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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

THERMOOXIDATIVE DEGRADATION OF NITRILE-BUTADIENE RUBBER

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Results are presented on: (a) the nonisothermal degradation of nitrile-butadiene rubber (NBR) from TG, DTG and DTA data; (b) the accelerated isothermal thermal degradation of NBR at 80°, 90° and 105° from the change in weight versus time data; (c) the accelerated isothermal thermal degradation of NBR at 80°, 90° and 105° from the change in relative elongation at break with time.

The thermal analysis data showed that the following processes occur successively during the nonisothermal heating of NBR in air: (1) the volatilization of the plasticizer and other ingredients; (2) the exothermic absorption of oxygen to yield nonvolatile oxidation products; (3) the decomposition of these products or their further interaction with oxygen to form volatile products.

The results obtained from the three kinds of measurements were correlated to give a realistic picture of the processes responsible for the changes in the mechanical properties of the material as a consequence of its heating.

The practical use of polymeric materials requires a knowledge of their behaviour under given environmental conditions (heat, light, nuclear radiation, humidity, etc.). In order to acquire such knowledge, one has to investigate the acceleretated ageing of these materials by following the changes in their mechanical properties (elongation at break, resistance to traction, resistance to compression, etc.) and their electrical properties (dielectric rigidity, dielectric losses, etc.) due to thermooxidative degradation. The results of accelerated ageing permit an evaluation of the lifetime of the material under the conditions of practical use [1]. For thermal degradation,

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the acceleration factor has to be chosen so that the mechanism of accelerated degradation of the material should be identical with that of the degradation under practical conditions. To solve such a problem, thermal analysis methods (TG, DTG and DTA) are very useful as they allow determination of the temperature range of thermal stability [2-7], the nonisothermal kinetic parameters of the degradation [8-10] and the changes undergone by the investigated polymeric materials as a consequence of accelerated ageing [3, 11, 12]. The nonisothermal kinetic parameters are very useful for determination of the thermal lifetime of polymeric materials [13, 14].

This paper presents results obtained in an investigation of the thermooxidative degradation of nitrile–butadiene rubber (NBR). The thermal degradation was investigated under nonisothermal conditions, and the isothermal accelerated degradation was studied by following weight losses and relative elongation at break. The isothermal and nonisothermal kinetic parameters were determined. These results were correlated with those obtained by investigation of the mechanical degradation. Conclusions were drawn concerning the processes responsible for the changes in the mechanical properties of the material as a consequence of heating.

Experimental

The nitrile-butadiene rubber used in these investigations was a CATC (Jilava, Romania) product.

The heating curves of the powdered samples were recorded by means of a Q–1500 D MOM Paulik–Paulik–Erdey derivatograph in static air atmosphere, in the temperature range 20-500° at heating between 0.75 and 5.5 deg/min.

The accelerated thermal ageing of the test specimens was performed in a WSU–200 oven with forced air circulation, in which the temperature was kept constant with an accuracy of ±2 deg.

The relative elongation at break of the initial test specimens and of specimens submitted to accelerated ageing was determined with an accuracy of ±1% by using a universal MONSANTO T–10/E machine.

The test specimens (dumb-bell-shaped test pieces) were prepared from NBR with a thickness of 1 mm according to ASTM D–412 requirements.

Results and Discussion

Derivatographic data

Figure 1 shows the thermal curves obtained at a heating rate $a = 2.8$ deg/min; for other heating rates, the curves are similar.

Inspection of the curves in Fig. 1 shows two changes, α and β, accompained by weight loss. Exothermic peak I corresponds to a process which takes place with a slight increase in sample weight. Change β is accompanied by exothermic peak II.

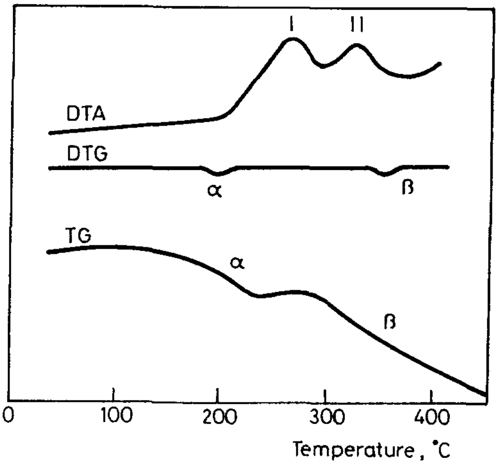

Fig. 1 The derivatogram of NBR in static air atmosphere at $a = 2.8$ deg/min

Change α corresponds to the volatilization of 3-4% of the NBR content, and is due to the loss of plasticizer and other ingredients.

The thermal curves of NBR in argon are given in Fig. 2.

From the curves in Figs 1 and 2, it may be concluded that exothermic peak I can be assigned to the oxidation of NBR to solid reaction products. Such processes have been suggested for the thermooxidation of EVA [12] and some elastomers [15]. In this oxidation step, mainly hydroperoxides are formed, probably as a result of singlet oxygen ($^1O_2$, $^1\Delta_g$) attack on methylene groups of diene monomeric units [16]. Figure 2 shows that thermal degradation in the inert atmosphere occurs in only one step, in which volatile compounds are evolved. As concerns the total weight loss, this is higher for thermooxidative degradation than for thermal degradation: at

350°, the weight loss is 22.3% for thermooxidative degradation and 9.2% for thermal degradation in argon.

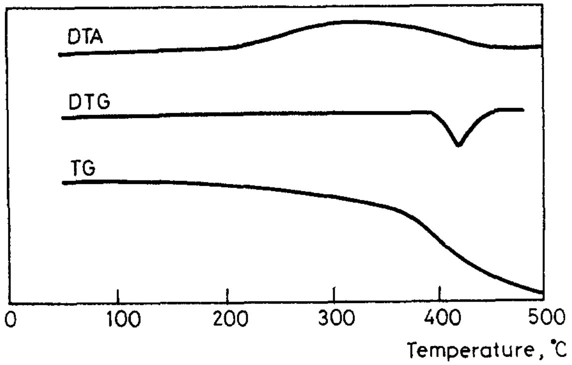

Fig. 2 The derivatogram of NBR in argon at $a=2.72$ deg/min

In order to evaluate the nonisothermal kinetic parameters for changes α and β (Fig. 1) and for the thermal degradation in the inert atmosphere (Fig. 2), which generate volatile reaction products, three methods have been applied:

– the Coats–Redfern method [17];

– the modified Coats–Redfern method [18];

– the Flynn–Wall method for constant heating rate [19].

The results obtained are listed in Table 1.

There is quite good agreement between the values of the nonisothermal kinetic parameters (activation energy, E_A, pre-exponential factor, A, and reaction order, n) obtained with the methods used. The changes in the nonisothermal kinetic parameter values with the heating rate could be assigned to mass transfer limitation at hihger heating rates, and to the change in the reaction mechanism on passing from lower to higher heating rates. A comparison of the nonisothermal kinetic parameters relating to the thermooxidative degradation and to the thermal degradation in argon shows no correlation between the mechanisms of the two processes.

From the results in Table 1, it can be concluded that, on the heating of NBR in a static air atmosphere, the following processes occur successively:

a) volatization of the plasticizer and other ingredients;

b) oxygen absorption leading to solid products (probably hydroperoxides);

Table 1 Values of nonisothermal kinetic parameters for processes α and β (Fig. 1) as well as for thermal degradation in argon

Process	Coats–Redfern					Modified Coats–Redfern				Flynn–Wall (a = ct)			
	a, K/min	E_A, kcal/mol	n	A, s^{-1}	r	E_A, kcal/mol	n	A, s^{-1}	r	E_A, kcal/mol	n	A, s^{-1}	r
α	0.75	10.8	0.2	27.558	0.9945	11.3	0.2	55.5	0.9956	11.9	0.2	24.5	0.9955
α	1.38	13.9	0.8	$2.617 \cdot 10^3$	0.9988	14.5	0.8	$5.6025 \cdot 10^3$	0.9988	14.9	0.8	$1.521 \cdot 10^4$	0.9995
α	2.80	19.8	1.6	$1.676 \cdot 10^4$	0.9988	20.5	1.6	$5.881 \cdot 10^4$	0.9988	20.6	1.6	$5.5424 \cdot 10^4$	0.9990
α	5.50	8.6	0.5	4.59	0.9999	9.5	0.6	14.92	0.9996	9.8	0.4	59.06	0.9993
β	0.69	66.7	1.9	$5.574 \cdot 10^{23}$	0.9940	64.0	1.8	$3.09 \cdot 10^{24}$	0.9927	65.4	1.9	$2.265 \cdot 10^{23}$	0.9943
β	1.32	57.8	2.3	$5.141 \cdot 10^{19}$	0.9876	57.5	2.3	$2.936 \cdot 10^{19}$	0.9884	57.5	2.2	$4.044 \cdot 10^{19}$	0.9869
β	2.39	35.5	2.1	$1.991 \cdot 10^{10}$	0.9939	35.4	2.0	$1.9648 \cdot 10^{10}$	0.9936	36.0	2.1	$3.241 \cdot 10^{10}$	0.9947
β	5.35	25.2	2.0	$1.837 \cdot 10^6$	0.9957	22.5	1.9	$2.738 \cdot 10^6$	0.9956	26.0	2.0	$6.333 \cdot 10^6$	0.9965
Thermal degradation in argon	2.72	10.0	0.2	$5.900 \cdot 10^{-1}$	0.9940	10.7	0.3	$1.319 \cdot 10^{-1}$	0.9952	11.6	0.1	$8.864 \cdot 10^{-1}$	0.9967

a – heating rate

E_A – activation energy, n – apparent reaction order, A – preexponential factor

r – correlation coefficient of the linear regression

c) decomposition of the solid through thermooxidation to volatile products.

The results of derivatographic analysis of NBR suggest the following temperatures for accelerated ageing: 80°, 90° and 105°.

The ageing process was followed via the weight change *vs.* time isotherms and via the relative elongation at break *vs.* time isotherms.

The weight loss vs. time isotherms

Figure 3 shows the weight loss (in percent) *vs.* ageing time isotherms at 80°, 90° and 105°. The first portion of the isotherms reveals a relatively fast weight loss due to the generation of volatile products. All the isotherms level off at the maximum values of the weight loss ($\%\Delta m$, $\%\Delta m_{max}$). The values of $\%\Delta m_{max}$ increase with the thermal ageing temperature (7% for 80°, 7.6% for 90°, and 7.8% for 105°).

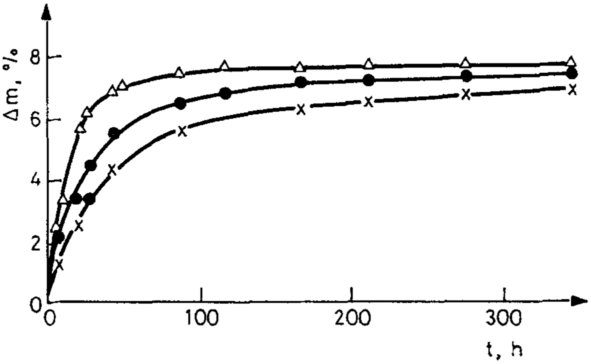

Fig. 3 The isotherms of weight loss of NBR during its thermal degradation x 80°C, ● 90°C, Δ 105°C

For kinetic analysis of the isothermal data, we used the classical rate equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where k is the rate constant, n is the reaction order and α is the degree of conversion, given by:

$$\alpha = \frac{\%\,\Delta m}{\%\,\Delta m_{max}} \tag{2}$$

The temperature dependence of the constant k is given by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_A}{RT}\right) \tag{3}$$

From the experimental data, using Eqs (1)-(3) in the temperature range 80-105°, we obtain $n = 1.65$, $E_A = 14.0$ kcal/mol and $A = 1.328 \cdot 10^7\ \mathrm{h}^{-1}$.

These isothermal kinetic parameter values are characteristic for elimination of the plasticizer and other ingredients.

To check the isothermal kinetic parameter values, we applied the method suggested by Doyle [20], which uses both isothermal and nonisothermal data, for the same process (α in Fig. 1). Straight lines log t_i *vs.* $1/T$, where t_i is the isoconversion time [20], were obtained for various heating rates associated with the 80° and 90° isotherms (Fig. 4).

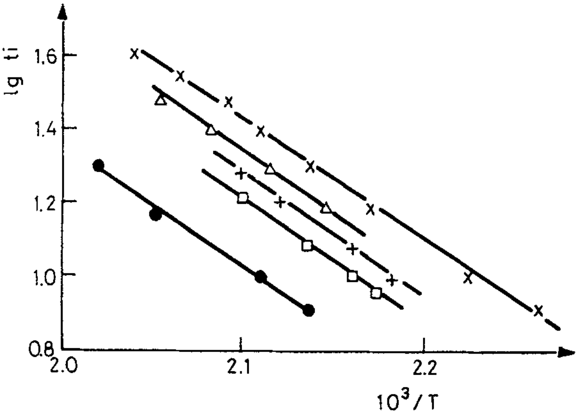

Fig. 4 Straight lines log t_i *vs.* $\frac{1}{T}$ for x $a = 1.38$ deg/min; $T_i = 80$°C, ● $a = 2.8$ deg/min; $T_i = 80$°C, △ $a = 0.75$ deg/min; $T_i = 80$°C, ☐ $a = 0.75$ deg/min; $T_i = 90$°C, + $a = 1.38$ deg/min; $T_i = 90$°C, T_i is the temperature at which the isotherm was recorded

From the slopes of these straight lines, activation energy values of 14.4-15.0 kcal/mol were obtained. Taking into account the experimental errors inherent in such measurements, it is obvious that these results are in satisfactory agreement with those obtained by using only isothermal data.

These results also show that the isothermal kinetic parameter values are characteristic for change α in Fig. 1.

The relative elongation at break vs. time isotherms

Figure 5 shows the variation of relative elongation at break $\frac{\varepsilon}{\varepsilon_o}$ vs. ageing time (ε is the elongation at break of the aged sample, and ε_o is the initial elongation at break for the unaged sample) for NBR at 80°, 90° and 105°.

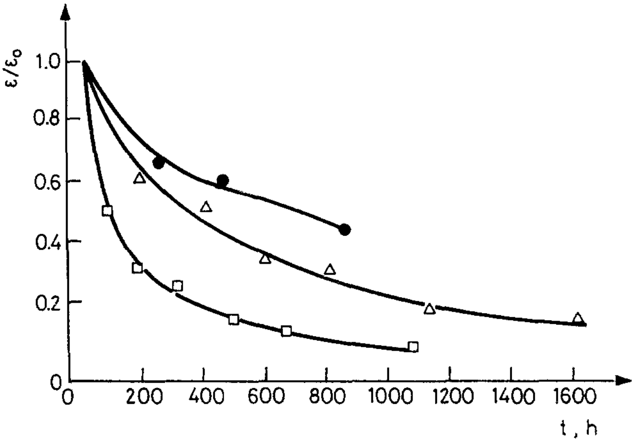

Fig. 5 The change in time of the relative elongation at break for thermally aged NBR in air
● 80°C, △ 90°C, □ 105°C

In order to analyze these data, the kinetic equation

$$-\frac{d\varepsilon}{dt} = k_\varepsilon \cdot \varepsilon^m \tag{4}$$

proposed by Dakin [21, 22] was used (k_ε is the overall rate constant; m is the overall order of the degradation process).

The shapes of the curves given in Fig. 5 for t >200 h suggest an exponential decrease in time of the relative elongation at break, corresponding to an apparent degradation order of unity. Such a value for the apparent degradation order has been obtained for other thermal degradations, such as the degradation of ethylene-propylene rubber (elongation at break) [23] or the degradation of glass-reinforced epoxy resin (flexural strength) [24].

As concerns our system, Fig. 6 gives the straight lines ln $\frac{\varepsilon}{\varepsilon_o}$ *vs.* ageing time. This linearity proves the decrease in time of the relative elongation at break.

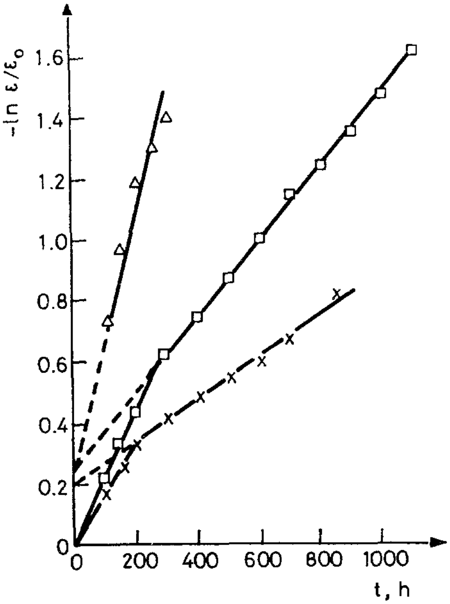

Fig. 6 Straight line $\ln\frac{\varepsilon}{\varepsilon_o}$ vs. ageing time x 80°C, □ 90°C, Δ 105°C

One should note the convergence of all straight lines at $t = 0$. This means that, after the plasticizer and other ingredients have been evolved, NBR turns into a material with another value of the initial elongation at break, ε_b

$$\varepsilon_o' = \frac{\varepsilon_o}{b} \tag{5}$$

where $b = 1.27$. This value was calculated from the intercept of the straight lines given in Fig. 6.

For the thermal degradation of many materials, the Arrhenius plot in the form

$$k_\varepsilon = A'\cdot\exp\left(\frac{-E'}{RT}\right) \tag{6}$$

has been checked [23, 26].

From relationships (4)-(6), one obtains

$$\frac{\varepsilon}{\varepsilon_o} = \frac{1}{b}\cdot\exp\left[-A't\cdot\exp\left(\frac{-E'}{RT}\right)\right] \tag{7}$$

The data necessary to test the application of Eq. (7) are given in Table 2. From these data, using Eq. (7), we obtain:

$$E' = 20.5 \text{ kcal/mol}; \quad A' = 3.11 \cdot 10^9 \text{ h}^{-1}$$

There is satisfactory agreement between the experimental and calculated values of $\frac{\varepsilon}{\varepsilon_O}$ for the following conditions of ageing:

$$t^\circ = 80^\circ; \quad 300 \text{ h} \le t \le 850 \text{ h}$$

$$t^\circ = 90^\circ; \quad 250 \text{ h} \le t \le 1500 \text{ h}$$

$$t^\circ = 105^\circ; \quad 100 \text{ h} \le t \le 400 \text{ h}$$

For 105°, Eq. (7) is not valid if $t > 400$ h. Thus, at the highest temperature of ageing, for $t > 400$ h, NBR undergoes thermooxidation described by another kinetic equation.

The value of E' (20.5 kcal/mol) differs from the value of E (14-15 kcal/mol) obtained from the weight loss data (Fig. 3). It is seen from Figs 3 and 5 that the mechanical degradation described by Eq. (7) begins after elimination of the plasticizer and other ingredients. Thus, it appears that the rapid mechanical degradation of NBR could be assigned to the initial loss of these components. On the other hand, Fig. 1 indicates that the loss of volatile compounds is followed by an exothermic oxidation leading to nonvolatile compounds (Fig. 1, peak I in the DTA curve). It is possible that this last process is responsible for the thermooxidative process described by Eq. (7).

Conclusions

The thermal stability of nitrile-butadiene rubber (NBR) was investigated.

Derivatographic analysis showed that, on progressive heating of NBR, the following processes occur:

1. Loss of the plasticizer and other ingredients.
2. The interaction of NBR with oxygen, leading to solid products (probably hydroperoxides).
3. Decomposition of these products or their interaction products with oxygen, leading to volatile products.

Table 2 Verification of equation (7) for results obtained in accelerated thermal ageing of NBR

$T=80^\circ C$			$T=90^\circ C$			$T=105^\circ C$		
$t(h)$	$\frac{\varepsilon}{\varepsilon_0}$		$t(h)$	$\frac{\varepsilon}{\varepsilon_0}$		$t(h)$	$\frac{\varepsilon}{\varepsilon_0}$	
	a	*b*		*a*	*b*		*a*	*b*
300	0.65	0.65	250	0.58	0.56	100	0.48	0.51
			300	0.54	0.52			
400	0.60	0.61	400	0.47	0.45	150	0.38	0.41
500	0.58	0.58	500	0.42	0.39	200	0.30	0.33
600	0.55	0.54	600	0.36	0.34	250	0.27	0.27
700	0.51	0.51	700	0.32	0.30	300	0.24	0.22
850	0.44	0.46	800	0.29	0.26	350	0.21	0.17
			900	0.26	0.22	400	0.19	0.14
			1000	0.23	0.19	500	0.14	0.09
			1100	0.20	0.17	600	0.12	0.06
			1200	0.17	0.15	700	0.10	0.04
			1300	0.16	0.13	800	0.08	0.025
			1400	0.15	0.11	900	0.07	0.02
			1500	0.14	0.10	1000	0.06	0.01

a = values resulted from curves of accelerated thermal ageing

b = values calculated using equation (7)

4. For processes 1 and 3, the nonisothermal kinetic parameter values were determined.

5. The weight loss *vs.* time isotherms allowed evaluation of the isothermal kinetic parameters. Kinetic analysis of the isotherms led to the conclusion that the weight loss *vs.* time curves correspond to volatilization of the plasticizer and other ingredients.

6. A relationship describing the exponential decrease in time of the relative elongation at break was derived. The results allowed assignment of the exponential mechanical degradation to the NBR oxidation which leads to nonvolatile products, probably hydroperoxides.

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Zusammenfassung — Es werden Ergebnisse über (a) den nichtisothermen Abbau von Nitril-Butadiengummi (NBR) anhand von TG-, DTG- und DTA-Daten; (b) den beschleunigten isothermen thermischen Abbau von NBR bei 80°C, 90°C und 105°C anhand von TG-Daten; (c) den beschleunigten isothermen thermischen Abbau von NBR bei 80°C, 90°C und 105°C aus der Abhängigkeit der relativen Elongation von der Zeit.

Die Daten der Thermoanalyse zeigten, daß beim nichtisothermen Erhitzen von NBR in Luft nacheinander folgende Prozesse ablaufen: (1) das Entweichen von Weichmacher und anderen Zusätzen; (2) die exotherme Absorption von Sauerstoff an den erhaltenen nichtflüchtigen Oxidationsprodukten; (3) die Zersetzung dieser Produkte oder ihre weitere Wechselwirkung mit Sauerstoff zur Bildung flüchtiger Produkte.

Die aus den dreierlei Messungen erhaltenen Ergebnisse wurden korreliert, um ein reales Bild über jene Prozesse zu geben, die als Folge des Erhitzens für die Veränderung der mechanischen Eigenschaften der Materialien verantwortlich sind.