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Properties of polyurethane coatings based on linseed oil phosphate ester polyols and expandable graphite

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Abstract. The effect of two grades of expandable graphite (EG 096 and EG 290) on the thermal decomposition and flammability of polyurethane (PU) coatings, based on two kinds of linseed oil phosphate ester polyols, was studied. Thermogravimetric analysis (TGA) and the cone calorimeter test at a heat flux of 35 kW/m² were used for this purpose. The chemical structure of the synthesized polyols was identified by Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (31P NMR) spectroscopy. The content of EG was varied from 0 up to 25%. For all characteristics of PU coatings, the maximum effect was reached at 25% of EG. It was found that PU coatings filled with EG 096 had higher char residue at thermal decomposition under nitrogen. The flame retardancy of the PU coating filled with EG 290, which generated more blowing gases at thermal decomposition and therefore had a higher expansion volume, was higher than the flame retardancy of the coatings filled with EG 096. The best characteristics were shown by filled PU coatings based on the polyol, which was phosphorylated in the presence of isopropyl alcohol and which, besides phosphate mono- and diesters, had phosphate triester and pyrophosphate monoester.

1. Introduction
To decrease the flammability of bio-based polyurethanes (PUs), phosphorus-containing polyols are used due to the strong carbonization effect of phosphorus in the condensed phase and the free radical quenching effect in the gaseous phase of polymer combustion [1]. For the synthesis of such polyols, different methods can be used [2, 3]. One of them is the phosphorylation of epoxidized vegetable oils, when firstly, the oil is oxidized with peroxyacids, and then ring-opening of the epoxy group is performed using phosphoric acid. The phosphorylation of epoxidized oils was investigated mainly for epoxidized soybean oil (ESO). Zhong, Guo et al. showed that PU coatings and foams based on phosphorylated ESO had not only good adhesive and mechanical characteristics [4–7], but also some decrease in the burning rate [8] and increase in the oxygen index [9] of PU foam samples.
To achieve a potentially greater effect on the flammability characteristics of PU coatings, epoxidation and phosphorylation of linseed oil (LO) has been investigated in a previous study [10]. Due to the higher content of double bonds in LO, it was possible to obtain epoxidized LO (ELO) with a higher value of epoxy equivalent to that of ESO and then, by phosphorylation, to incorporate more phosphate groups in the ester polyol structure. The main parameters of the flame retardancy of coatings, based on the synthesized polyols, were increased, but only up to 15–30%. To further enhance the flame retardancy of coatings, additional flame retardants would be used.
Among non-halogen flame retardants, expandable graphite (EG) is one of the most effective intumescent additives. It has an exfoliated structure intercalated with sulphuric acid into a graphite crystal structure. At high temperatures, the intercalated agent releases gases and graphite, expanded in
a perpendicular direction to the carbon layers in the crystal structure [11]. Most of the studies on the use of EG in urethane systems refer to PU foams. The effects of the particle sizes, expansion volume and percentage of EG on PU and PIR foams’ thermal degradation and flammability have been investigated in numerous works [12–15]. Duquesne et al. [16, 17] investigated the thermal degradation of PU coatings with EG and the mechanism of flame retardancy induced by EG in PU. Based on these studies, it has been concluded that the retardancy of EG results from the physical action rather than from the chemical one.

At the same time, the combination of EG with phosphorus-containing compounds may demonstrate the synergistic effect on polyurethane flame retardancy [18, 19]. In the present work, we will investigate the effect of two grades of EG, which differed in particle size and expansion volume, on the thermal degradation and flame retardancy of the PU coatings based on linseed oil phosphate ester polyols.

2. Experimental

2.1. Materials
For the synthesis of phosphorus-containing polyols, refined LO from Alberdingk Boley GmbH, Germany, and glacial acetic acid (CH₃COOH), 35% hydrogen peroxide (H₂O₂), ion exchange resin Amberlite IR-120 H, 85% phosphoric acid (H₃PO₄), isopropyl alcohol (IPA), diethylene glycol butyl ether (DGBE), and ethyl acetate (EtOAc), purchased from Sigma-Aldrich Chemie GmbH, Germany, were used. For PU coating preparation, polymeric diphenylmethane diisocyanate (p-MDI), grade Voratec SD 100 (NCO content 31.5%, functionality 2.7) from Dow Deutschland GmbH, Germany; Dabco T-12 Catalyst (dibutyltin dilaurate) from Fluka Analytical, Switzerland; toluene puriss (≥ 99.7%) from Sigma-Aldrich Chemie GmbH were used. Two grades of EG, EG 290 and EG 096, supplied by SINOGRAF SA, Poland, were used as the flame retardant.

2.2. Polyols synthesis and characterization
For comparison purposes, two kinds of polyols were synthesized in two stages. First, LO was epoxidized using 35% H₂O₂, CH₃COOH and ion exchange resin Amberlite IR-120 H as the catalyst. Then, phosphorylation of ELO with 2 wt% of H₃PO₄ was carried out in the presence of IPA (IPA polyol) or DGBE (DGBE polyol). The completion of the synthesis stages was monitored by the changes in the epoxy equivalent of the reaction products. The synthesis of polyols as well as the procedure of polyols washing, drying and separation from the water and solvents have been described in detail in a previous work [12]. It was shown that PU coatings based on IPA and DGBE polyols had different mechanical and thermal stability characteristics, but approximately the same flame retardancy.

The epoxy equivalent, hydroxyl (OH) number, and acid value of the polyols were determined according to ISO 3001:1999, ISO 14900:2001, and ISO 2114:2000 standards, respectively. The dynamic viscosity of polyols at 20°C was measured using a rotation HAAKE Viscotester 6L/R plus (Thermo Electron GmbH, Karlsruhe, Germany). The content of phosphorus was determined according to the AOCS Official Method Ca 12-55.

The chemical structure of the synthesized polyols was identified by FTIR spectroscopy using a Nicolet iS50 FTIR Spectrometer (Thermo Scientific Inc.) and ³¹P NMR spectroscopy using Varian 400-MR (161.9 MHz), and software Mnova 11.0 (Mestrelab Research).

2.3. Preparation and testing of polyurethane coating
Preparing PU coatings, EG was preliminary mixed in a 50% toluene solution of polyol. The content of EG was varied from 5% to 25% of the total coating mass. The premixed polyol composition was then mixed with p-MDI at a NCO/OH molar ratio of 1:1:1. For the thermogravimetric test, PU coatings were prepared in the form of free films, ~300 μm in thickness. For the flammability test, PU coatings
with the same thickness were applied on standard wood (pine) samples (100 × 100 × 16 mm). The consumption of the PU composition upon its applying to wood samples was controlled by the weight method (400 g/m²). All PU coatings were hardened at a temperature of 21 ± 2°C for 7 days.

The thermal decomposition of the coatings was studied by TGA under a nitrogen atmosphere using TGA/SDTA 851e Mettler Toledo. The samples (about 8 mg) were heated in aluminium oxide crucibles from room temperature up to 800°C at a heating rate of 10°C/min and a gas flow rate of 20 cm³/min. The fire behaviour of wood samples with PU coatings was studied using a FTT Cone Calorimeter (Fire Testing Technology Ltd.). Testing was performed at a heat flux of 35 kW/m², which is recommended in ISO 5660-1:2015 for exploratory testing. Test duration was 30 min.

3. Results and discussion

3.1. Characteristics of polyols

Both synthesized polyols were light yellow liquids. The OH number of DGBE polyol (295 mg KOH/g) was slightly higher than that of IPA polyol (283 mg KOH/g) due to the fact that the acid value of DGBE polyol also was higher (23.2 mg KOH/g in contrast to 11.5 mg KOH/g). The viscosity of DGBE polyol was 1200 mPa·s, while that of IPA polyol was much higher (26900 mPa·s). Such a big difference in viscosity was explained later owing to spectroscopic data. The content of phosphorus in the DGBE polyol (0.45%) was slightly lower than that in the IPA polyol (0.50%).

FTIR spectra of both IPA and DGBE polyols had the absorption bands of the P=O stretching vibration at 1140 cm⁻¹ and the P–O–C stretching vibration at 1024 cm⁻¹ for IPA polyol and 1029 cm⁻¹ for DGBE polyol. In other ranges of spectra, absorption bands spectra of both polyols were similar. The difference in the polyols’ structure was identified only by the ³¹P NMR spectra:

DGBE polyol ³¹P-NMR (162 MHz, δ, ppm): 15.90 [O=P(OR)(OH)]; 1.07 [O=P(OR)₂(OH) ]; 0.021 [O=P(OH)_₃].

IPA polyol ³¹P-NMR (162 MHz, δ, ppm): 15.90 [O=P(OR)(OH)]; 1.07 [O=P(OR)₂(OH)]; 0.021 [O=P(OH)_₃]; -0.91 [O=P(OR)₃]; -6.7 [O=P(OR)₂–O–P(OH)₂=O].

The ³¹P NMR spectra of both polyols had shifts at 15.90 and 1.07 ppm, assigned to phosphate mono- and diesters, and the chemical shift at 0.021 ppm was assigned to the traces of unreacted free phosphoric acid. The IPA polyol ³¹P NMR spectrum, besides these chemical shifts, had two more signals at -0.91 and -6.7 ppm, related to phosphate triester and pyrophosphate monoester. The reaction scheme of the formation and representative structure of the mentioned phosphate esters is presented in our previous work [12]. The difference in the polyols’ composition can be explained by the different polarity of the solvents. Due to the presence of phosphate triester and pyrophosphate monoester, which are formed in the medium of the less polar IPA, the viscosity of the IPA polyol was much higher.

3.2. TGA of polyurethane coatings

Two grades of expandable additives, EG 096 (EG1) with a particle size of 0–0.2 mm and EG 290 (EG2) with a particle size of 0.2–0.6 mm, had a declared expansion volume of 50–90 ml/g and 200–300 ml/g, respectively. Camino et al. [20] have shown that the graphite expansion process at thermal decomposition takes place due to the redox reaction between H₂SO₄ and carbon, which generates the blowing gases CO₂, SO₂ and H₂O. These gases escape through the edges of the graphite particles, leading to their irreversible expansion.

The expandability of EG, as follows from the manufacturer's declared characteristics and literature data, depends mainly on the particle size. As the particle size of EG gets smaller, it is difficult to keep and seal significant amounts of sulphuric acid inside the particles [21]. The experimental TGA curves of EG1 and EG2 under nitrogen follow this rule. The EG1 with smaller particles at thermal decomposition generated a smaller quantity of blowing gases and at 800°C lost only 14.8% of mass (Fig. 1). The mass loss of EG2 at this temperature was 23.7%. The redox and expansion process of these kinds of EG occurs mainly in the temperature range of 210–450°C and presents the maximal rate of mass loss at 233°C for EG1 and 235°C for EG2 (Figs. 3, 4).
To compare the effect of EG1 and EG2 filled PU coatings based on DGBE polyol, polyols with a lower viscosity were prepared. Afterwards, taking into account the results of the combustibility test, EG2 also was used only for filling of IPA coatings. TGA curves for DGBE polyol based neat PU coatings and those filled with 25 wt% of EG are presented in Fig. 1. The IPA coating had analogues TGA curves.

Figure 1. TGA curves for EG1, EG2, and filled with EGs and neat DGBE coatings.

Figure 2. Effect of the EG content on the char residue at 800°C of PU coatings.

Figure 3. DTG curves for EG1, EG2, and filled with EGs and neat DGBE coatings.

Figure 4. DTG curves for EG2, and filled with 25 wt% of EG and neat IPA coatings.

DTG curves for neat and filled coatings based on DGBE and IPA polyols are presented in Figs. 3 and 4, respectively. The thermal decomposition of neat PU coatings had three steps of mass loss. The first step took place in the temperature range of 215–370°C for DGBE and 230–370°C for the IPA coating, and presents the maximum rate of mass loss ($T_{1\text{max}}$) at 330°C and 326°C for DGBE and IPA coatings, respectively. This step is assigned to the primary scission of the urethane linkage and the phosphate ester bond [1]. In filled coatings in this temperature range, the redox and expansion process of EG also takes place. As a result of the summation of these processes at increasing EG content, $T_{1\text{max}}$ gradually decreased and reached its minimum value at 25 wt% (318°C and 320°C for DGBE and IPA coatings, respectively).

The second and the third steps of PU thermal decomposition, attributed to the polyester degradation and char residue formation, take place in the temperature range of 370–440°C and 440–540°C [10]. The char residue gradually increased with the addition of EG, reaching the maximum values at their content of 25 wt% (Fig. 2). The char residue at 800°C of the DGBE coating filled with 25% of EG1 (36%) was higher than the residue of the coating with 25% of EG2 (34%) due to smaller mass loss of
EG1. The char residue at 800°C of IPA coatings with 25% of EG2, despite the greater mass loss of EG2, was practically the same (36%) due to the slightly higher content of phosphorus and the presence of phosphate triester and pyrophosphate monoester in IPA polyol.

3.3. Cone calorimeter test of polyurethane coatings
The fire behaviour of wood samples with applied PU coatings was studied in the cone calorimeter test and was characterized in terms of mass loss (ML), peak of heat release rate (PHRR), total heat release (THR), mean effective heat of combustion (EHC), maximum average rate of heat emission (MARHE) and total smoke release (TSR).

Figure 5 presents HRR curves of wood samples with a neat DGBE and IPA coatings and those filled with 25 wt% of EGs, at the initial stage of combustion. The first stage of samples’ combustion (0–100 s) was attributed to the combustion of volatile products of thermal decomposition of PU coatings and wood. This stage of combustion was accompanied by the maximum HRR. With loading of EG, the PHRR of coatings gradually decreased (Fig. 6) and reached their minimum values at 25 wt% of EG. Time to the peak of HRR at increasing content of FR also decreased due to the thermal decomposition and high ability to absorb infrared radiation and thermal conductivity of EG [21]. The effect of EG1 loading on PHRR was lower than that of EG2. The PHRR of coatings with 25 wt% of EG2 decreased 2.5-fold, compared to the case of neat coatings.

![Figure 5. HRR curves of samples with neat and filled PU coatings. EG content 25 wt%.

With further exposure to heat flux, wood samples with the neat PU coating and the coatings with lower content of EG continued to burn, and extinguished only after 1300–1500 s. The coating with the EG content higher than 15 wt%, after ignition and the expansion of graphite, extinguished. However, after 300–400 s, the samples with the protective EG layer ignited again, because the pyrolysis of wood under the loose protective layer at constant heat flux exposition was continued, and flammable gases went out through this layer. Only some samples with the IPA coating filled with 25 wt% of EG2 did not ignite again.

Total and mean values of the main flammability parameters of wood samples with PU coatings for the whole period of the test time (0–1800 s) were decreased at increasing of EG content, like PHRR. All these parameters for samples with neat and filled coatings are listed in Table 1. The flammability parameters of samples filled with 25 wt% of EG were significantly lower than these parameters of wood samples without coatings. The effect of EG1 with lower expansion volume of flame retardancy was lower than that of EG2 with a higher expansion volume. Due to the presence of phosphate triester and pyrophosphate monoester in IPA polyol, the IPA coating filled with 25 wt% of EG2 had the lowest values of PHRR, mHRR, THR, mEHC, MARHE, ML and TSR, compared to filled DGBE coatings.
Table 1 Flammability parameters of wood samples with IPA and DGBE coatings

| Flame retardant Coating | IPA 0% | DGBE 0% | IPA 25% EG | DGBE 25% EG | IPA 25% EG1 | DGBE 25% EG1 |
|-------------------------|--------|---------|------------|-------------|------------|-------------|
| ML (wt%)                | 87     | 88      | 68         | 77          | 81         | 92          |
| PHRR (kW/m²)            | 255    | 260     | 98         | 102         | 122        | 190         |
| THR (MJ/m²)             | 120    | 124     | 56         | 82          | 100        | 131         |
| mEHC (MJ/kg)            | 13.7   | 13.6    | 8.7        | 10.8        | 12.7       | 14.5        |
| MARHE (kW/m²)           | 112    | 124     | 42.8       | 52.5        | 71.7       | 104         |
| TSR (m²/m²)             | 522    | 495     | 73.7       | 85          | 146        | 180         |

4. Conclusions

PU coatings reached the maximum char residue in the TGA test under nitrogen atmosphere at 25 wt% of EG. Due to a smaller mass loss of EG 096, the PU coating filled with it had a higher value of the char residue than the PU coating filled with EG 290. At the same time, EG 290, which at thermal decomposition generated more blowing gases and as a result had a higher expansion volume, had higher flame retardancy than EG 096. Minimum values of flammability parameters for all coatings were reached at the maximum content of EG (25 wt%). Due to the presence of phosphate triester and pyrophosphate monoester in the structure, IPA coatings filled with 25 wt% of EG 290 had the lowest values of all flammability parameters in the cone calorimeter test.

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