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A thermal degradation comparative study of polyesterurethane based on 4,4′-diphenylmethane di-isocyanate interacted with "d"-block metallic cations

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Abstract

A thermal degradation study of polyesterurethane based on 4,4′-diphenylmethane di-isocyanate interacted with "d"-block cations is presented. Studies were made of the influence of both the atomic number Z in the 3d series (Cr^{3+}, Fe^{3+}, Co^{2+} and Cu^{2+}) and of the principal quantum number $n = 3$, 4 and 5 (Cu^{2+}, Ag^{+}, Au^{3+}). For the relationship between the activation energy and the reacted fraction, an analytical equation that we proposed in a previous publication was verified. The physical parameter z^*/r, calculated using Slatter's rules, gives semi-quantitative information on the thermal behavior of these compounds.

INTRODUCTION

The present paper continues our investigations using thermal and photochemical degradation studies to determine the influence of metallic cations on the physico-mechanical properties of polyesterurethanic polymers [1]. In the present study, the polyesterurethane based on 4,4′-diphenylmethane di-isocyanate was investigated because it is the preferred polyurethane for synthetic skin. The present study investigates the influence on thermal degradation of metallic cations from the "d" block which could easily contaminate the polyurethane during different stages of its synthesis and subsequent processing.

During the synthesis, it is easy to regulate the porosity of the obtained films and, thus, it is possible to minimize contamination by noble metal cations from residual water. The metals can be recovered by thermal degradation of the samples, knowing that the great majority of noble metal compounds decompose to the elementary metal [2, 3].

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The ions Cr^{3+}, Co^{2+}, and Fe^{3+} were chosen, taking advantage of the possible recovery of their radioactive isotopes from residual water [4, 5].

EXPERIMENTAL

Materials

The polyurethane used was selected with reference to its characteristics as described in the literature [6], the starting materials being 4,4′-diphenylmethane di-isocyanate, poly(ethylene adipate) diol of molecular weight 2000, and ethylene glycol as chain elongator. The polyesterurethane contained 2.235×10^{-3} moles of urethanic groups per gram of polymer. Interaction with the metallic ions was performed according to literature specifications [7]. *N,N*-Dimethylformamide medium and aqueous solutions of equimolar concentrations were used. Any traces of metallic ions remaining in the polyurethane were determined by a radiochemical method, atomic absorption spectroscopy and flame emission spectroscopy [5].

Apparatus

Analyses were performed on a MOM-Budapest derivatograph, recording the weight losses (TG), the derivative (DTG), the differential thermal analysis (DTA) and the temperature increases (T). The investigations were performed in air at a heating rate of $9\ \mathrm{K\ min^{-1}}$, up to 900°C. In order to obtain comparable data, constant sensitivities for TG (50 mg), DTG (1/10), and DTA (1/10) were applied, and the same sample weight of about 50 mg was used.

RESULTS AND DISCUSSION

The thermogravimetric characteristics of the investigated samples are presented in Table 1, with the temperature ranges of the decomposition steps.

The comparison of the thermal stability of the samples was made using the Levi–Reich kinetic analysis method [8, 9]. The values of the reaction orders required in the calculations were estimated by the Coats–Redfern method [10]. Variations in the activation energy with the reacted fraction α for the basic polyurethane and for the interacted samples are presented in Fig. 1(a and b).

To describe analytically the variations in activation energy with reacted fraction, the equation proposed in our previous paper was used [1]

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

TABLE 1

Thermogravimetric characteristics and temperature intervals of the degradation of the basic polyurethane and of the samples interacted with "d"-block cations

Polyurethane P–M^{n+}	Weight losses (%) and temperature intervals (°C)				
	Overall weight loss	Step I	Step II	Step III	Step IV
P	85 [a]	–	–	–	–
P–Cu^{2+}	92.5	23.5	28	37	–
		180–320	320–420	420–600	
P–Ag^{+}	98.5	23	45.5	6.5	22
		160–320	320–420	420–460	460–590
P–Au^{3+}	85.5	29.75	21.75	10	21
		195–335	335–410	410–480	480–595
P–Cr^{3+}	94.5	6	44	11.5	31.5
		62–195	195–375	375–440	440–585
P–Fe^{3+}	89	23	29.25	33.5	–
		174–270	270–395	395–535	
P–Co^{2+}	96.5	1	1	58.5	32.5
		67–98	105–146	170–385	385–580

[a] The basic polyurethane presents just one degradation step between 220 and 560°C.

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

The results obtained are listed in Table 2. The cation constants of the samples containing Co^{2+} were determined using the experimental value for $\alpha \leqslant 0.202$.

The graphs of the analytical expression are presented in Fig. 2(a and b).

The equation describes the thermal degradation process fairly accurately for cations from the 3d series, the only exception being the samples interacted with Co^{2+} for $\alpha > 0.202$. This is also true of samples interacted with metallic ions of different series (3d, 4d, 5d), i.e. Cu^{2+}, Ag^{+}, and Au^{3+} for $\alpha \leqslant 0.35$. For $0.35 < \alpha < 0.6$, the equation gave average values for the activation energy, and the higher the atomic number Z, the higher the deviation. The same observation is valid for the 3d series.

At the beginning of the decomposition process ($\alpha < 0.08$), the activation energy of the pure polyurethane decreased to a value of 130 ± 2 kJ mol^{-1}, at least 30 kJ mol^{-1} higher than the activation energy values of any other samples in the range $0.08 < \alpha < 0.6$.

However, samples that had been interacted with metallic cations presented a minimum in activation energy for $\alpha < 0.35$.

Because of the different oxidation numbers of the studied cations, a physical parameter was used to compare the thermal stabilities [1], i.e. the

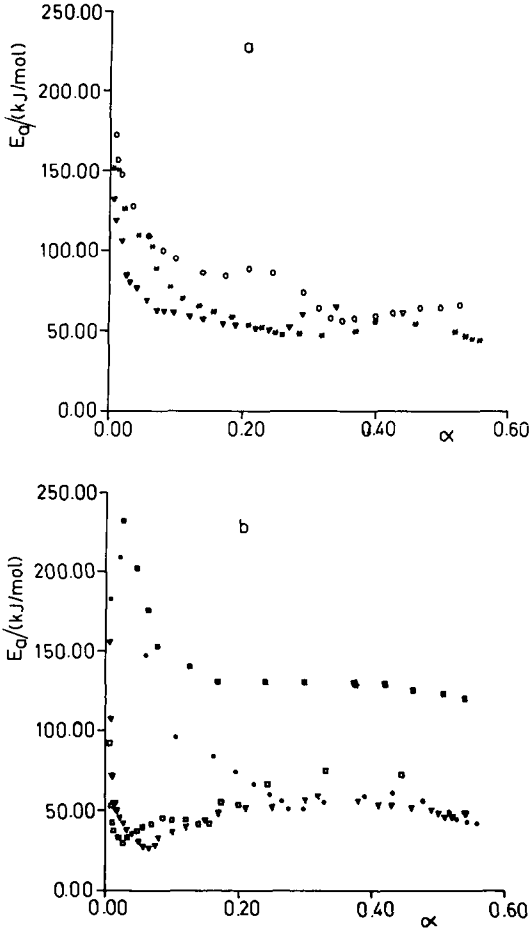

Fig. 1. Activation energy as a function of the fraction reacted α. Polyesterurethane interacted with Cu^{2+}, Ag^{+} and Au^{3+} (a); basic polyesterurethane and interacted with Cr^{3+}, Fe^{3+} and Co^{2+} (b). Key: ■, basic polyesterurethane; *, Cu^{2+}; ∇, Ag^{+}; ○, Au^{3+}; ▼, Cr^{3+}; ●, Fe^{3+}; and □, Co^{2+}.

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+}.

In Figs. 3 and 4, the minimum of the activation energy (for every sample) and the corresponding α value, respectively, are plotted against z^*/r.

In our previous paper [1], the following hypothesis was proposed: cations with z^*/r values between 7.5 and 9.5 have an increased contribution to the thermal degradation process. The cation Co^{2+} has a z^*/r value that is contained in this domain and Figs. 3 and 4 show that the sample with Co^{2+} ions confirmed the hypothesis.

TABLE 2

The constants from eqn. (1) and the maximum difference between the calculated and experimental values of the activation energy for the cations used

Cation	A	B	C	m	n	ε_{max}
Cu^{2+}	14.757	29.363	−5.158	0.381	0.34	7.62
Ag^{+}	37.972	10.122	1.808	0.248	0.667	10.57
Au^{3+}	39.448	−5.182	27.22	0.039	0.331	18.14
Cr^{3+}	74.814	−20.526	4.36	0.513	0.853	9.92
Fe^{3+}	14.51	30.37	−2.91	0.441	0.692	13.47
Co^{2+}	53.388	−2.2	0.143	0.795	1.355	6.54

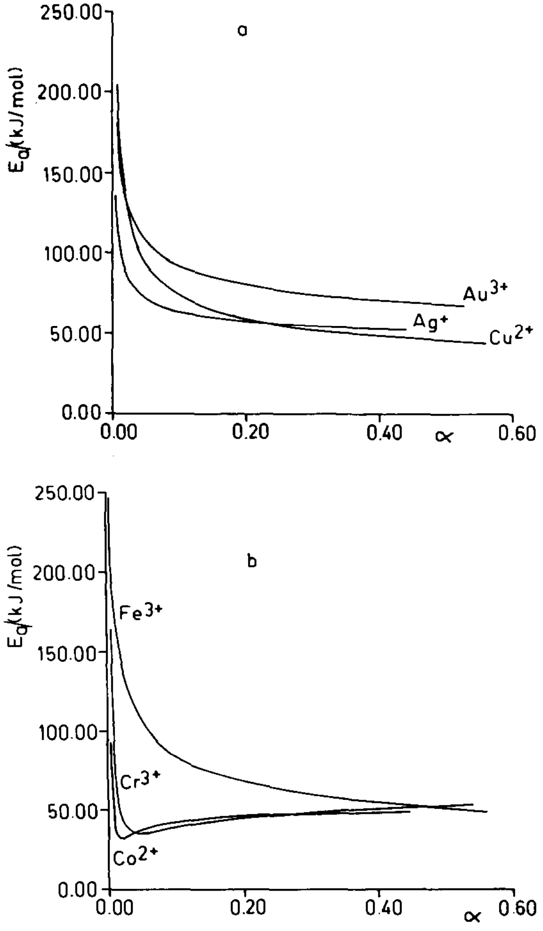

Fig. 2. Graphs of eqn. (1). Cu^{2+}, Ag^{+} and Au^{3+} (a); Cr^{3+}, Fe^{3+} and Co^{2+} (b).

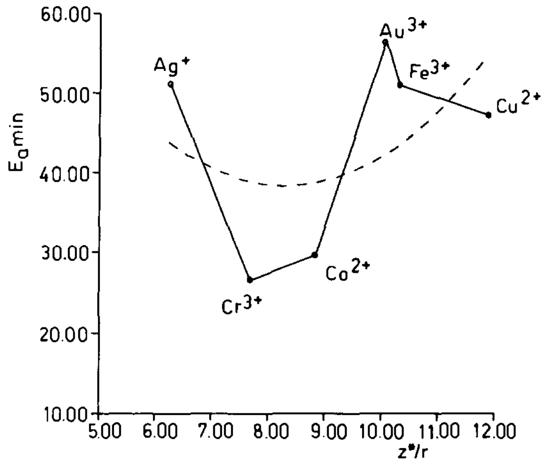

Fig. 3. Plots of minimum activation energy versus z^*/r.

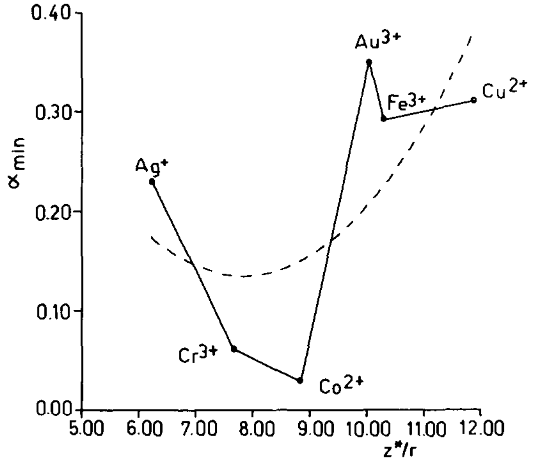

Fig. 4. Plots of the reacted fraction corresponding to the minimum of the activation energy versus z^*/r.

CONCLUSIONS

We can conclude that the range $7.5 < z^*/r < 9.5$ represents an interval in which the influence of the metallic cations on the thermal degradation processes of polyesterurethane can be expected to be quite appreciable. However, metallic cations that fall outside of this range could have undesirable influences on the thermal behavior of polyesterurethanes. The proposed equation for the degrading process can be applied for at least $\alpha < 0.2$, with small errors.

The effects of other cations on the thermal degradation of this class of polyurethanes will be the subject of subsequent studies.

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