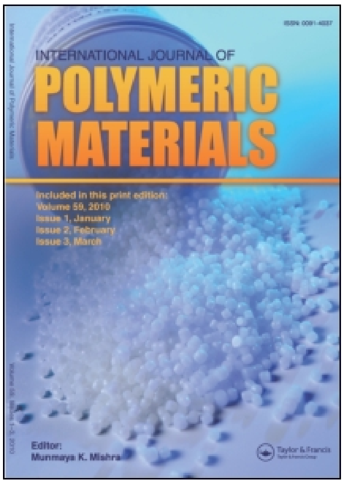

**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Thermal Stability of Polyesteric Precursors of Polyurethanes Interacted with Potassium Cations

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**To cite this Article** Moroi, Gabriela , Ciobanu, Constantin , Bilba, Nicolae , Palamaru, Mircea and Condratov, Vladimir(1998) 'Thermal Stability of Polyesteric Precursors of Polyurethanes Interacted with Potassium Cations', International Journal of Polymeric Materials, 39: 1, 141 — 149

**To link to this Article: DOI:** 10.1080/00914039808041039

**URL:** http://dx.doi.org/10.1080/00914039808041039

*Intern. J. Polymeric Mater.*, 1998, Vol. 39, pp. 141–149
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# Thermal Stability of Polyesteric Precursors of Polyurethanes Interacted with Potassium Cations

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*(Received 20 May 1997)*

The effect of potassium cations on the thermal stability of three aliphatic linear polyesters, i.e. poly(ethylene adipate)diol, poly(butylene adipate)diol and poly(hexamethylene adipate)diol, major precursors of polyesterurethanes, was investigated. The activation energy of the thermal decomposition processes of polymer/potassium ions interaction products and of parent polyesters was evaluated using the Levi-Reich thermal analysis method. It was found that the presence of potassium cations enhances the thermal stability of the studied polyesters.

*Keywords:* Thermal stability; activation energy; polyester; potassium cations; interaction

## INTRODUCTION

Polyurethane properties, such as thermal behavior [1], may be affected by the traces of metallic cations from residual catalysts and additives, when in the synthesis process metal-containing catalysts and additives are used [2–21]. In studying the interaction between polyurethanes and

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metallic ions, it is necessary to also investigate the influence of these ions on the polyesters, since the latter are, along with polyisocyanates and chain extenders, the basic precursors of polyesterurethanes, playing an important role in the polymer morphology evolution and having a significant effect on its processability and ultimate properties. The present study aims to establish whether the potassium cations could induce modifications in the thermal stability of three linear aliphatic polyadipates, i.e. poly(ethylene adipate)diol (PEA), poly(butylene adipate)diol (PBA) and poly(hexamethylene adipate)diol (PHA), which are widely employed for obtaining a large variety of polyurethanes with different applications. For this purpose, the change of activation energy ($E_a$) of the thermal decomposition was examined since, of the kinetic parameters which could be used to characterize the thermal stability, $E_a$ is the only one that could be considered as a semiquantitative factor [22, 23]. On the other hand, it is worth mentioning that the aliphatic polyester metallic complexes, such as those with alkali metal salts, can be employed as solid polymeric electrolytes [24–26].

## EXPERIMENTAL

The polyesters used in this study, namely, PEA, PBA, and PHA were synthesized from adipic acid and 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 ($M_n$) and polar groups (—OH, —COO—, —COOH) concentration, which were determined by methods described in the literature [27], are tabulated in Table I.

The interaction between polyesters and potassium cations, as potassium chloride, was carried out by the method reported elsewhere [28]. For each 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 potassium cations, ranging between 1:0.3 and 1:1, as well as a reference sample without KCl.

The potassium content of the interaction products was determined by means of flame emission spectroscopy, as well as indirectly, from

TABLE I Characteristics of polyesters

| *Polyester* | *OH NO.*[a] | *Acid No.*[a] | $M_n$[b] | $p_n$[c] | *Polar group concentration* × *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.

chlorine analysis, the results obtained by these two different methods being in agreement within the limits of experimental error.

The thermoxidative behavior of the interaction products and unmodified polyesters was followed on a MOM-Budapest derivatograph of Paulik-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.

## RESULTS AND DISCUSSION

The results of quantitative analysis of potassium in the interaction products are presented in Table II. For each polyester, the ratio of polar groups to potassium cations in the initial systems was adjusted to four distinct values, ranging from 1:0.3 to 1:1, by adding the appropriate amounts of potassium ions. However, all the resulting interaction products contain much lower quantities of potassium and, accordingly, the molar ratios are significantly higher; meanwhile, it can be observed that their potassium contents are quite close to each other, so that the values of the molar ratio lie within a much narrower range than initially. Since the amount of potassium cations remaining in the interaction products is low in comparison with that available in solution, it can be assumed that most of the polar groups along the polymer chains are inaccessible, presumably due to the sterical hindrance

TABLE II Potassium content of polyester/potassium cations interaction products

| *Composition* | *Symbol* | *Potassium content* % *wt* | | *Molar ratio polar groups/potassium cations* | |
|---|---|---|---|---|---|
| | | *added* | *retained* | *initial* | *final* |
| PEA/KCl | A | 11.33 | 1.10 | 1:0.3 | 1:0.023 |
| PEA/KCl | B | 16.50 | 0.87 | 1:0.5 | 1:0.018 |
| PEA/KCl | C | 20.52 | 1.44 | 1:0.7 | 1:0.031 |
| PEA/KCl | D | 25.10 | 2.63 | 1:1.0 | 1:0.0575 |
| PBA/KCl | E | 10.05 | 0.79 | 1:0.3 | 1:0.019 |
| PBA/KCl | F | 14.85 | 1.10 | 1:0.5 | 1:0.027 |
| PBA/KCl | G | 18.67 | 0.33 | 1:0.7 | 1:0.008 |
| PBA/KCl | H | 23.14 | 0.66 | 1:1.0 | 1:0.016 |
| PHA/KCl | K | 9.07 | 3.22 | 1:0.3 | 1:0.094 |
| PHA/KCl | L | 13.56 | 1.79 | 1:0.5 | 1:0.051 |
| PHA/KCl | M | 17.20 | 0.88 | 1:0.7 | 1:0.0245 |
| PHA/KCl | N | 21.54 | 1.67 | 1:1.0 | 1:0.047 |

caused by the conformations adopted by the macromolecules in solution during preparation.

The products with the highest potassium content correspond to different values of the initial molar ratio, i.e. 1:1, 1:0.5 and 1:0.3 for PEA, PBA and PHA, respectively; this fact is attributable to the specific conditions of preparation (concentration of cations and polyester in the solvent mixture) that provide the most important retention.

The thermoxidative decomposition of the parent polyesters and of their interaction products with potassium cations proceeds in two consecutive stages, the first step being the main one. The characteristic temperature ranges ($\Delta T$) and mass losses ($\Delta m$) are listed in Table III. It can be noticed that the initial decomposition temperatures of all the interaction products are higher than those of the corresponding unmodified polyesters.

In order to carry out a comparative investigation of thermal stability of studied products, the change of the activation energy of the decomposition process as a function of fractional extent of reaction ($\alpha$) was evaluated by using the Levi-Reich kinetic analysis method [29–31]. The values of the reaction order employed in these calculations were estimated by means of the Coats-Redfern method [32].

TABLE III Results of thermogravimetric analysis

| *Sample* | *Mass losses (in %) and temperatures (in °C)* | | | |
|---|---|---|---|---|
| | *Step I* | | *Step II* | |
| | $\Delta T^a$ | $\Delta m^b$ | $\Delta T^a$ | $\Delta m^b$ |
| PEA | 225–419 | 90.9 | 419–535 | 7.4 |
| A | 239–394 | 88.0 | 394–494 | 9.5 |
| B | 253.5–402 | 85.9 | 402–552.5 | 8.3 |
| C | 235–396 | 88.0 | 396–515.5 | 9.1 |
| D | 244–394 | 87.6 | 394–518.5 | 9.8 |
| PBA | 220–435 | 95.8 | 435–480 | 4.1 |
| E | 240–431.5 | 92.1 | 431.5–515.5 | 7.8 |
| F | 250–436 | 93.8 | 436–509 | 6.1 |
| G | 239–423 | 89.6 | 423–498 | 7.9 |
| H | 237–428.5 | 90.9 | 428.5–521 | 8.7 |
| PHA | 215–460 | 92.2 | 460–583 | 6.1 |
| K | 250–437 | 86.3 | 437–509 | 6.6 |
| L | 250–442 | 88.9 | 442–498 | 4.8 |
| M | 249–436.5 | 91.4 | 436.5–505 | 6.4 |
| N | 248–439 | 90.8 | 439–501.5 | 6.5 |

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

The dependence of activation energy on conversion for PEA and PEA/potassium cations interaction products is illustrated in Figure 1. All the interaction products show higher values of the activation energy than those corresponding to the original polyester over the entire conversion range. The product *B* exhibits the most pronounced rise in $E_a$, so it can be assumed that, although its potassium content is the lowest, the amount of potassium cations interacted with the polar groups is optimum so far as the increase of thermal stability is concerned. The highest potassium content of product *D* results in a closer behavior to that of PBA as compared to the other products, which supports the assumption that actually most of the potassium cations are physically retained and their influence on the thermal degradation process is very little (play the role of an inert filler).

The modifications, with $\alpha$, of the activation energy are presented in Figure 2 for the PBA/potassium cations interaction products, as well as for the unmodified polyester. Over the whole conversion range, the energies of activation for the interaction products are increased in

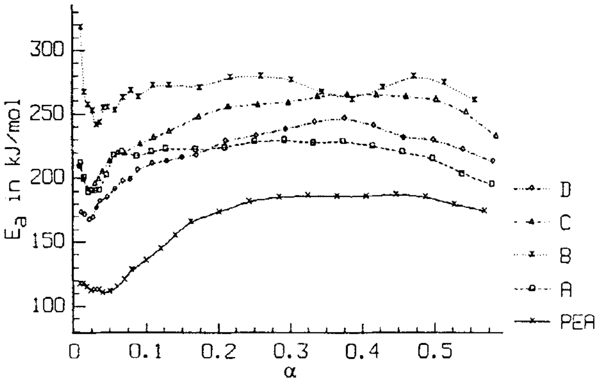

FIGURE 1 Activation energy $E_a$ as a function of fractional extent of reaction $\alpha$ for PEA and PEA/potassium cations interaction products.

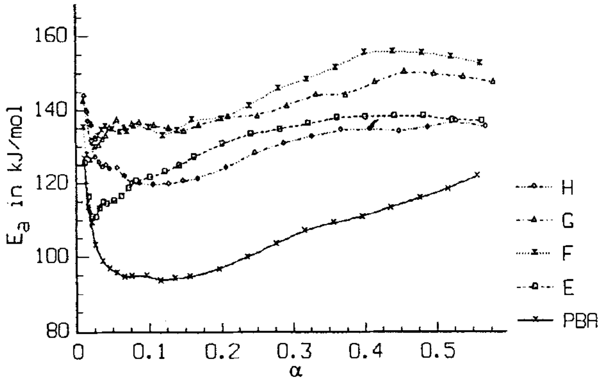

FIGURE 2 Activation energy $E_a$ as a function of fractional extent of reaction $\alpha$ for PBA and PBA/potassium cations interaction products.

comparison with those corresponding to PBA. The most stable product appears to be *F* which has the highest potassium content and probably also the largest quantity of potassium cations retained by the polar groups; the product *H* seems to contain the lowest amount of such ions since it shows the less different behavior from that of PBA.

For both PEA and PBA products, the original drop in activation energy is more abrupt and the minimum $E_a$ value is somewhat shifted towards lower conversions as compared with the parent polyesters, which suggests that the initial loss of the light decomposition compounds, such as $CO_2$ [33], occurs more rapidly in the presence of potassium cations.

Plots of $E_a$ vs. $\alpha$ for PHA and for its interaction products with potassium cations are represented in Figure 3. Except for the very little initial decrease, the activation energies of the interaction products gradually increase with increasing conversion, unlike the activation energy of PHA which after the original sharp drop exhibits little changes at conversions above 0.1. As compared to the unmodified polyester, all the products have superior values of $E_a$ over most of the conversion range; only at conversions below 0.04 the activation energies of the products are lower than those for PHA, which can be assigned to a slight catalytic action exerted by the potassium cations on the processes that occur at the onset of decomposition. Although there are rather little differences between the behaviors of the four products, it can be observed that the best thermal stability is shown by the product *L*.

The poor agreement between the compositional differences and the scatter of the $E_a$ vs. $\alpha$ curves is attributable, as already mentioned, to the fact that, besides the potassium cations interacting with polar groups, the products also include physically retained cations, which act as an inert filler, without affecting the thermal decomposition. According to the modifications in activation energy revealed by the

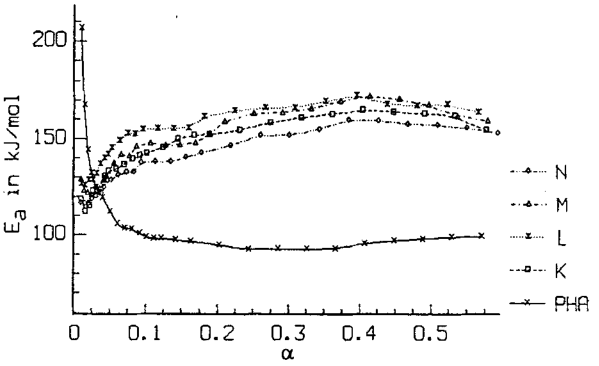

FIGURE 3 Activation energy $E_a$ as a function of fractional extent of reaction $\alpha$ for PHA and PHA/potassium cations interaction products.

present study, the products corresponding to the initial molar ratio 1:0.5 contain optimum quantities of potassium cations interacted with polar groups.

## CONCLUSIONS

The presence of potassium cations enhances the thermal oxidative stability of the three polyesters; in the case of PHA, the cations seem to also have a slight catalytic effect on the processes involved in the initial stages of decomposition. The most thermally stable products are obtained for the initial value 1:0.5 of the polar groups/potassium cations molar ratio.

A relationship between the extent of modification of thermal stability of the interaction products and their potassium content is difficult to establish due to the presence of physically retained cations that do not affect degradation; the increase in activation energy of the polyesters is induced exclusively by the small amounts of potassium cations interacted with polar groups.

The degree of retention of potassium cations depends not only on the concentration of polar groups, but also on other factors, such as conformational state of the interacting macromolecules.

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