

Some Aspects of Stabilization and Degradation of Nigerian Natural Rubber (II): The Environmental Degradation of DBHBT-Modified Unprocessed, Unvulcanized Nigerian Natural Rubber

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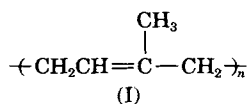
SYNOPSIS

3,5-Di-*tert*-butyl-4-hydroxybenzyl thioglycollate (DBHBT) was bound to the natural rubber (*Hevea Brasilenisis*) latex using 4,4'-azobiscyanovaleric (AZBN) acid-ferrous sulfate redox system. The degradation of various dilutions of the masterbatch as cast films under environmental influence has been investigated using spectroscopic method. Latex-bound DBHBT protects natural rubber latex against environmental degradation with an optimum concentration around 50%. The formation of C=O groups by some pathways independent of —OH groups and allylic hydrogen atoms has been suggested in the natural weathering of DBHBT-modified and unprocessed natural rubber.

INTRODUCTION

Generally *Hevea* rubber latex contains 30–36% (DRC) of *cis*-1,4-polyisoprene hydrocarbon as discrete particles ranging up to 3 μm in diameter. In addition it contains 0.3–0.7% ash, 1–2% protein, 2% resin, and 0.5% quebrachitol. The resin contains sterol esters, fatty acids, and carboxylic acids that strongly influence the rate of vulcanization with certain accelerating systems.^{1,2} Amino acids, enzymes, sugars, tannin, mineral acids, as well as carotenoids and lutoids have been found in natural rubber (NR). However, the composition of the latex varies from clone to clone and from one part of the tree to another. Season of the year affects both the quantity and composition of the latex as does the type of soil.

Pure *cis*-1,4-polyisoprene (I),



like the polyolefins, is transparent to visible and near UV radiations. However, chromophores, nearly al-

ways present as additives or impurities to absorb these radiations, get excited. Such excitation energy can be transferred directly or indirectly to nonabsorbing groups that may suffer numerous fates, notably dissociation. In addition, the reactive singlet oxygen can combine with olefin to produce hydroperoxides and their decomposition products.

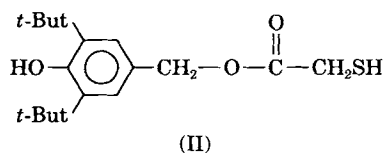
Though rubbers generally react slowly with oxygen at normal temperature and in the absence of light, thermal energy, like other radiations, may induce oxidation (thermal oxidation) and may act synergistically with electromagnetic radiations thereby hastening degradation.³ After initiation, both thermal and photooxidation proceed through free radical chain mechanism in which peroxides are believed to be important intermediates.

Following the pioneering works of Bateman⁴ and Bolland⁵ several workers have investigated the autooxidation of polydienes particularly the elastomers. Sakota et al.⁶ and Sato et al.⁷ demonstrated, using gel fraction studies, that synthetic isoprenes mostly undergo chain scission in heat aging, but both crosslinking and chain scission in UV aging. The rate of chain scission was found to be a function of molecular weight, incident light intensity, and hydroperoxide concentration. Golub⁸ and Bateman⁴ observed loss of unsaturation, *cis-trans* isomerism, crosslinking, and liberation of hydrogen in unphoton-sensitized photolysis of unsaturated polymers *in*

vacuo. Golub also showed that unsaturated polymers yield allylic hydroperoxides with shifted double bonds on photosensitized singlet oxygenation. Salomon⁹ had observed a broad —OH band at 3500 cm^{-1} , a C=O band at 1600 cm^{-1} , and a reduction in the intensity of the 860 cm^{-1} band on thermal oxidation of polyisoprene.

There are less documented works on the stabilization of unvulcanized natural *Hevea* rubber than on other rubbers. Hatchard¹⁰ and Kularatne and Scott¹¹ noted that a very low concentration of bound antioxidant in rubber can impart a significant level of oxidative stability even under aggressive conditions.

In the previous study,¹² 3,5-di-*tert*-butyl-4-hydroxybenzyl thioglycollate (DBHBT) (II)



was reacted with Nigerian Natural rubber latex at 65 + 1°C using 4,4'-azobis + cyanovaleric (AZBN) acid-ferrous sulfate redox system to obtain a binding efficiency of 13%. The bound DBHBT was found to protect unprocessed and unvulcanized Nigerian

rubber against UV degradation. In the current study the environmental degradation of DBHBT-modified Nigerian natural rubber has been investigated in the unprocessed, unvulcanized form.

EXPERIMENTAL

Materials

The natural rubber latex used in this work was collected in the month of July from Clones Harbel I and IJIRI, field MN4 of the Rubber Research Institute of Nigeria Iyanomo, Bendel State of Nigeria. It was preserved by adding 160 cm^3 of 25% ammonia solution to each 4.5 L of the fresh latex.

Hydrated 4,4'-azobis (4-cyanovaleric acid), stearic acid, formic acid, ferrous sulfate, trisodium pyrophosphate, glucose, absolute alcohol, and benzene were all of analytical grades and were supplied by the Aldrich Chemical Company. The DBHBT was prepared and kindly donated by Prof. E. G. Kolawole of Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria, and was used without further purification. The method of preparation has been reported elsewhere.¹³

Preparation of DBHBT Emulsion

A 0.5-g solution of stearic acid was melted with 4.0 g of DBHBT at 70–75°C. To the melted mixture

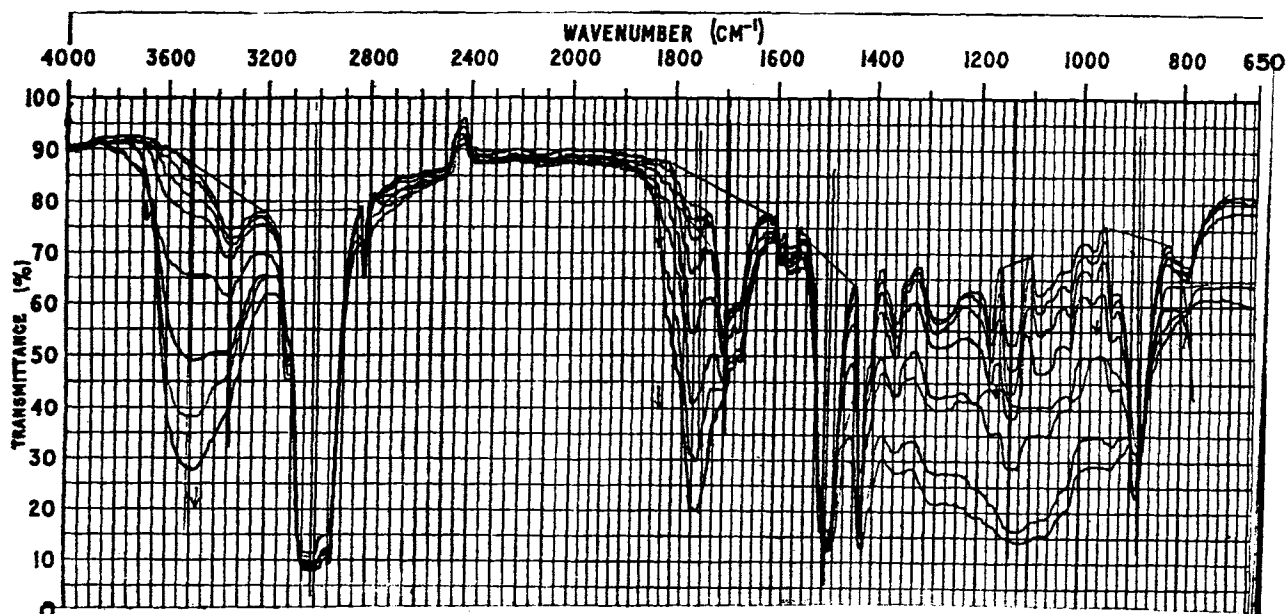


Figure 1 IR spectral changes in environmental degradation of a cast film of DBHBT-modified NR.

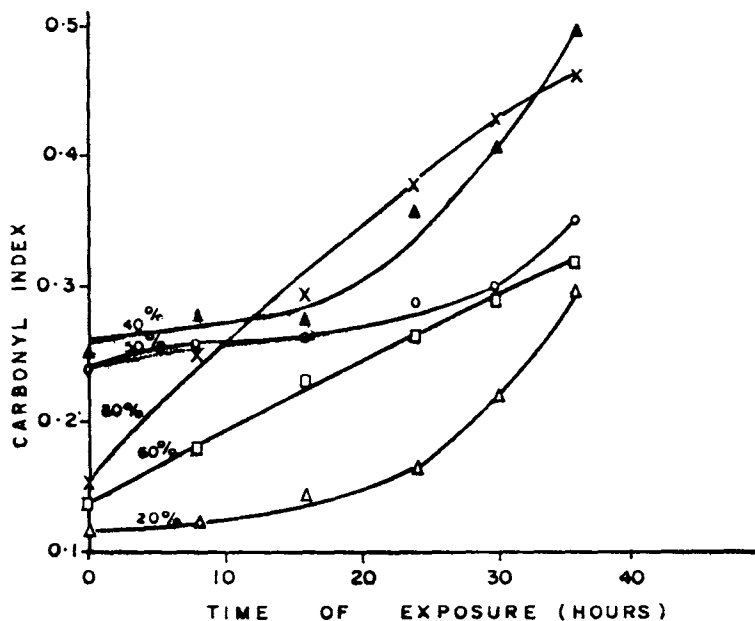


Figure 2 Effect of outdoor exposure on carbonyl indices of cast blends.

was slowly added 25.0 cm³ of 0.657M NaOH, and the mixture was thoroughly stirred. Stirring was continued for 2 min, and the resulting emulsion was quickly cooled in a cooling bath. The emulsion was remelted and purged before use.

Preparation of DBHBT-Bound Latex (Masterbatch)

The procedures earlier reported¹² were followed in the preparation of DBHBT-bound latex. Normal latex (146.37 g) of 34% solid content (i.e., 50 g of solid rubber) was diluted with distilled water and partially deammoniated to a pH between 8.0 and 8.5 by purging with nitrogen. The purged DBHBT-sodium stearate emulsion was added slowly to the stirred latex, which was kept at 60°C. After equilibrating for 15 min, the redox system (AZBN acid-FeSO₄, trisodium pyrophosphate, glucose) was added in aliquots over 2 h. The reaction was continued for another 7 h with the pH being maintained as closely as possible between 8.0 and 8.5 by the addition of dilute ammonia solution.

Table I IPS of Cast Blended Films from C=0 Indices

Blend	20%	40%	50%	60%	80%
IP (h)	13	16	20	—	—

The latex was coagulated by the addition of 1% formic acid, and the coagulum was washed several times with distilled water and dried at 25–30°C *in vacuo*. The dry modified coagulum was hot-extracted with analar absolute ethanol for 48 h in a soxhlet apparatus and dried at a temperature below 40°C *in vacuo*.

Preparation of Cast Films

The cast films were prepared from 2% solutions of various blends of masterbatch and ethanol-extracted natural rubber in benzene. Measured volumes of these solutions were placed on the surface of clean mercury contained in macro petri dishes of about 6 cm diameter and allowed to evaporate at room temperature. To get films that give about 60–80% transmittance, a number of layers of the solution depending on its viscosity were evaporated.

Natural Weathering Experiment

Cast films of the various blends mounted on cardboard paper frames were exposed outdoors in November during the day only. Structural changes were monitored by IR measurements.

Spectrophotometric Measurement

In all the aging experiments, the structural changes taking place in films of different thickness were

Table II Induction Periods (IP) of Cast Blends from Hydroxyl Index

Concentration of Masterbatch	20%	40%	50%	60%	80%
Approx IP (h)	20	23	23	25	28

monitored from the IR spectra¹³ in the 650- to 4000- cm^{-1} region recorded by the conventional double-beam IR spectrophotometer (Perkin-Elmer model 700). For each relevant band the peak intensities were measured by the baseline method. And to eliminate variations in the thickness of the films, the ratios of these peak intensities to that of an invariant reference peak at 3000, 2840, or 1500 cm^{-1} , called indices, were measured and plotted against exposure time.¹³

RESULTS AND DISCUSSION

Effect of Environmental Aging on IR Spectrum

Figure 1 shows the spectral changes in a cast film of DBHBT-modified NR as a function of time under environmental aging. The growth of the broad $-\text{OH}$ (3500 cm^{-1}) and the $\text{C}=\text{O}$ (1760 cm^{-1}) bands are quite noticeable as well as the decay of the $\text{C}=\text{C}$

(1680 cm^{-1}) peak. Pronounced spectral changes are also seen in the region between 700 and 1500 cm^{-1} , particularly in the allylic hydrogen (860 cm^{-1}) band. These spectral changes occur faster than in photo-degradation, and the extracted unmodified NR latex could withstand only a few hours of exposure to the environment.

Effect of Environmental Aging on Carbonyl Index

Figure 2 shows the plots of the $\text{C}=\text{O}$ index against outdoor exposure time for the various cast blends of the masterbatch with ethanol-extracted NR. The corresponding periods during which no change in index occurred, called induction periods (IP), are shown in Table I.

The induction period increases as the concentration of the masterbatch increases up to the 50% blend. Hence the optimum concentration of the masterbatch lies around this concentration. The 60 and 80% blends have no induction period and the latter grows at a faster rate. This fact may indicate that bound DBHBT shows some pro-oxidant action at high concentrations. The absence of induction period in the 60 and 80% blends, even though some exist from the allylic hydrogen index for these blends, may suggest a mechanism of carbonyl generation that does not involve allylic hydrogen abstraction at such high concentrations.

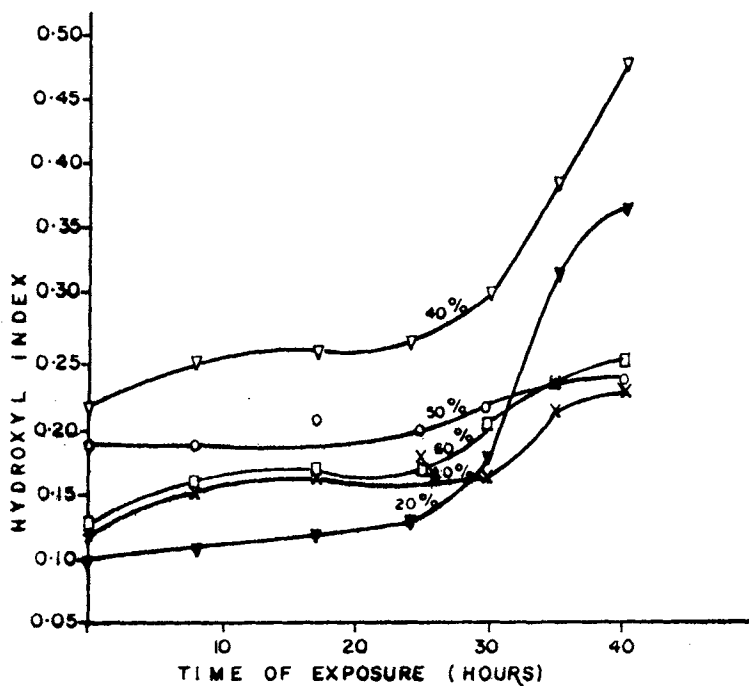


Figure 3 Effect of outdoor exposure on hydroxyl indices of cast blends.

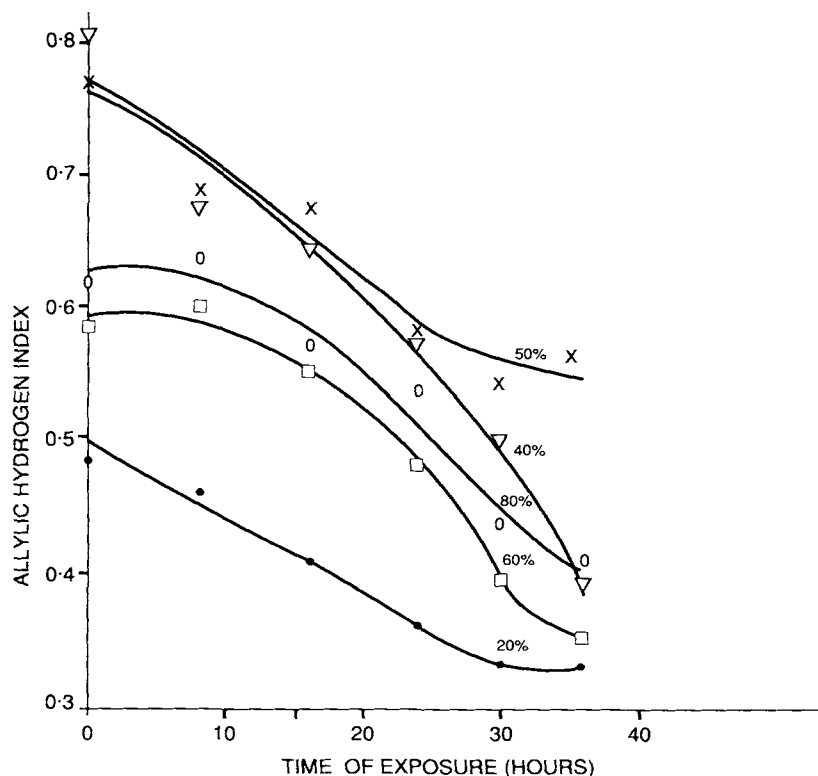


Figure 4 Effect of outdoor exposure on allylic hydrogen indices of cast blends.

As noted earlier¹² the IPS from the $C=O$ index are generally shorter than those from $-OH$ index contrary to the accepted theory of autooxidation. The difference in the minimum concentrations of $C=O$ and $-OH$ perceptible by IR spectra, which are said to be 0.5 and 0.1%, respectively,¹⁴ had been used to explain this contradiction then. It is, however, doubtful whether such large differences in $C=O$ and $-OH$ induction periods can be entirely due to differences in perceptibilities in the IR spectra. Another likely explanation is that natural rubber, in the presence of bound DBHBT, produces $C=O$ groups through pathways not involving $-OH$ or $-OOH$ groups. The absence of induction period for the 60 and 80% blends from the carbonyl index in spite of their large IPS of approximately 25 and 30 h, respectively, from the $-OH/-OOH$ index strongly supports this suggestion.

The IPS, where they exist, are generally shorter compared with their UV degradation counterparts because other degradation agents are involved in environmental aging in addition to UV radiation.

Effect of Environmental Aging on the Hydroxyl Indices

Figure 3 shows plots of hydroxyl indices against exposure time for the different blends. All the blends

show some induction period, which are shown in Table II.

The induction periods are found to increase with increase in the concentration of the masterbatch, and the rate of growth of the $-OH$ group after the IP appears to decrease with increase in concentration of masterbatch. This indicates that bound DBHBT may have some antioxidant activity that is approximately proportional to the concentration of masterbatch. This may involve both UV screening and hydroperoxide decomposition, especially at higher concentrations.

The IPS are longer than those based on other indices for each blend. And for the total exposure time of 40 h, all the blends show some retardation but no decay. This may indicate that the generation of $C=O$ groups is not related to the generation of $-OH$ groups or dependent on it as was pointed out earlier in the discussion. For example, while the generation of $-OH$ did not commence after 20 h for

Table III Induction Periods from Allylic Hydrogen Indices for Cast Blends

Blend	20%	40%	50%	60%	80%
IP (h)	—	—	—	5	8

the 80% blend, the production of C=O group had gone on throughout the period. A plausible explanation is that the —OH index exclusively represents the hydroxyl group, which is known to be one of the final degradation products, and not the peroxy group.

Effect of Environmental Aging on Allylic Hydrogen Indices

Figure 4 shows the plots of allylic hydrogen indices of the cast blends against exposure time. Unlike in their UV degradation counterparts¹² the blends with 60 and 80% of the masterbatch show little but remarkable induction periods that, in agreement with the accepted theory of photooxidation of pure natural rubber, are shorter than those from the hydroxyl index, which are shown in Table III.

The corresponding results from the carbonyl index do not, however, show the corresponding induction period. This may suggest, as was earlier stated, a mechanism of carbonyl group generation that is neither related to allylic hydrogen abstraction nor to hydroxyl group generation. After the induction period (approximately 10 h), all the blends lost their allylic hydrogen at about the same rate.

CONCLUSION

Latex-bound DBHBT protects NR latex against environmental degradation with an optimum masterbatch concentration of about 50%. The formation of C=O groups by some pathways independent of

—OH group and allylic hydrogen atoms has been suggested in the natural weathering of DBHBT-modified and unprocessed natural rubber.

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