ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 21, No. 2. 2015

Effect of Intumescent Flame Retardants on the Properties of Polyurethanes Based on Tall Oil Fatty Acids Esters

Vladimir YAKUSHIN [*], **Irina SEVASTYANOVA, Dzintra VILSONE, Mikelis KIRPLUKS**

Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006 Riga, Latvia

http://dx.doi.org/10.5755/j01.mm.21.2.5784

Received 25 November 2013; accepted 17 May 2014

The efficiency of using intumescent flame retardants in polyurethane coatings based on tall oil fatty acids esters was assessed. The influence of the content of each of the flame retardants (ammonium polyphosphate, melamine and pentaerythriol) separately on the flammability parameters of wood samples with polyurethane coatings in a cone calorimeter test, as well as on the thermal and mechanical properties of the polyurethane itself, was investigated. The effect of the ratios of double and triple combinations of the mentioned flame retardants on the specified properties was studied. It has been found that, for the given type of polyester urethane, ammonium polyphosphate decreases the flammability of polyurethane most. Melamine, and melamine in combination with ammonium polyphosphate decrease the smoke release upon polyurethane combustion.

Keywords: polyurethane, flammability, intumescent flame retardants.

1. INTRODUCTION

To decrease the flammability of polyurethanes, different flame retardants are used. The types of the used flame retardants are determined by the type of polyurethanes (rigid or flexible polyurethane foam, thermoplastic polyurethanes or polyurethane coatings) [1, 2]. In conditions of the limited use of halogenated flame retardants, to decrease the flammability of coatings, including those on the basis of biobased polyurethanes, halogen-free intumescent flame retardants are used increasingly often. The latter are divided into two types, depending on the mechanism of intumescence [3]. Thus, expandable graphite and similar substances are assigned to the type of retardants with the physical fire retardant mechanism [4, 5]. Retardants with the chemical fire retardant mechanism are related to the traditional type of intumescent flame retardants. The formulation of this type of flame retardants consists of three basic ingredients: an acid source, a char forming agent and a blowing agent [6].

For most intumescent formulations, ammonium polyphosphate (APP) is used as an acid source (precursor for catalytic acidic species). As a char forming agent, carbon-rich polyhydric compounds such as pentaerythritol (PER), starch, glucose and others are commonly used. As a blowing agent, nitrogen-releasing compounds such as melamine (Mel), urea and others are used [5].

The role of each ingredient in the mechanism of intumescence in fire retardant polymers and chemical processes, which occur upon heating typical intumescent systems, is considered in many studies. However, most of them are assigned to thermoplastic polypropylene (PP) and polyamide. Thus, Camino et al. [7], as in the previous studies, carried out a versatile study of intumescent PP-based formulations, containing the intumescent additives APP/PER. The effect of different blowing agents and fillers on the intumescence and combustion behaviour of intumescent polymer compositions has been evaluated by them [8, 9].

The mechanism of the interaction of APP with aliphatic polyamides, and the catalytic effect of talc and MnO_2 on the intumescent behaviour of these systems is considered in [10, 11] and other studies by Levchik et al. Catalytic effects of zeolites, natural clays and zinc borates in PP-based systems with the intumescent additives APP/PER, as well as the possibility to use polyamides and thermoplastic polyurethanes (TPU) as a char former in PP/APP systems are considered in [6, 12 – 15] and other works by Bourbigot et al. It has been shown that, in PP-based intumescent systems with polyamides or TPU, APP acts as both an acid source and a blowing agent.

APP is the main component also in polyurethane intumescent compositions. The mechanism of its fire retardancy in polyurethanes has been studied in detail in [16]. However, the use of only APP as an intumescent additive is not so efficient, and, to reach significant results, the incorporation of a sufficiently great amount of APP (30 wt. % – 40 wt. %) is required. In this case, the mechanical characteristics of filled polymers are considerably impaired.

More efficient is the use of APP in combination with the already mentioned PER and Mel owing to the synergism in pairs of these compounds [17, 18]. Data of these studies by Lewin are based on both the own results and the data of the studies by Camino, Levchik and Bourbigot mentioned earlier. It is exactly in these studies that the main combination of APP + PER in a ratio of 3 : 1 and that of APP + PER + Mel in a ratio of 3 : 1 : 1 for thermoplastics are proposed. In the case of using the combination of these three ingredients, the development of intumescent char starts with a reaction, above 200 °C, between APP and the carbon-rich PER to form phosphoric ester bonds. Further elimination of water and ammonia leads to the formation of carbon-phosphorus char.

---

[*] Corresponding author. Tel.: +371-26598999; fax.: +371-67550635.
E-mail address: *yakushin@edi.lv*. (V. Yakushin)

Melamine, which decomposes at a higher temperature, acts primarily as a blowing agent, expanding the char [19].

For polyurethanes, a typical ratio of these three ingredients is also 3 : 1 : 1 [20]. However, for a definite type of polyurethanes as a polymer, another ratio can better, because the definite contribution of a polymer in the process of the coating's intumescence directly depends on the chemical structure of the polymer itself. Therefore, in other studies, the effects of intumescence in polyurethanes and other polymers when using the three mentioned intumescent additives in very different ratios were investigated. In some cases, the greatest effect was reached at ratios, different from the typical one [21 – 23].

The aim of the present study was a search for a more efficient combination of three classical intumescent flame retardants (APP + PER + Mel) for polyurethanes based on tall oil fatty acids esters. The efficiency of intumescent flame retardants was evaluated using the cone calorimetry test and thermogravimetric analysis.

2. EXPERIMENTAL

2.1. Materials

Ammonium polyphosphate $(NH_4PO_3)_n$, with n > 1000 Exolit® AP 422 was supplied by Clariant International Ltd., BU Additives (Switzerland).

Melamine 99 % ALDRICH $(C_3H_6N_6)$, and Pentaerythritol 98 % ALDRICH $(C_5H_{12}O_4)$ were obtained from Sigma-Aldrich Chemie GmbH (Germany).

Polyisocyanate Voratec SD 100 (NCO content 31.5 %, functionality 2.7) was supplied by Dow Deutschland GmbH (Germany).

Tall oil fatty acids and triethanolamine ester (OH number 349 mg KOH/g), synthesized as in [24], was used as a polyol.

2.2. Preparation and testing of polyurethane coating

All intumescent additives were preliminary mixed in polyol. Polyurethane coatings were prepared from toluene solutions at the molar ratio NCO/OH = 1.1. Toluene (up to 50 %) was added to the premixed polyol with intumescent additives. For the thermal and mechanical test, polyurethane coatings were prepared in the form of free films [24]. For the flammability test, polyurethane coatings, 250 μm – 300 μm in thickness, were applied on (100×100×16) mm standard wood (pine) samples.

The consumption of the polyurethane composition upon its applying to both polypropylene plates (free films) and wood samples was controlled by the weight method. After applying the coating, the samples were immediately placed on a horizontal surface to ensure a uniform thickness of coatings till the gel formation. All polyurethane coatings were hardened at a temperature of 21 °C ±2 °C during 7 days.

Combustion performance of the polyurethanes was studied using a FTT Cone Calorimeter (Fire Testing Technology Ltd.). Testing was performed according to ISO 5660 at a heat flux of 35 kW/m^2. All samples were measured in a horizontal position. Test duration was 30 min.

Thermal stability of polyurethanes was determined using TGA/SDTA 851^e Mettler Toledo. Sample weight was about 8 mg; heating rate 10 °C/min. The test was carried out in the airflow of 20 cm^3/min. Tensile tests of polyurethane films were performed on a universal testing machine Zwick/Roell DO-FB0.5TS (500 N) according to the requirements of the standard ASTM D 882-10. The mentioned tests are described in more detail in [24].

3. RESULTS AND DISCUSSION

3.1. Cone calorimeter study

The ignition and combustion of all wood samples with polyurethane coatings during the tests occurred according to the following scenario. Firstly, under the action of the heat flux, volatile products of decomposition of the polyurethane coating released, which, in a definite period of time, flamed up, and the combustion of the coating itself started. Upon the combustion, the destructing coating intumescented. If melamine was present in the coating composition, then the coating combustion process was accompanied by a pronounced short boiling stage, connected with the release of the products of decomposition of melamine. After accomplishing this stage, the combined combustion of the wood sample with the intumescented carbonized coating continued. The combustion intensity gradually decreased and, after 20 min – 25 min, the flame extinguished.

The flammability parameters of wood samples with polyurethane coatings were measured in terms of time to ignition (t_{ig}), heat release rate (HRR), peak heat release rate (PHRR), mean mass loss rate (MLR) and total smoke release (TSR) [25, 26]. Additional parameters, which better characterized the flame resistance performance of materials such as maximum average rate of heat emission (MARHE) and fire growth index FGI = PHRR/t_{ig} [27], were also determined.

At first the effect of the addition of each intumescent flame retardant separately on the flammability of wood samples with polyurethane coatings was investigated. It has been found that, with increasing content of each of those additives up to 30 wt. %, the main flammability parameters of the samples, compared with those of the samples with a neat polyester urethane coating (without flame retardant additives), gradually decreased and reached their minimum at the content of flame retardants of about 25 %.

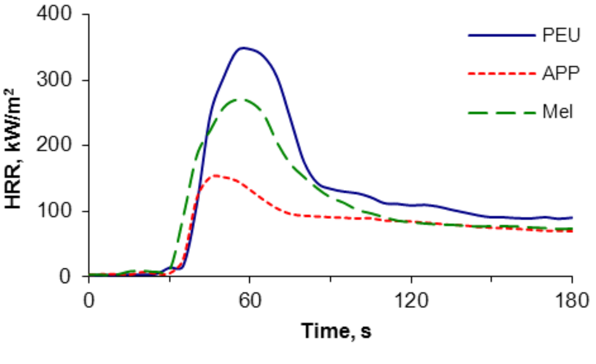

Fig. 1. HRR versus time for samples with coatings: neat polyester urethane (PEU) and PEU containing 25 wt. % of APP and Mel

The most considerable difference was observed in the indices, which characterized the initial stage of testing the samples (Fig. 1). Thus, PHRR for the samples with a polyurethane coating at the maximal content of APP and Mel decreased 2.4 and 1.2 times, respectively (Fig. 2). FGI and MARHE for the same samples, with increasing content of intumescent additives, changed in a similar way. In this case, for the samples with the coatings, containing APP and Mel, the decrease of FGI was 2.8 and 1.4-fold, respectively. The decrease of MARHE for the same samples was 1.75 and 1.4-fold, respectively.

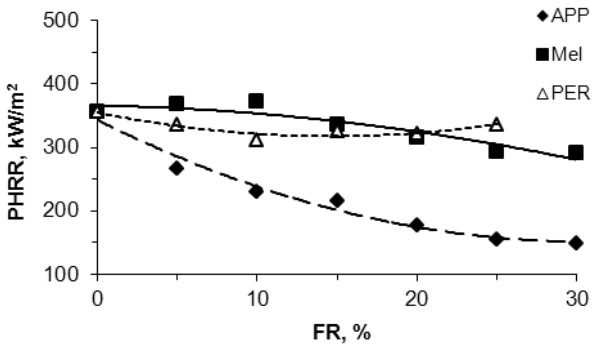

Fig. 2. PHRR versus flame retardants' (FR) weight content for samples with polyurethane coatings

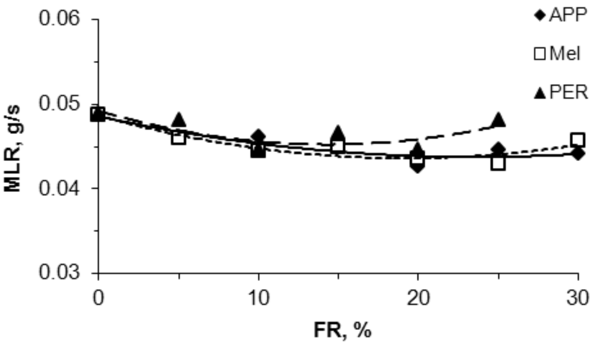

Fig. 3. Mean MLR versus flame retardants' weight content for samples with polyurethane coatings

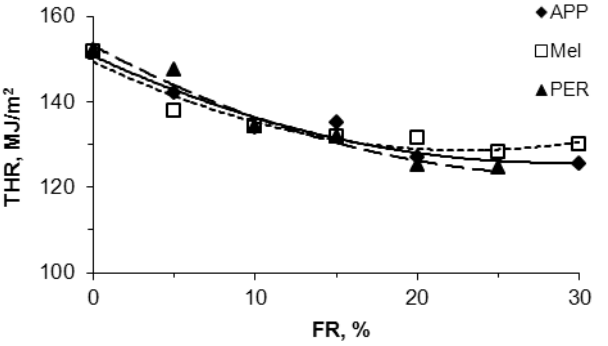

Fig. 4. THR versus flame retardants' weight content for samples with polyurethane coatings

In this case, mean MLR for the samples with the coating, containing APP and Mel, decreased only 1.1 times (Fig. 3). The THR of these samples also changed in a similar way; in this case, the decrease of THR for the samples with the coating, containing APP and Mel, was 1.2-fold (Fig. 4). No essential difference in the mentioned integral indices between the samples with the coatings, containing an equal amount of different flame retardants, was observed.

There was quite another pattern for the smoke release upon combusting samples with the polyurethane coating. If in the case of increasing content of APP or PER in the polyurethane till a definite concentration, the TSR of samples increased about 1.2 times, then, with increasing content of Mel in polyurethane, TSR decreased 1.3 times (Fig. 5). Correspondingly, in the investigated polyurethane based on tall oil fatty acids esters, APP decreased more efficiently the combustibility of the material, and Mel – its smoke release.

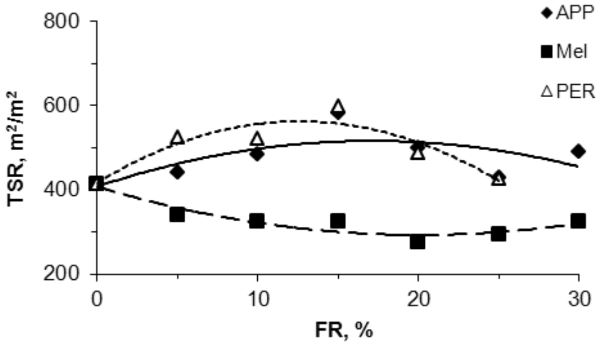

Fig. 5. TSR versus flame retardants' weight content for samples with polyurethane coatings

Further, taking into account all the obtained data, the maximal total content of intumescent flame retardants was limited to 25 %. And it was exactly such a total content of additives, at which the effect of the proportions in double and triple combinations of APP, PER and Mel was investigated.

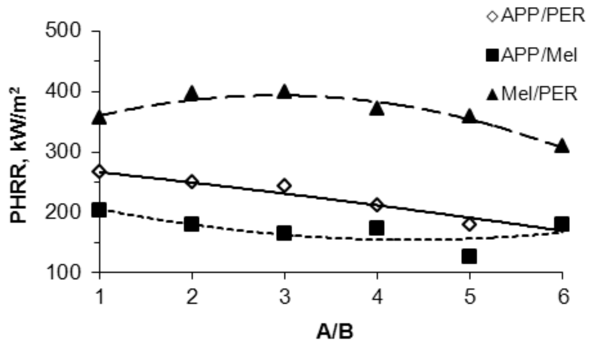

Fig. 6. PHRR versus flame retardants' ratio (A/B) for samples with polyurethane coatings

From the double combinations of intumescent flame retardants APP/PER, APP/Mel and Mel/PER, the combination APP/Mel appeared to be most efficient. The samples with the polyurethane coating, containing a combination of exactly those two flame retardants, had the lowest values of PHRR, FGI, MARHE and THR, and mean MLR. These parameters had the lowest value at ratios of APP/Mel equal to 3 : 1 and 4 : 1 (Fig. 6). In this case, some of them were on the level of the best parameters of the samples with the polyurethane coating, containing 25 % of APP. The TSR value (Fig. 7) of the samples with the addition of those two flame retardants (APP/Mel) was lower than the TSR value of the samples with the addition of only one APP, but somewhat higher than for the samples with the polyurethane coating with the addition of Mel alone.

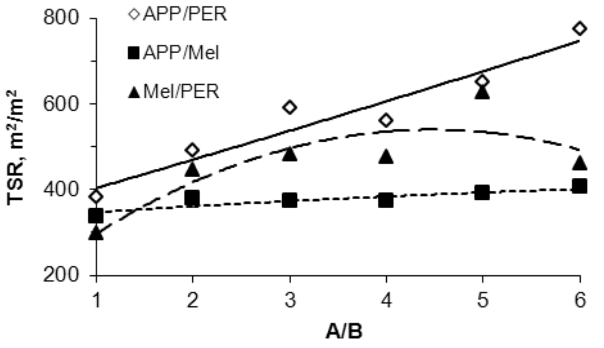

Fig. 7. TSR versus flame retardants' ratio for samples with polyurethane coatings

Correspondingly, for the given type of polyester urethane (PEU), the synergism of the system APP/Mel proved to be greater than that in the traditional APP/PER system. In this case, the synergism of the systems APP/Mel/PEU and APP/PER/PEU should be certainly spoken about more appropriately, because polyester urethane also directly participates in the combined processes of decomposition and char formation of the intumescent coating.

Table 1. Flammability parameters of wood samples with polyurethane coatings

Parameters	APP	APP/Mel		APP/PER/Mel	
	25%	3 : 1	4 : 1	3 : 1 : 1	3 : 1 : 2
PHRR, kW/m^2	155	165	174	198	208
FGI, kW/m^2·s	5.4	6.6	6.8	7.1	7.4
MARHE, kW/m^2	96.0	84.7	83.3	86.9	94.1
THR, MJ/m^2	127	126	124	138	139
TSR, m^2/m^2	489	373	374	322	420

Then samples with polyurethane coatings, containing all the three flame retardants simultaneously, were investigated. In this case, the ratio in the combinations APP/PER/Mel was varied in the ranges from 6 : 1 : X to 6 : 4 : X, where X varied from 1 to 6. The combinations, close to 3 : 1 : 1 (classic) and 3 : 1 : 2, appeared to be the most efficient ones. However, most of the flammability parameters of these samples were inferior or approximately on the level of the indices of the samples with polyurethane coatings, containing combinations of two flame retardants APP/Mel (Table 1). In terms of the main flammability parameters, neither of the tested triple combinations of flame retardants was superior to the mentioned double combinations of flame retardants. Hence, the presence of PER as a char forming agent in the system of intumescent additives for polyurethanes based on tall oil fatty acids esters did not give any significant effect. Because the polyurethane itself can act as a char forming agent, as shown in a range of studies [6], the additional char forming agent for the given type of polyurethane proved to be unnecessary.

3.2. Thermal and mechanical properties

Thermogravimetric analysis of polyurethanes with intumescent additives showed the following. Upon introducing of only Mel or PER, the decomposition of polyurethane upon heating occurs faster (Fig. 8) than the decomposition of neat polyester urethane. Respectively, also the height of the peaks corresponding to the temperature of the maximum rate of weight loss for the first step of decomposition on the DTG curve for those polyurethanes was higher than the height of the peaks of neat polyester urethane. The temperature of the maximum rate of weight loss for the final step of decomposition (T_{fMAX}), with increasing content of Mel or PER, decreased by 15 °C and 30 °C, respectively.

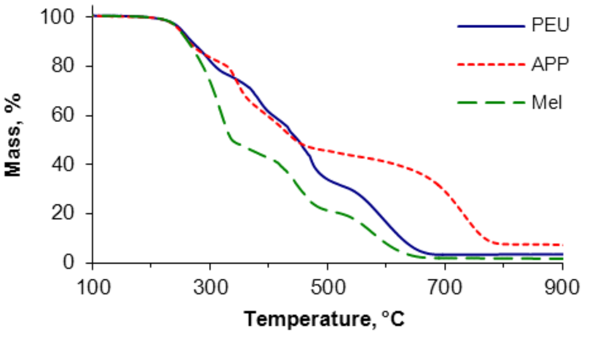

Fig. 8. TG curves for neat PEU and PEU containing 25 wt. % of APP and Mel

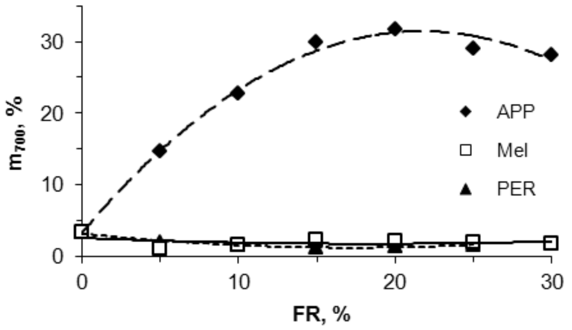

Fig. 9. Char yield at 700 °C for polyurethanes versus flame retardants' weight content

The decomposition of the polyurethane with an additive of APP occurred slower than that of neat polyester urethane, and upon increasing content of the flame retardant, the T_{fMAX} value of polyurethane increased from 590 °C (neat polyester urethane) to 735 °C (polyester urethane with 25 % of APP). The value of the char yield of polyurethanes also changed in a similar way. In particular (Fig. 9), the char yield at 700 °C (m_{700}) for polyester urethane, with increasing APP content, became much higher than the char yield of both neat polyester urethane and the polyurethanes with additives of Mel or PER. And it is known from the general theory [2] that the greater is the value of the char yield of a material, as a rule, the lower are the values of its flammability parameters.

Upon loading of APP combined with Mel or APP combined with PER into polyurethane, owing to synergism in these vapours, the decomposition of intumescent flame retardants at the final stage occurred slower than that of neat polyester urethane. In this case, at a ratio above 3 : 1, the value of the char yield was on the level of the indices for polyurethane, containing 25 % of APP. Also in this case, the data on the char yield (Fig. 10) correlated with the data of the flammability tests of polyurethane coatings.

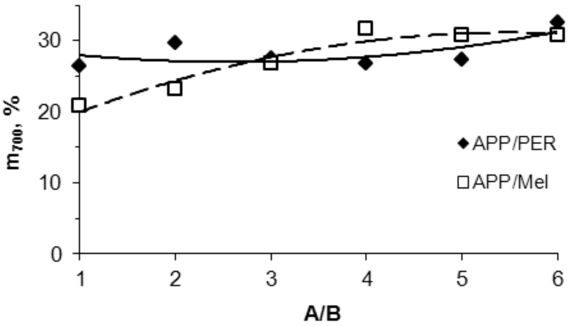

Fig. 10. Char yield at 700 °C for polyurethanes versus flame retardants' ratio

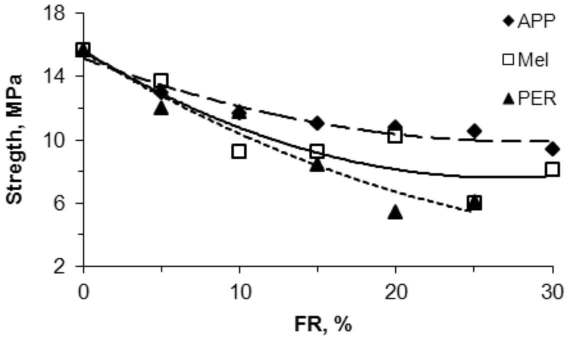

Fig. 11. Tensile strength of polyurethanes versus flame retardants' weight content

It is known that, upon loading of intumescent additives, as a rule, the mechanical properties of polymers are impaired. Also in this case, with increasing content of individual intumescent additives, tensile strength of polyurethane (Fig. 11) and its elongation at break considerably decreased. This occurred to a lesser extent upon loading of APP, the particles of which had the smallest sizes among all the flame retardants (particles <50 μm min. 95 %). These indices, with addition of Mel (particles <200 μm min. 90 %), were somewhat worse. The least strength was for the polyurethane with the addition of PER, the particles of which had the largest sizes (particles <250 μm min. 90 %). With increasing content of all the mentioned flame retardants, modulus of elasticity somewhat increased. The strength of the polyurethanes, containing a combination of the flame retardants APP/Mel in a quantity of 25 %, was on the level of strength for the polyurethane with 25 % of APP. If PER was used instead of Mel or additionally, then the tensile strength of polyurethanes considerably decreased.

4. CONCLUSIONS

To decrease the flammability of the given type of polyester urethane, ammonium polyphosphate was the most efficient additive. The efficiency of melamine was much lower; however, it was the only one among the investigated additives to reduce the total smoke release upon the combustion of polyurethane.

Approximately the same decrease of polyester urethane flammability, as in the case of ammonium polyphosphate, and the simultaneous reduction in total smoke release could be reached upon the loading of ammonium polyphosphate together with melamine at ratios of 3 : 1 and 4 : 1.

The lowest total smoke release was for the coatings with additives of flame retardants at a ratio of APP/PER/Mel equal to 3 : 1 : 1. However, upon adding of pentaerythriol to the combination of flame retardants, the other flammability parameters of polyurethane coatings, as well as their mechanical characteristics, were impaired.

Acknowledgments

The present study was financially supported in the framework of the State Research Program 5 "Sustainable Use of Local Resources (Mineral Deposits, Forest, Food and Transport) – New Products and Technologies (NatRes)".

REFERENCES

1. **Levchik, S. V., Weil, E. D.** Thermal Decomposition, Combustion and Fire Retardancy of Polyurethanes – a Review on the Recent Literature *Polymer International* 53 2004: pp. 1585 – 1610.
2. **Chattopadhyay, D. K., Webster, D. C.** Thermal Stability and Flame Retardancy of Polyurethanes *Progress in Polymer Science* 34 2009: pp. 1068 – 1133. http://dx.doi.org/10.1016/j.progpolymsci.2009.06.002
3. **Hao, J., Chow, W. K.** A Brief Review of Intumescent Fire Retardant Coatings *Architectural Science Review* 46 (1) 2003: pp. 89 – 95.
4. **Duquesne, S., Le Bras, M., Bourbigot, S., Delobel, R., Camino, G., Eling, B., Lindsay, C., Roels, T.** Thermal Degradation of Polyurethane and Polyurethane/Expandable Graphite Coatings *Polymer Degradation and Stability* 74 (3) 2001: pp. 493 – 499. http://dx.doi.org/10.1016/S0141-3910(01)00177-X
5. **Duquesne, S., Le Bras, M., Bourbigot, S., Delobel, R., Vezin, H., Camino, G., Eling, B., Lindsay, C., Roels, T.** Expandable Graphite: A Fire Retardant Additive for Polyurethane Coatings *Fire and Materials* 27 (3) 2003: pp. 103 – 117.
6. **Bourbigot, S., Le Bras, M., Duquesne, S., Rochery, M.** Recent Advances for Intumescent Polymers *Macromolecular Materials and Engineering* 289 2004: pp. 499 – 511.
7. **Camino, G., Costa, L., Martinasso, G.** Intumescent Fire-Retardant Systems *Polymer Degradation and Stability* 23 (4) 1989: pp. 359 – 376. http://dx.doi.org/10.1016/0141-3910(89)90058-X
8. **Camino, G., Costa, L., Trossarelli, L.** Study Of The Mechanism of Intumescence in Fire Retardant Polymers: Part III – Effect of Urea on the Ammonium Polyphosphate-Pentaerythritol System *Polymer Degradation and Stability* 7 (4) 1984: pp. 221 – 229. http://dx.doi.org/10.1016/0141-3910(84)90098-3
9. **Bertelli, G., Camino, G., Marchetti, E., Costa, L., Casorati, E., Locatelli, R.** Parameters Affecting Fire

Retardant Effectiveness in Intumescent Systems *Polymer Degradation and Stability* 25 (2 – 4) 1989: pp. 277 – 292. http://dx.doi.org/10.1016/S0141-3910(89)81012-2

10. **Levchik, G. F., Selevich, A. F., Levchik, S. V., Lesnikovich, A. I.** Thermal Behaviour of Ammonium Polyphosphate-inorganic Compound Mixtures. Part 1. Talc *Thermochimica Acta* 239 1 July 1994: pp. 41 – 49. http://dx.doi.org/10.1016/0040-6031(94)87054-3
11. **Levchik, G. F., Levchik, S. V., Sachok, P. D., Selevich, A. F., Lyakhov, A. S., Lesnikovich, A. I.** Thermal Behaviour of Ammonium Polyphosphate-inorganic Compound Mixtures. Part 2. Manganese Dioxide *Thermochimica Acta* 257 16 June 1995: pp. 117 – 125. http://dx.doi.org/10.1016/0040-6031(94)02210-F
12. **Bourbigot, S., Le Bras, M., Bréant, P., Trémillon, J.-M., Delobel, R.** Zeolites: New Synergistic Agents for Intumescent Fire Retardant Thermoplastic Formulations – Criteria for the Choice of the Zeolite *Fire and Materials* 20 (3) May 1996: pp. 145 – 154.
13. **Bugajny, M., Le Bras, M., Bourbigot, S.** New Approach to the Dynamic Properties of an Intumescent Material *Fire and Materials* 23 (1) January/February 1999: pp. 49 – 51.
14. **Almeras, X., Le Bras, M., Hornsby, P., Bourbigot, S., Marosi, Gy., Keszei, S., Poutch, F.** Effect of Fillers on the Fire Retardancy of Intumescent Polypropylene Compounds *Polymer Degradation and Stability* 82 (2) 2003: pp. 325 – 331. http://dx.doi.org/10.1016/S0141-3910(03)00187-3
15. **Bourbigot, S., Duquesne, S.** Fire Retardant Polymers: Recent Developments and Opportunities *Journal of Materials Chemistry* 17 2007: pp. 2283 – 2300.
16. **Duquesne, S., Le Bras, M., Bourbigot, S., Delobel, R., Camino, G., Eling, B., Lindsay, C., Roels, T., Vezin, H.** Mechanism Of Fire Retardancy Of Polyurethanes Using Ammonium Polyphosphate *Journal of Applied Polymer Science* 82 (13) 20 December 2001: pp. 3262 – 3274. http://dx.doi.org/10.1002/app.2185
17. **Lewin, M.** Synergistic and Catalytic Effects in Flame Retardancy of Polymeric Materials – an Overview *Journal of Fire Sciences* 17 January/February 1999: pp. 3 – 19.
18. **Lewin, M., Weil, E. D.** Mechanisms and Modes of Action in Flame Retardancy of Polymers. In: Horrocks, A. R., Price, D., (Eds.) Fire Retardant Materials. Woodhead Publishing Limited, Cambridge, 2001: pp. 31 – 68. http://dx.doi.org/10.1533/9781855737464.31
19. **Davis, J., Huggard, M.** The Technology of Halogen-free Flame Retardant Phosphorus Additives for Polymeric Systems *Journal of Vinyl and Additive Technology* 2 (1) March 1996: pp. 69 – 75.
20. **Levchik, S. V., Weil, E. D.** Commercial Flame Retardancy of Polyurethanes *Journal of Fire Sciences* 22 May 2004: pp. 183 – 210.
21. **Hassan, M. A., Kozlowski, R, Obidzinski, B.** New Fire-protective Intumescent Coatings for Wood *Journal of Applied Polymer Science* 110 (1) 5 October 2008: pp. 83 – 90.
22. **Gu, J., Zhang, G., Dong, S., Zhang, Q., Kong, J.** Study on Preparation and Fire-retardant Mechanism Analysis of Intumescent Flame-retardant Coatings *Surface & Coatings Technology* 201 2007: pp. 7835 – 7841. http://dx.doi.org/10.1016/j.surfcoat.2007.03.020
23. **Wang, F., Zhang, Z., ,Wang, Q., Tang, J.** Fire-retardant and Smoke-suppressant Performance of an Intumescent Waterborne Amino-resin Fire-retardant Coating for Wood *Frontiers of Forestry in China* 3 (4) December 2008: pp. 487 – 492.
24. **Yakushin, V., Stirna, U., Bikovens, O., Misane, M., Sevastyanova, I., Vilsone, D.** Synthesis and Characterization of Novel Polyurethanes Based on Tall Oil *Materials Science* (*Medžiagotyra*) (in press).
25. **Babrauskas, V., Parker, W. J.** Ignitability Measurements with the Cone Calorimeter *Fire and Materials* 11 (1) March 1987: pp. 31 – 43.
26. **Cogen, J. M., Lin, T. S., Lyon, R. E.** Correlations between Pyrolysis Combustion Flow Calorimetry and Conventional Flammability Tests with Halogen-free Flame Retardant Polyolefin Compounds *Fire and Materials* 33 (1) January/February 2009: pp. 33 – 50.
27. **Schartel, B., Hull, T. R.** Development of Fire-retarded Materials – Interpretation of Cone Calorimeter Data *Fire and Materials* 31 (5) August/September 2007: pp. 327 – 354.