

Effect of Vulcanization Systems and Antioxidants on Discoloration and Degradation of Natural Rubber Latex Thread Under UV Radiation

JAIMON K. KURIAN, N. R. PEETHAMBARAN, K. C. MARY, BABY KURIAKOSE

Rubber Research Institute of India, Kottayam-9, Kerala, India

Received 9 November 1999; accepted 14 December 1999

ABSTRACT: The effect of accelerator combinations and antioxidants on UV radiation degradation of natural rubber (NR) latex thread with a conventional and efficient vulcanization system is presented. Zinc diethyl dithiocarbamate (ZDEC), zinc dibutyl dithiocarbamate (ZDBC), zinc mercaptobenzothiazole (ZMBT), and tetramethyl thiuram disulfide (TMTD) were used as accelerators. The antioxidants used were reaction products of butylated *p*-cresol and dicyclopentadiene (Wingstay-L), Tris-nonylated phenyl phosphite (Crysol EPR 3400), styrenated phenol (SP), and polymerized 1,2-dihydro 2,2,4-trimethyl quinoline (HS). The thread samples were exposed to UV radiation and the appearance and physical properties of the thread were examined. The results indicated that the threads having ZDBC + ZDEC and ZDBC + ZMBT combinations as accelerators are more resistant to UV radiation than the thread having the ZDEC + ZMBT combination. The antioxidants Wingstay-L and SP + HS are effective in retaining the physical properties of the thread after UV exposure, and Crysol EPR 3400 is better in reducing discoloration. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 304–310, 2000

Key words: latex thread; accelerators; antioxidants; UV radiation; degradation; discoloration

INTRODUCTION

The properties of natural rubber (NR) latex thread mainly depend on the vulcanization system and antioxidant used in its production. The properties of the thread set out in IS:14424-1997 standard include the modulus, tensile strength, elongation at break, and resistance to degradation.¹ The modulus of the thread is very critical for its application in textiles.² The above properties of the thread are controlled to a great extent by the vulcanization system, which can be a conventional type using elemental sulfur (CV sys-

tem) or a system involving a sulfur donor accelerator (EV system).^{3,4} In order to improve the technical properties of the thread, different accelerator combinations are used and vulcanizates containing binary accelerator systems are reported to give superior physical properties.^{5–7}

NR latex thread is more vulnerable to degradation than other latex products because of its low bulk and large surface area. Degradation of the thread is caused by heat, light, oxygen, ozone, detergents, and so forth. The effect of heat and oxygen on the degradation aspects of the thread was already investigated in detail,⁸ but little was reported on the effect of light on the degradation of threads. It is reported that the UV radiation in sunlight causes discoloration and degradation of rubber products.^{9,10}

Correspondence to: N. R. Peethambaran.

Journal of Applied Polymer Science, Vol. 78, 304–310 (2000)
© 2000 John Wiley & Sons, Inc.

Table I Formulation of Latex Compounds: Accelerator Combinations

	CV System			EV System	
	CV ₁	CV ₂	CV ₃	EV ₁	EV ₂
60% Centrifuged NR latex	167	167	167	167	167
10% Potassium hydroxide solution	2	2	2	2	2
10% Potassium laurate solution	0.5	0.5	0.5	0.5	0.5
50% Sulfur dispersion	3.6	3.6	3.6	0.6	0.6
50% ZDEC	2.0	—	2.0	1.0	—
50% ZDBC	—	2.0	1.0	—	1.0
50% ZMBT	1.0	1.0	—	—	—
50% TMTD	—	—	—	4.0	4.0
20% Thiourea solution	—	—	—	3.5	3.5
50% Zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0

ZDEC, zinc diethyl dithiocarbamate dispersion; ZDBC, zinc dibutyl dithiocarbamate dispersion; ZMBT, zinc 2-mercaptobenzothiazole dispersion; TMTD, tetramethyl thiuram disulfide dispersion.

The present work presents the results of a systematic study on the effect of accelerator combinations and antioxidants on UV degradation of NR latex threads with conventional and efficient vulcanization systems.

EXPERIMENTAL

Centrifuged (60%) high ammonia type NR latex conforming to BIS 5430-1981 was used. Latex compounds were prepared according to the formulations given in Table I and the compounding ingredients used were of commercial grade. The latex was first stabilized by adding potassium hydroxide and potassium laurate solutions. The other compounding ingredients were

added as dispersions or emulsions. The compounds were then matured at 30°C for 96 h and sieved through a 100-mesh sieve. Each compound was then run on a pilot plant for thread manufacture through a 0.6-mm diameter glass capillary using 20% formic acid as the coagulant. The thread was then washed in hot water at 70°C, dried in a hot chamber at 90°C, wound on wooden frames, and vulcanized in boiling water. The threads with the conventional cure systems were vulcanized for 60 min, those with the efficient cure systems were vulcanized for 90 min, and they were finally dried in an air oven at 60°C. Cast latex 1-mm thickness films were also prepared from each latex compound. The films were then vulcanized in boiling water and dried as in the latex thread samples.

Table II Appearance and Physical Properties of Latex Thread Before and After UV Exposure

Properties	CV ₁				CV ₂				CV ₃			
	UV Irradiation Time (h)				UV Irradiation Time (h)				UV Irradiation Time (h)			
	0	24	48	96	0	24	48	96	0	24	48	96
Discoloration	Nil	Light yellow	Light yellow	Light yellow	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Physical properties												
Modulus (300%) (MPa)	1.6	1.57	1.54	1.1	2.3	2.2	2.2	1.90	2.1	2.2	2.1	2.0
Tensile strength (MPa)	23	20	17	8.75	22	17	16	13.1	21	18	16	15
Elongation at break (%)	1560	1500	1454	1192	1300	1280	1223	1039	1310	1250	1240	1091

Table III Appearance and Physical Properties of Latex Thread Before and After UV Exposure

Properties	EV ₁				EV ₂			
	UV Irradiation Time (h)				UV Irradiation Time (h)			
	0	24	48	96	0	24	48	96
Discoloration	Nil	Slightly yellow	Slightly yellow	Slightly yellow	Nil	Nil	Nil	Nil
Physical properties								
Modulus (300%) (MPa)	1.2	1.25	1.06	1.04	1.6	1.44	1.2	1.1
Tensile strength (MPa)	20	19	15	12	19	19	18	15
Elongation at break (%)	1590	1580	1550	1285	1550	1500	1403	1330

Portions of the thread and the film samples were then exposed to UV radiation from a UV source (Philips-TLD, 30 W, Holland) for 24, 48, and 96 h. The effect of UV light on the color and tensile properties of the thread was then examined. The color was graded visually and the tensile properties of the thread determined according to ASTM D412-98 using an Instron D-4411 universal testing machine. The thread and the film

samples after 24-h exposure to UV radiation were also subjected to heat aging at 100°C for 22 h, and its effect on color and tensile properties was determined. The film samples were tested for measuring the changes in crosslink density by the method suggested by Ellis and Welding.¹¹ The results are given in Tables II–V and Figure 1.

In order to assess the effect of the antioxidants on the degradation of thread samples under UV

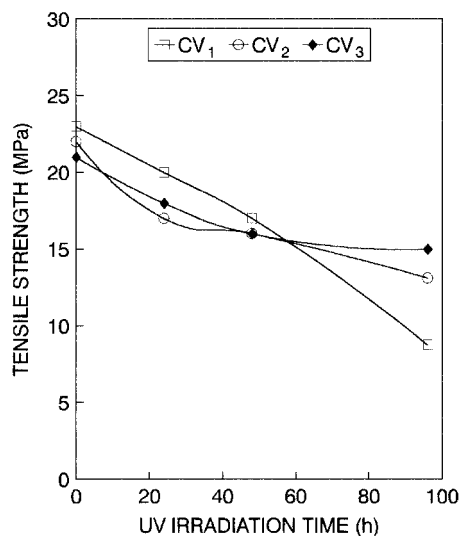
Table IV Appearance and Physical Properties of Latex Thread After 24-h UV Irradiation and Heat Aging at 100°C for 22 h

Formulations	Discoloration	Physical Properties after 24-h UV Exposure and Aging		
		Modulus (300%) (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
CV ₁	Yellow	1.0	6	1200
CV ₂	Yellow	2.0	12.5	1250
CV ₃	Yellow	1.95	12	1200
EV ₁	Yellow	1.25	9.5	1500
EV ₂	Yellow	1.3	13	1400

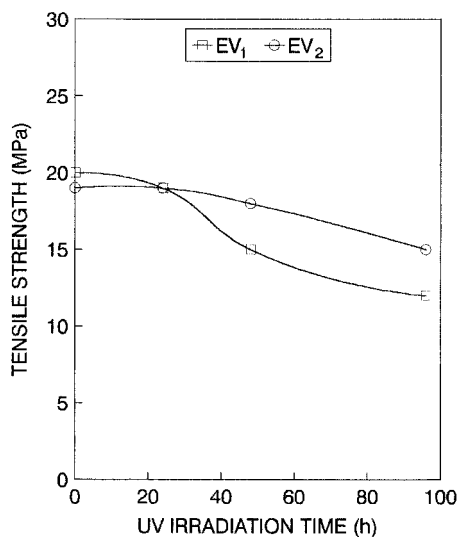
Table V Changes in Crosslink Density After 24-h UV Irradiation and Heat Aging at 100°C for 22 h

Formulations	Swell Index		
	Before UV Irradiation	After 24-h UV Irradiation	After 24-h UV Irradiation and Aging
CV ₁	3.9	3.9	4.4
CV ₂	3.8	3.6	3.8
CV ₃	3.9	3.8	3.9
EV ₁	4.7	4.6	5
EV ₂	4.8	4.6	4.8

The swell index is the weight in grams of benzene absorbed per gram of the sample.



(a)



(b)

Figure 1 The effect of UV irradiation on the tensile strength with different accelerator combinations.

radiation, two typical mixes (CV₁ and EV₁) were selected. Latex compounds containing each of the antioxidants Wingstay-L (reaction product of butylated *p*-cresol and dicyclopentadiene), Tris-nonylated phenyl phosphite (Crystol EPR 3400), styrenated phenol (SP), and polymerized 1,2-dihydro 2,2,4-trimethyl quinoline (HS) were prepared according to the formulations given in Table VI. The thread samples were then prepared as described above and subjected to UV radiation for 24, 48, and 96 h. The color and tensile properties

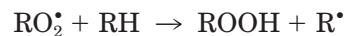
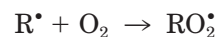
were then examined as described earlier. The results are given in Table VII and Figure 2.

RESULTS AND DISCUSSION

Effect of Accelerator Combinations

The properties of latex thread samples with different accelerator combinations before and after exposure to UV radiation are given in Tables II and III. It is observed that there is no discoloration for all the thread samples before exposure to UV light. It is also evident that the modulus of the thread produced using zinc dibutyl dithiocarbamate (ZDBC) + ZMBT and ZDBC + zinc diethyl dithiocarbamate (ZDEC) combinations is higher than that of the ZDEC + ZMBT combination in the conventional system. In the efficient system the tetramethyl thiuram disulfide (TMTD) + ZDBC combination is also better than the TMTD + ZDEC combination for attaining higher modulus for the threads. This is attributed to the higher activity of ZDBC in crosslink formation as reported earlier.² The values of the swell index, which is a measure of crosslink density of the cast latex film samples given in Table V, also support this. It was also observed that the sample containing the ZDEC + ZMBT combination in the CV system turned light yellowish more than the thread sample containing the TMTD + ZDEC combination on UV irradiation. The thread with the other accelerator combinations retained almost their original color. We also observed that all the thread samples turned slightly opaque on UV exposure, and this may be due to surface oxidation.

During UV irradiation chain scission may occur as a result of the following reactions^{10,12}:



The importance of hydroperoxide in the photooxidation process is well established and the rate is proportional to the initial hydroperoxide

Table VI Formulation of Latex Compounds: Antioxidants

	CV System			EV System		
	CV _{1a}	CV _{1b}	CV _{1c}	EV _{1a}	EV _{1b}	EV _{1c}
60% Centrifuged NR latex	167	167	167	167	167	167
10% Potassium hydroxide solution	2	2	2	2	2	2
10% Potassium laurate solution	0.5	0.5	0.5	0.5	0.5	0.5
50% Sulfur dispersion	3.6	3.6	3.6	0.6	0.6	0.6
50% ZDEC	2.0	2.0	2.0	1.0	1.0	1.0
50% ZMBT	1.0	1.0	1.0	—	—	—
50% TMTD	—	—	—	4.0	4.0	4.0
20% Thiourea solution	—	—	—	3.5	3.5	3.5
50% Zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0	1.0
50% Wingstay-L dispersion	2	—	—	2	—	—
50% Crystol EPR 3400 emulsion	—	2	—	—	2	—
50% Antioxidant (SP emulsion + HS dispersion)	—	—	2	—	—	2

ZDEC, zinc diethyl dithiocarbamate dispersion; ZMBT, zinc 2-mercaptobenzothiazole dispersion; TMTD, tetramethyl thiuram disulfide dispersion.

concentration.¹³ The protective action of a chemical against UV light depends on several factors such as enhanced catalytic activity for hydroperoxide decomposition, UV absorption and deactivation of the absorbed light, better light stability, and increased solubility of the chemical in the polymer. In the region of 290–350 nm, which is the critical region of the sun's spectrum responsible for sensitization of photooxidation, ZDEC is reported to absorb much less light. In addition to this, ZDBC has a better solubility in NR because of its higher alkyl chain length compared to ZDEC. The action of ZMBT as a catalyst for decomposition of hydroperoxide is very much dependent on the molar ratio of the hydroperoxide to ZMBT.¹⁴ At lower ratios, ZMBT is reported to have a prooxidant effect. Hence, the higher degradation effect of the ZDEC + ZMBT combination over that of ZDBC + ZMBT could be attributed to the combined effect of the lower solubility of ZDEC in NR, its lower level of UV absorption, deactivation of the absorbed light, and the higher prooxidant activity of ZMBT under UV irradiation. Furthermore, the CV₁ system is slightly more yellow than the EV₁ system after UV exposure and this may be due to the high sulfur content in the former system, which can produce more colored species with other organic ions or groups. ZDBC may be capable of incorporating more sulfur into the crosslinks so that less discoloration and a higher modulus for the thread is obtained.

The effect of UV radiation for longer periods on the physical properties of the thread is depicted in

Figure 1. It can be seen that UV light causes considerable deterioration of the tensile strength of the thread. Among the different accelerator combinations, the ZDBC + ZDEC combination is found to be better in retaining the tensile properties on long-term UV irradiation. In the EV system, TMTD + ZDBC is better than TMTD + ZDEC in retaining the tensile properties. The thread samples with the ZDEC + ZMBT combination showed the most deterioration in the CV system. The combined effect of UV light and heat also indicated that samples containing ZDEC + ZMBT underwent more degradation than the other systems.

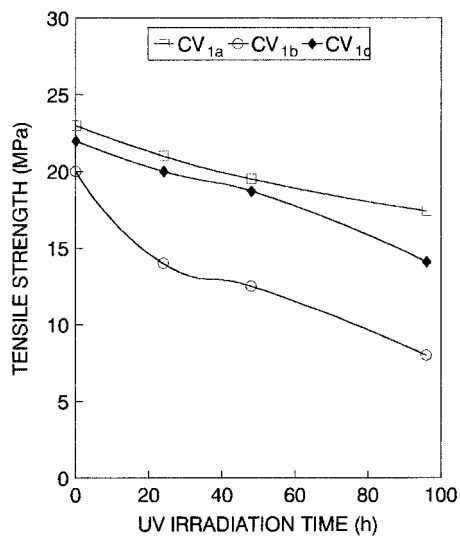
Effect of Antioxidants

The test results of the threads with various antioxidants in the CV₁ and EV₁ compounds are given in Table VII and Figure 2. The results show that the antioxidant (SP + HS) combination imparted discoloration to the thread under UV radiation. But Crystol EPR 3400, which is a phosphite-type antioxidant, reduced the discoloration to a considerable level. This can also be attributed to an action similar to the one described in the case of ZDBC reducing radical formation. However, as an antioxidant it was found to be less powerful at the dosage used in the formulation. Wingstay-L gave better protection to the thread under long-term UV irradiation than the (SP + HS) system, and the effect of antioxidant was more pronounced in the CV system.

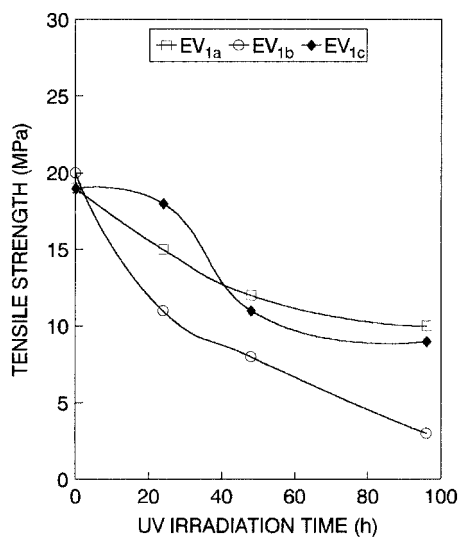
Table VII Appearance and Physical Properties of Thread with Different Antioxidants Before and After UV Irradiation

Properties	Antioxidant	CV ₁					EV ₁				
		UV Irradiation Time (h)					UV Irradiation Time (h)				
		0	24	48	96	96	0	24	48	96	
Discoloration	Wingstay-L	Nil	Light yellow	Light yellow	Light yellow	Light yellow	Nil	Slightly yellow	Slightly yellow	Slightly yellow	
Physical properties											
Modulus (300%) (MPa)		1.58	1.57	1.20	1.05	1.25	1.40	1.15	1.0		
Tensile strength (MPa)		23	21	19.5	17.4	19	15	12	10		
Elongation at break (%)		1610	1556	1461	1447	1620	1580	1571	1454		
Discoloration	Crystal EPR 3400	Nil	Slightly yellow	Slightly yellow	Slightly yellow	Nil	Nil	Nil	Nil		
Physical properties											
Modulus (300%) (MPa)		1.20	1.30	1.14	1.06	1.28	1.0	0.9	0.4		
Tensile strength (MPa)		20	14	12.5	8.0	20	11	8.0	3		
Elongation at break (%)		1700	1680	1648	1558	1640	1630	1513	1011		
Discoloration	SP + HS combination	Light yellow	Yellow	Yellow	Yellow	Slightly yellow	Yellow	Yellow	Yellow		
Physical properties											
Modulus (300%) (MPa)		1.50	1.54	1.5	1.35	1.25	1.32	1.30	1.2		
Tensile strength (MPa)		22	20	18.7	14.1	19	18	11	9		
Elongation at break (%)		1650	1670	1499	1551	1630	1500	1450	1425		

Discoloration index: yellow > light yellow > slightly yellow.



(a)



(b)

Figure 2 The effect of UV irradiation on the tensile strength with different antioxidants.

CONCLUSION

In conclusion, we observed that the effect of accelerator combinations on discoloration and degradation of latex threads under UV radiation depends on the type of accelerators. The ZDBC

+ ZDEC and ZDBC + ZMBT combinations were found to be better in giving better color and degradation resistance to the thread than the ZDEC + ZMBT combination under the CV system. Similarly, under the EV system the TMTD + ZDBC is better than the TMTD + ZDEC combination. We also observed that the antioxidants Wingstay-L and (SP + HS) combinations are more effective in retaining the physical properties of the thread than Crystol EPR 3400 under long-term UV irradiation, and the phosphite-type antioxidant Crystol EPR 3400 is better in reducing the discoloration under UV radiation.

The authors are grateful to Dr. N. M. Mathew, Director, Rubber Research Institute of India, and to Mr. K. S. Gopalakrishnan, Director (T and TC), Rubber Board, for their valuable help and encouragement in conducting this study.

REFERENCES

1. IS:14424-1997, Indian Standard, Rubber Threads-Specification; Bureau of Indian Standards, New Delhi.
2. Collins, J. L.; Gorton, A. D. T. *NR Technol* 1984, 15(4), 69.
3. Blackley, D. C. *Polymer Latices*; Chapman & Hall: London, 1997; Vol. 3, p 544.
4. Gorton, A. D. T. *NR Technol* 1975, 6(3), 52.
5. Blokh, G. A. *Organic Accelerators in the Vulcanization of Rubber*; IPST: Jerusalem, 1968; p 299.
6. Collins, J. L.; Gorton, A. D. T. *NR Technol* 1985, 16(3), 52.
7. Dogadkin, B. A.; Shersheev, B. A. *Rubber Chem Technol* 1962, 35(1), 1.
8. Gorton, A. D. T. *NR Technol* 1989, 20(4), 65.
9. Melotto, M. A. *The Vanderbilt Rubber Handbook*, 13th ed.; Ohm, R. F., Ed., R. T. Vanderbilt Company: Norwalk, CT, 1990; p 538.
10. Morton, M. *Introduction to Rubber Technology*; Van Nostrand Reinhold: New York, 1959; p 130.
11. Ellis, B.; Welding, G. N. *Techniques of Polymer Science*; Society of Chemical Industry: London, 1964; Vol. 17, p 46.
12. Saito, Y. *Int Polym Sci Technol* 1995, 22(12), 47.
13. Morand, M. M. E. *J. Rubber Chem Technol* 1966, 537.
14. Scott, G. *Development in Polymer Stabilization—6*; Applied Science Publishers: London, 1983; p 73.