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Aspects of polyesterurethanes interaction with metallic ions. I. Influence of sodium cations on thermal behavior of some aliphatic linear polyesters

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Abstract

The influence of sodium cations on the thermal behavior of three aliphatic linear polyesters, namely poly(ethylene adipate)diol, poly(butylene adipate)diol and poly(hexamethylene adipate)diol, the major constituents of polyesterurethanes, was studied by investigating the activation energy of the thermal degradation processes of polymer/sodium ions interaction products in comparison with that of parent polyester, using the Levi–Reich method. © 1997 Elsevier Science B.V.

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1. Introduction

In polyurethanes synthesis, metal-containing catalysts or additives can be used [1–15], but the presence of the traces of metallic cations from residual catalysts or additives may cause changes in the final polymer properties, such as thermal behavior [16]. It was found that, of the kinetic parameters which could be used to characterize thermal stability, only the activation energy (E_a) could be considered as a semiquantitative factor [17,18]. Polyesters are, besides polyisocyanates and chain extenders, the basic starting components of polyesterurethanes, playing a major role in the morphology development and having a pronounced effect on processability and ultimate physical and mechanical properties of the polymer. It is consequently necessary, in studying the interaction between polyurethanes and metallic ions, to also consider the influence of these ions on the polyester properties. The purpose of the present paper is to investigate whether the alkali metal ions, namely sodium ions, could induce changes in the activation energy of three linear aliphatic polyesters: poly(ethylene adipate)diol (PEA), poly(butylene adipate)diol (PBA) and poly(hexamethylene adipate)diol (PHA), these adipates being one of the most widely used polyesters for obtaining a large variety of polyurethanes with different applications. On the other hand, it is worth mentioning that the possibility of employing aliphatic polyester metallic complexes as solid polymeric electrolytes has already been reported [19–22].

2. Experimental

The polyesters used in this study, namely, PEA, PBA, and PHA were synthesized from adipic acid and

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Table 1
Characteristics of polyesters

Polyester	OH No. [a]	Acid No. [a]	$\bar{M}_n$ [b]	$\bar{p}_n$ [c]	Polar groups concentration $\times 10^3$ in mol g^{-1}		
					–COO–	–OH	–COOH
PEA	56.20	3	1964	11.05	11.248	1.018	0.053
PBA	56.74	3	1978	9.43	9.533	1.011	0.053
PHA	63.83	3	1778	7.27	8.178	1.124	0.053

[a] In mg KOH/g.
[b] Number-average molar mass.
[c] Number-average degree of polymerization.

ethylene glycol, 1,4-butandiol and 1,6-hexandiol, respectively, by melt polycondensation. The characteristics of these polyesters, i.e. hydroxyl number (OH No.), acid number (Acid No.), number-average molar mass $(\bar{}_n)$ and polar groups (–OH, –COO–, –COOH) concentration, which were determined by methods described in the literature [23], are tabulated in Table 1.

The interaction between polyesters and sodium cations was brought as follows. To a vigorously stirred solution of polyester in acetone, a solution of NaCl in deionized water was added dropwise, at room temperature. The resulting system was kept under continuous stirring for five more minutes and then, while it was allowed to stand, it separated into two colorless immiscible liquid layers. After 12 h, the interaction product, a white solid formed in the organic phase, was filtered off and subsequently dried at 105°C under vacuum. For every polyester a series of four interaction products were prepared by using various molar ratios of the polar groups (–OH, –COO–, –COOH) in the polymer chains to sodium cations, ranging between 1 : 0.3 and 1 : 1, as well as a reference sample without NaCl. The final products were white powders.

3. Analysis

The sodium content of the interaction products was determined by means of flame emission spectroscopy, as well as indirectly, from chlorine analysis, the results obtained by these two different methods being quite similar.

The thermoxidative behavior of the interaction products and unmodified polyesters was followed on a MOM-Budapest derivatograph of the Paulik–Erdey type. The thermoanalytical curves (TG, DTG, DTA) were recorded simultaneously in air at an average heating rate of 12°C min^{-1}, up to 600°C. In order to obtain comparable data, the thermal analyses were performed in the same conditions for all the studied samples.

4. Results and discussion

The results of quantitative analysis of sodium in the interaction products are summarized in Table 2. The amounts of sodium cations initially added in the systems were adjusted so that, for the same polymer, four different quantities of ions (ranging from 0 to 1 mol) correspond to one mole of polar groups. However, all the resulting interaction products contain much lower amounts of sodium (several times higher molar ratios of polar groups to sodium cations). Meanwhile, the values of the sodium content are very close to each other (their molar ratios lying within a much narrower range than one mole). As the quantity of sodium cations remaining in the products is low relative to that available in solution, it can be assumed that most of the polar groups along the chains are not accessible, probably due to the steric hindrance caused by the conformations addopted by the chains in solution during preparation. It can be observed that usually the products obtained for the ratio 1 : 1 differ from the others by the largest sodium content, which can be explained by the specific preparation conditions (concentration of cations and polyester in the solvent mixture) that provide the most important retention.

In the thermoxidative decomposition of the parent polyesters and of their interaction products with

Table 2
Sodium content of polyester/sodium cations interaction products

Composition	Symbol	Sodium content, %wt		Molar ratio polar groups/sodium cations	
		added	retained	initial	final
PEA/NaCl	A	6.99	3.26	1 : 0.3	1 : 0.125
PEA/NaCl	B	10.41	3.13	1 : 0.5	1 : 0.12
PEA/NaCl	C	13.18	2.66	1 : 0.7	1 : 0.10
PEA/NaCl	D	16.47	6.34	1 : 1.0	1 : 0.27
PBA/NaCl	E	6.16	1.17	1 : 0.3	1 : 0.05
PBA/NaCl	F	9.30	1.30	1 : 0.5	1 : 0.055
PBA/NaCl	G	11.89	1.26	1 : 0.7	1 : 0.05
PBA/NaCl	H	15.04	3.21	1 : 1.0	1 : 0.14
PHA/NaCl	K	5.54	2.67	1 : 0.3	1 : 0.13
PHA/NaCl	L	8.44	2.08	1 : 0.5	1 : 0.10
PHA/NaCl	M	10.89	3.54	1 : 0.7	1 : 0.18
PHA/NaCl	N	13.90	3.36	1 : 1.0	1 : 0.17

Table 3
Results of thermogravimetric analysis

Sample	Mass losses (in %) and temperatures (in °C)				
	Overall mass loss	Step I		Step II	
		ΔT [a]	Δm [b]	ΔT [a]	Δm [b]
PEA	98.3	225–419	90.9	419–535	7.4
A	93.4	231–419	85.4	419–509	8.0
B	91.1	239–414	84.1	414–534	7.0
C	89.5	230–414	81.9	414–525	7.6
D	88.6	230–466	81.5	466–566	7.1
PBA	99.9	220–435	95.8	435–480	4.1
E	96.0	209–412	89.2	412–474	6.8
F	98.3	221–438	91.8	438–510	6.5
G	97.2	221–447	92.0	447–512	5.2
H	93.2	221–435	87.2	435–511	6.0
PHA	98.3	215–460	92.2	460–583	6.1
K	93.2	201–469	89.3	469–538	3.9
L	97.7	190–470	94.1	470–512	3.6
M	94.6	185–471	89.8	471–536	4.8
N	89.7	209–462	86.0	462–524	3.7

[a] Temperature range.
[b] Mass loss.

sodium cations, two consecutive stages can be distinguished; the main stage being followed by a final one. The characteristic temperature ranges (ΔT) and mass losses (Δm) are listed in Table 3.

In carrying out a comparative investigation of thermal decomposition of studied products, the change of the activation energy as a function of fractional extent of reaction (α) was followed by using the Levi–Reich kinetic analysis method [24–26]. The values of the reaction order employed in these calculations were estimated by means of the Coats–Redfern method [27].

The modifications, with α, of the activation energy for the PEA/sodium cations interaction products, as well as for the unmodified polyester, are presented in Fig. 1. Although all the interaction

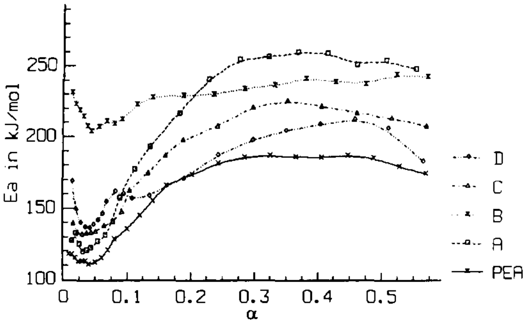

Fig. 1. Activation energy E_a as a function of fractional extent of reaction α for PEA and PEA/sodium cations interaction products.

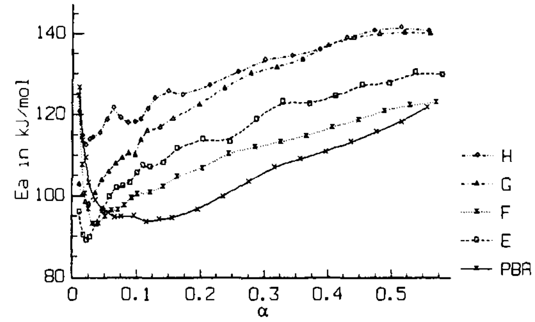

Fig. 2. Activation energy E_a as a function of fractional extent of reaction α for PBA and PBA/sodium cations interaction products.

products show higher values of the activation energy than those corresponding to PEA over the entire conversion range, in general little changes occur in the initial stage (α<0.1). The more stable product seems to be B which exhibits a pronounced rise in E_a even at low conversion. It can be assumed that its content of sodium cations retained by the polar groups is optimum so far as the increase of thermal stability is concerned. As compared to the other products, the behavior of D, in spite of the highest sodium content, is closer to that of PEA probably because most of the sodium cations are physically retained, their influence on the thermal decomposition being very little (play the role of an inert filler).

Plots of E_a vs. α for PBA and for its interaction products with sodium cation are represented in Fig. 2. The initial stages ($\alpha < 0.06$) of interaction products decomposition occur generally with values of E_a below that for the original polyester, while the activation energies for the resulting structures are higher than those for PBA. Also, the original drop is more abrupt and the minimum E_a value is lower for the products than for PBA, so it seems that the sodium cations accelerate the loss of the light decomposition compounds, such as CO_2 [28]. The product H which exhibits the best thermal stability has the highest sodium content and probably the largest amount of sodium cations interacted with polar groups.

The dependence of activation energy on conversion is illustrated in Fig. 3 for PHA and PHA/sodium cations interaction products. As compared to PHA, the interaction products present lower values of E_a in the first part of the decomposition, especially at the very beginning of the process. After reaching a minimum, their activation energies show a slight, gradual rise and at $\sim 95\ \mathrm{kJ\,mol^{-1}}$ become superior to the corresponding values of the parent polyester, which after the original sharp decrease exhibit little changes at conversions above 0.1.

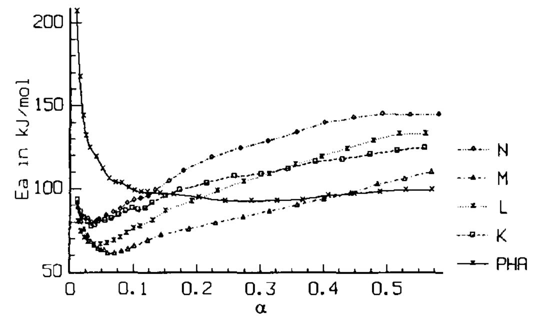

Fig. 3. Activation energy E_a as a function of fractional extent of reaction α for PHA and PHA/sodium cations interaction products.

As it can be noticed, the agreement between the compositional differences and the scatter of the E_a vs. α curves is rather poor, which is attributable, as mentioned before, to the fact that, besides the sodium cations interacting with polar groups, the products also contain physically retained cations, which act as an inert filler, without affecting the thermal decomposition. The products obtained for the ration 1 : 1 exhibit the largest amounts of physically retained sodium cations.

5. Conclusions

The degree of retention of sodium cations depends not only on the concentration of polar groups, but probably on other factors such as conformational modifications of the polymer chains that occur in solution during preparation.

The sodium cations do not cause very important changes in the activation energy of thermal degradation of the three polyesters. However, their presence enhance the thermal stability of PEA. As for PBA and PHA, the sodium cations seem to exert a catalytic effect (more pronounced for PHA) on the processes involved in the initial stages of decomposition, but increase the activation energy for the resulting compounds.

A correlation between the extent of modification of thermal behavior of the interaction products and their sodium content is rather difficult since the products also contain physically retained cations that do not affect degradation.

References

[1] F. Hostettler and E.F. Cox, Ind. Eng. Chem. 52 (1960) 609.

[2] J.W. Britain and P.G. Gemeinhardt, J. Appl. Polym. Sci. 4(11) (1960) 207.

[3] H.A. Smith, J. Appl. Polym. Sci. 7(1) (1963) 85.

[4] J. Robins, J. Appl. Polym. Sci. 9(3) (1965) 821.

[5] S.L. Reegen and K.C. Frisch, J. Appl. Polym. Sci., Part A1 8 (1970) 2883.

[6] T.E. Lipatova and L.A. Bacalov, J. Macromol. Sci. Chem. 4 (1970) 743.

[7] R. Sojecki, Acta Polymerica 40(12) (1989) 715.

[8] E.B. Richter and C.W. Macosko, Polym. Eng. Sci. 18(13) (1978) 1012.

[9] C.-S. Chern, J. Appl. Polym. Sci. 40 (1980) 2189.

[10] L.S. Kangas C.W. Stobbie, Eur. Pat. Appl. EP 344, 912, 1989..

[11] D.R. Hall D.J. Keller, Eur. Pat. Appl. EP 308, 683, (1989)..

[12] P.H. Markusch, J.W. Rosthauser and M.C. Beatty, U.S., US 4, 788, 262, 1988..

[13] Y. Takeuchi and Y. Chihara, Jpn. Kokai Tokkyo Koho JP 01,204,974 (84,204,974), 1989.

[14] K. Kanetani, Jpn. Kokai Tokkyo Koho JP 02 06,519 (90,06,519), 1990.

[15] C. Ciobanu, C. Adumitresei and A. Caraculacu, Patent RSR 68415, 1978.

[16] O.G. Tarakanov, V.A. Orlov and V.K. Belyakov, J. Polym. Sci., Part C 23 (1968) 117.

[17] Z. Pietrzyk, L. Kulesza and M. Jasieniak, J. Therm. Anal. 33 (1988) 1135.

[18] M. Palamaru, I. Rusu, L. Pruna and C. Ciobanu, Thermochim. Acta 230 (1993) 235.

[19] F. Huang, X. Wang and S. Li, J. Macromol. Sci. Chem. A28(2) (1991) 175.

[20] M. Watanabe, M. Rikukawa, K. Sanui and N. Ogata, Macromolecules 19 (1986) 188.

[21] R. Dupon, B.L. Papke, M.A. Ratner and D.F. Schriver, J. Electrochem. Soc. 131 (1984) 586.

[22] F. Huang, X. Wang and S. Li, HuaDong HuaGong XueYuan XueBao 16 (1990) 415.

[23] D.J. David and H.B. Staley, Analytical Chemistry of the Polyurethanes, Vol. XVI, Part III, Wiley-interscience (1969) p.278.

[24] L. Reich and D.W. Levi, Makromol. Chem. 66 (1963) 102.

[25] L. Reich, J. Inorg. Nucl. Chem. 31 (1969) 789.

[26] E. Segal and D. Fátu, Introducere n cinetica proceselor neizoterme (Introduction to nonisothermal kinetics), Ed. Acad. R.S. Romania, Bucureşti, 1983, p.147.

[27] A.W. Coats and J.P. Redfern, Nature 201 (1964) 68.

[28] C. Caşcaval, Studiul polimerilor prin piroliză şi cromatografie de gaze (Study of polymers by pyrolysis and gas chromatography), Ed. Acad. R.S. Romania, Bucureşti, 1983, p.125.