

The Influence of Anilino-Substituted Salicylanilide on the Physicomechanical Properties of Ultraviolet-Aged Natural Rubber

W. M. KHALIFA and M. A. EL-AZMERLY, *National Research Centre, Dokki, Cairo, Egypt*; S. E. MORSI* and S. BARSOUM, *Department of Chemistry, Faculty of Science, University of Tanta, Tanta, Egypt*

Synopsis

The effect of nine derivatives of salicylanilides on the elastic properties of ultraviolet-aged natural rubber have been investigated. The results are compared with similar blends without additives and also with reference samples containing phenyl salicylate. The compounds showed variable effects, but both *o*-Cl and *p*-OCH₃ derivatives showed remarkable effects. They both help in the thermal crosslinking. Also, natural rubber samples containing these derivatives showed remarkable stability in tensile stress, elongation, and swelling.

INTRODUCTION

In a previous communication we have correlated the spectra of salicylanilides with their structure.¹ In this communication we shall report the effects of these compounds on the elastic properties of natural rubber blends.

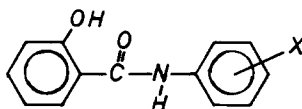
Natural rubber was used in this study since it is a good vehicle for testing photostabilizers because its properties are easily modified by ultraviolet radiation. The possible electronic transitions in natural rubber may result in singlet oxygen addition or it may result in *cis-trans* isomerization at the π -bonds.

EXPERIMENTAL

Materials

Natural rubber (pale crepe) was used to prepare a formulation containing 100 parts natural rubber, 6 zinc oxide, 3.5 sulfur, 0.5 stearic acid, 0.5 mercaptobenzothiazole, and 2 phr of the test stabilizer.

The ultraviolet stabilizers used had the general structure given in formula 1,



Formula 1

General structure of Salicylanilides Used as Ultraviolet Stabilizers

where $x = o$ -Cl (II), H (III), p -Cl (IV), o -OCH₃ (V), m -OCH₃ (VI), p -OCH₃ (VII), p -CH₃ (VIII), p -OH (IX), and m -OH (X).

Phenyl salicylate was used as the reference stabilizer.

Control samples used were of natural rubber without any stabilizer.

* To whom correspondence should be addressed.

Some samples were prepared by using stabilizers on acetone-extracted natural rubber.

Methods

Mixing. All mixes were prepared on a two-roll mill, diameter 470 mm, working distance 300 mm, speed of the slow roll 24 rpm, gear ratio 1.4. In all mixes, the temperature was kept at 30°C. The compounded rubber was left for at least 12 hr before vulcanization. The time of mastication was controlled by measuring the intrinsic viscosity of the raw rubber in benzene at $25 \pm 0.1^\circ\text{C}$ using the Ubbelohde suspended-level viscometer, modified by Ravikov,² and the molecular weight was calculated.³ The average mastication time was about 7 min.

Sample Preparation. Sheets 1 mm thick were made in clean, polished moulds in an electric press. Vulcanization was conducted at 143°C under a pressure of 160 kg/cm². The cured sheets were left for 24 hr, following which standard dumbbell-shaped specimens were cut.

Acetone Extracts. The extracts were prepared according to a method described elsewhere.⁴

Density. The density was determined using the buoyancy method.⁵

Swelling. The swelling was determined volumetrically in benzene in the presence of phenyl- β -naphthylamine (0.5 g PBN/50 ml benzene) at $25 \pm 0.1^\circ\text{C}$.

Molecular Weight Between Crosslinks (\bar{M}_c). This quantity was determined from swelling and density (d) data, using the Flory-Rehner equation⁶⁻⁸:

$$\bar{M}_c = \frac{-dV_0 V_r^{1/3}}{\ln(1 - V_r) + V_r + uV_r^2}$$

where V_0 is the molar volume of the solvent at 25°C , V_r is the volume fraction of the rubber in swollen material, and $u = 0.37$ is the interaction constant⁹ for benzene.

Accelerated Light Aging. An apparatus for testing rubber under accelerated light aging was used.¹⁰ Samples of defined dimensions (length 50 mm, width 6 mm, and thickness about 0.12 mm) were stretched on the apparatus for different deformations from 5 to 200% strain. The shortest failure time of the samples was found at 40% deformation. The source of ultraviolet radiation was a Hanovia lamp (type SH 616 A) with resonance lines of 248–366 nm¹¹ and quantum energies ranging between 3.48 and 5.0 eV. The distance between the light source and samples was 250 mm. The properties of the natural rubber were measured at different irradiation times up to 192 hr.

Physicomechanical Properties. Modulus, tensile strength, and elongation were measured by standard procedures.¹² Different concentrations of 2, 4, 6, and 8 parts stabilizer/100 parts natural rubber (phr) were used. The 2-phr concentration was found to be the most convenient since formulations containing concentrations below this value did not have stabilization effect, and concentrations above this value have impaired the mechanical properties and did not add extra stabilization effects. The optimum vulcanization time was 20 min.

RESULTS AND DISCUSSION

Modulus of Elasticity

Both control and experimental samples containing additives show an increase in the modulus of elasticity with increasing irradiation time. The control sample shows a progressively linear increase; compound VII showed a small rate of increase, whereas compound II showed negligible difference (Fig. 1). Since the elasticity of natural rubber depends on the presence of highly folded chains, an increase in modulus indicates the occurrence of crosslinking reactions. The decrease in extent of folding could result from an increase of crosslinking, a decrease in chain length, or a *cis-trans* isomerization. Both crosslinking and chain scission could go through the intermediate formation of hydroperoxide as a result of singlet oxygen reaction with the double bonds.

There are two observations on the elasticity results. (1) The moduli for nonirradiated samples differ according to the type of additive, and, in general, it is markedly greater in the case of compounds II and VII. (2) Samples of some compounds showed a break in the moduli-irradiation time curves forming two linear parts. The part of higher slope occurs at shorter irradiation times.

At this stage we should differentiate between the thermal effects of additives that should occur during the curing of the natural rubber mixes and those occurring photochemically during ultraviolet irradiation. Thus, by comparison of moduli values for nonirradiated samples, it is shown that formulations containing II and VII have higher values of moduli. This increase is attributed to the extra thermal crosslinking that takes place during curing as a result of the addition of II and VII.

The first parts of the moduli-irradiation time curves, which show higher slopes, are attributed to the acceleration in photostimulated isomerization and crosslinking due to the presence of additives. The second part with smaller slope indicates that the main process occurring at that stage is the photolytic chain scission, which subsequently decreases the extent of folding and thus increase the moduli.

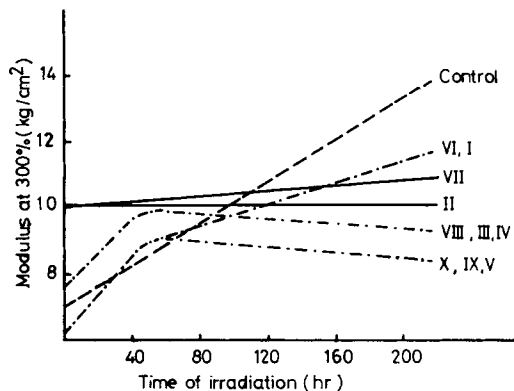


Fig. 1. The influence of ultraviolet aging on the moduli of natural rubber formulations.

Tensile Strength

Tensile strength-radiation time curves are shown in Figure 2. In the control samples an increase towards the maximum followed by a decrease occurs. In the first part, crosslinking and isomerization dominate; both lead to an increase in tensile values. This part is followed by a range in which photolytic chain scission occurs and tensile decreases. The formulation containing I showed an increase in tensile strength with two different rates (Fig. 2). It is well known¹³ that phenyl esters undergo photo Fries rearrangement to ketones. Thus, phenyl salicylate rearranges in ethanol to 37% *o*-hydroxy benzophenone, 42% *p*-hydroxybenzophenone, and 15% polymer. Because of this rearrangement, the crosslinking rate is decreased and crosslinking occurs throughout the irradiation period. The tensile strength results show that the most photoresistant formulations are those containing II and VII.

Percentage Change in Elongation

The percentages of change in elongation are represented in Figure 3; there are four classes of formulations: (1) those resulting in an exponential increase in elongation with increasing irradiation, (2) those giving a linear increase, (3) those possessing an induction time, and (4) those that are stable during the irradiation times used. Thus, the control and formulations containing V, VI, IX, and X belong to class (1), III and VIII belong to class (2), I and IV to class (3), and II and VII to class (4). The elongation increase is due to chain length increases resulting from either decreased linking or recombination of two radical chains. Compounds showing an induction time may indicate that photochemical fatigue in the processes responsible for efficient deactivation of the excited state occur. In I, the photochemical fatigue is represented by the Fries rearrangement that results in the destruction of intramolecular hydrogen-bonded chelate.

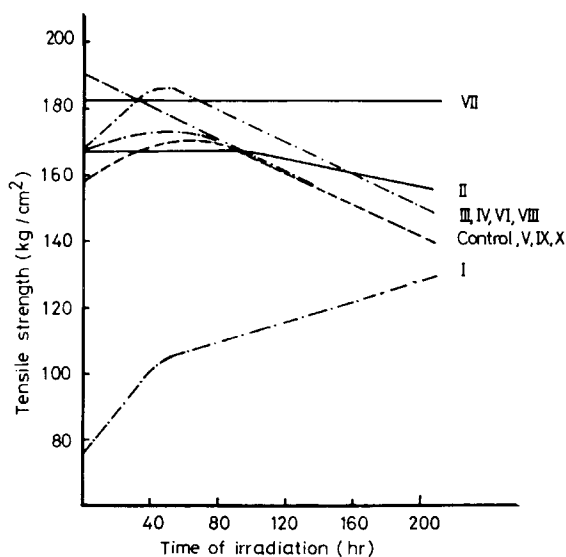


Fig. 2. The influence of ultraviolet aging on the tensile strengths of natural rubber formulations.

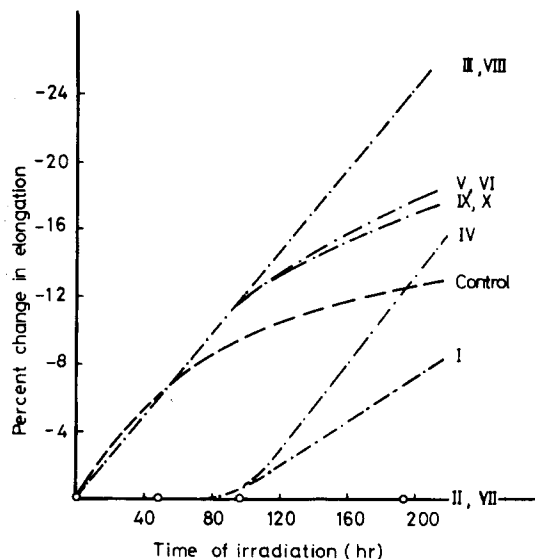


Fig. 3. The influence of ultraviolet aging on the elongation of natural rubber formulations.

Swelling

From the above-mentioned physicochemical measurements, it seemed that the formulations that are most resistant to photodegradation are those containing II and VII. For this reason we have taken samples of formulations containing those compounds together with a control sample and another containing VI for comparison. We have determined the influence of ultraviolet radiation on the amount of absorbed benzene in these samples. The results are represented in Figure 4, which shows that both the control and VI formulations lead to a decrease in swelling time curves down to a minimum that is then followed by an increase. This agrees with the above-mentioned results showing that, at the beginning of irradiation, crosslinking predominates and leads to a decrease,

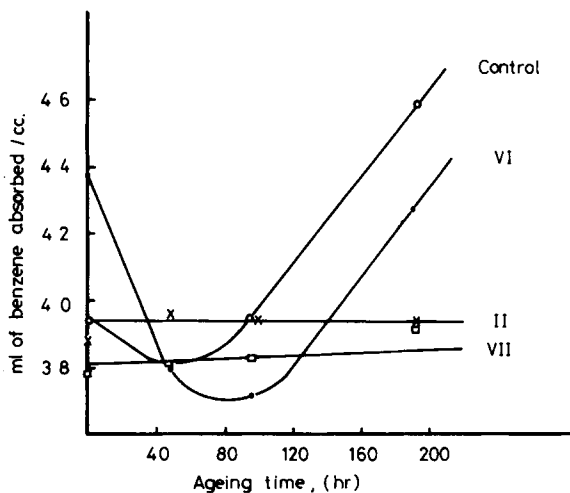


Fig. 4. Swelling vs ageing time for some natural rubber formulations.

whereas in the later stages of irradiation the swelling increase is due to photolysis and degradation. In formulations II and VII, in which thermal crosslinking as well as photostabilization occur, the swelling properties did not show any significant change upon increasing the time of irradiation. The calculated average molecular weights between every two crosslinks show that for the control and for VI the M_c values decrease to a minimum and then increase, whereas those for II and VII do not show any significant change (Table 1). These results are in agreement with all the results given above.

Physicomechanical Tests on Acetone-Extracted Rubber

Since natural rubbers usually contain natural stabilizers, we have carried out a comparison between formulations containing acetone-extracted natural rubber. The results indicate that the control samples failed the test during the irradiation period, whereas those containing II and VII did not (Table II).

CONCLUSION

The results show that the most efficient stabilizers among the anilino-substituted salicylanilides are the *o*-chloro and *p*-methoxy. In general, electron-releasing groups increase the efficiency because they decrease the ionization

TABLE I
Molecular Weight Between Every Two Crosslinks (M_c)

Irradiation time (hr)	Formulation			
	Control	II	VI	VII
0	6363	6289	7530	5996
48	5984	6387	5912	6050
96	6363	6363	5712	6050
192	8198	6385	7267	6130

TABLE II
Physicomechanical Properties of Ultraviolet-Irradiated, Acetone-Extracted Natural Rubber Formulations

	Formulation		
	Control	II	VII
Ingredients			
acetone-extracted natural rubber	100.0	100.0	100.0
zinc oxide	6.0	6.0	6.0
sulfur	3.5	3.5	3.5
stearic acid	0.5	0.5	0.5
<i>o</i> -chlorosalicylanilide	—	2.0	—
<i>p</i> -methoxysalicylanilide	—	—	2.0
Properties after irradiation ^a			
modulus 300% (kg/cm ²)		10.00	10.80
tensile strength (kg/cm ²)		130.00	140.00
elongation at break (%)		600.00	600.00
permanent set (%)		10.00	10.00
swelling (ml/cm ³)		4.83	3.99
M_c		9074.00	6473.00

^a Duration, 192 hr.

potential on the imino nitrogen. The *o*-substituents have an additional effect favoring stabilization, since it involves the intramolecular ring chelate with imino hydrogen. This explains the reason for the enhanced efficiency of the *o*-chloro over the *p*-chloro derivative. In case of the *o*-methoxy group, which possesses a larger van der Waals radius, the anilide and the salicyl moieties may not become coplanar. This will decrease conjugation, and, in this case, the *p*-methoxy is more efficient than the *o*-methoxy derivative.

References

1. M. A. El-Azmerly, S. E. Morsi, R. M. Issa, and S. Barsoum, *Eur. Polym. J.*, **11**, 95 (1975).
2. S. R. Ravikov, *Vysokomol. Soedin.*, **1**, 1558 (1959).
3. S. R. Ravikov, *Methods of Determination of Molecular Weights and Polydispersity of High Molecular Weight Compounds*, Academic, Moscow (1963).
4. ASTM Designation, D 297-61 T, April (1967).
5. ASTM Designation, D 297-55 T, p. 1179 (1958).
6. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943).
7. R. G. Bauman, *J. Appl. Polym. Sci.*, **2**, 328 (1959).
8. R. G. Bauman and J. W. Born, *J. Appl. Polym. Sci.*, **1**, 351 (1959).
9. S. M. Miller, M. W. Spindler, and R. L. Vale, *J. Polym. Sci., Part A*, **1**, 2537 (1963).
10. A. A. Yehia, N. A. Ghanem, and W. D. Khalifa, *Rubber World*, April, 68 (1971).
11. Hanovia, Inc., Lamp Division, Newark, N.J.
12. ASTM Designation, D 412-66 T (1967).
13. D. Bellus and Hrdlovic, *Chem. Rev.*, **67**, 599 (1967).

Received July 30, 1977

Revised April 10, 1978