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A comparative study by thermal analysis of polyurethanes interacted with metallic ions

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Abstract

The influence of some cations from the s and d blocks on the thermal degradation of a polyurethane based on 4,4′-dibenzyl di-isocyanate, poly(ethylene adipate) diol and ethylene glycol was studied. The thermogravimetric data were analysed using the Levi–Reich method. The results obtained were processed on a computer; a mathematical relation and a physical parameter are proposed to characterize the processes.

INTRODUCTION

It is well known that to obtain bulk polyurethanic foams, catalysts which contain metals or metallic cations have to be used [1]. Because of the traces of metallic cations from the residual catalysts, the polyurethanes obtained present sensitivities different from that of uncatalysed polyurethane to hydrolytical, thermal and photochemical degradation [2].

The literature includes studies on model urethanes and polyurethanes that elucidate the thermal degradation and protection mechanisms of these polymers, but there are fewer studies regarding the effect of the metallic ions on the thermal degradation. One of these studies [3] concluded that of the kinetic parameters which could be used to determine the thermal stability of polyurethanes, only the activation energy E_a could be considered as a semi-quantitative factor.

The aim of the present paper is to present a way in which the action of different metallic cations on the thermal degradation of the studied polyurethane can be estimated.

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EXPERIMENTAL

Materials

The reference polyurethane was a polyesterurethane obtained from 4,4′-dibenzyl di-isocyanate, poly(ethylene adipate) diol, with a molecular weight of 2000, and ethylene glycol. The content of urethanic groups was 2.24×10^{-3} moles of urethanic groups per gram of polymer [4]. The interaction of the polyurethane with the metallic ions was performed using techniques described in the literature [5]. A medium of *N,N*-dimethylformamide and aqueous solutions of equal molar concentrations were used. The traces of metallic ions remaining in the polyurethane (10^{-5}–10^{-7} gram ions of cation per gram of polymer) were determined by a radiochemical method, by atomic absorption spectroscopy and by flame emission spectroscopy [6].

Apparatus

The analyses were performed on a MOM-Budapest derivatograph, with recording of the weight losses (TG), the derivative (DTG), the differential thermal analysis (DTA) and the temperature increases (T). The thermal curves were recorded in air at a heating rate of 12 K min^{-1}, up to 600°C. In order to obtain comparable data, the same sensitivities for TG (50 mg), DTG (1/10) and DTA (1/10), and the same sample weight of about 50 mg, were used throughout.

RESULTS AND DISCUSSION

The thermogravimetric characteristics including the temperature ranges are listed in Table 1.

As discussed above, for comparison of the thermal stabilities of the polyurethanes, we preferred to use the Levi–Reich kinetic analysis method [7, 8]. The values of the reaction order used in these calculations were estimated by means of the Coats–Redfern method [9]. The variations of the activation energy with α (the reacted fraction), for the basic polyesterurethane and for those interacted with cations from the s block (Na^+, K^+, Mg^{2+}, Ca^{2+}) and the d block (Cu^{2+}, Ag^+, Au^{3+}, Fe^{3+}, Cr^{3+}), are presented in Figs. 1 and 2.

The samples interacted with metallic ions, showing a sharp decrease in activation energy during the initial decomposition stage ($\alpha < 0.2$). In all cases, a minimum in the activation energy appeared which is probably due to the formation of some compounds unstable under the degrading conditions.

To compare the curves, i.e. the thermal behaviour of the samples, we

TABLE 1

Thermogravimetric results (weight losses) and temperature ranges for the basic polyurethane and the samples interacted with metallic cations

Polyurethane P–M^{n+}	Weight loss (%) and temperature ranges in °C					
	Overall weight losses	Step I	Step II	Step III	Step IV	Step V
P	84[a]	–	–	–	–	–
P–Na^+	81.5	2.75	38.5	12.5	16	12
		30–50	230–324	360–375	410–452	470–600
P–K^+	61.5	3	29.5	13.5	15.5	–
		30–50	240–318	375–406	494–560	
P–Mg^{2+}	87.5	5.5	35	15.5	13	18.5
		40–165	200–269	323–359	400–455	481–520
P–Ca^{2+}	85.5	13.5	43	29	–	–
		34–77	200–297	425–495		
P–Cu^{2+}	93	7.5	54	30.5	–	–
		175–220	265–400	465–527		
P–Ag^+	89	3.5	6.5	39.5	39.5	–
		40–60	133–190	320–385	390–600	
P–Au^{3+}	86.5	3.5	19	39.5	24.5	–
		50–70	168–248	315–378	380–600	
P–Fe^{3+}	89.5	7	15.5	20.5	13	33.5
		35–150	192–221	265–325	370–440	450–478
P–Cr^{3+}	91.5	10	59.5	22	–	–
		40–69	241–378	475–600		

[a] The basic polyurethane has just one weight loss step between 230 and 530°C.

tried to deduce the equations which best describe the processes. Taking into account the features of these curves, a general equation

$$E_a(\alpha) = A + B/\alpha^m + C/\alpha^n \tag{1}$$

where E_a is the activation energy (in kJ mol^{-1}), α the reacted fraction, and A, B, C, m, n are cation constants, is proposed.

The constants A, B, C, m, and n, and the maximum difference between the calculated and experimental values for the activation energy (for all cations) are listed in Table 2.

The graphs of eqn. (1) for cations from the s and d blocks, respectively, are presented in Fig. 3(a) and (b).

A better approximation for the experimental value could be obtained using high-degree polynomial equations (Fig. 4). Although this is a better fitting method, it would be extremely difficult, if even impossible to compare the results obtained in this way.

Taking into account that the metallic ions have different physical and

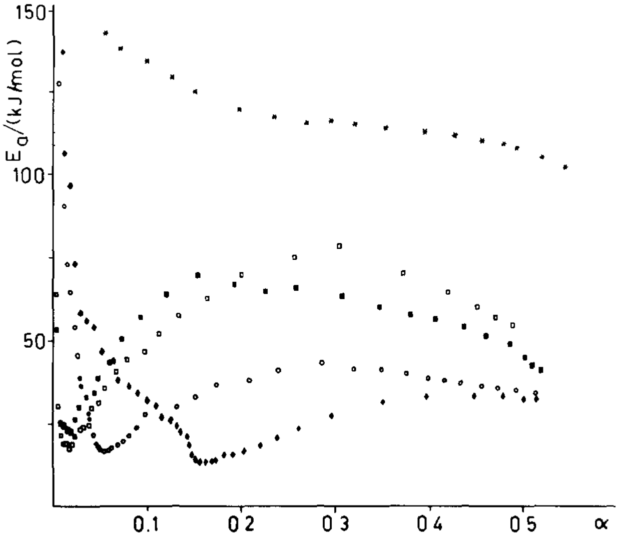

Fig. 1. Activation energy E_a for the basic polyesterurethane and of those interacted with Na^+, K^+, Mg^{2+} and Ca^{2+}, as a function of the reacted fraction α: *, basic polyurethane; □, Na^+; ■, K^+; ○, Mg^{2+}; ◆, Ca^{2+}.

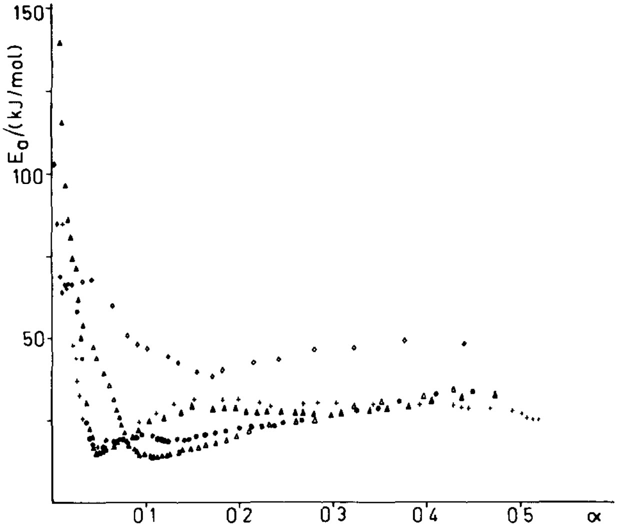

Fig. 2. Activation energy E_a for the polyesterurethanes interacted with cations from the "d" block as a function of the reacted fraction α: ◇, Cu^{2+}; △, Cr^{3+}; ▲, Au^{3+}; ●, Ag^+; +, Fe^{3+}.

TABLE 2

The constants of eqn. (1) and the maximum difference $\varepsilon_{\max}$ between the calculated and measured values of the activation energy

Cation	A	B	C	m	n	$\varepsilon_{\max}$
Na^+	83.94	−7.75	0.433	0.677	1.2	14.6
K^+	62.57	−0.658	0.005	1.05	1.95	15.05
Mg^{2+}	167.18	32.4	−144.6	0.497	0.222	12.3
Ca^{2+}	22.04	0.37	−0.061	1.93	1.59	13.6
Cu^{2+}	16.29	19.22	−0.0001	0.293	2.29	10.72
Ag^+	20.12	0.219	−0.011	1.397	1.858	15.74
Au^{3+}	21.66	0.095	−0.09	2.71	2.69	23.21
Fe^{3+}	120.56	−88.27	21.92	0.31	0.597	9.43
Cr^{3+}	21.57	0.081	−0.019	2.3	2.01	15.85

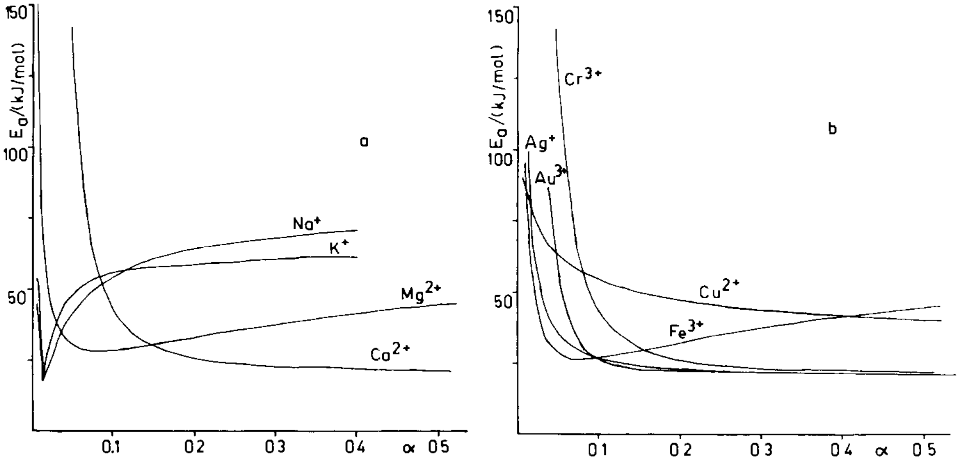

Fig. 3. The graphs of eqn. (1) for (a) "s" block cations, and (b) "d" block cations.

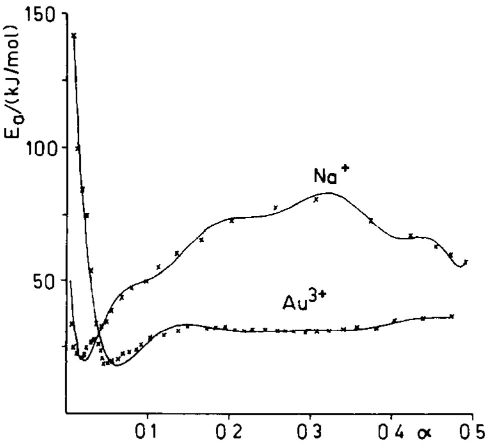

Fig. 4. The polynomial fitting method applied to the samples containing Na^+ and Au^{3+} ions.

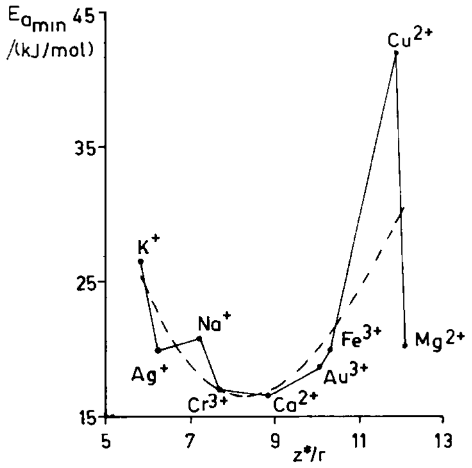

Fig. 5. Plots of the minimum activation energies vs. z^*/r.

chemical properties, we tried to determine a parameter with which to compare their influence on the thermal stability of the polyesterurethane. A suitable parameter seemed to be the one used by Maitra [10] who applied the electrostatic potential experienced by an outermost electron in an M^{n+} ion, expressed as z^*/r, where z^* is the effective nuclear charge calculated using Slatter's rules [11] and r is the ionic radius [12] for M^{n+}.

If we plot the minimum activation energy for every sample against z^*/r (Fig. 5), a minimum-value field for $7.5 < z^*/r < 9.5$ is apparent. The different behaviour of the Cu^{2+} ion, whose minimum energy during the degrading process has the highest value, is noticeable.

For the final stages of decomposition, we can consider the limiting case when the reacted fraction tends to 100%. Thus eqn. (1) becomes

$$\lim_{\alpha \to 1} E_a(\alpha) = \lim_{\alpha \to 1} (A + B/\alpha^m + C/\alpha^n) = A + B + C \qquad (2)$$

Plotting, in this case, the activation energy versus z^*/r (Fig. 6), a field of minimum value for $7.5 < z^*/r < 9.5$ can once again be observed.

It may be fortuitous but, as depicted in Fig. 7, the higher the z^*/r value, the higher the α value corresponding to the minimum in the activation energy.

CONCLUSIONS

Analysing the results obtained, we can conclude that the activation energy for the degradation processes of basic polyurethane is higher than the activation energies for the polyurethane interacted with metallic ions which suggests that the metallic ions of the system are catalysts for the processes of thermal degradation.

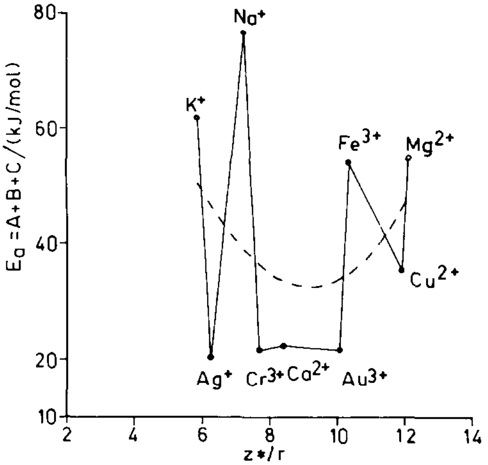

Fig. 6. Plots of the minimum activation energies vs. z^*/r for the final stages of decomposition.

The sample which contained Cu^{2+} ions has a higher minimum activation energy value than the other samples. However, this minimum is displaced to higher values of the reacted fraction. The parameter z^*/r which was proposed to characterize comparatively the thermal degradation processes of the studied samples, would seem to be a suitable parameter for this purpose.

Thus, for this type of polyurethane, metallic ions having a z^*/r value outside the interval 7.5–9.5, have a more reduced contribution to the thermal degradation processes. However, from the industrial point of

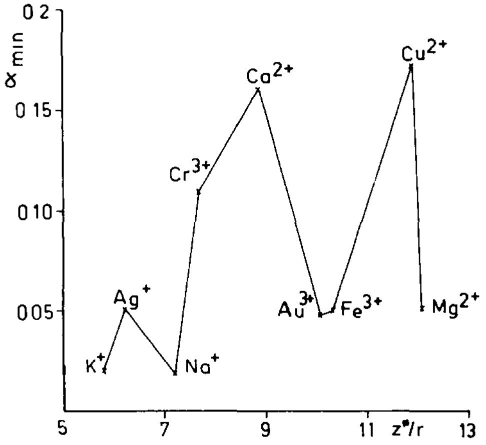

Fig. 7. The reacted fraction that corresponds to the minimum of the activation energy α_{min} as a function of z^*/r.

view, the presence could cause degradation processes which would be very difficult to control.

The influence of other cations on polyurethanes will be the topic of subsequent studies.

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