Effect of melamine phosphate on the thermal stability and flammability of bio-based polyurethanes

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Abstract. The effect of melamine phosphate (MP) on the thermal stability of bio-based polyurethane and the flammability parameters of wood samples with polyurethane coatings was studied. Thermogravimetric analysis and cone calorimeter test at a heat flux of 35 kW/m² were used for this purpose. The main characteristics of the thermal stability and flammability of the coating with addition of MP were compared with the characteristics of analogous coatings with addition of ammonium polyphosphate (APP), as well as APP in combination with melamine. It was found that the use of MP as an intumescent additive allows a considerable decrease of most of the flammability parameters of the polyurethane based on tall oil fatty acids, like APP. To reach the maximum effect, it is enough to load in the polyurethane 20% of MP. In contrast to APP, MP reduces also the smoke release of the samples. Using MP in combination with APP at definite weight ratios, it is possible to essentially reduce the flammability parameters of polyurethane coatings, such as PHRR, THR and MARHE.

1. Introduction
Melamine is successfully used in flexible PU foams and other polymers as a halogen-free flame retardant (FR) [1–3]. The melamine itself, upon combusting of a polymer, acts only as a blowing agent, which dilutes flammable volatile products, released upon the decomposition of a polymer at high temperature [4]. To reach a greater effect and owing to synergism of nitrogen and phosphorus, it is often used in combination with ammonium polyphosphate, which acts as charring catalysts in intumescent FR systems. Another type of FR, based on the well-known phosphorus/nitrogen synergism [5], are phosphorous salts of melamine.

Melamine phosphate and melamine polyphosphates of different grades under various names are commercially available. They are mainly used in different thermoplastics, such as polypropylene and polyamide [6, 7]. It is recommended to use melamine phosphate also in thermosets, both unsaturated polyester and epoxies [8, 9]. At the same time, there is not so great experience of using melamine phosphate in cross-linked polyurethanes [10, 11].

In the present study, the efficiency of melamine phosphate as an intumescent FR in a polyurethane coating based on triethanolamine esters of tall oil fatty acids was assessed. The effects of the melamine phosphate content and the weight proportions in its combination with other FRs on the main parameters of the thermal stability and flammability of polyurethane coating were studied. The mentioned parameters of the new coatings were compared to the parameters of similar polyurethane
coatings with most often used intumescent FRs – single ammonium polyphosphate, as well as ammonium polyphosphate in combination with melamine.

2. Experimental

2.1. Materials
Melamine phosphate (P > 12%, N > 42%) was purchased from Tianjin Aokatet Chemical Co., Ltd. (China). Ammonium polyphosphate, grade Exolit® AP 422 (P 31.5%, N 14.3%) was obtained from Clariant International Ltd., BU Additives (Switzerland). Melamine 99% (N 66.8%) was purchased from Sigma-Aldrich Chemie GmbH (Germany).

Polyisocyanate Voratec SD 100 (NCO content 31.5%, functionality 2.7) was obtained from Dow Deutschland GmbH (Germany). Triethanolamine esters of tall oil fatty acids (OH number 349 mg KOH/g), synthesised as in [12], were used as a polyol.

2.2. Preparation and testing of polyurethane coating
Melamine phosphate (MP), in mixture with polyol, did not behave as inert filler; therefore, it was preliminary mixed in polyisocyanate. Ammonium polyphosphate (APP) and its mixtures with melamine (MEL) like in [13] were preliminary mixed in polyol. Then toluene (up to 50%) was added to the polyol or polyisocyanate premixed with intumescent additives. Polyurethane coatings were prepared at the molar ratio NCO/OH = 1.1. For the thermal test polyurethane coatings were prepared in the form of free films. For the flammability test, polyurethane coatings, 250-300 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. All polyurethane coatings were hardened at a temperature of (21 ± 2)°C during 7 days.

TGA/SDTA 851e METTLER TOLEDO was used for thermal gravimetric analysis (TGA) of polyurethane coatings. Sample weight was about 8 mg; heating rate 10°C/min. The test was carried out in the airflow of 20 cm³/min. FTT Cone Calorimeter (Fire Testing Technology Ltd.) was used for the combustibility test of wood samples with applied coatings. Testing was performed according to ISO 5660 at a heat flux of 35 kW/m² like in [13]. All samples were arranged in a horizontal position. Test duration was 30 min.

3. Results and discussion

3.1. TGA of intumescent polyurethane coatings
At first, the effect of the content of each flame retardant separately on the thermal stability of polyurethanes was investigated. It was found that, although the decomposition temperature of MP (350°C) is higher than that of APP (300°C), the type of the flame retardant did not exert any essential effect for the first step of filled polyurethanes’ decomposition. With increasing content of both the flame retardants, both the initial decomposition temperature and the temperature of the maximum rate of weight loss for the first steps of decomposition of polyurethanes remained practically on the same level (~230°C and 260°C, respectively). Actually, both those temperatures were determined by the lower initial temperature of destruction of the polyurethane itself.

The effect of the flame retardant’s type manifested itself only for the final step of polyurethane decomposition. At an equal content of flame retardants, the char yield for the APP-containing polyurethane was much higher than that for the polyurethane, containing the same amount of MP (Fig. 1). This was because the content of phosphorus in APP was almost 2.6 times higher than in MP. No significant effect of the much higher content of nitrogen in MP (2.9-fold) on the final results of destruction was found.

Then the effect of the weight ratio of flame retardants in the combinations APP/MP and APP/Mel at the same total content of flame retardants (25 wt.%) was investigated. It was exactly this content of
flame retardants, at which most of the investigated indices of polyurethanes reached their optimum values. With varying ratio, in the mentioned combinations, no essential difference in the indices, characterising the first step of polyurethane decomposition, was observed. At the same time, by varying the weight ratio from 1:1 to 6:1 in the mentioned combinations of FRs (A/B), the char yield at 600°C ($m_{600}$) of filled polyurethanes slightly increased (Fig. 2). In this case, it exceeded the value of the char yield of polyurethane, filled with single MP, and approximated the value of the char yield of polyurethane, filled with single APP.

Figure 1. Char yield at 600°C for polyurethanes versus FRs’ weight content.

Figure 2. Char yield at 600°C for polyurethanes versus FRs’ weight ratio.

3.2. Cone calorimeter study of polyurethane coating

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), total heat release (THR), mean mass loss rate (MLR) and total smoke release (TSR) [14]. Additional parameters, which better characterised the flame resistance of materials such as maximum average rate of heat emission (MARHE) and fire growth index $FGI = PHRR/t_{ig}$ [15], were also determined.

Comparing the mentioned parameters of combustion of the samples with polyurethane coatings with the addition of one of the flame retardants, it was found that in terms of the indices, MP as a flame retardant is as efficient as APP. With increasing content of both the flame retardants up to 30 wt.%, the main flammability parameters of polyurethanes varied approximately equally, despite the much lower (2.6-fold) content of phosphorus in MP.

Figure 3. HRR versus time for polyurethane coatings with 25% of FR and without FR (PEU).

Figure 4. PHRR versus APP and MP weight content for wood samples with coatings.

The parameters, characterising the initial period of burning of the wood samples with polyurethane coatings, varied to a greater extent (Fig. 3). Thus, with increasing content of both MP and APP up to 25%, PHRR for the samples with a polyurethane coating decreased 2.3 times (Fig. 4). The decrease of
the FGI of the samples with polyurethane coatings, containing 25% of MP or APP, was still greater, namely, 2.8-fold.

The flammability parameters, characterising the behaviour of samples for the full time of the test, did not decrease so much. Thus, MARHE for the wood samples with a polyurethane coating, with increasing content of FRs up to 25%, decreased 1.8 times (Fig. 5). However, THR and MLR at loading of the same amount of MP or APP decreased only 1.2 and 1.1 times, respectively.

The almost equal efficiency of those two flame retardants was obviously explained by the additional action of another element in the composition of flame retardants during combustion, namely, nitrogen, as well as its synergistic action with phosphorus. The comparatively moderate content of phosphorus in MP, in comparison with APP, was compensated by the much higher content of nitrogen. The total content of nitrogen and phosphorus in MP was also higher (1.2-fold) than in APP.

Owing to the high content of nitrogen MP had one distinct advantage. As in the case of adding of melamine (blowing agent) [13], the TSR of samples with polyurethane coatings, containing the additions of MP, were much lower than those for the same ones with additions of APP. With increasing content of MP up to 20%, TSR of the samples decreased sequentially (Fig. 6). With the further increase of the MP content, TSR of the samples with a polyurethane coating increased, probably due to the insufficiently good dispersion of MP in the coating at its high content.

Taking into account the lower smoke release, MP, as a single flame retardant, appeared to be more preferable than single APP. In this case, the content of MP, at which the flammability parameters of polyurethane compositions reached their minimum, was lower (20%) than for APP (25%).

**Figure 5.** MARHE versus APP and MP weight content for samples with coatings.

**Figure 6.** TSR versus APP and MP weight content for wood samples with coatings.

**Figure 7.** THR versus FRs’ weight ratio for wood samples with coatings.

**Figure 8.** PHRR versus FRs’ weight ratio for wood samples with coatings.
Varying the weight ratio in double combinations of FRs, it was found that most of the flammability parameters of samples with coatings, containing the combination APP/MP, were better than the parameters of the samples with coatings, containing the combination APP/MEL. This could have been expected, because, at the same weight ratio of those FRs in the polyurethanes with the addition of the APP/MP mixture, the content of phosphorus is higher than that in the polyurethanes with the addition of the APP/MEL mixture. With increasing weight ratio in the mentioned combinations from 1:1 to 6:1, the phosphorus content in the polyurethanes with the addition of APP/MP increased from 5.4% to 7.2%, but in the polyurethanes with the addition of APP/Mel, the phosphorus content grew from 3.9% to 6.8%. The total content of phosphorus and nitrogen in the polyurethanes with the addition of APP/MEL was only slightly higher than that in polyurethanes with the addition of APP/MP.

Increasing the weight part of APP in combinations of APP/MP and APP/MEL MLR, TSR and MARHE of the samples with polyurethane coatings changed in the same manner, like THR (Fig. 7). In this case, most of the parameters’ values did not reach the levels of the parameters of the samples with a polyurethane coating with the same amount of single MP or APP. Only THR and MARHE of samples, containing the combination APP/MP, was lower by 20% than that of the samples with single MP.

Decreasing the weight ratio in the mentioned FRs’ combinations, PHRR of the samples with APP/MEL increased, but with APP/MP decreased (Fig. 8). In the range of the ratios from 3:1 to 1:1, PHRR of the samples, containing the combination APP/MP, was lower by 10-20% than for samples, containing single MP. In this case, these values of THR, MARHE and PHRR were the best of all the earlier obtained results of testing the samples with polyurethane coatings, containing single intumescent FRs or their various combinations [13].

4. Conclusions

Thus, MP as single intumescent FR, decreases most of the flammability parameters of the polyurethane coatings based on tall oil fatty acids, like single APP. It was found that the maximum effects on flammability parameters took place at loading 20% of MP into the polyurethane coating. In contrast to APP, the addition of MP reduces also the smoke release of the samples. Using MP in combination with APP (up to 50% from the total amount of FRs) it is possible to essentially reduce the flammability parameters of polyurethane coatings, such as PHRR, THR and MARHE.

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