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THERMAL CHARACTERISTICS OF NOVEL $NaH_2PO_4/NaHSO_4$ FLAME RETARDANT SYSTEM FOR POLYURETHANE FOAMS

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Thermal behaviour of $NaH_2PO_4/NaHSO_4$ flame retardant system for polyurethane (PU) rigid foams was investigated by simultaneous TG/DTA under dynamic conditions. It has been found that the most probable mode of action of 5:3 (mass/mass) $NaH_2PO_4/NaHSO_4$ system, which proved to be most efficient in PU flame retardation (in comparison with other $NaH_2PO_4/NaHSO_4$ compositions), is based on formation of char-promoting phosphoric acids and on thermal stabilisation of PU macrochains by an excess of sodium dihydrogenphosphate.

Keywords: *flame retardation, polyurethane, sodium dihydrogenphosphate, sodium hydrogensulfate, thermal decomposition*

Introduction

Polyurethanes (PU) are a class of polymers with broad range of properties and applications. Some of the most important polyurethane-based materials are rigid PU foams that are commonly used for building engineering applications and for thermal insulation in domestic and commercial refrigeration, as well as furniture components and decorative panelling [1]. Such a broad spectrum of applications has led to concerns about the flammability which needs to be thoroughly re-addressed after the replacement of chlorofluorocarbons with other blowing agents that have lower environmental impact but may support the fire propagation [2]. Generally, phosphoric acid haloalkyl esters are commonly used as PU flame retardants [3], but there is tendency to withdraw halogen-containing systems due to formation (in their presence) of toxic decomposition products during fire [4]. Effective nonhalogen flame retardants are dimethylmethylphosphonate and other phosphorus-containing organic compounds [2]; besides, ammonium polyphosphate (APP), red phosphorus (RP) and expandable graphite (EG) are applied as flame retardants of PU foams [3, 5, 6] – e.g. the mixture of APP or RP with EG was found to be very effective [7, 8], but its black colour is disadvantageous for a number of applications. Apart from ammonium salts of phosphoric acid, attention was also paid to other inorganic phosphates - our previous results have shown that sodium dihydrogenphosphate flame retards PU foams by dilution and cooling effects, as well as by inducing cross-linking reactions [9]. Additionally, we have reported that sodium dihydrogenphosphate and sodium hydrogensulfate show synergistic effect when used jointly [10]; it was supposed that they react with phosphoric acids formation [11] that are known to be active both in gas and condensed phase during polymer combustion [2,12–15]. Recently action of other acid forming inorganic FR agents has been also described; results of TG-MS study of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ influence on the pyrolysis of pinus needles were published [16]. On the other hand, thermal decomposition of various PU materials is presently intensively studied, as described in [17–19]. The influence of $NaH_2PO_4/NaHSO_4$ flame retardant (FR) system on thermal decomposition of ethoxylated bisphenol A-based polyetherurethanes blown with pentane was recently described [20, 21]. DRIFTS, TG-MS, TG-FTIR and GC-MS data indicate that mixture of sodium dihydrogenphosphate and sodium hydrogensulfate causes change of degradation mechanism of PU at the start of degradation (180–250°C) – more thermally stable groups are formed by urethane bond decomposition reaction leading to formation of secondary amines and CO_2, while base foam (without addition of the FR system) degrades with first order amines, vinyl bonds and CO_2 formation [20, 21]. Additionally, the FR system catalyses cross-linking reactions those lead to intensive char formation.

Thus, the aim of this work was to explain the mechanism of interaction of NaH_2PO_4 and $NaHSO_4$ by

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thermal analysis methods in order to apply the knowledge gained during systematic thermal studies for even more effective flame retardation of rigid PU foams.

Experimental

Materials

Sodium dihydrogenphosphate (NaH_2PO_4) and disodium pyrophosphate ($Na_2H_2P_2O_7$), which is a by-product of NaH_2PO_4 thermal degradation, were products of Chemical Works 'Alwernia S.A.', Alwernia, Poland, and sodium hydrogensulfate ($NaHSO_4$) was obtained from POCh, Gliwice, Poland.

Novel flame retardant system formulation

$NaH_2PO_4/NaHSO_4$ flame retardant system was obtained by grinding of 5 mass parts of NaH_2PO_4 with 3 parts of $NaHSO_4$ in porcelain mortar. Burning tests of PU foam modified with 20% of $NaH_2PO_4/NaHSO_4$ have shown synergistic effect of these compounds; the highest efficiency was obtained at 5:3 (mass/mass) ratio of components [11].

Techniques

Thermal analyses were carried out using simultaneous thermogravimetric/differential thermal analyser TA Instruments 2960 at a heating rate of 5 K min^{-1} under air atmosphere. Samples' mass was ca. 20 mg. FTIR spectra were obtained for 10 mg samples in 300 mg KBr disk using Unicam's spectrometer Mattson 3000.

Results and discussion

A comparison of the endothermal peaks in DTA curve of sodium dihydrogenphosphate decomposition (Fig. 1) with the corresponding peaks in DTA profile of disodium pyrophosphate (Fig. 2) shows that the latter is an intermediate product, formed during sodium dihydrogenphosphate thermal degradation.

Dehydration of sodium dihydrogenphosphate into pyrophosphate form should stoichiometrically proceed with 7.5% of sample mass decrease – in our experiment we have observed only 6.84% mass loss. Besides, 13.84% of the total mass loss was found, while stoichiometric sodium dihydrogenphosphate full dehydration requires 15%. We suppose that the difference arises from other phosphates presence in an industrial-grade sample. Conclusion of disodium pyrophosphate formation agrees with recent Vlase *et al.* results [22]. Thermal decomposition of the second component of flame retardant system analysed in the course of this work (sodium hydrogensulfate) is displayed in Fig. 3.

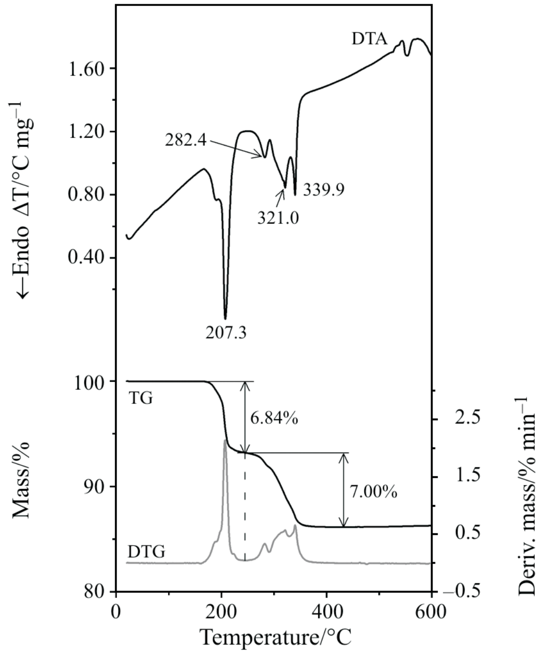

Fig. 1 Results of thermal analysis of sodium dihydrogenphosphate. Heating rate 5 K min^{-1}

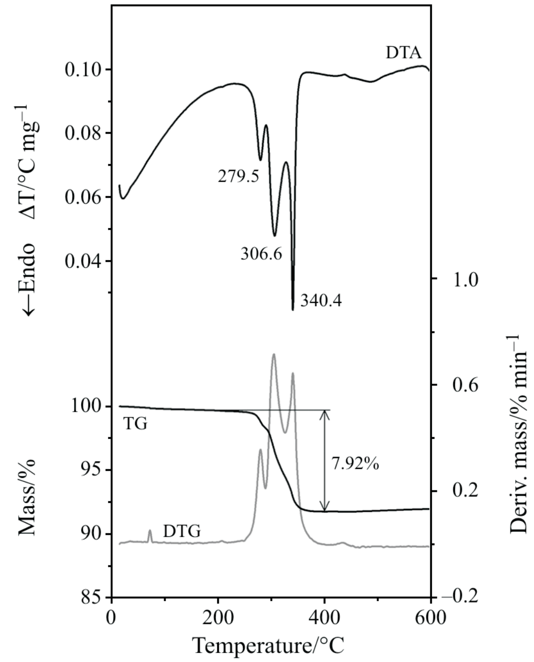

Fig. 2 Results of thermal analysis of disodium pyrophosphate. Heating rate 5 K min^{-1}

In the first stage, 3.04% of hygroscopic water was lost, followed by melting and dehydration leading to the formation of solid $Na_2S_2O_7$. Dehydration of anhydrous $NaHSO_4$ into $Na_2S_2O_7$ should cause 7.5% of mass loss; in Fig. 3 can be seen that in this degrada-

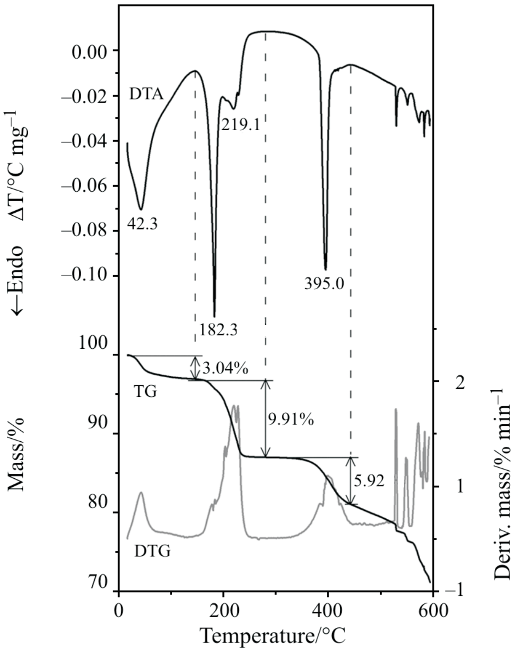

Fig. 3 Results of thermal analysis of sodium hydrogensulfate. Heating rate 5 K min^{-1}

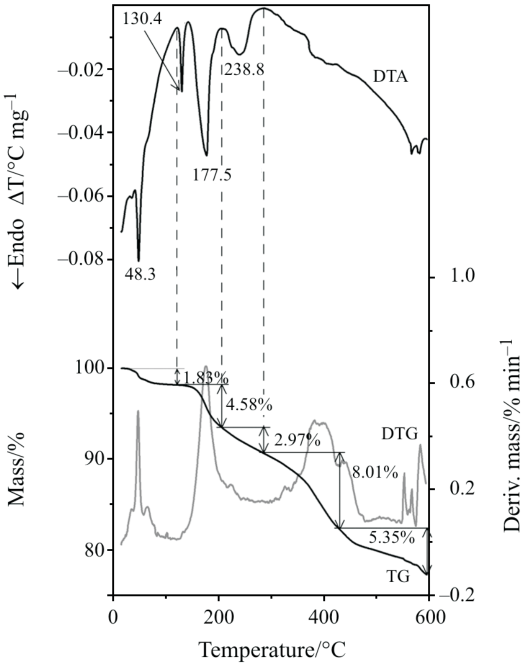

Fig. 4 Thermal degradation of NaH$_2$PO$_4$/NaHSO$_4$ 5:3 (mass/mass) mixture. Heating rate 5 K min^{-1}

tion step the sample lost 9.91% of mass – such a difference is caused by the presence of monohydrate of sodium hydrogensulfate in the investigated sample. In the next step, sodium pyrosulfate melts and degrades with SO$_3$ evolution.

After analysis of the individual components, thermal degradation of 5:3 (mass/mass) NaH$_2$PO$_4$/NaHSO$_4$ mixture was studied and results are shown in Fig. 4.

Hygroscopic water evolution (1.83%) is followed by an endothermic effect at 130.4°C (not connected with any mass loss) which is could be a repercussion of reaction (1); such endothermic effect does not appear during thermal analysis of mixture's components. Next degradation steps are also other than it could be concluded from the thermal degradation route of separated components of mixture – the reaction of sodium dihydrogenphosphate with sodium hydrogensulfate can proceed as presented in reactions (1) and (2).

$$NaH_2PO_4 + NaHSO_4 \rightarrow H_3PO_4 + Na_2SO_4 \quad (1)$$

$$NaH_2PO_4 + H_3PO_4 \rightarrow NaH_3P_2O_7 + H_2O\uparrow \quad (2)$$

Maximum efficiency of NaH$_2$PO$_4$/NaHSO$_4$ mixture as a flame retardant (when only first reaction occurs) should be observed at the mass proportion of 1:1, while, when first and second reaction are running both, mixture ought to be the most active at 2:1 mass ratio. Correlation of the highest activity at 5:3 mass ratio with the thermal analysis result suggests the presence of Na$_2$H$_5$P$_5$O$_{16}$ as intermediate active component, which is formed by no-water producing reaction at 130°C, followed by two dehydration steps giving overall reaction (3)

$$5NaH_2PO_4 + 3NaHSO_4 \rightarrow$$

$$\rightarrow Na_2H_5P_5O_{16} + 3Na_2SO_4 + 4H_2O \quad (3)$$

If flame retardant contains 1.83% of hygroscopic water then reaction (3) yields 7.36% of water, while two dehydration steps at 177 and 239°C produce 7.55% of water (Fig. 4) – the small difference is due to the influence of next dehydration step and presence of small amount of NaHSO$_4$·H$_2$O. FTIR spectra do not show differences between thermally untreated sample of flame retardant and sample heated up to 140°C (Fig. 5). It suggests that endothermic effect at 130°C is not an effect of chemical reaction, but is resulted from melting of a new, previously formed component in FR system. Phosphoric acid formation would be rather connected with dehydration step.

Summarizing the results obtained, the most probable idea assumes melting effect at 130°C and, during the following dehydration step, phosphoric acid formation, which acts as charring agent during burning, while an excess of NaH$_2$PO$_4$ increases PU thermal stability – it agrees with the our previous results (NaH$_2$PO$_4$ improves alkyloxylate-based PU foams thermal stability and influences the degradation mechanism [10] – it can be assumed that NaH$_2$PO$_4$ presence stabilizes PU macrochains) and with the present results – the flame retardant system under investigation loses water by the way which is more similar to phosphoric acids than to a salt.

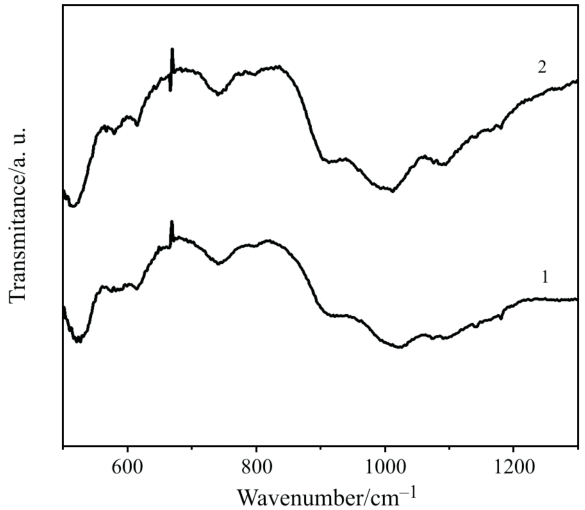

Fig. 5 Comparison of FTIR spectra of $NaH_2PO_4/NaHSO_4$ 5:3 (mass/mass) mixture 1 – under ambient conditions and 2 – after conditioning for 2 h at 140°C

Conclusions

Sodium dihydrogenphosphate normally decomposes with sodium pyrophosphate formation, but in the presence of sodium hydrogensulfate it melts before the decomposition occurs – it is manifested by an endothermal effect at ca. 130°C. Sodium dihydrogenphosphate and sodium hydrogensulfate give synergistic flame retardation effect – the most probable mode of action is based on char-promoting phosphoric acids formation and thermal stabilization of PU units by an excess of sodium dihydrogenphosphate.

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References

1 O. Gunter, Polyurethane Handbook, Hanser, Munich, 1994.
2 A. F. Grand and C. A. Wilkie (Eds.), Fire Retardancy of Polymeric Materials, Marcel Dekker, New York, 2000.
3 J. Green, J. Fire Sci., 14 (1996) 353.
4 J. Murphy, Reinf. Plastics, 45 (2001) 42.
5 M. Modesti, F. Simioni and P. Albertini, Cell. Polym., 13 (1994) 113.
6 R. William and H. Bell, US patent 2168706 A, 25/06/1986.
7 S. Duquesne, R. Delobel, M. Le Bras and G. Camino, Polym. Degr. Stab., 77 (2002) 333.
8 M. Modesti and A. Lorenzetti, Polym. Degr. Stab., 78 (2002) 167.
9 K. Pielichowski, K. Kulesza and E. M. Pearce, J. Polym. Eng., 22 (2002) 196.
10 K. Pielichowski, K. Kulesza and E. M. Pearce, J. Appl. Polym. Sci., 88 (2003) 2319.
11 K. Pielichowski and K. Kulesza, Thermal stability and flame retardancy of rigid polyurethane foams, The 14th Annual BCC Conference on Flame Retardancy – Recent Advances in Flame Retardancy of Polymeric Materials, Stamford, CT, June 2–4, 2003.
12 G. Camino, L. Costa and M. P. Luda di Cortemiglia, Polym. Degr. Stab., 33 (1991) 131.
13 J. Green, J. Fire Sci., 10 (1992) 470.
14 E. D. Weil, Handbook of Organophosphorus Chemistry, Ed. R. Engel, Marcel Dekker, New York, 1992.
15 S. Lu and I. Hamerton, Prog. Polym. Sci., 27 (2002) 1661.
16 A. Pappa, K. Mikedi, N. Tzamtis and M. Statheropoulos, J. Therm. Anal. Cal., 84 (2006) 655.
17 K. Pielichowski, D. Słotwińska and J. Pielichowski, J. Therm. Anal. Cal., 63 (2001) 317.
18 E. F. S. Vieira, A. R. Cestari, S. F. Zawadzki and S. M. Rocha, J. Therm. Anal. Cal., 75 (2004) 501.
19 W. W. Sułkowski, S. Mistarz, T. Borecki, M. Moczyński, A. Danch, J. Borek, M. Maciążek and A. Sułkowska, J. Therm. Anal. Cal., 84 (2006) 91.
20 K. Kulesza and K. Pielichowski, J. Anal. Appl. Pyrolysis, 76 (2006) 249.
21 K. Kulesza, K. Pielichowski and K. German, J. Anal. Appl. Pyrolysis, 76 (2006) 243.
22 T. Vlase, G. Vlase and N. Doca, J. Therm. Anal. Cal., 80 (2005) 207.

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