Polymer Bulletin 6, 175-181 (1981)

Polymer Bulletin

Effect of Copper Chelates on U.V. Stability of Butyl Rubber and SBR Rubber

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ABSTRACT

An investigation of the photo-oxidative degradation and stabilization of IIR and SBR in the temperature range of 258 to 313°K in air with a monochromatic light of 366 nm in the absence and presence of various concentrations of the different copper chelates has been described. The stabilizer performance in IIR and SBR was accessed by carbonyl index and quantum yield measurements. The changes of IIR and SBR during the irradiation with an ultra-violet light (366 nm) have been conducted by viscometrically and actinometric techniques. Irradiations were conducted on the films at 0, 2, 4, 6, 8, 10, 12 and 14 hours and various parameters were obtained.

INTRODUCTION

The deterioration of rubber and polymeric materials is mainly due to the ultraviolet portion of sun-light reaching the earth. Unsaturated synthetic elastomers, being highly sensitive to oxidation, require the addition of stabilizers to provide protection during processing, storage and end use. SCHMITT et al. (1963) and BHATNAGAR et al. (1976) have studied the photo-oxidation and stabilization in solid state for only a few copolymers in air. The photolytic chain scission for poly(α-methyl-styrene), poly(methyl isopropyl ketone) and butyl rubber have been reported by STOKES et al.(1962), WISSBRUN (1959) and BHATNAGAR et al.(1977) and CHANDRA et al.(1979), respectively.

The stabilizers in common use for elastomers include aromatic amines, phosphites and phenolic anti-oxidants. This report is a summation of investigation on the effectiveness of cuprous-isopropyl dithiophosphate for butyl rubber and copper(II) bis(pyrrole-isopropanolamine) for poly(styrene-co-butadiene). The optimum concentrations for both the stabilizers which would achieve a saturation limit in photo-stabilization of both the elastomers have been determined. The carbonyl index and quantum yield for

0170-0839/81/0006/0175/$01.40

random chain scission have also been determined.

EXPERIMENTAL

(i) Materials: Butyl rubber [IIR], a copolymer of isobutylene (96.5%) and isoprene, and poly(styrene-co-butadiene) [SBR], a copolymer of styrene (23.5%) and butadiene, supplied through the courtesy of M/s. Swastic Rubber Company, Poona and synthetic Chemicals Ltd., Bariely, respectively, were cut into small pieces and subjected to acetone and methanol extraction for 75 hours in a soxhlet. The samples were purified by SINGH (Commun.), dried in vacuo to a constant weight and preserved in black pointed desiccator at room temperature. The chelates, cuprous di-isopropyl dithiophosphate [CDIP] and copper(II) bis(pyrrole-isopropanolamine) [CPIA] were synthesised according to literature procedures of BURN (1966) and SYAMAL et al.(1975). SINGH et al. (1981) have described the method of rubber film (215μ) preparation, incorporation of the stabilizers into film matrix, the method of film dissolution and photoirradiation with a monochromatic light of 366 nm wavelength.

(ii) Procedures: The unirradiated and irradiated films in the absence and presence of the stabilizer were dissolved in chlorobenzene (A.R. grade). Viscosity measurements were carried out in a Ubbelohde viscometer at 30.0 ± 0.05°C and intrinsic viscosities $[\eta]$ were calculated for both, IIR and SBR solutions. Film solutions were separately pipetted out into the viscometer and sufficient time is given for thermal equilibrium. Flow-times were determined for chlorobenzene and for IIR and SBR solutions separately. Flow-times of rubber solutions were determined at five different concentrations. The quantum yields for photo-oxidative degradation and stabilization were determined with potassium ferri-oxalate actinometry.

RESULTS AND DISCUSSION

The intrinsic viscosities $[\eta]$ of the irradiated films in the absence and presence of 0.1 wt.-% CDIP in IIR and 0.1 wt.-% CPIA in SBR in the temperature range of 258 to 318°K in air were determined by extraploting reduced viscosities to zero concentration.

Table 1 shows that $[\eta]_t$ decreases as a function of irradiation time for IIR and SBR films irradiated in the absence and presence of 0.1 wt.% CDIP in IIR and 0.1 wt.% CPIA in SBR as a photostabilizer in air at 288°K with a light intensity flux of 1.68×10^{-8} einstein sec.$^{-1}$ cm^{-2}. The table shows a rapid decrease in $[\eta]_t$ initially which then slows down and the decrease in $[\eta]_t$ is greater of the irradiated film in the absence of the stabilizers as compared with the corresponding values of IIR and SBR films in its presence. This indicates that CDIP retards degradation of IIR and CPIA of SBR. The initial rapid drop is due to scission of weak links. JELLINEK et al. (1970) and CAMERON et al. (1962) also have contended that initial change in $[\eta]_t$ in such cases is due to the scission of weak bonds by the attack of oxygen. There is increase in $[\eta]_t$ at longer irradiations suggesting that crosslinking predominates at longer exposures.

TABLE 1

Intrinsic viscosities $[\eta]_t$ in dl.g^{-1} for photo-oxidative degradation and stabilization of IIR and SBR in the absence and presence of 0.1 wt.-% of CDIP and CPIA,respectively,at 288°K in air.

Light intensity flux = 1.68×10^{-8} einstein sec.$^{-1}$ cm.$^{-2}$

Irradiation wavelength (λ) = 366 nm.

Time of irradiation (hrs)	IIR	IIR + CDIP	SBR	SBR + CPIA
0.0	1.31	1.31	2.48	2.48
2.0	1.23	1.27	2.39	2.43
4.0	1.17	1.23	2.31	2.34
6.0	1.10	1.18	2.19	2.23
8.0	1.03	1.13	2.10	2.15
10.0	0.98	1.09	2.03	2.09
12.0	0.97	1.10	1.97	2.11
14.0	0.98	1.11	1.96	2.13

Quantum yields were determined by potassium ferrioxalate actinometry. Quantum yield for chain scission is given by:

$$\phi_{cs} = \frac{\left[\left([\eta]_o/[\eta]_t\right)^{1/\alpha} - 1\right] m}{\bar{M}_{no}\, I} \qquad .. \quad (1)$$

where ϕ_{cs} is the quantum yield, $[\eta]_o$ and $[\eta]_t$ are the intrinsic viscosities of the unirradiated and irradiated films, respectively; α is the viscosity expansion factor, m is the weight of irradiated film, $\bar{M}_{no}$ is the number average molecular weight of the polymer before irradiation and I is the intensity of the irradiation in einstein. AMERIK et al. (1971) have shown that for small changes in viscosities:

$$\left([\eta]_o/[\eta]_t\right)^{1/\alpha} \approx \bar{M}_{no}/\bar{M}n \qquad .. \quad (2)$$

The viscosity average molecular weight $\bar{M}_o$ of irradiated IIR and SBR in the absence and presence of different stabilizers in chlorobenzene were calculated from the experimentally determined values of $[\eta]$ at 30° ± 0.05°C using the following relations:

$$[\eta] = 6.83\text{x}10^{-4}\ \bar{M}_v^{0.56} \qquad \text{(IIR + CDIP system)} \quad .. (3)$$

and

$$[\eta] = 30.46\text{x}10^{-5}\ \bar{M}_v^{0.71} \qquad \text{(SBR + CPIA system)} \quad .. (4)$$

BAMFORD et al. (1958) have converted $\bar{M}_v$ to $\bar{M}_n$ by using the relation:

$$\frac{\bar{M}_v}{\bar{M}_n} = \left[\frac{\Gamma(3+a)}{2(1+a)}\right]^{1/a} \qquad .. (5)$$

where $\Gamma(3+a)$ is the gamma function of (3+a) and a is the exponent in Mark-Houwink's relation.

The quantum yields in the absence and presence of CDIP in IIR and CPIA in SBR as a function of temperature is given in Figure 1. The quantum yield increases with increasing temperature which is probably due to the increased mobility of the polymer chain at higher temperature. The figure also shows that larger quantum yields are of base IIR and SBR at all temperatures and the smaller are of stabilizers incorporated in the film matrix where UV absorption occurs at CDIP in IIR and CPIA in SBR. A saturation limit in photostabilization is achieved at 0.7 wt.-% of CDIP in IIR and 0.8 wt.-% CPIA in SBR. The value of quantum yield, less than unity, clearly indicates that the number of moles of degradation products are less than the number of photon absorbed by the polymer.

The lifetimes of IIR and SBR films containing various concentrations of CDIP and CPIA, respectively are shown in Figure 2. Increasing the concentration beyond 0.7 wt.-% CDIP in IIR and 0.8 wt.-% CPIA in SBR, brings a saturation limit in photo-stabilization. Figure 1 also confirms that saturation protective action in UV stability is reached at the above mentioned concentrations.

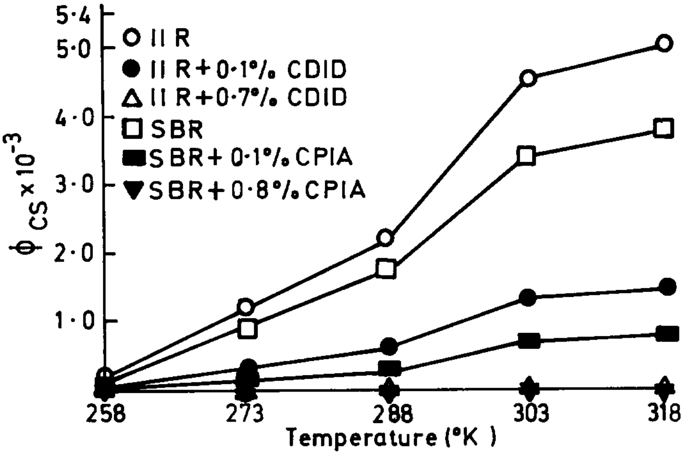

Fig. 1. Quantum yields for photo-oxidative degradation and stabilization of IIR and SBR in the absence and presence of stabilizer versus temperature

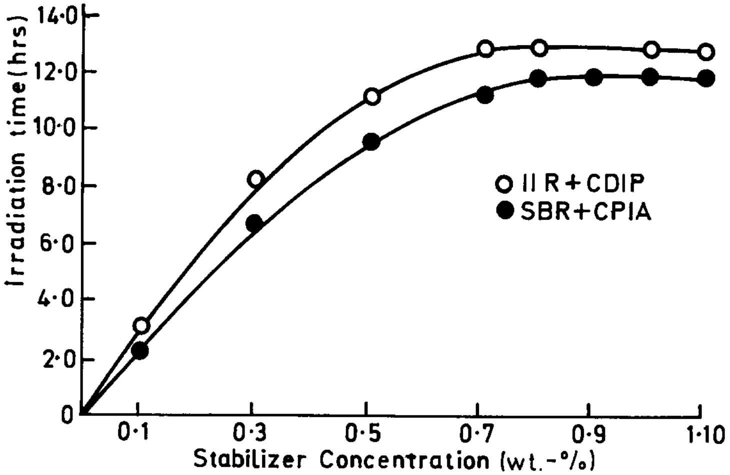

Fig. 2. Effect of stabilizer concentration on film photostabilization

The rate of photo-oxidative degradation was measured by means of a carbonyl index at 1721 cm^{-1} using a Perkin-Elmer (Model 21) infrared spectrophotometer:

$$\text{Carbonyl index} = [(\log I_o/I_t)/d] \times 100 \qquad .. \quad (6)$$

where I_o is the intensity of incident light, I_t is the transmitted light intensity and d is the film thickness in microns. Table 2 shows that the contents of carbonyl index of the irradiated film is lower in the presence of 0.1 wt.-% CDIP in IIR and 0.1 wt.-% CPIA in SBR as compared to the corresponding values of base IIR and SBR at 288°K.

TABLE 2

Carbonyl index [CI] for photo-oxidative degradation and stabilization of IIR and SBR in the absence and presence of 0.1 wt.% of CDIP and CPIA, respectively at 288°K in air.

Light intensity = 1.68×10^{-8} einstein $sec.^{-1}$ $cm.^{-2}$.
Irradiation wavelength (λ) = 366 nm.

Time of irradiation (hr)	IIR ($CI \times 10^{-2}$)	IIR+CDIP ($CI \times 10^{-2}$)	SBR ($CI \times 10^{-2}$)	SBR+CPIA ($CI \times 10^{-2}$)
0.0	0.00	0.00	0.00	0.00
2.0	0.16	0.09	0.11	0.04
4.0	0.21	0.12	0.15	0.08
6.0	0.31	0.17	0.23	0.13
8.0	0.43	0.31	0.36	0.21
10.0	0.54	0.39	0.49	0.32
12.0	0.63	0.47	0.58	0.44
14.0	1.12	0.86	1.03	0.74

Thus CDIP and CPIA stabilize IIR and SBR, respectively, by interference with the propagation reaction by absorption of UV light and decomposition of the macromolecule peroxides and hydroperoxides. By minimizing the light energy absorbed by the polymer, the primary photochemical processes are prevented. In addition to this the chelates inhibit the initiation process by electron transfer and formation of charge-transfer inert complexes.

ACKNOWLEDGEMENTS

The author wishes to thank Prof. A. Syamal for providing facilities and helpful discussions. The financial support for this work by C.S.I.R. New Delhi is gratefully acknowledged.

REFERENCES

AMERIK, Y. and GUILLET, J.E., Macromol., 4, 375 (1971)

BAMFORD, C.H., BARB, W.G., JENKINS, A.D. and ONYON, P.F., The Kinetics of Vinyl Polymerisation by Radical Mechanism, Butterworths Scientific Publications, London, 301 (1958)

BHATNAGAR, H.L. and CHANDRA, R., Ind.J.Chem., 14A, 469 (1976)
BHATNAGAR, H.L. and CHANDRA, R., Ind.J.Technol., 15, 318 (1977)
BURN, A.J., Tetrahedron, 22, 2153 (1966)
CAMERON, G.G. and GRASSIE, N., Makromal.Chem., 53, 72 (1962)
CHANDRA, R. and SINGH, R.P., Ind.Chem.J., 13, 13 (1979)
JELLINEK, H.H.G. and FLAGSMAN, F., J.Polym.Sci., 8, 711 (1970)
SCHMITT, R.G. and HIRT, R.C., J.Appl.Polym.Sci., 7, 1565 (1963)
SINGH, R.P., CHANDRA, R. and SYAMAL, A., Proc.Ind.Acad. Sci., 90, 93 (1981)
SINGH, R.P., Polym.Photochem. (Commun.)
STOKES, S. and FOX, R.B., J.Polym.Sci., 56, 507 (1962)
SYAMAL, A. and KALE, K.S., Curr.Sci., 44, 256 (1975)
WISSBRUN, K.F., J.Am.Chem.Soc., 81, 58 (1959)

Received September 3, 1981
Revised and accepted November 17, 1981