Thermo-oxidative Behaviour of Epoxidised Natural Rubber

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Epoxidised natural rubber (ENR) was specially formulated for improving NR basic properties, namely its resistance to fuels and oils, gas permeability and compatibility with polar elastomers. NR with various degrees of epoxidation was submitted to accelerated ageing tests; its behaviour was observed by means of IR spectroscopy and oxyluminiscence, and its processing characteristics were evaluated in a Brabender Plastograph. The influence of the degree of epoxidation on the thermo-oxidation behaviour was investigated.

rubber exhibits Natural outstanding mechanical properties compared to synthetic rubbers but, due to its high unsaturation, it shows a great reactivity towards various chemical agents, particularly to thermooxidation. These shortcomings may be avoided to some extent by chemical modification of the elastomeric chain by the introduction of polar groups, particularly by epoxidation which is also applicable to other diene elastomers'. By this method, it was intended to diminish gas permeability and increase the resistance to petroleum derivatives to an extent similar to specialpurpose elastomers². Another method involves polymer modification by improving ageing stability.

By increasing the degree of epoxidation, the elastomer becomes polar and its solubility in non-polar solvents is restricted³. Some of the desired properties are augmented with the degree of epoxidation, for instance with 25 mole % epoxy groups there is better compatibility with polar elastomers and, at 50 mole % epoxy units, ENR exhibits a resistance to petroleum derivatives similar to acrylonitrile butadiene rubber and its gas permeability approaches that of butyl rubber. At the same time, ENR is very sensitive to variations in pH; in acid medium, scission of the oxyranic cycle occurs, followed by crosslinking of the elastomer by means of ether bridges, leading to an increase in gel content of ENR^{4.5}.

Studies of the oxidation of ENR^{6,7} confirmed that chemically modified NR, with lower gas permeability and diminished unsaturation, is less prone to attack by oxygen than NR itself; however, during the production of ENR, the antioxidants naturally occurring in NR are lost, and the stability of ENR to thermo-oxidative destruction results from a balance of these factors7. The degradation of vulcanised ENR was proved⁶ to be closely related to the curing system used (conventional, semi-EV, EV); their ageing was accelerated by the by-products resulting in the reaction of the epoxy units with sulphur, leading to an increase in the acidity of the medium.

The thermo-oxidative behaviour of some grades of ENR with various degrees of epoxidation, and the kinetics following the formation and accumulation of oxygenated groups are discussed.

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EXPERIMENTAL

The elastomers studied are:

- Natural rubber, grade RSS-1
- Synthetic polyisoprene, type Carom 2200 (Carom S.A., Romania) containing 95% cis-1,4 units
- Epoxidised natural rubber containing 25 mole % and 50 mole % epoxy units, respectively, ENR-25 and ENR-50 (Malaysia).

Rubber samples were purified by extraction and precipitation in appropriate solvents. Casting films on NaCl windows were prepared from purified elastomers and IR spectra were recorded using a 577 Perkin-Elmer spectrograph, in the region 4000 cm⁻¹ to 600 cm⁻¹. Recordings were made initially and during ageing at 80°C – 120°C; the total duration of thermo-oxidation was enough to ensure 80% absorption of the carbonyl/ carboxyl groups (γ_{co} 1720 cm⁻¹) for each elastomer tested.

The content of hydroperoxy groups was determined by the oxyluminiscence method, the light emission being assigned to the oxidation process. A Harshaw 2000 apparatus (USA) was used in isothermal conditions at 100°C for the oxidation process, 50 s air heating time, with 0.01 g of the investigated substance.

The processing behaviour was evaluated in a Brabender Pl-3S Plastograph (Brabender OHG, Germany), at 100°C, for 20 min, at a shear rate corresponding to 80 rotations/ min; the gel content was also determined.

RESULTS AND DISCUSSION

IR Spectra of ENR

Isoprenic elastomers (natural and synthetic) exhibit characteristic absorption peaks due to the symmetrical and asymmetrical stretching vibrations of CH_2 groups in the range 3000 – 2800 cm⁻¹, of unsaturated CH = CH units as 3025 cm⁻¹ and 1660 cm⁻¹ of substituted unsaturated units at 845 cm⁻¹ and 840 cm⁻¹, the last two peaks being

assigned to the *trans* and *cis* 1,4-isomers, and the absorption at 890 cm⁻¹ corresponding to isopropenyl $-C(CH_3) = CH_2$ groups^{8,9}. In the ENR spectrum, some of these peaks remained unchanged, but significant modifications also occurred. Thus, the peak at 3025 cm⁻¹ (C = C units) exhibited a marked decrease with increasing degree of epoxidation; the same comment may be applied to the 1660 cm⁻¹ peak, as evidenced by the unsaturation reduction following epoxidation. The most affected spectral region as a consequence of epoxidation is that of the backbone unsaturation; in this case, an important diminution in the 840 cm^{-1} absorption band (*cis*-1,4 units) and the corresponding increase in the 875 cm⁻¹ absorption peak which was assigned to the epoxy groups placed on the polymer backbone¹⁰ were noticed. Modifications in the 900 - 800 cm⁻¹ region of IR spectra are illustrated in *Figure 1*.

Thermo-oxidation of ENR

The induction time for thermo-oxidation in air was measured at various temperatures. The kinetic curves in Figure 2 illustrate the formation and accumulation of C = O groups at a degradation temperature of 100°C. From the kinetic curves, the induction time was deduced and the oxidation rate and activation energy of the overall degradation process were computed (Table 1).

The degradation process followed firstorder kinetics in the initial stage; as the oxidation progressed, the reaction order approached zero, indicating an auto-catalytic subsequent stage.

The data show a reduction of the resistance to degradation of ENR-25 compared with NR; the increase in the degree of epoxidation up to 50 mole % was of little significance.

During the thermo-oxidation process, the oxygen in singlet active form reacts with the hydrocarbon chain of the polyisoprene, resulting in various hydroperoxide structures evidenced by the new absorption bands appearing in the region 3400 - 3380 cm⁻¹ and



Wave number, γ (cm⁻¹)

Figure 1. Modifications in 900-800 cm⁻¹ region of IR spectra.

Dubber	Induction period (min)			Rate constant at 100°C	Activation energy
Rubber	80°C	100°C	120°C	(min ⁻¹)	(kJ. mol ⁻¹)
NR	900	340	9 0	2 × 10 ⁻⁴	84
IR	700	120	70	3 × 10 ⁻⁴	75
ENR-25	580	90	10	1.8×10^{-2}	34
ENR-50	320	60	15	2.4×10^{-2}	38

TABLE 1. KINETIC DATA FOR THE THERMO-OXIDATIVE DESTRUCTION OF THE RUBBERS STUDIED

assigned to -OOH groups; subsequently, the band intensity decreases and a band appears in the region 1720 cm⁻¹ assigned to C = Ogroups, a new band also appears at 3445 cm⁻¹ attributed to -OH groups. In this connection, the chemiluminiscence intensity is dependent on the concentration of hydroperoxides formed during the initial stage which, in their turn, participate in the propagation stage of the destruction process¹¹.



Figure 2. Formation and accumulation of C = O groups at a degradation temperature of $100^{\circ}C$.

In a general scheme of the thermooxidative process^{12,13}, the propagation stage is represented by reactions of the form:

$$R^{\bullet} + O_2 \xrightarrow{k_2} ROO^{\bullet}$$
$$ROO^{\bullet} + RH \xrightarrow{k_3} ROOH + R^{\bullet}$$

The rate constant k_3 is deduced assuming that the chemiluminiscence intensity is directly proportional to the concentration of the formed hydroperoxide in circumstances when the emission surface of the sample remains unmodified¹⁴:

$$I_t = C [\text{ROOH}]_t$$
 ... 1

where I_t is the chemiluminiscence intensity at time t C is the proportionality constant [ROOH]_t is the hydroperoxide concentration at time t. Computing the specific luminiscence and plotting it against time, the resulting curve can be described by the equation:

$$I(t) = C_1 \cdot \exp(-kt)$$
 ... 2

where C_1 is a pre-exponential factor

k is the rate constant of the firstorder reaction.

From the ascending part of the curve, the dependence *I versus* time was deduced and the plot in semi-logarithmic coordinates is a straight line having the slope equal to k_3 [*RH*]. Mathematical treatment of the experimental results gave the values grouped in *Table 2*. These data show that the oxidation rate in the propagation step increases by increasing the degree of epoxidation; at the same time, as expected, the induction time decreases.

The rate of oxidation for the initiation step, based on IR spectral data varies in the same way as those obtained by luminiscence measurements; obviously, the two cited reaction rates refer to the evolution of different chemical groups, carbonyl/carboxyl and hydroperoxy, respectively.

TABLE 2.	KINETIC DATA	DETERMINED BY
	LUMINISCENCI	e method

Rubber	Induction period at 100°C (min ⁻¹)	Rate constannt at 100°C (min ⁻¹)	
NR	6.0	2.1×10^{-2}	
IR	5.0	3.0×10^{-2}	
ENR-25	3.2	3.3×10^{-2}	
ENR-50	2.1	7.3×10^{-2}	

The data obtained from processing in the Brabender Plastograph at 100°C (Table 3) are in agreement with the results of previously discussed thermo-oxidative tests. In contrast with the behaviour of NR and synthetic polyisoprene, for the case of ENR the gel content increased in all our experiments (Table 4). These experimental results may suggest that the reactions involved in mechanical processing of ENR are different in some respects from that assigned for isoprenic rubbers^{15,17}. The gel

TABLE 3. MECHANO-DESTRUCTION DURING PROCESSING IN BRABENDER PLASTOGRAPH

Rubber	Destruction index ^a
NR	10
IR	14
ENR-25	7.2
ENR-50	8.6

*Destruction index¹⁶

$$I_{d} = \frac{M_{i} - M_{20}}{20}$$

where M_i - initial torque value

 M_{20} - torque value after 20 min

TABLE 4. 0	GEL CO	NTENT	OF RU	JBBERS	AFTER
THER	MO-OX	IDATIVI	E DES	TRUCTIO	ON

Destruction temperature (°C)	NR	IR	Gel content ENR-25	ENR-50
Initial	2	5	20	28
80	3	12	40	45
100	1	8	71	67
120	1	10	83	90

content and the destruction index determined from Brabender processing data suggest that crosslinking prevailed, compared to chain scission.

The crosslinking reactions can be enhanced by the presence in the structure of ENR, besides the main oxyran groups, of small amounts of other groups resulting in secondary reactions during epoxidation of NR¹; significant amounts of gel are present even in the initial ENR. During thermooxidative degradation of ENR, an increase in the content of the C-O-C group was evidenced by the band at 1100 cm⁻¹ in the IR spectrum, even at 80°C. The new oxygenated groups can be intra- or inter-chain but the increase of the gel content during ageing supports the assumption that an important portion (if not all) of the new C-O-C bonds represent crosslinks in the gel structure.

CONCLUSION

The behaviour of ENR-25 and ENR-50 on thermo-oxidation was investigated and compared to unmodified isoprene rubbers. It was found that the oxidation rate depends on the degree of epoxidation. Epoxidised rubber is less resistant to degradation compared to unmodified rubber. The increase in gel content suggests the participation of the oxyranic groups in crosslinking reactions during thermo-oxidative degradation and mechanical processing by the formation of ether bridges.

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