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THERMAL BEHAVIOUR OF BINARY SYSTEMS OF POLYOXYETHYLENE AND SODIUM (POTASSIUM) IODIDE

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Abstract

The influence of a wide range of concentrations (0.1–40 mass%) of Na(K)I on both the thermal behaviour and melt indexes of polyoxyethylene (POE) in a broad temperature interval was investigated by combined dynamic thermal analysis and with an extrusion plastometer.

It was found that addition of 2–5 mass% of alkali salts resulted in the optimum thermal stability of POE and increased the melt index of high molecular POE, regardless of the mode of introduction of the additives into the polymer.

Keywords: binary mixtures, melt indexes, polyoxyethylene-sodium(potassium) iodide, thermal analysis

Introduction

Studies of binary systems based on polyoxyethylene (POE) and alkali metal salts have been concentrated on their ionic complexes (IC) of high conductivity [1–5]. The IC of POE with Na(K)SCN and with Na(K)I are comparatively well known and have been studied previously [6–8]. The thermal stability of POE is known to increase in the presence of alkali metal salts [9, 10]. The thermal behaviour of these systems in the solid phase, however, has not been studied in detail [10, 11]. In our previous studies we have found that very low concentrations of Na(K)SCN increase the thermal stability of POE in air, the effect being close to that of the IC containing much higher concentrations of the salts (35–40 mass%). Moreover, a considerable increase in the melt index (MI) of high-molecular POE was found in the presence of Na(K)SCN [13]. Further studies of similar systems can be useful for clarifying the mechanism of the stabilizing effect mentioned above, and in the processing of these systems into manufactured articles.

The aim of the present work was to follow the influence of a wide range of concentrations of NaI and KI on the thermal behaviour and melt indexes of POE in a broad temperature interval.

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Experimental

Binary systems of three types of POE with different average viscosity molecular masses ($\overline{M}$v) denoted as POE1 ($\overline{M}$v=$1.8\cdot10^6$), POE2 ($\overline{M}$v=$2\cdot10^4$) and POE3 ($\overline{M}$v=$7\cdot10^3$) were analyzed. The high molecular POE (HMPOE) – POE1 was a commercial product of Chimic (Dimitrovgrad, Bulgaria), POE2 (Merck, Germany) and POE3 (Verila, Sofia, Bulgaria).

NaI and KI (reagent grade) were commercial products of Reachim (Ukraine) and were used as received. Their concentrations in the mixtures varied from 0.1 to 40 mass%.

Binary mixtures were prepared in two ways [12], i.e. by grinding the initial components in the solid state in a mortar and by mixing solutions of POE and the salts in methanol followed by evaporation of the solvent.

A combined dynamic thermal analysis instrument (OD – 102 Derivatograph, MOM, Hungary), was employed under the following conditions: heating rate of 6°C min^{-1}; sample mass 100±0.5 mg (powder or foil kept in the presence of a drier); Pt crucible as a holder without standard substance; medium-air (static) and nitrogen flowing over the sample at a rate of 17 1 h^{-1}.

Using the TG and DTG curves obtained, the apparent activation energies of the thermal decomposition (E_a) of the samples under study were determined [14, 15]. The total areas of the exothermal peaks for the complete oxidative decomposition of the thermally active components (ΔS) were calculated by graphical integration employing the mass method.

MI were obtained by means of an extrusion plastometer according to the requirements of ASTM – D – 1238 – 65T. The melt indexes of HMPOE and its mixtures containing 2 and 5 mass% of alkali salts were determined under a loading of P=21.6 kg at 200, 250, 265 and 280°C. The MI values at 200°C of mixtures that have already been passed through the extruder at the above temperatures (the so-called secondary MI) were also determined.

Results and discussion

Derivatographic analyses

Initial components

The influence of atmospheric oxygen was found to be of crucial importance in the initial stages of thermal decomposition of POE with different $\overline{M}$v up to ca. 320°C [12]. The corresponding curves are shown for comparison (curves 1 and 2, Fig. 1). In air the decomposition took place in two principal stages within the temperature intervals 180–320°C and 320–500°C and was accompanied by wide and strong exothermal peaks and followed by complete burning. The decomposition in nitrogen took place in one stage within a narrower temperature interval, 330–420°C. The apparent E_a of the basic thermal decomposition was much higher than the corresponding E_a value for the decomposition in air (260 kJ mol^{-1} in nitrogen *vs*. 50 kJ mol^{-1} in air).

No peaks corresponding to mass loss were observed up to 600°C on the experimental thermal curves for the initial NaI and KI under the same conditions of analysis (Fig. 1, curve 5 and Fig. 2, curve 4). The DTA curves only showed the endothermal peaks of the melting of the salts at 640 and 680°C.

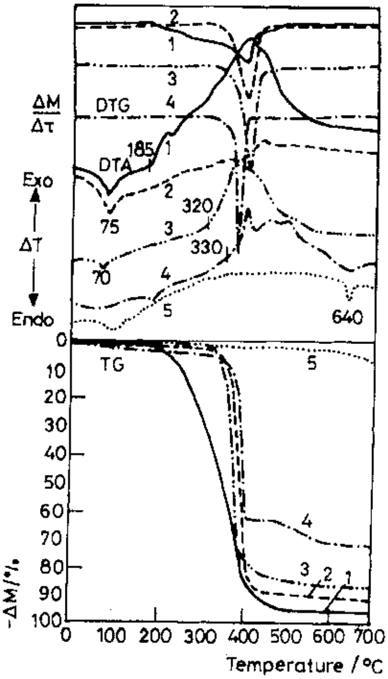

Fig. 1 Thermal curves of POE1 in air-(curve 1), and in nitrogen-(curve 2), mixture of POE1 and 5 mass% NaI-(curve 3); ionic complex of POE1 and NaI-(curve 4); NaI-(curve 5)

Binary mixtures of POE1 and NaI

The results of the thermal analyses of mixtures of POE1 and NaI (Figs 1 and 3 and Table 1) showed considerable changes in their thermal characteristics associated with both the mass loss and heat release in the thermooxidative decomposition reactions as compared with those of the initial POE1. At very low concentrations of NaI (0.1 and 0.5 mass%) the initial temperatures of oxidation ($T_{i.o}$) and mass loss (T_o) for the compositions increased considerably in comparison with those of the initial POE1. These two temperatures were almost the same and corresponded to the induction period (τ_{ind}) established from the onset of the first exothermal peak in the DTA curves (Table 1).

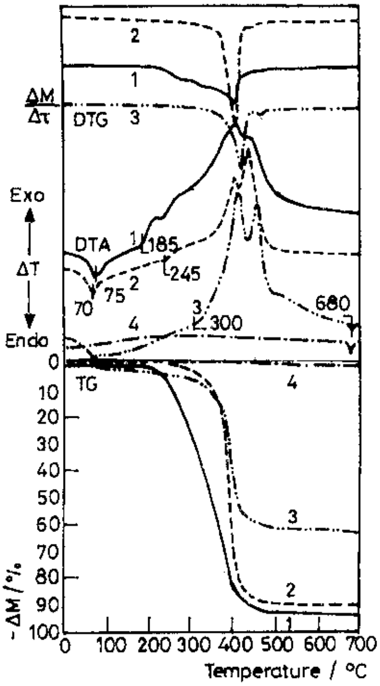

Fig. 2 Thermal curves of POE1 in air-(curve 1), mixture of POE1 and 1 mass% KI-(curve 2); ionic complex of POE and KI-(curve 3); KI-(curve 4)

The increase in NaI concentration led to a higher temperature of initial decomposition (T_o) which increased by 130°C. The temperature of 10% decomposition increased by ca. 100°C. At the same time, the temperature of 50% decomposition ($T50$) and the temperature corresponding to the maximum decomposition rate (T_{max}) increased only by 40 and 10°C, respectively (Fig. 3). An increase in the alkali salt content resulted in higher thermal stability and higher values of E_a for the basic thermooxidative decomposition (50 kJ mol^{-1} for the initial POE1 *vs*. 188 kJ mol^{-1} for POE containing 5 mass% of NaI, *vs*. 226 kJ mol^{-1} for the IC (Table 1).

The DTA curves of the samples (Fig. 1) indicate that besides a considerable shift towards higher temperatures, there was also a certain reduction of the initial exothermal peaks of the oxidation of POE. When the content of the salt was within 2–5 mass%, the first exothermal peaks vanished almost completely and sharp reductions were observed for the other mixtures. The general heat release and the areas of the exothermal peaks, $\Delta S\%$, were reduced by more than 50% in comparison with those for the initial POE1 (Table 1). Following that a slight increasing trend of the peaks was observed. The endothermal peak at 190°C (Fig. 1, curve 4) was due to the melting of the crystalline IC of POE1 and NaI.

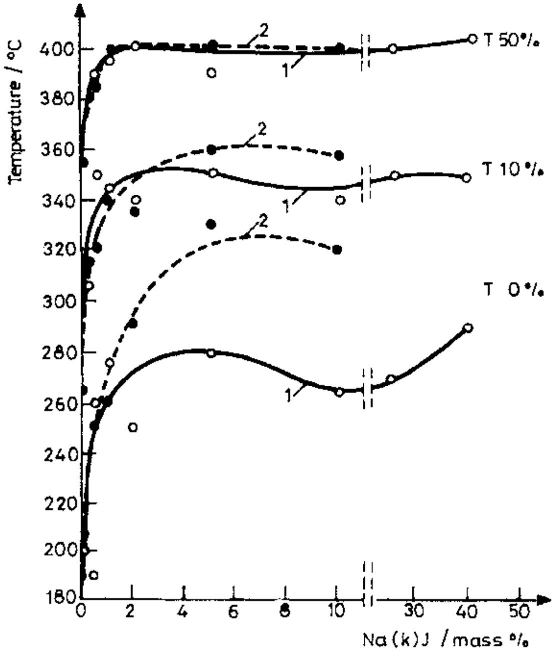

Fig. 3 Dependence of the characteristic temperatures of the decomposition of mixtures based on POE1 and KI-(curves 1) and POE1 with NaI-(curves 2), on the salts content

When the content of NaI was more than 5 mass%, a separate stage appeared for the decomposition of the by-product formed after the basic decomposition of the samples (Fig. 1, curves 3 and 4). Curve 4 also revealed that in the case of the IC of POE1 and NaI, the high-temperature exothermal peak of the residual prod-

Table 1 Thermal characteristics of binary systems of POE1 and NaI

NaI content/ mass%	$\tau_{ind.}$/ min	$T_{i.o.}$/	T_o/	T_{max}/	$-\Delta S$/ %	E_a/ kJ mol^{-1}	Correlation coefficient
			°C				
0	24	185	190	395	0	50	0.9996
0.1	24	185	205	395	37	80	0.9998
0.5	36	235	250	395	51	92	0.9998
1.0	40	250	260	400	63	92	0.9997
2.0	45	300	290	385	57	134	0.9998
5.0	48	330	330	400	70	188	0.9998
10.0	44	320	320	400	52	172	0.9998
35.0*	49	330	320	390	82	226	0.9996

*IC of POE1 and NaI (melt temperature 190°C) uct of burning was bimodal, and the corresponding step in the TG curve in the temperature interval 480–600°C was completely separated and shifted by more than 50°C towards higher temperatures.

Binary compositions of POE1 and KI

The thermal curves and the resulting thermal characteristics of the POE1-KI compositions (Figs 2, 3 and Table 2) revealed a considerable shift of the thermooxidative decomposition towards higher temperatures at very low KI content. The increase in thermal stability was found to be greater for mixtures containing 5 mass% KI, and for the IC of POE and KI (Fig. 3, curve 1, Table 2).

Table 2 Thermal characteristics of binary systems of POE1 and KI

KI content/ mass%	$\tau_{ind.}$/ min	$T_{i.o.}$/	T_o/	$T_{max.}$/	$-\Delta S$/ %	E_a/ kJ mol^{-1}	Correlation coefficient
			°C				
0	24	185	190	395	0	50	0.9996
0.1	24	170	200	395	39	79	0.9994
0.5	38	260	260	390	43	111	0.9989
1.0	32	245	275	400	52	143	0.9995
2.0	31	250	250	400	44	116	0.9995
5.0	28	250	280	390	50	119	0.9995
10.0	28	250	265	400	33	93	0.9999
25.0	38	270	270	400	35	105	0.9993
40.0	44	290	290	400	33	92	0.9997
40.0*	44	300	290	410	39	105	0.9992

*IC of POE1 and KI (foil)

It should also be noted that for mixtures of POE and KI, no other high-temperature step of the decomposition appeared in the corresponding curves. This holds true for the IC, too (Fig. 2, curve 3). A decrease in the heat release was observed up to 300°C. After that, the amount of heat released was sufficient to catalyse the burning of the polymer almost completely at about 450°C.

When the IC of POE and KI was heated, a mass loss was observed before the principal decomposition of the sample, which could not be explained by a release of moisture alone. This mass loss could also be accounted for by the formation of low-molecular fragments. They cannot recombine because of the amorphous structure of the IC of POE and KI, unlike the fragments of the IC of the other salts whose crystalline structure favours the recombination of free radicals.

Regardless of the molar mass of POE, for binary mixtures the resulting stabilizing effect of the salts was found to cause changes in the thermal characteristics (Table 3).

Table 3 Thermal characteristics of binary system of POE2 with NaI and KI

Salt content /mass%	τ_{ind}/ min	$T_{i.o}$/	T_o/	$T50$/	T_{max}/	$-\Delta S$/ %	E_a/ kJ mol^{-1}	Correlation coefficient
		°C						
0	22	150	180	350	390	0	38	0.9995
1% NaI	28	200	200	390	395	15	132	0.9993
2% NaI	35	290	280	400	395	20	113	0.9989
5% NaI	47	320	310	400	400	37	170	0.9994
5% KI	45	300	290	395	395	30	139	0.9995

Determination of melt indexes

The results of studies of the MI reveal interesting behaviour of these systems as far as the requirements for their thermal stability and processability are concerned. The MI of the initial HMPOE is very low, i.e., MI esceeded lg 10 min^{-1} only at 280°C and maximum loading. After the second extrusion at 250°C and at maximum loading, the MI of POE changed to ca. 1 g 10 min^{-1}. The above results, however, showed that long before these temperatures were reached, the initial POE had already been decomposed to a considerable degree. For this reason the initial HMPOE cannot be processed by moulding under pressure and extrusion.

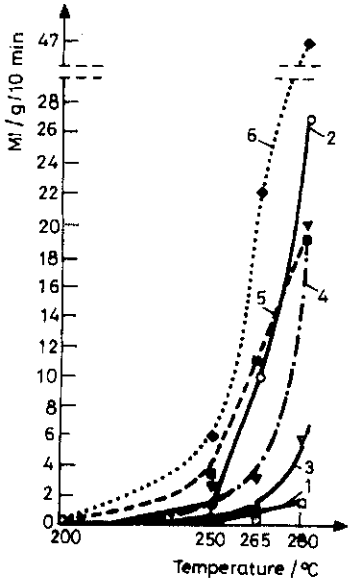

Fig. 4 Increase of the MI *vs.* the temperature of extrusion; for the initial POE1-(curve 1); secondary MI for the initial POE-(curve 2); for a mixture of POE1 and 5% KI-respectively (curves 3 and 4); for a mixture of POE1 and 5% NaI-(curves 5 and 6)

In the presence of alkali salts the MI of HMPOE increased considerably. The increase in MI was found to be higher for the mixtures containing NaI, (Fig. 4, curves 5 and 6) as compared to the mixtures with KI (Fig. 4, curves 3 and 4).

The considerable increase in the thermal stability for the mixtures and their better flow characteristics are important advantages in their processing into manufactured articles.

Conclusions

1 – The thermal behaviour of POE on dynamic heating in the presence of a wide range of concentrations (0.1–40 mass%) of Na(K)I was studied.

2 – It was proved that NaI and KI exhibit an appreciable thermal stabilizing effect on POE in air, regardless of the mode of their introduction into POE.

3 – The optimum thermal stabilizing effect was observed for NaI and KI contents of 2–5 mass%.

4 – The alkali salts studied, introduced in optimum concentrations within 2–5 mass% were found to improve the melt index of high-molecular POE considerably.

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