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THERMAL PROPERTIES OF N-ETHYL-N-PHENYL-DITHIOCARBAMATES AND THEIR INFLUENCE ON THE KINETICS OF CURE

D. Ondrušová[1], *E. Jóna*[1] *and P. Šimon*[2]

[1]Department of Chemistry and Technology of Inorganic Materials, Faculty of Industrial Technologies, University of Trenčín, 020 32 Púchov, Slovak Republic
[2]Department of Physical Chemistry, Slovak Technical University, 812 37 Bratislava, Slovak Republic

Abstract

The thermal properties (in the temperature range of 100–250°C) of N-ethyl-N-phenyldithiocarbamate complexes of Zn(II), Co(III), Ni(II), Cu(II) and Pb(II) and their influence on the kinetics of cure have been studied by differential scanning calorimetry (in nitrogen). It was found that Zn(II), Co(III) and Pb(II) dithiocarbamates melted without further effects, while the melting of Ni(II) and Cu(II) dithiocarbamates is accompanied with decomposition. From the kinetic point of view, the dithiocarbamates decrease the values of the reaction order and the values of rate constants follow this order (with respect to the metal ion): Zn(II)<Cu(II)<Pb(II)<Ni(II)<Co(III).

Keywords: differential scanning calorimetry, kinetics of vulcanization, N-ethyl-N-phenyldithiocarbamates

Introduction

A number of metal dithiocarbamates have been synthesized and characterized in recent years. Special interest in the study of metal dithiocarbamates was aroused because of the striking structural features presented by this class of compounds and also because of its diversified applications, such as high pressure lubricants in industry, fungicides and pesticides, and also as accelerators in vulcanization [1]. Dithiocarbamates used in the process of vulcanization of rubber compounds form a group of ultra-accelerators of the curing process [2]. Since different metal ions can occur in the curing process in the manufacture of tyres (for example, Co(II) ions are found in adhesion promoters, Cu(II) and Zn(II) salts are formed in a reaction between the brass coating on the reinforcing steel cord) [3–5], it is assumed that in the course of vulcanization a considerable number of various compounds between metal ions and dithiocarbamates may be formed which have not been studied yet.

Therefore, several metal N-ethyl-N-phenyldithiocarbamates, $M(epdtc)_n$ (*M*=Zn(II), Co(III), Ni(II), Cu(II), Pb(II), *epdtc*=N-ethyl-N-phenyldithiocarbamate), have been especially prepared and their influence on the kinetics of cure was studied.

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This paper is devoted to the study of thermal properties of N-ethyl-N-phenyl-dithiocarbamates and their influence on the kinetics of cure, by means of differential scanning calorimetry (DSC).

Experimental

Preparation of the dithiocarbamates

The dithiocarbamates were prepared by extraction of aqueous solutions of the inorganic salts of corresponding metal ions with a chloroform solution of the commercially manufactured vulcanization accelerator $Zn(epdtc)_2$ (commercial designation Vulkacit P Extra), in an exchange reaction, according to the following general pattern:

$$Zn(epdtc)_2+M^{n+} \rightarrow M(epdtc)_n+Zn^{2+};\ M= \text{Co(III), Ni(II), Cu(II), Pb(II)}$$

By recrystallization from a chloroform solution, crystals of products were obtained.

Thermal properties

The Perkin Elmer Differential Scanning Calorimeter DSC-7 was used for the thermoanalytical study. The experimental conditions were as follows: the mass of samples 1.5–5 mg, the scanning rate of 5°C min^{-1}, nitrogen atmosphere. Temperature calibration was carried out using In and Zn, enthalpy calibration by using In.

Kinetic analysis of vulcanization

To evaluate the kinetics of vulcanization, kinetic equation [6] is frequently used

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

where α is the degree of vulcanization, k is the rate constant and n is the order of reaction. To evaluate the dynamic curves obtained by differential scanning calorimetry, it is necessary to express the dependence of the rate constant on temperature by the Arrhenius equation:

$$k=A\exp\left[-\frac{E_a}{RT}\right] \tag{2}$$

where A and E_a are the pre-exponential factor and the activation energy of vulcanization, respectively. For the dynamic conditions of measurement with a linear increase of temperature, Eq. (2) may be transformed into the following form:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left[-\frac{E_a}{RT}\right](1-\alpha)^n \tag{3}$$

The degree of vulcanization is determined as the ratio of the reaction enthalpy at temperature T to the total reaction enthalpy:

$$\alpha = \frac{\Delta H_T}{\Delta H_{total}} \quad (4)$$

When evaluating the experimental data, it is assumed that the vulcanization stage starts after reaching the temperature T_i which corresponds to the completion of the induction period. The rate constant being expressed by Arrhenius Eq. (2), the rate equation of non-isothermic vulcanization with a constant increase in temperature is expressed by Eq. (3). The degree of vulcanization is expressed by Eq. (4). The integration of experimental data was carried out by the trapezoidal method. Changes in the baseline depending on the degree of vulcanization were taken into account in the integration, which was carried out iteratively.

The integration of Eq. (3) was performed by the fourth order Runge–Kutta method. The degrees of vulcanization obtained from Eq. (4) were compared with the degrees calculated from Eq. (3). The kinetic parameters were obtained by the non-linear method of least squares and minimization of the sums of the squares of differences between theoretical and experimental values of the degree of vulcanization was performed by the simplex method. The minimised kinetic parameters were A, E_a, n and T_i.

Results and discussion

Analytical results

The content of N, C, S and H was determined by elemental analysis and the contents of metals were established by complexometric titration. The analytical data of the compounds reported in Table 1, shows a good agreement between the experimental and calculated data.

Table 1 Analytical data of N-ethyl-N-phenyldithiocarbamates

Compound	Elemental analysis									
	Theoretical/%					Experimental/%				
	C	H	N	S	M	C	H	N	S	M
$Zn(epdtc)_2$	47.2	4.4	6.1	28.0	14.3	46.9	4.0	5.8	26.9	13.9
$Co(epdtc)_3$	50.0	4.5	6.5	28.4	9.1	49.7	4.4	6.6	29.6	9.4
$Ni(epdtc)_2$	47.9	4.5	6.2	28.4	13.0	47.2	4.1	6.2	26.1	12.8
$Cu(epdtc)_2$	47.4	4.4	6.1	28.1	13.9	46.9	4.22	5.9	26.0	14.0
$Pb(epdtc)_2$	36.0	3.4	4.7	21.3	34.5	36.1	3.2	4.5	19.9	33.1

Thermal properties

Recent thermal studies on metal-dithiocarbamates indicate [1, 7] that formation of the metal-thiocyanate intermediate is the essential step in the decomposition of the majority of dithiocarbamate complexes. Thermal decomposition of metal-dithiocarbamates generally proceeds (over 200°C) through the following steps:

1. Decomposition of dithiocarbamate to thiocyanate:
   $M(R_2NCS_2) \rightarrow M(NCS)_n$
2. Decomposition of thiocyanate to sulphide:
   $M(NCS)_n \rightarrow MS_{n/2}$
3. Oxidation of sulphide to metal or metal oxide:
   $MS_{n/2} \rightarrow M$ or $MO_{n/2}$

or volatilization of metal sulphide.

From the vulcanization point of view it was interesting to study the thermal properties of individual metal dithiocarbamates in the temperature range of ~100–250°C by differential scanning calorimetry (DSC). From the DSC data of all the dithiocarbamates studied (Fig. 1, Table 2), a considerable influence of the metal atom in these compounds is evident. The clear sharpness of the peaks at ~209°C in $Zn(epdtc)_2$, ~232°C in $Co(epdtc)_3$, and ~177°C in $Pb(epdtc)_2$ is characteristic for the melting of these compounds [8]. In $Zn(epdtc)_2$ the melting endotherm is accompanied by another endotherm at ~141°C (without mass loss) attributed to a crystalline change [9]. A marked influence of Ni(II) and Cu(II) ions on the thermal behaviour of the compounds studied has the consequence of a complex shape of the corresponding DSC curves. In the case of $Ni(epdtc)_2$ the two endothermic peaks at ~197 and 204°C are due to decomposition but the broad second peak with a shoulder can be also ac-

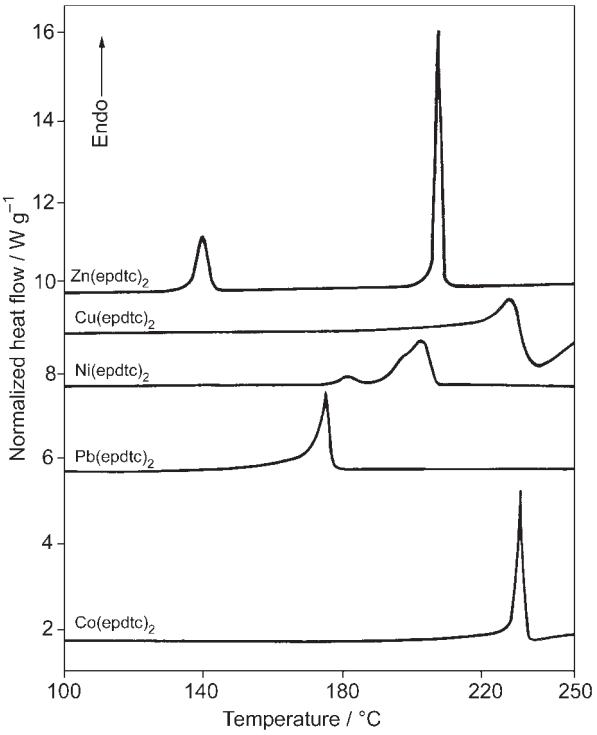

Fig. 1 DSC curves of N-ethyl-N-phenyldithiocarbamates

companied by melting. The broad endothermic peak at ~229°C for $Cu(epdtc)_2$ may be interpreted likewise.

Table 2 DSC data of N-ethyl-N-phenyldithiocarbamates

Compound	Onset/°C	Peak/°C	ΔH/kJ mol^{-1}
$Zn(epdtc)_2$	137.8 207.7	141.2 209.4	14.7 28.4
$Co(epdtc)_3$	229.4	232.1	41.0
$Ni(epdtc)_2$	184.0 196.3	197.3 204.3	5.4 39.8
$Cu(epdtc)_2$	223.8	229.0	19.6
$Pb(epdtc)_2$	174.8	177.1	27.4

Kinetic analysis of vulcanization

The kinetic parameters obtained are shown in Table 3. The values of A and E_a lead to the values of rate constants of vulcanization of the same order; for example, for 150°C the values of rate constants are within $(3.1–7.2)\cdot10^{-4}$ min^{-1} for all compounds. However, the promoters cause a decrease in the reaction order. For the compound without promoter, the reaction order is 0.72 which is the value quite close to the first-order reaction kinetics widely used for the description of vulcanization. The compounds with promoters have the reaction order of 0.03i0.29. This range points out the zero-order kinetics where the rate of vulcanization is constant, not depending on the extent of vulcanization. This difference between reaction orders for the compounds without and with the promoters suggests a dramatic change in the reaction mechanism of vulcanization in the presence of promoters.

Table 3 Kinetic parameters of the rubber compounds with the addition of N-ethyl-N-phenyldithiocarbamates

No.	Rubber compound	ΔH/ J g^{-1}	$A\cdot10^9$/ min^{-1}	$E_a\cdot10^3$/ kJ mol^{-1}	n	T_i/°C	$k\cdot10^{-4}$ (150°C)/ min^{-1}
0	with no accelerator	–52.6	6.49	107.7	0.72	164.5	3.24
1	with $Zn(epdtc)_2$	–30.0	2.46	104.4	0.03	173.3	3.13
2	with $Co(epdtc)_3$	–67.4	0.03	87.4	0.06	170.1	4.33
3	with $Ni(epdtc)_2$	–14.1	0.03	85.6	0.18	180.7	7.09
4	with $Cu(epdtc)_2$	–23.0	1.18	100.3	0.29	180.1	4.89
5	with $Pb(epdtc)_2$	–11.8	0.04	86.7	0.08	181.6	7.22

An analysis of the vulcanization stage has shown that the frequently used model of the n^{th}-order reaction describes the vulcanization kinetics satisfactorily, it is how-

ever necessary to include in it the existence of the induction period expressed by introducing the parameter T_{ind}. This kinetic equation is sufficient for the modelling of the vulcanization process, however, for a deeper understanding of the process it would be necessary to analyse the reaction mechanism of vulcanization in more detail, to establish the kinetic equation on the basis of the findings, and to obtain the basic kinetic parameters from experimental data. Such a procedure would make it possible to find those reaction stages in the vulcanization mechanism that dominantly influence the quality of products.

Conclusions

Thermal behaviour of the metal N-ethyl-N-phenyldithiocarbamates and their influence on the kinetics of vulcanization has been studied in this paper.

According to the results of DSC measurements (in the temperature range of 150–250°C), the studied compounds, $M(epdtc)_n$ (*epdtc*=N-ethyl-N-phenyldithiocarbamates, *M*=Zn(II), Co(III), Ni(II), Cu(II), Pb(II)), may be divided into two groups:

a) only melting of these compounds proceeds (*M*=Zn(II), Co(III), Pb(II))

b) the process of melting is accompanied by decomposition (*M*=Ni(II), Cu(II)).

(The DSC curve for $Zn(epdtc)_2$ exhibited another effect at ~141°C attributed to a crystalline change.)

Kinetic study shows that N-ethyl-N-phenyldithiocarbamates decrease the reaction order. Difference between reaction orders for the compounds without and with the promoters suggests a dramatic change in the reaction mechanism of vulcanization in the presence of promoters. The values of rate constants follow this order (with respect to the metal ion): k(Zn(II))<k(Cu(II))<k(Pb(II))<k(Ni(II))<k(Co(III)). The influence of Ni(II) and Co(III) N-ethyl-N-phenyldithiocarbamates on the reaction rate is evident.

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