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THE THERMAL BEHAVIOUR OF HIGH-MOLECULAR POLYOXYETHYLENE-UREA BINARY MIXTURES

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Abstract

The thermal behaviour (from 20 to 500°C) of high-molecular polyoxyethylene-urea mixtures which formed a molecular complex was investigated by means of a derivatograph. Under the conditions of the investigation, there were no indications of an interaction between the thermal decomposition products and the initial components, or of new intermediates with a thermostabilizing effect. A linear coorelation was obtained between the mass loss at 250°C and the urea content of the mixture, which may be used to determine the urea content of similar mixtures.

Keywords: high-molecular polyoxyethylene-urea mixtures, molecular complex

Introduction

The readiness of polyoxyethylene (POE) to undergo oxidation is known to decrease in the presence of various organic and inorganic substances. A number of reports have been published on the use of a variety of nitrogen-containing compounds, such as urea and its derivatives, as low-temperature stabilizers of the molecular weight of POE [1–4]. When POE and urea are mixed, a molecular complex (MC) is obtained [5–7], in which the molecular ratio of POE to urea is 1:2. The temperature of fusion and some structural characteristics have been determined [7]. Reports on the thermal behaviour of binary mixtures of high-molecular POE and urea above the temperature of fusion of the MC are unknown. Accordingly, it appears of interest to clarify the possibility of interaction between products of the thermal decomposition of the components. It seems prob-

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able that heating of the initial components leads under certain conditions to the formation of nitrogen-containing intermediates with a thermostabilizing effect.

In the present study, the thermal decomposition of binary mixtures of high-molecular POE and urea was investigated in a wide temperature interval.

Experimental

High-molecular POE with a mean viscosity molecular mass M_v of 2.7×10^6 and p.a. urea (Ridelharn, Germany) were used. The binary mixtures investigated were prepared in two ways:

1) By homogenizing mixtures of the components in definite ratios (Table 1A) by grinding in the solid state at room temperature for one hour.

2) By mixing a solution (1%) of POE in methanol with a solution (10%) of urea in benzene in definite ratios (Table 1B), evaporating and then drying the residues. The actual contents of urea in these mixtures were determined by elementary analysis (Carlo Erba, Italy) of nitrogen, carbon and hydrogen contents (Table 1B).

TG, DTG, and DTA curves were obtained with an OD-102 derivatograph (MOM, Budapest) under the following conditions: temperature range 20–550°C, heating rate 6 deg·min^{-1}, sample weight 100±0.5 mg, a medium of static air, a ceramic-metal crucible as holder, no inert substance. The areas of the total exotherms of the oxidative decomposition (S_{ox}), obtained from DTA curves recorded under identical experimental conditions, were measured by graphical integration.

Results and discussion

Thermal decomposition of initial components

The thermal decomposition of urea involves a complicated mechanism, which may differ with conditions such as temperature, rate of heating, sample weight, layer thickness, rate of lead-off of the gases formed, etc. [8, 9]. In a range of about ±15°C deg near the melting temperature, urea decomposes during 20–40 hours, generating cyanuric acid, biuret or triuret and ammonia [9] according to reactions (1), (3) and (4):

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \quad (1)$$

$$CO(NH_2)_2 \rightarrow H_2O + H_2CN_2 \quad (2)$$

Table 1 Urea-content and melting temperatures of the mixtures

A Mechanical mixtures											
Numbers of the mixtures	1	2	3	4	5	6	7	8	9	10	11
Urea-content / mass.%	0	10	20	30	45	58	70	73.2	80	90	100
T_{melt} of POE '/ °C	80	70	65	70	70	75	75	65	65	70	–
T_{melt} of urea / °C	–	–	130	145	135	135	–	130	135	140	145
T_{melt} of MC / °C	–	–	–	–	150	150	150	140	140	–	–

B Mixtures, obtained as insoluble fraction										
N-s of the mixtures	1	2	3	4	5	6	7	8	9	10
Urea-content elem. anal. / mass.%	1.0	8.1	15.8	57.8	58.7	61.7	62.5	68.0	70.9	76.5
Urea-content term. anal. / mass.%	2.0	10.0	18.0	50.5	57.5	61.5	72.5	77.0	80.0	77.5
T_{melt} of POE / °C	75	70	75	65	65	65	–	–	–	–
T_{melt} of urea / °C	–	–	–	145	–	–	–	–	–	–
T_{melt} of MC / °C	–	–	–	160	150	150	155	160	155	165

$$CO(NH_2)_2 + HNCO \rightarrow NH_2CONHCONH_2 \tag{3}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{4}$$

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{5}$$

The decomposition of urea by fast heating proceeds mainly without formation of biuret, and in the presence of moisture biuret formation is also prevented [9, 10]: reactions (4) and (5). IR spectroscopy reveals that the gas phase over melted urea at 140°C consists of cyanuric acid, ammonia and CO_2 [9]. From the thermal curves obtained on dynamic heating (Fig. 1, TG curve 4), it may be cal-

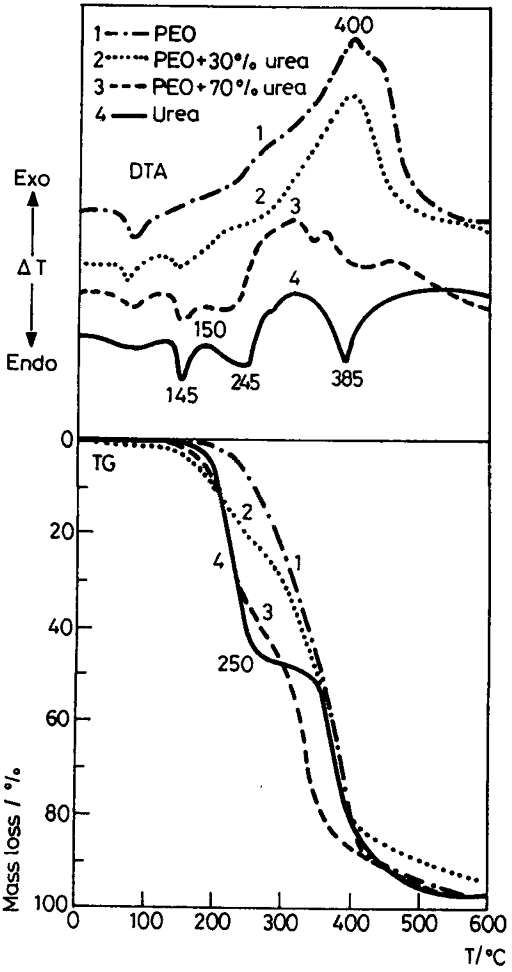

Fig. 1 DTA and TG curves of the initial components and some mixtures

culated that the gaseous products eliminated from the sample up to 250°C comprise about 46% of the initial weight of the sample, i.e. much more than in the case of biuret formation according to (1) and (3). Otherwise, predominantly ammonia would be eliminated, i.e. about 28% of the initial weight of the sample. Therefore, other reactions occur simultaneously under the studied conditions.

DTA curve 4 shows that under these conditions urea decomposes with the absorption of heat. The melting temperature is registered at 145°C. The thermal curves indicate two basic steps of decomposition, with endothermic peaks at 245 and 385°C.

The decomposition of the initial POE is extremely exothermic because of the thermooxidative reactions throughout the temperature interval 150–500°C. Measurable mass loss begins at 180°C and ends at about 410°C.

Thermal decomposition of POE-urea systems

The thermal characteristics of the mixtures show the special features in the decomposition of the components. Figure 2 reveals that an increase of the urea content up to 30 mass % leads to decreasing characteristic temperatures T_0 (beginning) and T_{10} (10% decomposition) in comparison with those for the initial POE. This is not the case for T_{50} (50% decomposition) and $T_{\mathrm{max\ rate}}$ (maximum rate of decomposition).

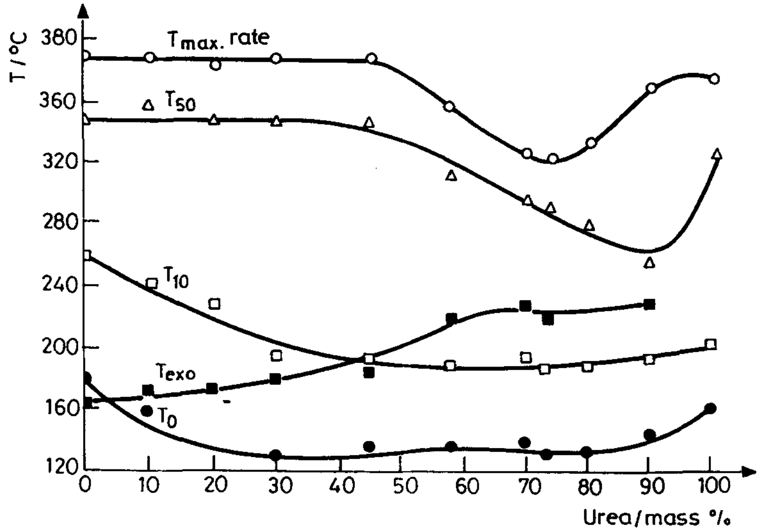

Fig. 2 Dependence of some thermal characteristics of the mechanical blends on the urea-content

Figure 2 demonstrates that T_0 and T_{10} continuously decrease up to 30% urea content. From 30 to 80% urea, they remain steady, and above 80% urea they increase slightly, but are still lower than those for the initial components. In the initial stage of decomposition, the hydrolytic decomposition reactions probably play a dominant role. It is possible that water vapour eliminated by decomposition of one component influences the decomposition of the other component, this reflecting the ratio of the components. It is also important which contribution (POE or urea) to the mass loss is decisive. In the initial stages of decomposition, as can be seen from the thermal curves of the initial products (Fig. 1), the decomposition of urea is decisive.

T_{50} and $T_{\max\ \text{rate}}$ (Fig. 2) are unaltered up to 50% urea content, but at concentrations of urea around the MC (73.2% urea) they decrease considerably. The stability of these two temperature characteristics for other concentrations of urea is an indicator of retention of the mechanism of decomposition, i.e. the absence of important interaction between POE and urea over the temperature of fusion, or the formation of new intermediates which exert a thermal stabilizing effect on the system.

In order to confirm or to reject the above statements, the mass losses were calculated up to a certain temperature, corresponding to the end of the first stage in the TG curve (250°C) for the initial urea or its blends with POE (Fig. 1). It was found that the total mass losses of the blends for these temperature intervals are additive and comparable to the calculated mass losses, according to those for the separate components in each of the blends (Fig. 3). The linear dependence obtained between the mass losses may be used to determine the urea content in blends containing unknown ratios of the components. Urea contents determined in this way are compared with the results of elementary analysis in Table 1B. For some of the samples, the data are identical. The differences between the experimental and calculated mass losses for mechanical blends are within ±3 mass%. This method may be used with a specific TG stage (involving lower systematic errors) for determination of the urea content in such cases.

The variation in the total heat released relative to unit mass loss, presented in Fig. 4 as a function of the urea content, shows a steady fall. This has a bearing on the mechanical blends, and the blends obtained by precipitation. The decrease in the total heat release in some cases reaches 50% of that for the initial POE. The DTA curves do not display any thermal effects connected with the formation of new interactions. The thermal characteristics obtained under the investigation conditions have an approximately additive character.

There are therefore no indications of measurable anomalous deviations of the mass loss, or the appearance of new thermal peaks, or shifts in the typical thermal peaks, which would be indicative of new interactions between the prod-

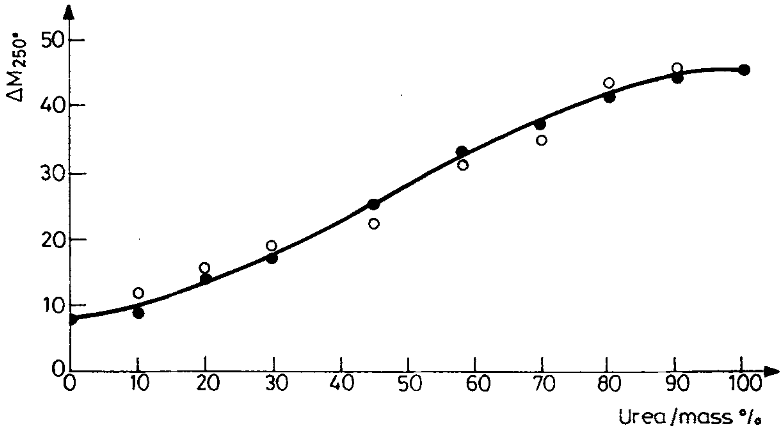

Fig. 3 Dependence of the mass losses by 250°C on the urea-content: • – ΔM_{250} experimental mass losses; o– ΔM_{250} calculated additive mass losses

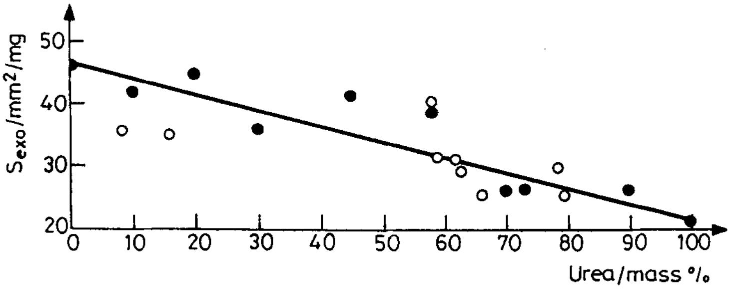

Fig. 4 Dependence of the total heat release, relevented to unit of mass loss upon the urea- content: • – for mechanical blends; o – for the blends, obtain as insoluble fraction

ucts of thermal decomposition and the initial components, leading to thermal stabilization of the system. On the contrary, destabilization was observed in the mutual presence of POE and urea, which was probably due to the effect of mixing, and to the presence of water from the thermal decomposition in the system.

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Zusammenfassung — Mittels eines Derivatografen wurde das thermische Verhalten (von 20 bis 500°C) von hochmolekularen Polyoxyethylen-Harnstoff-Gemischen untersucht, die einen Molekülkomplex bilden. Unter den Versuchsbedingungen gab es keinerlei Hinweise auf eine Wechselwirkung zwischen den thermischen Zersetzungsprodukten und den Ausgangsverbindungen, noch auf neue Zwischenprodukte mit einem thermostabilisie- renden Effekt. Zwischen dem Gewichtsverlust bei 250°C und dem Harnstoffgehalt des Gemisches erhielt man eine lineare Korrelation, die zur Bestimmung des Harnstoffgehaltes in ähnlichen Gemischen verwendet werden kann.