At prolonged exposure the relatively large amounts of gel indicate that in SBR with and without FeSt₃ the predominant process is crosslinking. The gel formation is not reversible as the crosslinking reaction may occur through formation of peroxide bridges or carbon–carbon bonds, depending on the mode of polymer–hydroperoxide decomposition.

Figure 3 also shows loss of relative elongation for irradiated SBR films. The unstabilized sample showed a slight elongation gain at 200 h which may be due to the early presence of crosslinking reactions and to the slight increase in crystallinity of the polymer caused by photo-oxidation degradation. The decrease in elongation after 200 h may be due to the high quantum yield of some bond formed by the recombination of oxygenated free radicals, which may decrease the average strength of the molecular chain.

The increase in density at the same time could be explained by the fact that a considerable amount of low molecular weight material is formed simultaneously. The shorter and more mobile molecular chains will have an increased probability of attaining a closer packing in the amorphous region and hence increase the density. The increase in secondary bond forces by polar group (oxygenated) formation also supports the formation of a

more ordered structure. The increase in elongation at a later stage may be due to an increase in the crystallinity of neat SBR as highly ordered structures are formed on prolonged u.v. ageing. The polymer samples with synergistic mixtures of BHBM/PBHBT show the characteristic delayed ageing curves for the polymer in the absence and presence of 0.05 wt.% FeSt₃.

The iodometric analysis of hydroperoxide groups (–OOH) formation in polymer samples is shown in *Figure 4*. The presence of hydroperoxy groups in irradiated SBR films is also visible from i.r. spectra in the range 3600–3100 cm^{-1}. During degradation, hydroperoxide groups increased rapidly to a maximum after about 300 h u.v. exposure followed by an equally rapid fall. The fall in hydroperoxide suggests that the initially formed hydroperoxide breaks down to give stable oxygen-containing end products in the polymer (notably carbonyl and hydroxyl groups) and even after prolonged exposure at 90°C the absorption band at 1720 cm^{-1}, due to carbonyl groups, and at 3440 cm^{-1} attributed to hydroxyl groups (–OH) are retained. The absorption band of the hydroxyl groups at ~3440 cm^{-1} partially overlaps the absorption band of the hydroperoxy groups at 3400–3380 cm^{-1}, due to band broadening. In i.r. studies of irradiated SBR samples the growing or diminishing bands also centred around the double bands at 965 and 912 cm^{-1}.

Figure 4 also shows the dependence of carbonyl and hydroxyl functional groups upon u.v. exposure with time for an unstabilized and stabilized SBR in the absence and presence of FeSt₃. The carbonyl and hydroxyl groups increase quite rapidly with time for neat SBR sample. The amounts of hydroperoxy, and corresponding carbonyl and hydroxyl groups formed, are smaller in the presence of a synergistic mixture of BHBM/PBHBT and the resulting ageing curves for hydroxyl and carbonyl groups show an even longer induction period for the degraded SBR in the presence of BHBM/PBHBT than the curve for the sample with FeSt₃ and with BHBM/PBHBT.

In the degradation mechanism for SBR it was speculated that prior thermal-oxidative treatment during processing led to a reduction in the autocatalytic period which proceeded rapidly during photo-oxidation and in
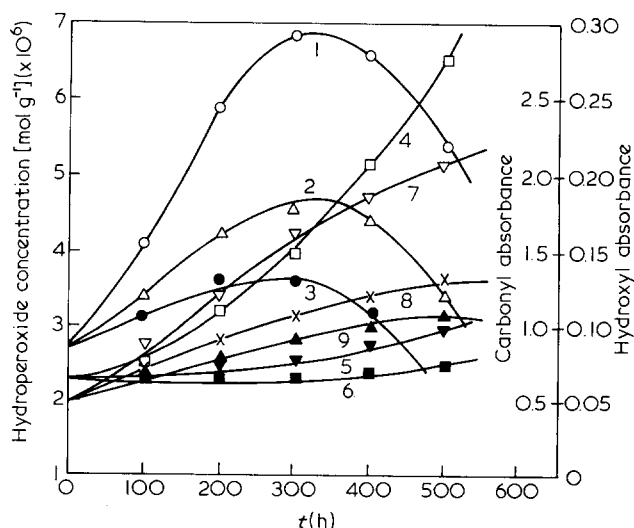

Figure 4 Effect of PBHBT in combination with BHBM on the hydroperoxide, carbonyl and hydroxyl groups at 365 nm photo-oxidative degraded SBR films at 90°C in the absence and presence at 0.05 wt % FeSt₃

the presence of $FeSt_3$. In the i.r. spectra the unsaturation is also decreased during thermal oxidative degradation confirming that the allylic groups are involved in the activation process on u.v. irradiation, the unsaturation of an unoxidized sample decayed autocatalytically but again oxidation in air removed the auto-catalytic period. This result would be expected if allylic hydroperoxides were responsible for degradation. Hydroperoxide was found to be formed in the polymer as a result of processing, rising to a maximum concentration during u.v. irradiation. It appears, therefore, that thermally produced hydroperoxide rather than derived carbonyl compounds are the source of photo-instability in SBR. The $FeSt_3$ catalyses the radical-forming decomposition of hydroperoxides generated during ageing, thus supplying new radicals to the radical-type ageing process.

In view of the significance of hydroperoxides in the photo-oxidative degradation process, it is to be expected that the stabilizers BHBM/PBHBT which function by destroying hydroperoxides will be effective in extending the induction period to the degradation. These stabilizers not only behave as inhibitors but they also retard the linear stage of the photo-oxidation, the linear rate decreasing with increasing concentration of BHBM and PBHBT. This behaviour is characteristic of the u.v. screening agents and is consistent with the behaviour of BHBM and PBHBT which behave as u.v. screens and metal deactivators as well as peroxide decomposers in combination. PBHBT is also a chelating agent which deactivates metal ions, such as ferric ions, by the formation of an iron complex with $FeSt_3$ and behaves both as a thermal and u.v. stabilizer due to a combination of different kinds of activity in the same molecule. A more detailed study of the stabilization mechanisms of BHBM and PBHBT will be presented separately in a later publication.

CONCLUSIONS

The bound antioxidant and the u.v. stabilizer are concentrated in the SBR and cannot be readily extracted.

A comparison of the resulting molecular weight, degree of degradation, gel content, elongation-to-break, density, hydroperoxide, carbonyl and hydroxyl groups of a sample without ferric stearate and without BHBM/PBHBT shows that the effectiveness of the stabilizers BHBM and PBHBT is sufficient for SBR in the presence and absence of $FeSt_3$. These physical, mechanical and chemical properties were found to depend on the concentration of the added stabilizers. In the case of synergistic mixtures, the mixture containing 0.5 wt.% BHBM and 1.0 wt.% PBHBT in SBR gave the best performance under processing and 365 nm irradiation in air at 90°C.

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