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# The comparative kinetic analysis of non-isothermal degradation process of acrylonitrile–butadiene and ethylene–propylene–diene rubber compounds. Part I

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ABSTRACT

The non-isothermal degradation processes of acrylonitrile–butadiene and ethylene–propylene–ethylidenenorbornene rubber compounds were investigated with thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG), using the different calculation procedures. It was found that the acrylonitrile–butadiene (NBR) and the ethylene–propylene–diene (EPDM) rubber degradations represent the complex processes, where there are conversion regions with a constant value of the apparent activation energy ($E_a$). It was established that the NBR and EPDM degradation under nitrogen atmosphere can be described by the one and a half order ($n = 3/2$) and the first order ($n = 1$) reaction kinetics, respectively. A linear dependence was observed between $\ln A$ and $E_a$ at every heating rate, known as the artificial compensation effect (*art*-CE). It was found that the calculated differential conversion curves are in good agreement with the experimental ones, for each of the observed heating rates, thus confirming the correctness of the obtained reaction models for the NBR and EPDM degradation processes.

## 1. Introduction

Today there is a wide variety of rubber polymers, each with its own set of characteristic attributes, and each offered with modifications designated to enhance one or more of those attributes. In most cases, nevertheless, the elastomer by itself lacks one or more property necessary to produce a saleable product. A number of materials must be added to make it commercially useful. Compounding is the means by which elastomer and additives are combined to ensure efficient manufacture of the best possible product. The compounding of rubber products starts with the choice of elastomer, filler (reinforcing or extending), crosslinking chemicals, and various additives which, when mixed together, will provide a compound with the desired properties and performance [1,2]. Mixing is followed by forming operations such as milling, extrusion, and calendering. These lead to the final processing step of vulcanization or curing in which the compound changes from a thermoplastic to a thermoset or crosslinked state [2,3]. The most commonly used elastomers in polymer industry are acrylonitrile–butadiene (NBR) and ethylene–propylene–diene (EPDM) rubbers [2].

We have focused our attention on the comparative kinetic analysis of degradation processes of the acrylonitrile–butadiene (NBR) and ethylene–propylene–diene (EPDM) rubbers under non-isothermal conditions, in an inert atmosphere. In order to obtain more accurate kinetic triplets for investigated degradation processes, the thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were used.

Kinetic study of thermal degradation provides useful information for the optimization of the successive treatment of polymer materials in order to avoid or at least limit thermal degradation. The analysis of the degradation process becomes more and more important due to an increase in the range of temperatures for engineering applications, recycling of post-consumer plastic waste, as well as the use of polymers as biological implants and matrices for drug delivery, where de-polymerization is an inevitable process affecting the lifetime of an article.

Acrylonitrile–butadiene rubbers (NBR) release degradation products from the butadiene-rich areas, acrylonitrile-rich areas and interphase areas in the rubber where butadiene and acrylonitrile are adjoined. Alekseeva [4] reported that NBR rubbers could be identified on the basis of acrylonitrile, butadiene and

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ethenylcyclohexene in the pyrolysate. Hummel et al. [5] characterized a number of copolymer rubbers, including NBR rubber, using Py-MS. They proposed a fragmentation scheme to account for many of the major ions in the mass spectrum of NBR rubber. Dynamic (non-isothermal) thermogravimetry was used to investigate the thermal degradation kinetics of butadiene rubber in a nitrogen atmosphere at constant nominal heating rates over the temperature range 175–575 °C [6]. Two distinct mass change stages in the thermogravimetric curves indicated that the degradation of butadiene rubber might be attributed to two reactions [6]. The prediction of the lifetime for a thermal degradation analysis of NBR was carried out by Kawashima and Ogawa [7] using FT-IR technique.

The degradation of EPDM and its blends has been studied under a variety of conditions including non-isothermal [8] and isothermal degradation [9] under a nitrogen atmosphere, photo-oxidation [10,11], radiochemical oxidation [12–14], thermo-oxidation [15,16] and ultraviolet irradiation [17]. The influence of the factors on the degradation of EPDM such as metallic oxides [18] and carbon black [19,20], have also been investigated. It was shown that the structural effects can influence on the thermal properties and degradation behavior of EPDM [21,22].

Therefore, the present study focuses on the comparative kinetic investigations of degradation processes for the pure (without the presence of fillers) cross-linked NBR and EPDM rubbers. In order to determine the values of kinetic parameters and the proper function of the reaction mechanism, the different kinetic methods [23] were used. Based on the kinetic results, the differences in the degradation mechanisms and thermal stabilities of the observed patterns are discussed. The presented kinetic results of degradation processes of considered rubber compounds can be useful for engineering applications, in order to explain the complex degradation mechanisms at high temperatures, using simple overall kinetic expressions.

## 2. Experimental

### 2.1. Materials

*Network precursors*: (a) acrylonitrile–butadiene rubber (NBR), Kraynac 34-50 (“Polysar”, Canada) with acrylonitrile content 33.2%, (b) ethylene–propylene–ethylidenenorbornene rubber (EPDM), Vistalon 2504 (“Exxon”, Belgia) with 4% ethylidenenorbornene, ethylene content 58%. *Accelerators*: N-cyclohexyl-2-benzothiazole sulphenamide (CBS); tetramethylthiuram disulphide (TMTD). *Antioxidants*: N-isopropyl-N-phenyl-p-phenylenediamine (Vulkanox 4010 NA). *Curing agent*: Sulphur. *Activators*: zinc oxide and stearic acid. The compound formulations (Table 1) expressed in part per hundred parts of rubber, phr.

### 2.2. Mixing procedure

The compounds (Table 1) were prepared using a laboratory mixing roll mill of dimensions 400 mm × 150 mm at a speed ratio of the rollers $n_1/n_2 = 28/22$, at a roller temperature of 40–50 °C. The rubber should be masticated for a few minutes. The activators, zinc oxide, stearic acid and sulphur were then added, as well CBS and TMTD together with an anti-ageing agent (4010 NA).

### 2.3. Sample preparation

After mixing, the elastomer compounds were moulded into 2 mm thick slabs. The slabs were moulded in a hydraulic press using moulding conditions previously determined from the torque data, obtained by a Monsanto Rheometer 100 S at 160 °C. The cure time for each compound was defined as the time interval at which 90% of its maximum torque was reached. The test specimens were dying cut from test slabs.

### 2.4. Vulcanization

The vulcanizates were prepared by curing at 150 °C for optimum cure time using an electrical press under a pressure of about 60 MPa.

### 2.5. Thermal measurements

The thermal stability of the NBR and EPDM samples were investigated by non-isothermal thermogravimetric (TG) analysis using a Perkin Elmer TGS-2 instrument. The samples with approximately $m \approx 10–15$ mg were heated at three different linear heating rates of $\beta = 10$, 20 and 40 °C min$^{-1}$, in a dynamic nitrogen atmosphere (the flow rate of 25 cm$^3$ min$^{-1}$), in the temperature range from 25 °C up to 600 °C.

## 3. Theoretical background

### 3.1. Kinetic analysis

The rate of degradation reaction can be described in terms of two functions, $k(T)$ and $f(\alpha)$ thus:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $\alpha$ is the degree of conversion ($\alpha = (m_o - m_t)/(m_o - m_f)$, $m_o$, $m_t$ and $m_f$ are the initial, actual and final mass of the sample in the TGA curves, respectively), $t$ is the reaction time, $k(T)$ is the rate constant and $f(\alpha)$ is the type of reaction or function of reaction mechanism. By substitution of the Arrhenius equation, $k(T) = A\exp(-E_a/RT)$, the following equation results:

$$\frac{d\alpha}{dt} = A\,\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{2}$$

where $A$ is the pre-exponential factor, $E_a$ is the apparent activation energy, $R$ is the gas constant and $T$ is the absolute temperature in K.

After introduction of the constant heating rate $\beta = dT/dt$ and rearrangement, one obtains

$$\frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right)\exp\left(-\frac{E_a}{RT}\right)dT. \tag{3}$$

A subsequent integration of Eq. (3) leads to the equation in the form:

$$g(\alpha) = \int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_o}^{T}\exp\left(-\frac{E_a}{RT}\right)dT \tag{4}$$

where $g(\alpha)$ is integral form of the reaction mechanism function and $T_o$ is the starting temperature of non-isothermal experiment. Eq. (4) cannot be expressed by a simple analytical form since its right-hand side corresponds to a series of infinite $\gamma$ functions. In mathematical practice, Eq. (4) can be expressed in the following form [24]:

$$g(\alpha) = \frac{A}{\beta}\int_0^{T}\exp\left(-\frac{E_a}{RT}\right)dT = \frac{AE_a}{\beta R}p(x) \tag{5}$$

where $T_o$ is introduced as an approximation for the lower limit of the integral on the right-hand side of Eq. (4) as $T_o \to 0$, bearing in mind that the value of temperature $T_o$ in practical cases is very small. The variable $x = E_a/RT$ is the reduced apparent activation energy, while $p(x)$ represents the temperature or exponential integral which cannot be exactly calculated [25]. For the different solid state reaction mechanisms, $f(\alpha)$ and $g(\alpha)$ have different expressions [26]. The most frequently cited kinetic models used in this work are summarized in Ref. [26].