

Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

THERMAL DEGRADATION OF POLYCHLOROPRENE RUBBER UNDER ISOTHERMAL AND NON-ISOTHERMAL CONDITIONS

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Abstract

The results of a kinetic investigation of the non-isothermal degradation and the isothermal degradation of the residual deformation under constant deflection for polychloroprene rubber are presented. A relationship was derived between the degree of non-isothermal conversion and the value of the investigated mechanical property.

Keywords: compensation effect, kinetic parameters, polychloroprene rubber, thermal degradation

Introduction

In order to design equipment with components made from polymeric materials, it is necessary to know their thermal lifetimes. In order to estimate these, the investigated materials must be submitted to thermally accelerated aging, and the isotherms showing the changes in time of the chosen property (mechanical or electrical) must be recorded. Through statistical analysis of the results, the thermal lifetime under the conditions of use can be obtained [1]. This method for the prediction of the thermal lifetime requires 8–10 months of gathering experimental data for a given material and a given property. This is the reason why faster procedures (which have not yet received general acceptance) have been tried [2–7]. Some of these methods make use of thermal analysis, which allows a fast evaluation of the kinetic parameters of degradation of the polymeric material. It has been shown [5] that in many cases the values of the apparent activation energy obtained from non-isothermal data are practically equal to those obtained from the data concerning the isothermal degradation of a mechanical property. For such cases, a relationship between the degree of conversion and the value of

the mechanical property should be found. In the present work, we try to find such a dependence for the thermal degradation of polychloroprene rubber, material for which results relating to the non-isothermal degradation from thermal analysis data [8, 9] and to the isothermal degradation of residual deformation under constant deflection [10–12] were earlier reported.

The non-isothermal degradation of polychloroprene rubber

In a previous paper [8] we showed that the non-isothermal degradation of polychloroprene rubber up to 350°C occurs in a single exothermic step, with the generation of volatile products (mainly hydrogen chloride). In order to evaluate the apparent activation energy, the isoconversional methods of Friedman [13] and Flynn-Wall-Ozawa [14, 15] have been used. As shown in Fig. 1, the results of both methods reveal that the apparent activation energy, E , depends on the degree of conversion.

The values of the apparent activation energy obtained by Friedman's method are higher than those obtained by the Flynn-Wall-Ozawa method. As demonstrated in a relatively recent paper [16], if the activation energy depends on the degree of conversion, one should expect different values for the activation energy estimated by means of these two isoconversional methods. We appreciate that in such cases the use of Friedman's method is more suitable, as it is based on the

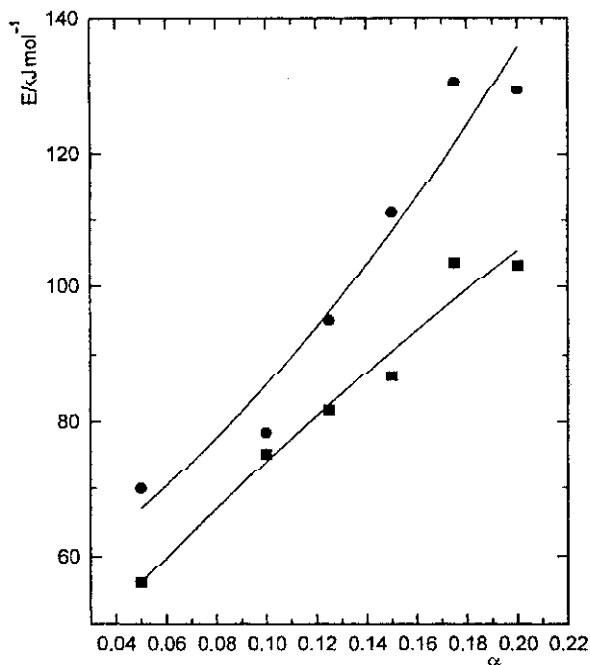


Fig. 1 The dependence $E = E(\alpha)$ for the non-isothermal degradation of polychloroprene rubber; ● – Friedman's method, ■ – Flynn-Wall-Ozawa method

rate equation. The Flynn-Wall-Ozawa method requires integration of the rate equation, considering that the activation parameters do not depend on the degree of conversion (α).

An increase of E with α was found for the non-isothermal degradation of poly(vinylchloride) [17], in which hydrogen chloride is released as in the case of polychloroprene rubber. It was considered [17] that 'structural irregularities such as allylic and tertiary chlorine' are responsible for the relative low values of the apparent activation energy at low values of the degree of conversion.

The isothermal degradation of the residual deformation under constant deflection

A previous paper [10] presented the isotherms of degradation of the residual deformation under constant deflection for polychloroprene rubber. In order to evaluate the apparent activation energy, an integral method was used. The values of the apparent activation energy were obtained from the slopes of the straight lines $\ln t$ vs. $1/T$ for $\epsilon = \text{constant}$ (ϵ is the chosen relative property). The obtained values of the apparent activation energy depend on ϵ . The equation on which this method is based is obtained through integration of the Dakin rate equation for the thermal degradation of the given property [18]:

$$-\frac{d\epsilon}{dt} = A_{\epsilon} f(\epsilon) \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where A_{ϵ} is the pre-exponential factor and $f(\epsilon)$ is the differential function of the degradation.

The integration of this equation is performed by presuming constant values of the activation parameters. However, it has been shown that these parameters (A_{ϵ} and E) depend on ϵ . This is the reason why, for such cases, the correct values of these parameters should be determined by using the degradation rate equation in its logarithmic form:

$$\ln\left(-\frac{d\epsilon}{dt}\right) = \ln A_{\epsilon} f(\epsilon) - \frac{E}{RT} \quad (2)$$

Thus, a plot of $\ln(-d\epsilon/dt)$ vs. $1/T$ for $\epsilon = \text{constant}$ is a straight line whose slope and intercept allow the values of E and $\ln A_{\epsilon} f(\epsilon)$ to be obtained. Obviously, under such conditions, in order to calculate the activation energy, it is not necessary to know the analytical form of $f(\epsilon)$. As shown earlier [12] for the degradation of polychloroprene rubber:

$$f(\epsilon) = \epsilon \quad (3)$$

a result which was checked by comparing the theoretical and experimental isotherms of degradation.

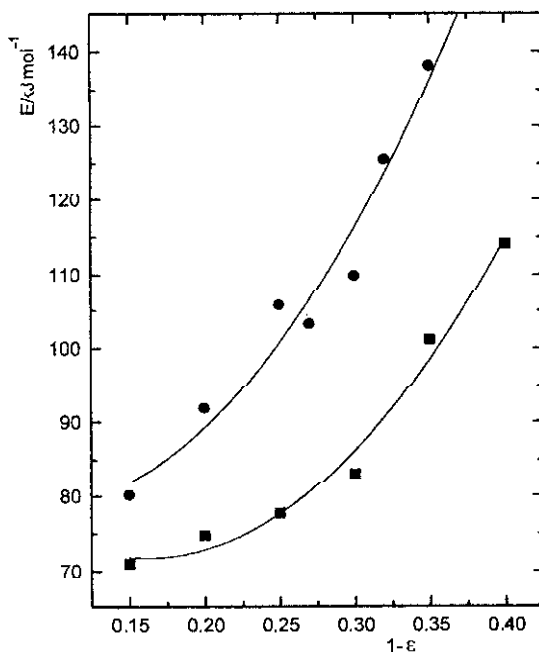


Fig. 2 The change in the apparent activation energy with $(1-\epsilon)$ for polychloroprene rubber; ● - E determined using the differential method, ■ - E determined using the integral method

As depicted in Fig. 2, both the differential and the integral method lead to apparent activation energy values which depend on the degree of degradation of the mechanical property. The differential method leads to higher values of the apparent activation energy. As shown previously, the differential method leads to the correct dependence of the apparent activation energy on the degree of degradation of the mechanical property.

Since $f(\epsilon)$ is given by relationship (3), the values of the pre-exponential factor for various values of ϵ were calculated from the intercepts of the straight lines $\ln(-d\epsilon/dt)$ vs. $1/T$ [12]. It was shown [12] that the activation parameters are correlated through the relationship of the compensation effect:

$$\ln A_{\epsilon} = a_{\epsilon} + b_{\epsilon} E \quad (4)$$

where $a_{\epsilon} = -10.72$ (A_{ϵ} expressed in s^{-1}) and $b_{\epsilon} = 0.31 \text{ mol kJ}^{-1}$.

The kinetic correlation of the isothermal and non-isothermal data

Figures 1 and 2 demonstrate that, for the same method (differential or integral) the range of values of E obtained from the isothermal data is close to that obtained from the non-isothermal data. This suggests a biunivocal relationship

between the degree of conversion corresponding to the non-isothermal degradation and the degree of isothermal degradation of the mechanical property. In other words, a given value of E corresponds to a given pair (α, ϵ) . The existence of a relationship between α and ϵ is the basis of the quasichemical approximation leading to the derivation of Dakin's equation (Eq. (1)). Starting from this, Audouin and Verdu [19] showed that the apparent activation energy corresponding to the degradation of a polymeric material property is equal to the activation energy of the overall chemical degradation process responsible for the change in this property.

Let us consider that

$$\epsilon = g(\alpha) \quad (5)$$

As the degradation of the property is expressed by $(1-\epsilon)$, for $\alpha \rightarrow 0$, $\epsilon = g(\alpha) \rightarrow 1$, and for $\alpha \rightarrow 1$, $\epsilon = g(\alpha) \rightarrow 0$.

From relationships (1), (3) and (5), it turns out that

$$\frac{d\alpha}{dt} = A_r \frac{-g(\alpha)}{dg(\alpha)/d\alpha} \exp\left(-\frac{E}{RT}\right) \quad (6)$$

whose logarithmic form is

$$\ln \frac{d\alpha}{dt} = \ln A_e + \ln \frac{-g(\alpha)}{dg(\alpha)/d\alpha} - \frac{E}{RT} \quad (7)$$

On the other hand, Friedman's method for evaluating the activation energy from non-isothermal data is based on the relationship

$$\ln \frac{d\alpha}{dt} = \ln A_{TG} + \ln f(\alpha) - \frac{E}{RT} \quad (8)$$

where A_{TG} is the pre-exponential factor evaluated from non-isothermal data and $f(\alpha)$ is the differential conversion function.

With the condition that a given pair (α, ϵ) should correspond to each E value, and with the dependence $E=E(\alpha)$ and $E=E(\epsilon)$, as obtained by the mentioned differential methods, we obtained the following expression:

$$\epsilon = g(\alpha) = \exp(-105.2\alpha^3) \quad (9)$$

which fulfils the previous boundary conditions (for $\alpha \rightarrow 0$, $\epsilon \rightarrow 1$; for $\alpha \rightarrow 1$, $\epsilon = 2.05 \cdot 10^{-46}$ (practically 0)).

From relationships (7)–(9), we obtain

$$\ln \frac{d\alpha}{dt} = \ln A_\epsilon - 5.75 + \ln \alpha^{-2} - \frac{E}{RT} \equiv \ln A_{TG} - \frac{E}{RT} + \ln f(\alpha) \quad (10)$$

Correspondingly:

$$\ln A_{TG} = \ln A_{\epsilon} - 5.75 \quad (11)$$

and

$$f(\alpha) = \alpha^2 \quad (12)$$

From relationship (12) and the values of the intercepts for the straight lines $\ln(d\alpha/dt) = \ln\beta(d\alpha/dT)$ vs. $1/T$ for α -const. (β is the heating rate), according to Friedman's method, the values of A_{TG} for $0.05 \leq \alpha \leq 0.20$ were calculated. As shown in Fig. 3, the non-isothermal activation parameters are correlated through the relationship of the compensation effect:

$$\ln A_{TG} = a_{TG} + b_{TG}E \quad (13)$$

where $a_{TG} = -16.09$ (A_{TG} expressed in s^{-1}) and $b_{TG} = 0.27 \text{ mol kJ}^{-1}$ ($r = 0.9988$).

On the other hand, from relationships (11) and (13) it turns out that

$$\ln A_{\epsilon} = a_{TG} + 5.75 + b_{TG}E = -10.34 + 0.27E \quad (14)$$

These parameters of the straight line $\ln A_{\epsilon}$ vs. E exhibit values close to the compensation parameters a_{ϵ} and b_{ϵ} . This is confirmation of the correctness of the analytical form of the function $\epsilon = g(\alpha)$.

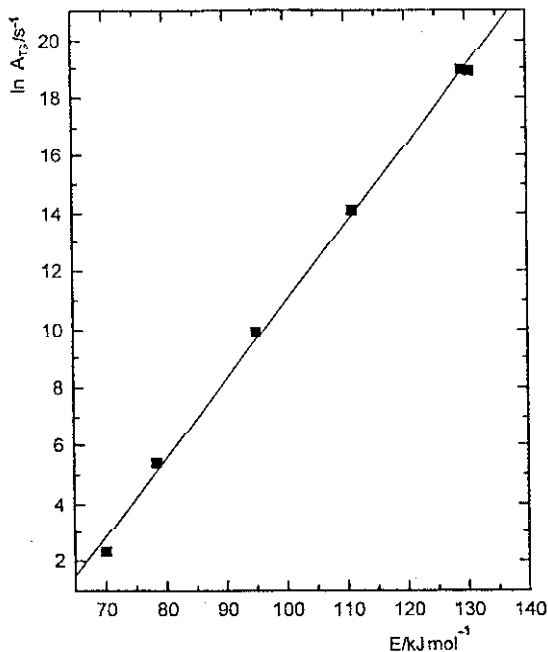


Fig. 3 The straight line $\ln A_{TG}$ vs. E for the non-isothermal degradation of polychloroprene rubber

Conclusions

1 Results relating to the kinetic interpretation of the non-isothermal curves of the mass loss and of the isothermal curves of the deformation under constant deflection for polychloroprene rubber are presented.

2. It has been shown that, for the non-isothermal degradation, the apparent activation energy increases with the degree of conversion and, for the isothermal degradation, the apparent activation energy increases with the degree of degradation of the mechanical property.

3. A relationship has been derived between the degree of conversion and the value of the mechanical property.

4. This relationship and the values of the compensation effect parameters obtained from non-isothermal data were used to calculate the values of the compensation parameters corresponding to the isothermal degradation of the investigated mechanical property. The values obtained for the compensation effect parameters are in satisfactory agreement with those found directly by kinetic analysis of the isotherms of the thermal degradation of the deformation under constant deflection.

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