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THE THERMOOXIDATIVE STABILITY OF AN ISOBUTYLENE-ISOPRENE ELASTOMER

*G. Balázs**, *S. Doszlop**, *O. Biró** and *L. Palotás***

*DEPARTMENT OF PLASTIC AND RUBBER, TECHNICAL UNIVERSITY OF BUDAPEST,
BUDAPEST, HUNGARY
**"TAURUS" RUBBER CO., BUDAPEST, HUNGARY

It has been proved that the basic oxidative stability of butyl elastomer can be evaluated of isothermal calorimetry. Similarly, the effects of ozone and of thermooxidation can be followed by this method. The isothermal curves for the photooxidation of the elastomer gave a complex pattern, so here it seems necessary to use other methods (IR, UC, GPC dissolving/swelling, DTA, etc.) to determine the remaining stability.

Knowledge of the thermooxidative stability of an elastomer is of considerable technical importance in the rubber industry. As this property determines the possible storage conditions of the material, the allowed mixing temperature range during the compounding process and finally the stability of the rubber product are partly governed by the stability of the elastomer.

Nonisothermal DSC and DTA in air or oxygen are popular methods for determining the oxidative stability of elastomers. In our work we attempted to apply isothermal calorimetry (by DSC) to evaluate the basic and the remaining oxidative stability of an elastomer, because as far as we know, this method has not been used earlier in rubber research.

The elastomer was a butyl rubber (IIR), an isobutylene - isoprene copolymer with about 1.2 % isoprene content (Butyl BK, industrial grade).

The isothermal calorimetric measurements were performed with a Perkin-Elmer DSC-2 instrument in a constant (20 cm^3/min) air stream, using samples with identical geometry. The DTA measurements were performed with a Derivatograph-C at heating rate of $V_h = 5$ deg/min.

In addition to the determination of the basic stability of the elastomer, the remaining oxidative stability of samples pre-degraded under known conditions was evaluated, too.

The methods of laboratory aging were the standard ones used in the practice of the rubber industry.

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Thermooxidation: Geer oven; $T = 135^{\circ}$, air atmosphere.
Photooxidation: Xenotest 150.
Ozone treatment: Orec 300, c: 200 pphm.

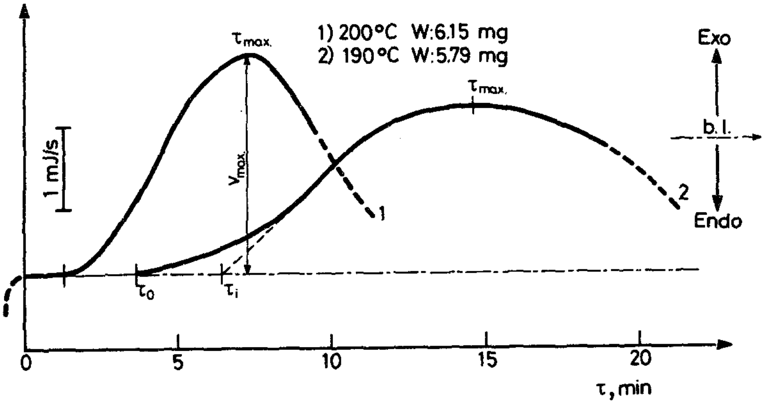

Fig. 1 Oxidation of a "Butyl BK" elastomer

Table 1 The thermooxidative stability of a "Butyl BK" elastomer

Temps of is., °C	τ_0 (min)	τ_i (min)	τ_{max} (min)	$V_{max\ ox.}$, mJ/sg
200	1.4	2.2	7.2	414
190	3.6	6.5	14.5	351
180	23.5	28.6	49.0	223
170	92.6	98.4	128.0	137

$T_{0,\ ox}$ (by Derivatograph): 201°C

The results of the isothermal oxidation of the starting (not pre-degraded) elastomer can be found in Fig. 1 and Table 1. The fast oxidation process at every temperature applied started only after a well-defined induction time (τ_i). The fast oxidation can be due to the accumulation and decomposition of hydroperoxides and the consumption of the antioxidant originally present in the elastomer. Thus, the thermooxidative stability of the elastomer can be characterized at a given temperature by the induction time, and within this time the material may be regarded as a stable one, it can be handled, stored, etc. Further, by measuring τ_i at different temperatures and using the expression $\ln \tau_i$ - $1/T$, some extrapolations can be made to the lower temperature region, not forgetting the rule that the error in evaluating τ_i, the time of stability, increases strongly with increasing difference between the measured and the extrapolated temperature.

The oxidation isotherms contain other important characteristics of the process (τ_{max}, v_{max}), but from a practical point of view τ_i may be considered most useful.

Pre-degraded butyl samples were also evaluated in order to obtain information about the change caused in the original thermooxidative stability by these processes, as the remaining stability would determine, for example, the processability of such a material.

Ozone

Table 2 contains the onset temperatures of oxidation, determined with a derivatograph. Ozone would attack all the polymers containing double bonds, so in this elastomer the isoprene units would be damaged. In response to ozone, the remaining thermooxidative stability of the elastomer decreased, but this was true only after the first few days of ozone aging. For 15 days τ_i decreased, but after 28 days in the ozone chamber τ_i increased. However, 28 days meant a very severe degradation, and we consider that all the double bonds have already reacted with ozone, and thus all those labile hydrogens which support, the most sensitive sites for oxidation have also disappeared.

Table 2 Effect of ozone treatment on the thermooxidative stability of "Butyl BK" elastomer

Time of O_3 treatment (days)	τ_o (min)	τ_i (min)	τ_{max} (min)	$V_{max,\ ox.}$, mJ/sg	$T_{o,\ ox,}$* °C
	23.5	28.6	49.6	223	201
3	11.1	17.0	35.4	311	199
15	9.1	12.0	34.0	193	
28	0 > 60				211

$T_{isotherm}$: 180°C, * Determined by derivatography

Thermooxidation (Table 3)

On increase of the duration of the degradation, the remaining oxidative stability (τ_i) decreased. The derivatograph gave similar results.

Photooxidation (Table 4, Figs 2 and 3)

This process can be considered the most complex one, for the hydroperoxides formed are sensitive to UV light, as can be seen from the results. Even irradiation for 3 days strongly decreased τ_i (τ_i was practically zero at 170°) and a process of oxidation appeared with increasing rate. Only at 150° did the material have some residual stability

Table 3 Effect of thermal treatment ("Geer" oven, $T = 135^\circ$C, air) on the thermooxidative stability of "Butyl BK" elastomer

Time of treatm. (days)	Temp. of isoth., °C	τ_o (min)	τ_i (min)	τ_{max} (min)	V_{max}, mJ/sg	$T_{o,\,ox}$* °C
3	170	67.0	73.5	101.3	203	195
7		12.2	15.4	39.5	192	187
28		2.2	2.6	11.8	49	150
7	180	0	2.2	16.0	294	
	170	12.2	15.4	39.5	192	
	160	26.0	30.0	85.6	132	

* Determined by derivatography

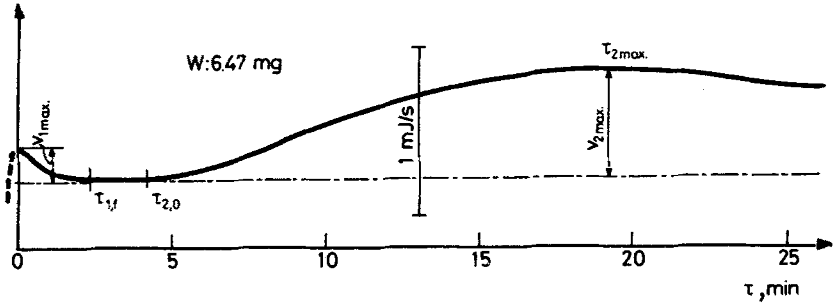

Fig. 2 Oxidative stability (T_{is}: 170°C) of a "pre-degraded" "Butyl BK" elastomer. Irradiation: 7 days/Xenotest

Longer irradiation times gave isotherms with different behaviour. After 7 days (Fig. 2) two more or less separated oxidation processes appeared, while after 28 days only one strong oxidation process was detected, having a continuously decreasing rate at 170° (Fig. 3).

Table 4 Effect of Xenotest irradiation on the thermooxidative stability of "Butyl BK" elastomer

Irrad. time (days)	Temp. of isoth., °C	$\tau_{1,f}$ (min)	$\tau_{2,0}$ (min)	$\tau_{2,i}$ (min)	$\tau_{2,max}$ (min)	$V_{1,max}$, mJ/sg	$V_{2,max}$, mJ/sg	$T_{o,ox}$* °C
3	170		0	0	16.2		174	166
7		2.3	4.0	4.3	19.2	28	96	162
28		5.7				376		143
3	170		0	0	16.2		174	
	160		0	0	32.2		115	
	150		6.0	6.2	45.6		78	

* Determined by derivatography

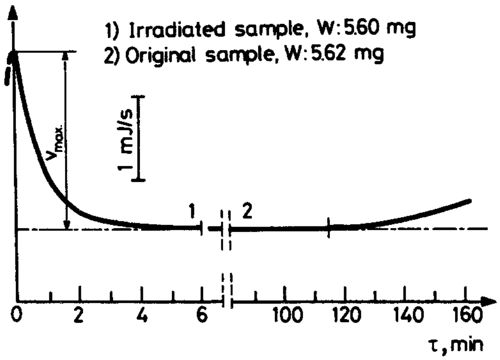

Fig. 3 Oxidative stability (T_{is}: 170°C) of a "pre-degraded" "Butyl BK" elastomer. Irradiation: 28 days/Xenotest

A comparison of the different degradation processes revealed that the butyl elastomer is very sensitive to light, but its stability against ozone attack or thermooxidation seems to be much higher.

Zusammenfassung — Es wurde erwiesen, daß die grundlegende oxidative Stabilität von Butylelastomeren mittels isothermer Kalorimetrie ermittelt werden kann. Analog können mit diesem Verfahren der Einfluß von Ozon und Thermooxidation untersucht werden. Isotherme Kurven für die Photooxidation der Elastomere liefern ein kompliziertes Bild, hier scheint die Anwendung anderer Methoden (IR, UC, GPC, Löslichkeit, Quellvermögen, DTA usw.) erforderlich zu sein, um die verbleibende Stabilität zu bestimmen.