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CHANGES IN THE THERMAL BEHAVIOUR OF *NBR* DUE TO ACCELERATED γ-RADIATION-INDUCED AGEING

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Abstract

Thermal investigation has allowed us to show the changes undergone by a sort of nitrile-butadiene rubber (*NBR*) as a consequence of γ-radiation-induced ageing. The parameters of the processes, which occur at progressive heating of the investigated samples, were determined. It was shown that for γ-irradiated samples the activation parameters corresponding to the thermo-oxidative process leading to solid products are correlated through the relation of compensation effect. Also, it was shown that, by γ-irradiation, *NBR* undergoes a relatively rapid change of its thermal behaviour which can be due to structural changes.

Keywords: compensation effect, γ-radiation-induced ageing, non-isothermal kinetics

Introduction

In some previous papers [1–4] we showed that the accelerated thermal γ-radiation-induced ageing of some polymeric materials determines the changes in the thermal behaviour of these materials which were put in evidence in TG, DTG and DTA curves. The results obtained by thermal analysis were correlated with those relating the variation of some mechanical properties of the investigated materials as a consequence of the accelerated ageing.

This paper presents the results obtained at the determination of the thermal characteristics of a sort of nitrile-butadiene rubber (*NBR*) from thermal analysis data following γ-radiation ageing.

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Experimental

A sort of vulcanized *NBR*, produced by CATC-Jilava-Romania was investigated. This rubber contains 33% acrylonitrile, carbon black, plastifiers, antioxidants, zinc oxide.

The γ-irradiation of the *NBR* samples was performed at room temperature using ^{60}Co source.

The thermoanalytical curves, TG, DTG and DTA, of the powdered samples of *NBR* were recorded by means of MOM-Budapest-Type C-Paulik–Paulik–Erdey derivatograph in a static air atmosphere, at a heating rate of 5 K min^{-1}. The mass of the analyzed samples was in the range 41–49 mg.

Results and discussions

The ageing of *NBR* in γ-radiation field was performed under the following conditions:

1. at a dose rate of 0.1 Mrad h^{-1} with ageing times: 60 and 120 h;
2. at a dose rate of 0.6 Mrad h^{-1} with ageing times: 50, 75, 100, 125 and 200 h.

Simultaneous thermoanalytical curves were recorded for the initial test sample as well as for the aged ones.

Figure 1 shows the TG, DTG and DTA curves of the non-aged sample. The thermal curves for γ-radiation aged *NBR* are similar to those shown in this figure.

Inspection of the curves in Fig. 1 shows two changes I and III accompanied by mass loss. At a temperature located between those corresponding to these two changes, an exothermic change (peak II in the DTA curve) occurs. The change II is

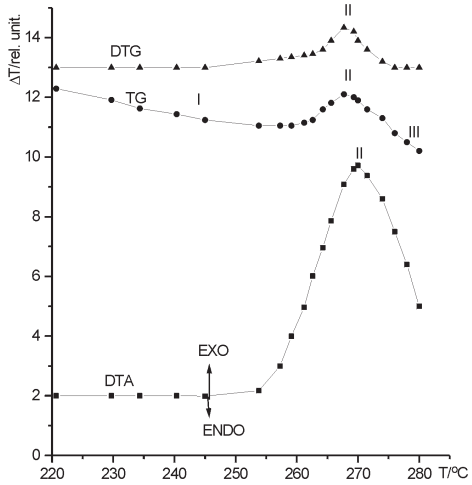

Fig. 1 TG, DTG and DTA curves of non-aged *NBR* in static air atmosphere, at a heating rate of 5 K min^{-1}

accompanied by a slight increase of the sample mass which was very satisfactory confirmed by thermal curves obtained at relatively small heating rates (0.65 K min^{-1} and 1.4 K min^{-1}) and a higher mass of the analyzed sample (≈100 mg).

The change I corresponds to volatilization of ≈5% from *NBR*, and is due to the loss of the plasticizer and other ingredients.

In order to account for the change corresponding to the peak II in DTA curve, thermal curves of *NBR* were recorded in argon atmosphere. These curves no longer exhibit peak II. Thus, the exothermic peak II corresponds to the thermo-oxidation of *NBR* with generation of solid products, probably hydroperoxides, due to the attack of the singlet oxygen ($^1O_2$, $^1\Delta_g$) on the methylene groups of diene monomeric units [5]. At higher temperatures, thermo-oxidative degradation with generation of volatile products occurs. The total mass loss is ≈95%.

Such a thermo-oxidative degradation characterized by two kinds of oxidation (one accompanied by a slight mass increase and other by release of volatile compounds) was previously reported in connection with the thermo-oxidative degradation of certain polymeric materials [1, 3, 6–10].

Table 1 lists the conditions of accelerated ageing and the characteristics of the DTA exothermic peak. From this table, one can see that T_{max} has a higher value for non-aged *NBR* than those corresponding to aged ones. This means that after γ-irradiation the investigated material turns in another one with other properties. In addition, the rate of thermo-oxidation, expressed by $\Delta T_{max}/m$, exhibits an irregular variation with D_I, which can be assigned to the complex character of the thermo-oxidative process (cross-linking of *NBR* leading to reactive centers, scission of the macromolecular chain, etc.).

Table 1 The parameters of the exothermic DTA peak of non-aged and aged *NBR*

D/MRad h^{-1}	T/h	D_I/Mrad	T_{max}/K	$\frac{\Delta T_{max}}{m}$/K mg^{-1}
0.0	0	0	551	0.38
0.1	60	6	540	0.35
0.1	120	12	540	0.31
0.6	50	30	534	0.26
0.6	75	45	540	0.42
0.6	100	60	543	0.30
0.6	125	75	541	0.42
0.6	200	120	540	0.46

D=dose rate; t=ageing time; D_I=integrated dose; T_{max}=maximum temperature in the process II; m=mass of the analyzed sample; ΔT_{max}=the maximum value of the temperature change in the process II

In order to evaluate the activation parameters of the change II, the following relation which grounds the Piloyan *et al.* [11] method will be used:

$$\ln\Delta T=\ln\left[\frac{Af(\alpha)}{C}\right]-\frac{E}{R}\frac{1}{T}\equiv\ln A_{a}-\frac{E}{R}\frac{1}{T} \quad (1)$$

where: A is the pre-exponential factor, α is the degree of conversion, $f(\alpha)$ is the differential function of conversion, C is the proportionality constant between $d\alpha/dt$ and ΔT, E is the activation energy, R is the gas constant and T is the temperature.

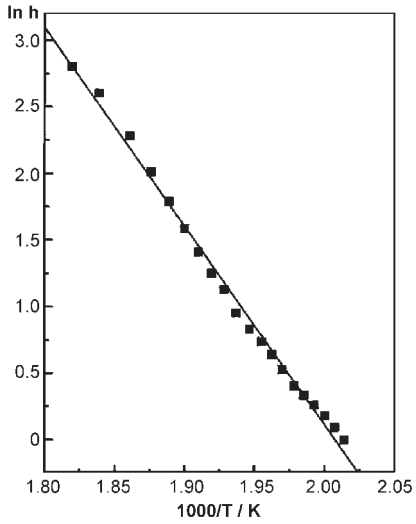

Fig. 2 ln$h$ vs. 1/T for the initial non-aged *NBR*. h is proportional with ΔT

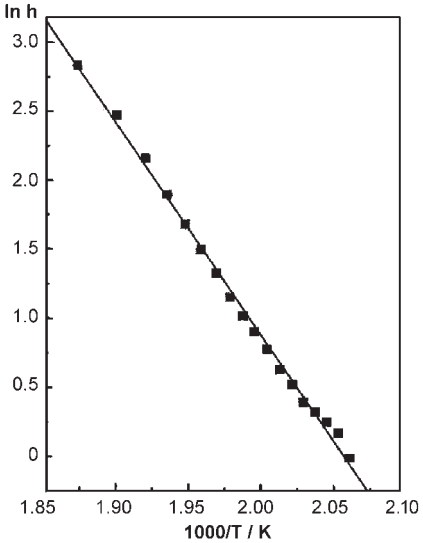

Fig. 3 ln$h$ *vs.* 1/T for γ-irradiated *NBR* (0.6 MRad h^{-1}; 200 h)

For low degree of conversion, the differential conversion function, $f(\alpha)$, exhibits a slow dependence on α. Under these conditions, $[Af(\alpha)]/C \equiv A_a$ is practically independent on α and can be assimilated with an apparent pre-exponential factor. It turns out that the activation energy and the apparent pre-exponential factor can be evaluated from the slope and the intercept of the straight line $\ln\Delta T$ *vs.* $(1/T)$ recorded for low values of α. Two of these straight lines obtained for initial non-aged *NBR* and γ-irradiated *NBR* (0.6 MRad h^{-1}; 200 h) are shown in Figs 2 and 3. The correlation coefficients of the linear regression for all the obtained straight lines is higher than 0.995. The values of $\ln A_a$ and E calculated from the parameters of these straight lines depend on the conditions of accelerated ageing, although a regular variation of the activation parameters with the integrated dose was not observed. Nevertheless, as shown in Fig. 4, $\ln A_a$ and E values corresponding to the γ-irradiated samples are correlated by the relationship:

$$\ln A_a = aE + b \tag{2}$$

where: a=0.242 mol kJ^{-1} and b=0.664 with r=0.9991.

Relation (2) corresponds to the well-known *compensation effect* observed in many heterogeneous solid-gas chemical reactions (see, for example, the review paper [12] in which some problems concerning the compensation effect in the kinetics of non-isothermal degradation of polymers are discussed).

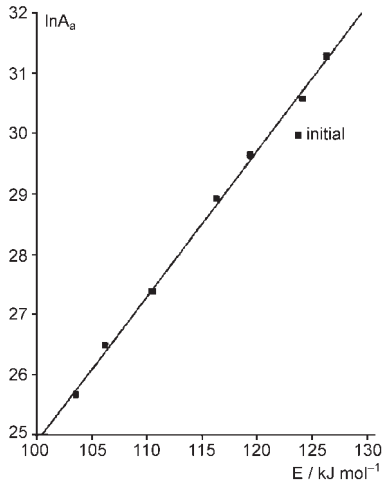

Fig. 4 The plot $\ln A_a$ *vs.* E for the thermo-oxidative process II

One can notice that the point ($\ln A_a$, E) corresponding to the non-aged *NBR* is not on the straight line shown in Fig. 4. This proves once again that after γ-irradiation the investigated material turns in another one with other properties.

The existence of the compensation effect for γ-irradiated *NBR* shows that these samples undergo similar reactions of thermo-oxidative degradation, the perturbing parameters which causes the effect being the dose rate and time of irradiation.

The isokinetic temperature was calculated from the slope of the straight line $\ln A_a$ *vs. E*, using the relation [12]:

$$T_i = \frac{1}{Ra} \tag{3}$$

The obtained value is T_i=497 K which is in the range of the thermo-oxidation temperatures.

Agrawal [13] states that the compensation effect requires, besides verification of relationship (2), the intersection of the Arrhenius plots in a single point. This criterion is not checked for our data. Zsakó and Somasekharan [14] have shown that only for a straight line $\ln A_a$ *vs. E* with r=1 do the Arrhenius straight lines intersect in a single point. This is the reason why Agrawal's criterion is not fulfilled in our case.

Conclusions

The parameters of the non-isothermal thermo-oxidative degradation of non-aged and γ-irradiated *NBR* were evaluated.

Thermal analysis showed that, at progressive heating of all investigated *NBR* samples, the following changes occur: I. loss of the plasticizer and other ingredients; II. interaction of *NBR* with oxygen, leading to solid products; III. decomposition or thermo-oxidation of these solid products leading to volatile products.

For change II the non-isothermal activation parameter values were determinated. Except the non-aged *NBR*, the values of $\ln A_a$ and E are correlated through the relation of compensation effect.

The differences in the thermal behaviour of non-aged *NBR* in comparison with the accelerated aged ones can be attributed to a relative rapid change of *NBR* structure as a consequence of γ-irradiation.

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