

**DETERMINATION OF RATE CONSTANTS
AND ACTIVATION ENERGIES
FOR EMISSION OF ORGANIC COMPOUNDS
FROM POLYOXYMETHYLENE**

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SUMMARY

Emission of organic compounds from two types of polytrioxane (colorless and black-smoke pigmented) has been measured by using a 20-cm³ chamber connected directly to a gas chromatograph. Measurements were performed at 40, 60, and 80°C at a flow rate of 0.45 cm³ min⁻¹. High surface to volume ratio and a relatively large sample loop (3 cm³) enabled detection of signals from organic substances present at low concentrations (~μg cm⁻³). The results obtained revealed that for the pigmented polytrioxane the rate of emission of organic compounds and the rate constants for the process were higher than for the colorless form. In contrast, the activation energy was slightly higher for emission of trioxane from the pigmented material. For trioxepane emission activation energies were similar. Results show the pigment had no retardant activity on emission of organic compounds from the polymer. The activation energies determined for emission of organic compounds were in the range 15 to 60 kJ mol⁻¹. The rate constants (from 7.6 × 10⁻¹⁰ to 9.2 × 10⁻⁸ cm⁻² s⁻¹) suggest diffusion or desorption are occurring within the polymer matrix.

INTRODUCTION

In recent years there has been much interest in the emission of volatile organic compounds (VOC) from polymeric materials [1–4]. Emission has usually been measured at 23°C and with single exchange of the air within a chamber every hour, although higher temperatures and higher air-

exchange ratios have also been used [3]. It is well known that the organic compounds present inside these synthetic materials are residues from manufacture or products of thermal, chemical, photochemical, or microbial degradation [4].

Polyoxymethylene (POM) is a useful polymer, characterized by high (70 %) crystallinity and good mechanical properties [5–7], which is used for machine construction [7] and as a medical material [8]. POM is manufactured by polymerization of formaldehyde or by copolymerization of trioxane and ethylene oxide, which furnishes a more thermally stable form. At the start of polymerization dioxolane and trioxepane have been observed [9]. Thermal degradation of the copolymer polyacetal resin occurs above 400°C [10–14] with formaldehyde as the main decomposition product. Recently, because of increased interest in this polymer, practical studies of thermal [15–17] and mechanical [16] degradation, photooxidation [17], and thermal oxidation [18] have been performed. Use of a modern pyrolytic system at 400°C reveals the degradation products to be dioxolane and trioxepane [19]. Over 50 thermal degradation products have been revealed by pyrolytic study of POM at 700 and 900°C [20]. Apart from formaldehyde, dimethylformaldehyde, and formic acid a wide variety of low-molecular-weight methoxy oligomers and 1,3,5-trioxanes with methoxy substituents were detected.

In this study direct chromatographic analysis has been used to measure organic compounds emitted from polyoxymethylene. This technique enables simultaneous, flexible determination of several compounds at different concentrations. No additional analytical procedures, for example sampling or solvent extraction, are needed. Results are obtained quickly with small time intervals (30 min) between measurements. Further calculation enables estimation of the rate constants and activation energies for emission of specific compounds. Energies of activation related to diffusion of low-molecular-weight compounds through the polymeric matrix are in the range 10 to 100 kJ mol⁻¹ [21]. Knowledge of activation energies for emission and information about thermal degradation and organic residues from manufacture are helpful in revealing the origin of the organic compounds present within polymeric materials.

EXPERIMENTAL

Apparatus

The experiment was performed with a constant flow rate of helium through the chamber containing the sample and the sample loop. The sam-

ple loop was connected to a Hewlett–Packard HP 6890 gas chromatograph equipped with a 60 m × 0.25 mm i.d. HP-5MS (5% diphenyl, 95% dimethylpolysiloxane) column and connected to an HP 5973 quadrupole mass spectrometric detector. Data recording was performed by monitoring ions characteristic of formaldehyde, dioxolane, trioxane, and trioxepane – m/z 29, 73, 31, and 73, respectively. Vials of capacity 20 cm³ sealed with silicone rubber septa were used as measurement chambers. An HP 7694E HeadSpace autosampler was used to identify particular compounds. The measurement system is depicted in Fig. 1.

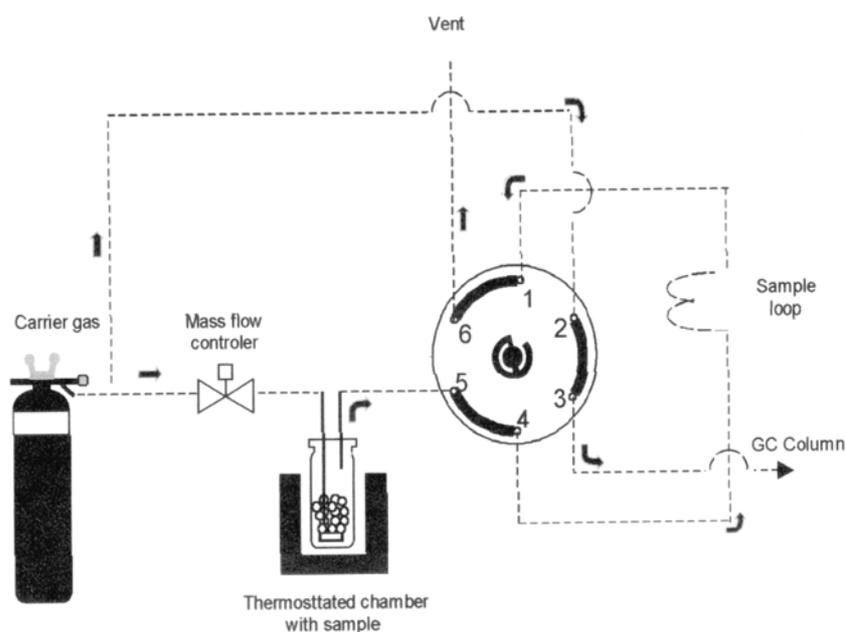


Fig. 1

Measurement system for continuous study of the emission of organic compounds from polymeric materials

Between measurements the carrier gas flows through a needle into a sealed vial, flows over the granules in the vial, and flushes the sample loop. When the position of the six-port valve is changed the carrier gas transports the emitted compounds from the sample loop into the chromatograph inlet. The total capacity of the vial, connecting tubes, and loop was 25.3 cm³. The flow rate of the gas (F_c) through the system was adjusted by use of a bubble flow meter. Application of this device necessitates ta-

king into account the effect of water vapor pressure and temperature when reading the direct flow rate (F_m).

$$F_c = \left(\frac{T_c}{T_m} \right) \frac{(p_m - p_w)}{p_m} F_m \quad (1)$$

where T_c is the temperature of the vial and of the connecting tubes, T_m is the ambient temperature, and p_m and p_w represent, respectively, the external pressure and the saturated water vapor pressure at T_m . The tubes connecting the carrier gas and the vial were pierced through the septa into the vial which was thermally preconditioned. This started the flow of the carrier gas through the vial.

Reagents

Two forms of polytrioxane were investigated, colorless and material containing smoke-black pigment, both manufactured by Nitrogen Works in Tarnów under the trade name Tarnoform 300. The materials were studied one month after manufacture. For both materials the density was 1.40 g cm^{-3} ; they were in granular form with average dimensions of 0.322 mm and 0.0814 cm^2 . High-purity helium with 2 ppm oxygen content, containing less than 3 ppm moisture, was used as the carrier gas.

Procedure

Four hundred granules were placed in the vials (chambers), which were then sealed with silicone septa. Perforated stainless-steel supports separated the granules from the vial bottom. For identification of compounds by use of the HeadSpace instrument vials were thermostatted at 140°C for 60 min and spectra were recorded in full-scan mode in the m/z range from 10 to 120. Identification was based on use of reference standards and on the Wiley library of spectra (6th edition). For dynamic measurements (Fig. 1) the time required to fill the loop, at a flow rate of $0.45 \text{ cm}^3 \text{ min}^{-1}$, limited the moment of initiation of chromatographic measurement and the first read-out commenced after 6.7 min. Flow of gas was initiated by connection of the tube which transferred the carrier gas from the vial. Measurements were performed at temperatures of 40, 60, and 80°C .

The reference sample was prepared by weighing approximately 1 mg 1,3-dioxolane, 1,3,5-trioxane, and 1,3,5-trioxepane (pure standards) directly into a sealed vial. The vial was thermostatted at 140°C for 15 min for complete evaporation of the standards. It was then connected to the tubing that

initiated gas flow through the assembled measurement system. The method of exponential dilution was used to calculate the concentrations of reference compounds in the chamber for a given value of F_c [22]:

$$c_t = c_0 \exp\left(\frac{-tF_c}{V_k}\right) \quad (2)$$

where c_0 signifies the starting concentration of the reference compound and c_t is the concentration after time t . V_k symbolizes the volume of the measurement chamber without sample, tubes, and sample loop.

RESULTS AND DISCUSSION

Formaldehyde, 1,3-dioxolane, 1,3,5-trioxane, and 1,3,5-trioxepane were the main volatile components released from the polytrioxane sample. In Fig. 2 the retention times of these substances were, respectively, 3.61, 4.35, 5.82 and 7.75 min at a carrier gas flow of $1 \text{ cm}^3 \text{ min}^{-1}$. Identification of four compounds only was possible, because of low intensities of the other peaks.

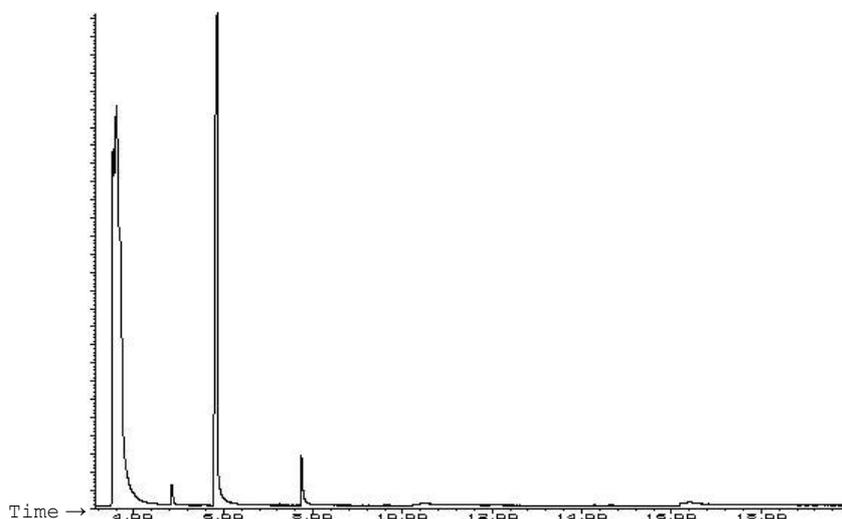


Fig. 2

Chromatogram developed for identification of organic substances emitted from colorless polytrioxane

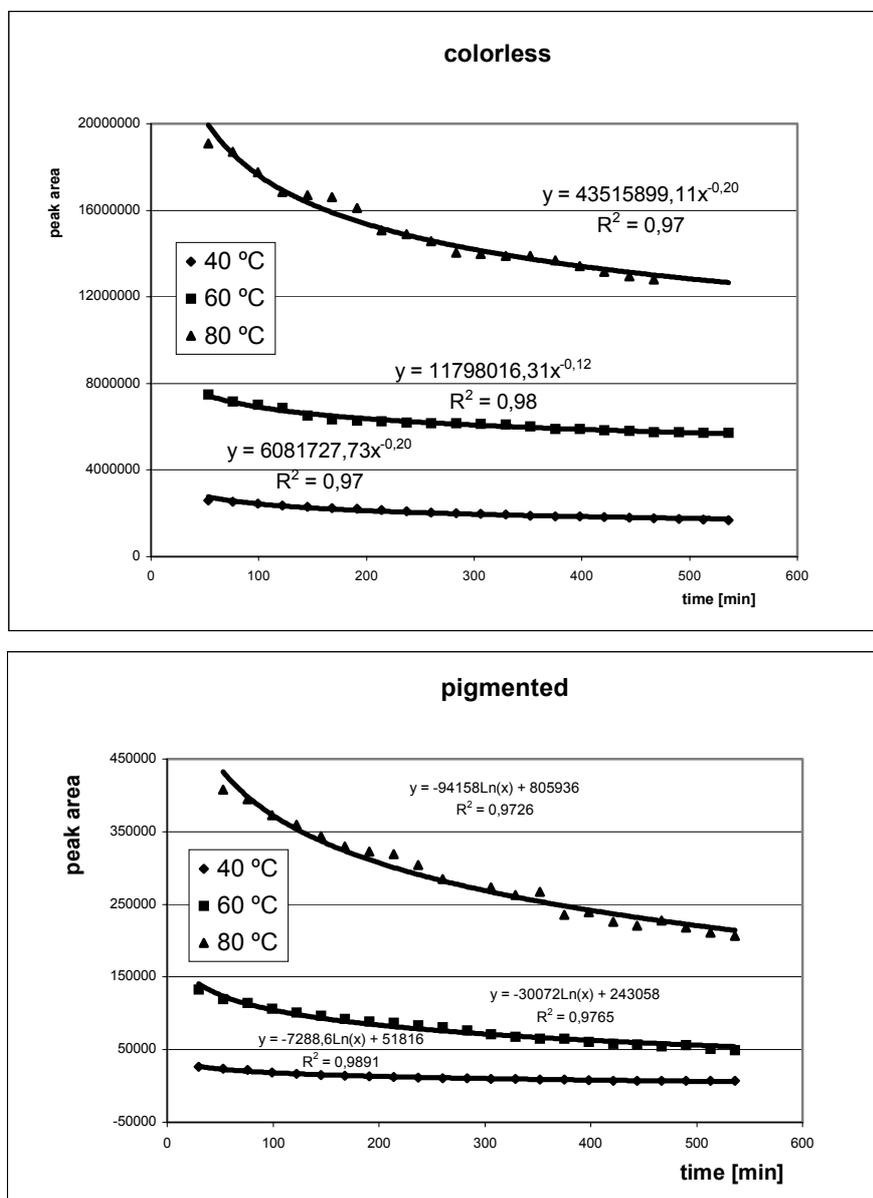


Fig. 3

Data points and adjustments for dependence of trioxane peak area on time for emission from colorless and pigmented polytrioxane

Under the experimental conditions used the released compounds were systematically removed from the measurement system. Data recorded for trioxane peak area during the time of the experiment have the character of a disappearance function (Fig. 3). For further calculation of the constant values for the process it was necessary to adjust the continuous functions of concentration in the measurement chamber in relation to the measurement time. The dependence on measurement time of concentrations in the gas phase surrounding the granules was first-order exponential decrease for all compounds. For all compounds R^2 exceeded 0.97.

The peak area obtained for formaldehyde (Fig. 4) excluded this compound from further consideration. Formaldehyde is a reactive, readily polymerized compound. As was remarked above, formaldehyde makes a significant contribution to the substances emitted. The low flow rate used ($0.45 \text{ cm}^3 \text{ min}^{-1}$) enables accumulation of formaldehyde inside the chamber. The relatively small peak areas recorded and comparison of the expected and non-typical emission profiles at $80 \text{ }^\circ\text{C}$ suggest that formaldehyde is transformed into another material.

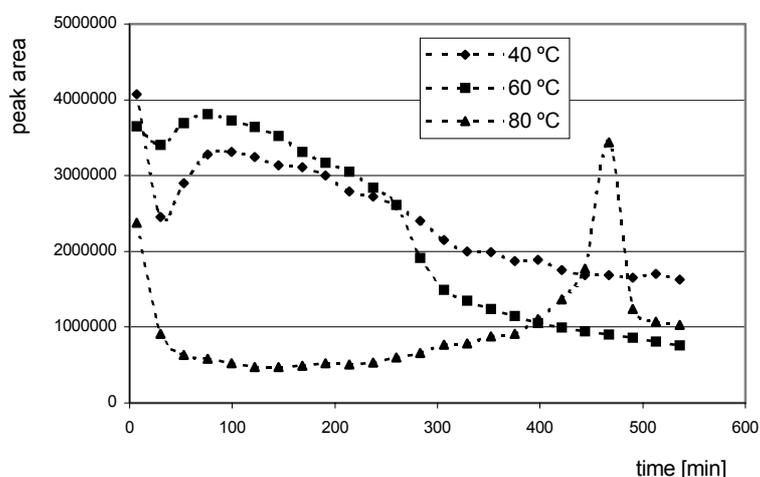


Fig. 4

Dependence on time of peak areas of formaldehyde emitted from colorless polytrioxane

The rates of emission under the flow conditions used are described by Eq. (3):

$$-u_m = kSc \exp\left(\frac{-tF_c}{V_k}\right) \quad (3)$$

where u_m symbolizes the rates of change of the concentration of the organic compounds in the gaseous phase in $\mu\text{g cm}^{-3} \text{s}^{-1}$, k represents the constant rate of emission of organic compounds from the polymeric material,

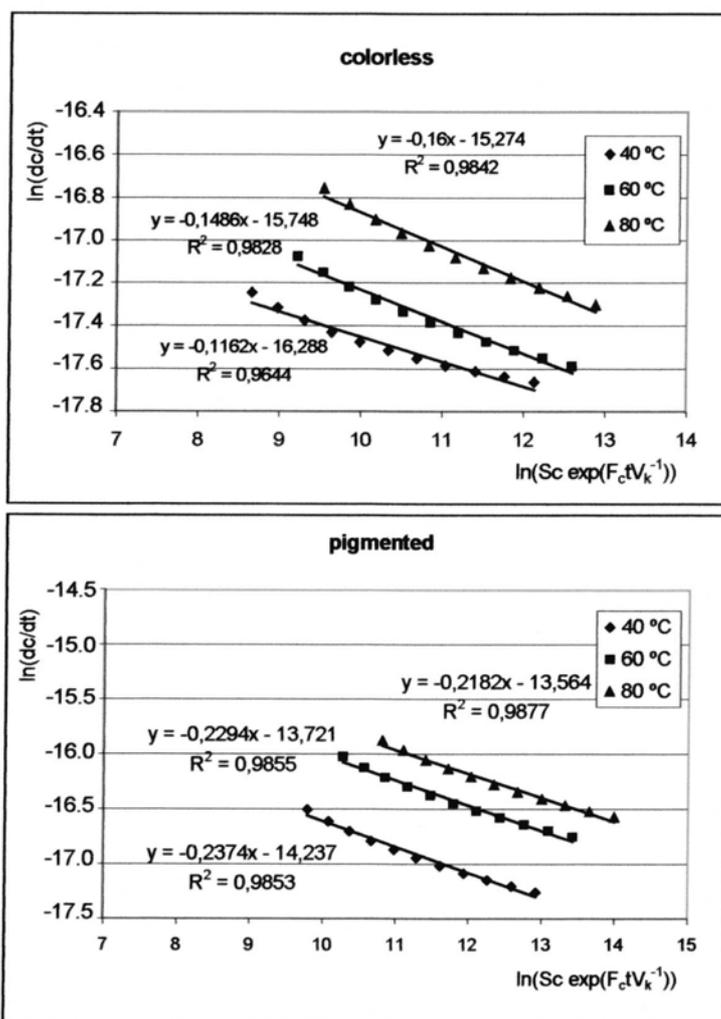


Fig. 5

Logarithmic dependencies used to determine rate constants for emission of trioxane from the colorless and pigmented forms of polytrioxane

and S is their surface area. From the dependence of concentration on time the rate constants were determined on the basis of Eq. (3). For linearization derived from Eq. (3) plots of the logarithm of the process rate against the logarithm of the product of surface area and exponential concentration were prepared. An example chart for trioxane is shown in Fig. 5. The logarithm of the rate constant is given by the slope; calculated rate constants are listed in Table I.

Table I

Rate constants for the emission process at different temperatures

Emitted compound	Rate constant, k ($\text{cm}^{-2}\text{s}^{-1}$)		
	40°C	60°C	80°C
Trioxane / colorless	6.6×10^{-7}	1.1×10^{-6}	1.3×10^{-6}
Trioxane / dyed	8.4×10^{-8}	1.4×10^{-7}	2.3×10^{-7}
Dioxolane / colorless	5.5×10^{-10}	1.2×10^{-8}	6.9×10^{-8}
Trioxepane / colorless	3.7×10^{-8}	6.0×10^{-8}	1.1×10^{-7}
Trioxepane / dyed	1.6×10^{-9}	2.7×10^{-9}	4.3×10^{-9}

Differences between rate constants for emission of the same compounds from different types of polytrioxane decrease with increasing temperature. Rate constants for the heavier compound, trioxepane, were significantly lower than for trioxane. Emission of dioxolane from pigmented polytrioxane was not observed.

For steady flow conditions in the measurement system the total amount of organic compound released between any two measurements must consist of amount calculated on the basis of the observed process rate and the amount washed out by gas flowing through the chamber. The rate of emission, R , describing the amount of substance emitted from unit surface area of sample in unit time under the conditions specified was calculated by use of Eq. (4):

$$R = \frac{\left\{ \int_{t_1}^{t_2} u_m dt \left[1 + \exp \left(\frac{-(t_2 - t_1) F_c}{V_k} \right) \right] \right\} V_k}{S(t_2 - t_1)} \quad (\mu\text{g cm}^{-2} \text{min}^{-1}) \quad (4)$$

where t_1 and t_2 are the times of successive measurements in min, V_k is the sum of the volumes of the chamber (without sample volume), tubes, and

sample loop in cm^3 , and S represents the surface area of the weighed amount of granules, expressed in cm^2 . The rates of emission determined are highly dependent on the type of polytrioxane sample and the temperature (Fig. 6). More trioxane is released from the colorless material than from the pigmented material. The same trend of emission was observed for other compounds.

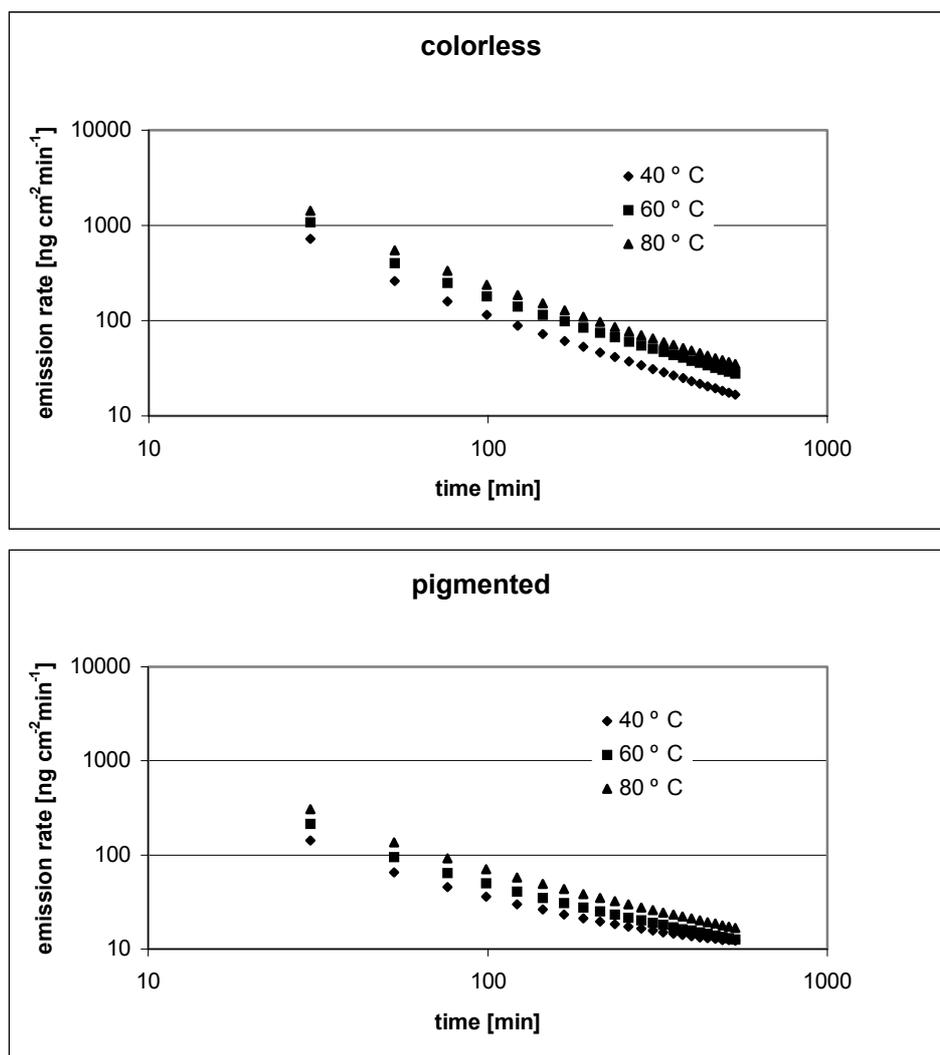


Fig. 6

Dependence on time of rates of emission of trioxane from colorless and pigmented polytrioxane

Values of the logarithm of the rate constants derived at different temperatures enabled calculation of activation energies, E_a , for the emission process on the basis of the Arrhenius equation. The results and measurement uncertainty of E_a are presented in Table II. For trioxane the activation energy was slightly higher for the dyed material but for trioxepane no significant difference was observed. The highest activation energy was obtained for emission of dioxolane from colorless material.

Table II

Activation energies and measurement uncertainty for emission of organic compounds from polytrioxane

Emitted compounds	Energy of activation (kJ mol ⁻¹)	Measurement uncertainty (kJ mol ⁻¹)
Trioxane / colorless	15.6	2.3
Trioxane / dyed	23.3	0.9
Dioxolane / colorless	49.2	11.3
Trioxepane / colorless	23.9	3.6
Trioxepane / dyed	22.3	4.0

CONCLUSION

Our investigation considered two similar polymeric materials manufactured at the same time, by very similar procedure, and with the same mechanical and thermal properties. The different rate constants and activation energies for the materials reveal the importance of the pigment in the emission process. The absolute value of the activation energy for emission from both materials does not exceed 60 kJ mol⁻¹. On this basis it can be concluded that the observed emission of organic compounds at temperatures between 40 and 80°C is a physical process. Lower emissions of organic compounds from the pigmented form must be a result of escape of emitted compounds during coloring, because of the use of a higher temperature during manufacture.

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