

# Properties of Polyurethane Coatings Based on Linseed Oil Phosphate Ester Polyol

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**ABSTRACT:** Linseed oil was epoxidized using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), acetic acid (AcOH) and ion exchange resin Amberlite IR-120 as a catalyst. Epoxidized oil was separately dissolved in isopropyl alcohol (IPA) or diethylene glycol butyl ether (DGBE) and phosphorylated with different amounts of phosphoric (H<sub>3</sub>PO<sub>4</sub>) acid (1%, 2%, 3% and 5%). The formation of phosphate polyesters was confirmed by Fourier-transform infrared (FTIR) and <sup>31</sup>P nuclear magnetic resonance (NMR) spectra. Based on the synthesized polyols, polyurethane (PU) coatings were prepared. PU coating based on linseed oil diethylene glycol ester polyol was used as the reference. For the characterization of coatings, mechanical tests and thermogravimetric analysis (TGA) were used. The flammability parameters of wood samples with PU coatings at a heat flux of 35 kW/m<sup>2</sup> were determined. It was found that PU coatings based on IPA polyols had higher mechanical characteristics, char residue upon thermal decomposition and flame retardancy.

**KEYWORDS:** Linseed oil epoxidation, linseed oil phosphate polyol, PU coatings, flame retardancy

## 1 INTRODUCTION

Polyols that are obtained from vegetable oils by different methods are commonly used for production of bio-based polyurethanes (PU). Transesterification of vegetable oils with polyhydric alcohols is one of the most popular reactions. Another popular method of oil epoxidation is using peroxyacids and the subsequent ring opening of epoxidized oil with different alcohols [1]. Most of bio-based PU foams and coatings have good properties, but unfortunately, they have poor flammability properties. To decrease the flammability of bio-based PU, phosphorus-containing polyols are synthesized by different methods and used in bio-based PU coatings and foams, because sometimes the use of halogenated flame retardants is limited [2].

Epoxidation of vegetable oils has been studied in numerous works, and the effect of the concentrations of hydrogen peroxide formic and acetic acids and molar ratios on the epoxy group content in epoxidized oils is well investigated [3-9]. The kinetics of oil epoxidation is also studied because the effect of different types of catalysts and their concentrations may vary the epoxy group yield [10-12]. Phosphorylation of epoxidized vegetable oils is one of the methods to introduce phosphorus-containing molecules. The synthesis of phosphorus-containing polyols is carried out in two stages. First, the oil is epoxidized, and then epoxy ring opening, using phosphoric acid, is performed.

Most of reactions of oil epoxidation and phosphorylation of epoxidized oils were mainly investigated based on soybean oil. The role of different solvents and the concentration of phosphoric acid in the epoxy ring opening kinetics was reported in [13-15], showing that, based on soybean oil phosphate ester polyol, coatings with good properties could be obtained. In other studies [16-18], the properties of PU foams based on analogous polyols were investigated. Regarding the properties of PU foams, some other ways of bio-based polyol synthesis were reported in [19-23]. The flammability of coatings has not yet been tested; however, some tests were performed for PU foam. In particular, Heinen et al. [24] studied the effect of the phosphorus content in soybean phosphate ester on the oxygen index of PU foam. To decrease the flammability of compounds, it is necessary to introduce more phosphate groups in the polyol structure. Potentially, this is possible using linseed oil (LO), which contains more unsaturated bonds than soybean oil.

The objectives of the present work were to study (1) the kinetics of LO epoxidation as well as the ring opening reaction using different concentrations of phosphoric acid in the presence of two solvents, and (2) the mechanical properties, thermal degradation and flame retardancy of PU coatings based on LO phosphate ester polyols.

## 2 EXPERIMENTAL

### 2.1 Materials

Refined LO with the iodine value 181 g/100 g was obtained from Alberdingk Boley GmbH, Germany. Acetic acid (purity higher than 99.8%) (AcOH) from

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Honeywell Fluka (Germany), and hydrogen peroxide (35%), ion exchange resin Amberlite IR-120 H, phosphoric acid (85%), isopropyl alcohol (99%) (IPA), diethylene glycol 99% (DEG), diethylene glycol butyl ether (99%) (DGBE) and ethyl acetate (99.5%) (EtAc) from Sigma-Aldrich Chemie GmbH (Germany) were used for the synthesis of phosphorus-containing polyols. MDI-based isocyanate Voratec SD 100 (NCO content 31.5%, functionality 2.7), and Dabco T-12 Catalyst (dibutyltin-dilaurate) for polyurethane coating preparation were purchased from Dow Deutschland GmbH (Germany) and Fluka Analytical (Switzerland), respectively.

## 2.2 Epoxidation of Linseed Oil

Epoxidation of LO was carried out in a four-necked round bottom flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a water cooling condenser. First, the calculated amounts of AcOH and ion exchange resin Amberlite IR-120 H, as the catalyst, were added to LO and heated till 40°C. Then, the calculated amount of H<sub>2</sub>O<sub>2</sub> solution was added to the reactants dropwise over 30 min, maintaining the temperature not higher than 60°C. After the additions were completed, the reaction mixture was stirred at 600 rpm, and the stirring was continued at a temperature not higher than 65°C. The samples were periodically taken from the flask, and the epoxy group content test was performed until the iodine value dropped below 5 g/100 g. The reaction product, epoxidized linseed oil (ELO), was filtered to remove the ion exchange resin and washed with distilled water to remove free acid and separated from water in a separating funnel.

## 2.3 Phosphorylation of Epoxidized Oil

Taking into account the previous studies [16], kinetics of phosphorylation was carried out in two different solvents with different polarity. For phosphorylation, 100 g of ELO was dissolved in 50 g of IPA or DGBE and heated till the boiling point of the solvents. Then, the calculated amount of H<sub>3</sub>PO<sub>4</sub> (1%, 2%, 3% and 5% of epoxidized linseed oil mass) dissolved in 10 g of water was added to the reactants dropwise for 10 min, maintaining the temperature of the appropriate solvent at the boiling point. After that the reactants were heated at the boiling point and the reaction was continued for 6 h.

The product was dissolved in EtAc and washed with distilled water to remove unreacted phosphoric acid. After the water was separated, the polyol solution was dried for 12 h with anhydrous sodium sulphate. To remove the solvent, the polyol solution was distilled at

60°C and 180 mbars, and polyol was dried at 60°C and 10 mbars using a vacuum rotary evaporator.

## 2.4 Preparation of PU Coatings

Based on the synthesized LO phosphate polyols and isocyanate, PU coatings with the isocyanate index 110 were prepared. The concentration of Dabco T-12 Catalyst was 0.04 wt% of the total coating mass. PU coatings were prepared from mixed toluene solutions of polyol and p-MDI using a NCO/OH molar ratio of 1.1:1. For the thermogravimetric and mechanical test, polyurethane coatings were prepared in the form of free films, using polypropylene plates as the substrate and a 4-sided applicator frame with a gap of 350 µm in height and 100 mm in width. For the flammability test, polyurethane coatings, ~250 µm in thickness, were applied on standard wood (pine) samples (100×100×16 mm). The consumption of the polyurethane composition upon its application to wood samples was controlled by the weight method. All polyurethane coatings were hardened at a temperature of 21±2°C for 7 days. The reference PU coating was synthesized from the same ELO and DEG using molar ratios 1:1.1, to give linseed oil diethylene glycol ester (LDEG).

## 2.5 Methods for Polyol and PU Coating Characterization

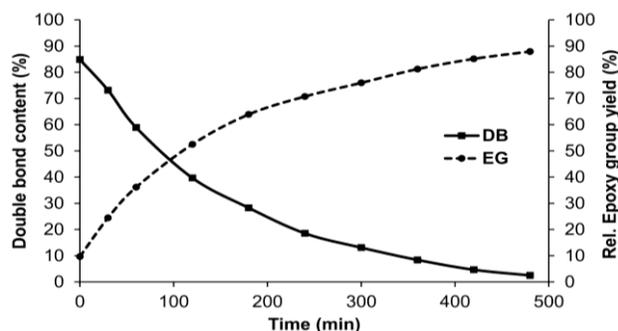
The iodine value and epoxy group content (weight percent of epoxide) of the synthesized products were determined according to ISO 3961:2013 and ASTM D1652-11. The hydroxyl (OH) number and acid value of polyols were determined according to ISO 14900:2001 and ISO 2114:2000. For the characterization of polyols, a Nicolet iS50 Analytical FTIR Spectrometer (Thermo Scientific Inc.) was used. <sup>31</sup>P NMR spectra were measured with a Varian 400-MR spectrometer at 161.9 MHz using chloroform as a solvent.

The tensile test of PU coatings was performed on a universal testing machine Zwick/Roell DO-FB0.5TS (500 N) according to ASTM D 882-10. The thermal stability of PU was tested using TGA/SDTA 851e METTLER TOLEDO. The glass transition temperature of polyurethanes was determined using DSC 851e METTLER TOLEDO. Both tests were carried out at a heating rate of 10 °C/min in nitrogen atmosphere. In these tests, coatings in the form of free films were used. Fire behaviour of wood samples with applied PU coatings 250 µm in thickness was studied using a FTT Cone Calorimeter (Fire Testing Technology Ltd.). Testing was performed according to ISO 5660-1:2015 at a heat flux of 35 kW/m<sup>2</sup>. Test duration was 30 min.

### 3 RESULTS AND DISCUSSION

#### 3.1 Epoxidation Reaction

For the epoxidation of LO, 20 parts by weight (PBW) of ion exchange resin Amberlite IR-120 H were added to 100 PBW of oil. During the epoxidation with 35%  $\text{H}_2\text{O}_2$ , the molar ratio of LO (double bonds) to  $\text{H}_2\text{O}_2$  and AcOH was 1:1.5:0.5. These epoxidation parameters were chosen based on literature data [7,25] and the results of control syntheses. The moment when the last droplet of the hydrogen peroxide solution was added to the reaction mixture was considered to be the start time of the reaction kinetics. The samples for kinetics measurements were taken at 0 min, 30 min, 60 min, 120 min, 180 min, 240 min, 300 min, 360 min, 420 min and 480 min. Using these parameters, the maximum epoxy group content (24.2%) was obtained after 8 h when the iodine value dropped below 5 g  $\text{I}_2/100$  g. The relative epoxy group yield (EG) reached 87.9% and content of double bonds (DB) decreased to 2.5% (Figure 1).

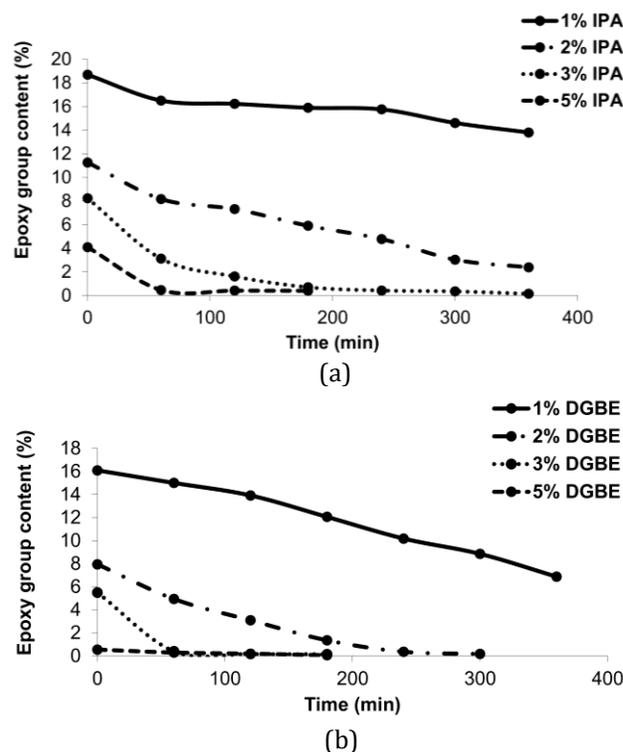


**Figure 1** Relative epoxy group content and double bond content versus reaction time.

#### 3.2 Ring-Opening Reaction with $\text{H}_3\text{PO}_4$

ELO was phosphorylated in both solvents with different amounts of  $\text{H}_3\text{PO}_4$  (1%, 2%, 3% and 5%). It was found that, with increasing concentration of  $\text{H}_3\text{PO}_4$ , ring-opening and phosphate ester formation reactions were accelerated (Figure 2). Similarly, the moment when the last droplet of the  $\text{H}_3\text{PO}_4$  solution (1%, 2%, 3% and 5%) was added to the reaction mixture was considered to be the start time of the reaction kinetics. The samples for kinetics measurements were taken at 0 min, 60 min, 120 min, 180 min, 240 min, 300 min and 360 min or until complete oxirane ring cleavage was reached. The fastest was the ring opening reaction using 5%  $\text{H}_3\text{PO}_4$  in both solvents, and complete oxirane ring cleavage was reached after 3 h. It can be noted that, using DGBE

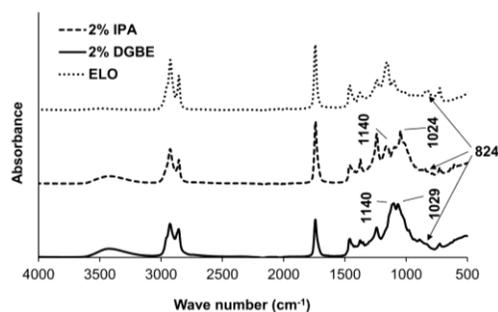
as a solvent, ring opening is slightly faster and more complete than with the IPA solvent. In both cases, using 1%  $\text{H}_3\text{PO}_4$  in similar reaction conditions, ring opening was incomplete and the hydroxyl value of both polyols was lower. The synthesized polyols were yellow coloured liquids. Polyols based on the use of different solvents such as IPA and DGBE, and phosphorylated with 1%, 2%, 3% and 5%  $\text{H}_3\text{PO}_4$  are named as 1% IPA, 2% IPA, 1% DGBE, 2% DGBE, etc. The characteristics of the polyols phosphorylated in the presence of IPA (IPA polyols) and DGBE (DGBE polyols) are listed in Table 1.



**Figure 2** Effect of the  $\text{H}_3\text{PO}_4$  concentration on the epoxy group content versus reaction time of (a) IPA and (b) DGBE polyols.

It could be seen that, using IPA as a solvent instead of DGBE, polyols had lower OH values, probably due to the phosphate triester and polyphosphate in the polyol structure discussed below (see  $^{31}\text{P}$ -NMR Measurements). It was also observed that, with increasing  $\text{H}_3\text{PO}_4$  concentration, the overall acid values were higher, probably due to some form of free phosphoric acid still present in the mixture (see  $^{31}\text{P}$ -NMR Measurements). The idealized chemical structure of polyols is presented in Figure 3.

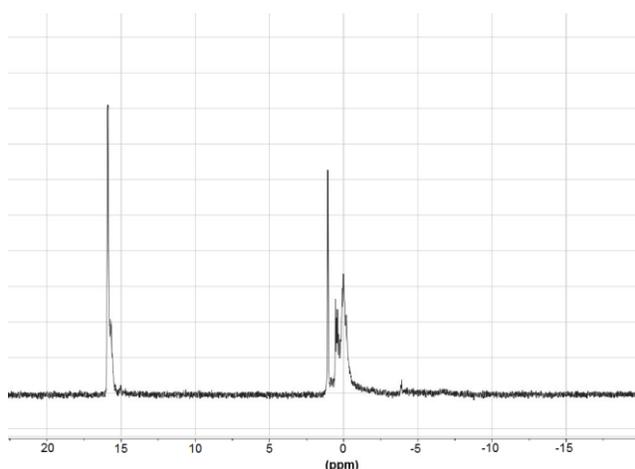




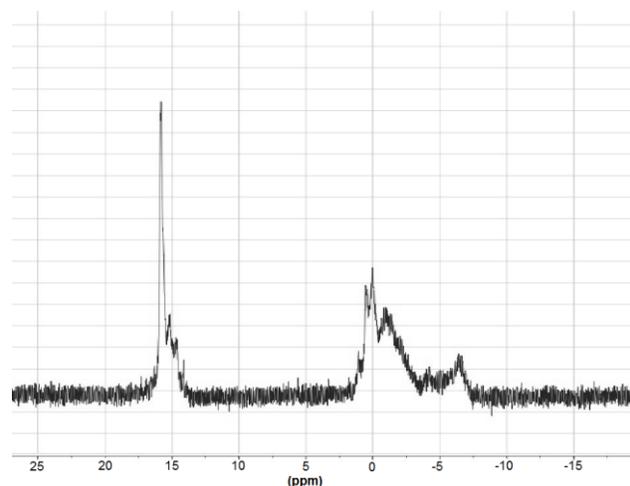
**Figure 5** Full FTIR spectra of ELO as well as IPA and DGBE polyols, phosphorylated with 2%  $H_3PO_4$ .

### 3.4 $^{31}P$ -NMR Measurements

$^{31}P$ -NMR spectroscopy, which is a more sensitive technique, was performed to confirm the incorporation of phosphorus into the structure of the polyol. Figures 6 and 7 show the  $^{31}P$ -NMR spectra of ELO-DGBE polyol and ELO-IPA polyol using 2%  $H_3PO_4$ , respectively. Both spectra present two signals at 1.07 ppm and 15.89 ppm for ELO-DGBE 2%, and 1.08 and 15.81 ppm for ELO-IPA 2%, assigned to phosphate mono- and diester. This may indicate that  $H_3PO_4$  is attached to the skeleton of the polyol. Chemical shifts at 0.02 in the spectra demonstrate that some form of free phosphoric acid is still present in the mixture. In the case of using IPA as a solvent, two more peaks appear at -6.7 ppm in the form of polyphosphate and -0.91 for phosphate triester. Such a difference in the polyols' composition can be explained by the different polarity of the used solvents. In the medium of the more polar DGBE, as a result of the reaction, only phosphate mono- and diesters are formed. In the medium of the less polar IPA, besides that, phosphate triesters and polyphosphates are formed.



**Figure 6**  $^{31}P$ -NMR spectrum of DGBE polyol phosphorylated with 2%  $H_3PO_4$ .



**Figure 7**  $^{31}P$ -NMR spectrum of IPA polyol phosphorylated with 2%  $H_3PO_4$ .

### 3.5 Mechanical Properties of Polyurethane Coatings

The tensile properties of the average values of 6 tested samples of PU coatings are presented in Table 2, in which the PU coatings based on IPA and DGBE polyols phosphorylated with 1%, 2%, 3% and 5%  $H_3PO_4$  are named as 1% IPA, 2% IPA, etc. The coefficient of variation was not higher than 8% for strength and modulus of elasticity, and not higher than 12% for elongation at break. It was found that the PU coatings based on the 2% IPA, 3% IPA and 5% IPA polyols had rather greater tensile strength and modulus of elasticity than in the case of the reference LDEG PU. Obviously, the rigidity of the network of those cross-linked polyurethanes, containing phosphate triester and polyphosphate groups, is higher than that of the reference LDEG PU, in which the isocyanate groups formed as a result of the reaction with the primary OH group of DEG are introduced in the PU cross-linked structure via a thermodynamically flexible short ethylene chain-  $(CH_2)_2$ -. In favour of this assumption says also the higher glass transition temperature ( $T_g$ ) of those phosphate based PU compared with the  $T_g$  of the reference PU (Table 2).

The coatings based on 2% IPA and 3% IPA had the highest tensile strength and modulus of elasticity. For the coatings based on 5% IPA, these characteristics are somewhat lower. It is probably due to the movement of the equilibrium of the reactions (Figure 3) more towards to the phosphate monoester formation at a higher  $H_3PO_4$  concentration. The coatings based on DGBE polyols, containing phosphate mono- and diesters, had lower tensile strength than the LDEG PU as well as IPA polyols based coatings.

**Table 2** Mechanical properties of PU based on LO polyols.

Polyols	LDEG	1% H <sub>3</sub> PO <sub>4</sub>		2% H <sub>3</sub> PO <sub>4</sub>		3% H <sub>3</sub> PO <sub>4</sub>		5% H <sub>3</sub> PO <sub>4</sub>	
		IPA	DGBE	IPA	DGBE	IPA	DGBE	IPA	DGBE
Strength (MPa)	37.5	8.5	2.8	50.6	29.40	49.90	35.4	39.7	33.8
Modulus (MPa)	1350	225	20.6	1600	1100	1570	1150	1170	1060
Elongation (%)	12.6	8.0	63.5	8.3	7.8	5.5	6.4	5.1	11.4
T <sub>g</sub> (°C)	56.4	52.4	-2.1	65.6	56.2	67.0	58.3	62.9	60.1

**Table 3** Thermal properties of polyurethane coatings.

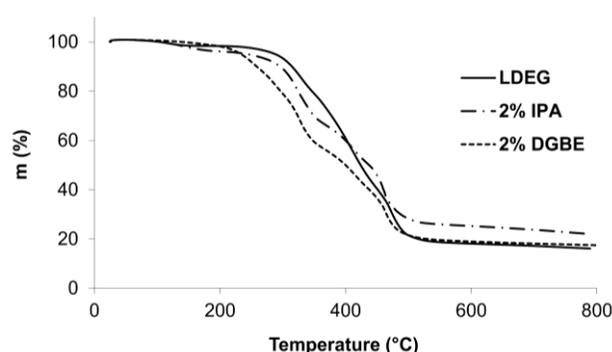
Polyol	LDEG	1% H <sub>3</sub> PO <sub>4</sub>		2% H <sub>3</sub> PO <sub>4</sub>		3% H <sub>3</sub> PO <sub>4</sub>		5% H <sub>3</sub> PO <sub>4</sub>	
		IPA	DGBE	IPA	DGBE	IPA	DGBE	IPA	DGBE
T <sub>1max</sub> (°C)	331	325	231	323	329	316	325	296	318
T <sub>2max</sub> (°C)	410	410	342	411	413	407	413	394	411
T <sub>3max</sub> (°C)	472	463	462	460	463	458	461	457	457
m <sub>600</sub> (%)	18.0	18.1	17.2	25.2	17.8	20.0	18.8	19.5	17.2
m <sub>800</sub> (%)	16.0	16.0	16.2	21.8	16.7	18.1	17.3	18.3	16.1

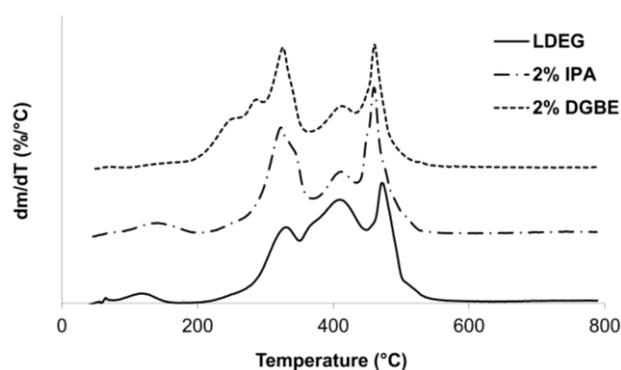
The coatings based on 1% IPA as well as 1% DGBE polyols had the lowest mechanical properties, probably due to the low crosslinking density of the PU networks. The reason for this is the incompleteness of the ring opening reaction within the reaction time, and as a result lower hydroxyl values of both polyols (Table 1). The PU based on the 1% DGBE polyol, containing phosphate mono- and diesters, has the lowest strength and modulus of elasticity, because it is in the rubbery state at room temperature (T<sub>g</sub> = -2.1°C).

### 3.6 Thermal Decomposition of Polyurethane Coatings

Figures 8 and 9 show TGA and DTG curves for IPA and DGBE coatings, which have three steps of thermal decomposition. The first step occurred in the temperature range of 230-370°C for IPA and LDEG coatings and 215-370°C for the DGBE coating, and presented the maximum rate of mass loss at the temperature T<sub>1max</sub>. This step of thermal decomposition was assigned to the dissociation of the urethane bond to alcohols and isocyanates for all coatings and the cleavage of the phosphate groups of IPA and DGBE coatings [26]. In the first step, phosphate ester PU had a higher mass loss than the reference LDEG PU. For IPA and DGBE coatings, mass losses were about 28% and 38%, respectively, in contrast to the mass loss of 20% for the reference PU. Phosphate ester PU had lower T<sub>1max</sub> than the reference LDEG coating (Table 3). With increasing concentration of H<sub>3</sub>PO<sub>4</sub>, T<sub>1max</sub> decreased. The second step of PU thermal decomposition was attributed to polyester

degradation [27]. In the temperature range of 370-440°C, the maximum mass loss was for the LDEG coating (39%). The temperature of the maximum rate of mass loss of this step T<sub>2max</sub> is presented in Table 3. The third decomposition step was in the temperature range of 440-540°C, when the residues formed during the first and second degradation steps further degraded to form a char residue [28]. The temperature of the maximum rate of mass loss for the final step of decomposition (T<sub>3max</sub>) was lower for phosphate ester polyols. T<sub>3max</sub> slightly decreased when the concentration of H<sub>3</sub>PO<sub>4</sub> in the polyols synthesis increased (Table 3). Average values of 3 tested samples are also presented in Table 3.

**Figure 8** TGA curves for PU coatings.

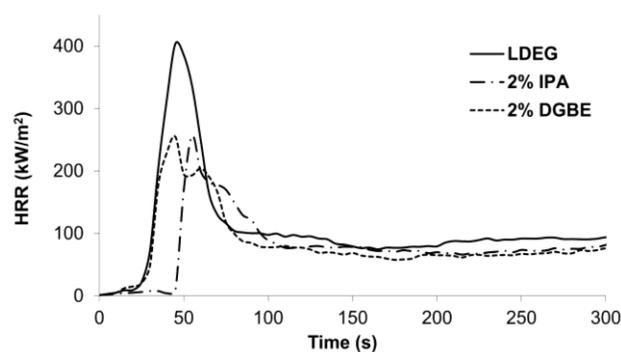


**Figure 9** DTG curves for PU coatings.

The char residue at 600°C and 800°C ( $m_{600}$  and  $m_{800}$ ) for DGBE coatings was approximately the same as for the reference LDEG coating, but the char yield for IPA was higher than that for DGBE and the reference, probably due to the presence of phosphate triesters and polyphosphate in polyols (Table 3). The highest char residue was for the 2% IPA coating. It can be noted that the char yield is a more significant thermal decomposition indicator, which generally correlates with the flame retardancy of materials.

### 3.7 Flammability Properties of Polyurethane Coatings

The fire behaviour of wood samples with PU coatings was studied in a cone calorimeter test and characterized in terms of mass loss (ML), heat release rate (HRR), peak of heat release rate (PHRR), total heat release (THR), mean effective heat of combustion (mEHC), total smoke release (TSR), and CO and CO<sub>2</sub> yield (COY and CO<sub>2</sub>Y).



**Figure 10** HRR versus time for PU based on LDEG, 2% IPA and 2% DGBE.

Figure 10 presents HRR curves of samples with reference PU coatings and the coatings based on phosphorylated polyols in the initial part of combustion (0-300 s). It is the stage of combustion of volatile products of the coating and wood thermal decomposition. Then, combustion continued in the condensed phase, and HRR decreased. After 1300-1500 s, the flame was out, and small heat releases were attributed to sample smouldering. The total and mean values of the main flammability parameters of wood samples with PU coatings for the whole period of the test (0-1800 s) are listed in Table 4. The burning intensity of wood samples with PU coatings based on LO phosphate ester polyols was lower than that of the samples with the reference coating. With increasing H<sub>3</sub>PO<sub>4</sub> concentration, flammability parameters such as ML, THR and HRR decreased (Table 4). Moreover, PHRR decreased 1.7 fold with increasing H<sub>3</sub>PO<sub>4</sub> concentration (Figure 11).

**Table 4** Flammability parameters of wood samples with PU coatings.

Polyol	LDEG	1% H <sub>3</sub> PO <sub>4</sub>		2% H <sub>3</sub> PO <sub>4</sub>		3% H <sub>3</sub> PO <sub>4</sub>		5% H <sub>3</sub> PO <sub>4</sub>	
		IPA	DGBE	IPA	DGBE	IPA	DGBE	IPA	DGBE
THR (MJ/m <sup>2</sup> )	141	121	132	127	127	119	131	121	131
mEHC (MJ/kg)	15.0	13.5	14.2	13.8	13.7	13.1	14.0	13.3	14.1
ML (%)	90.4	86.9	88.6	86.8	87.8	86.6	87.0	86.6	86.7
TSR (m <sup>2</sup> /m <sup>2</sup> )	470	537	573	493	458	386	695	538	540
COY (kg/kg)	0.06	0.07	0.07	0.08	0.07	0.07	0.07	0.07	0.07
CO <sub>2</sub> Y (kg/kg)	2.24	2.41	2.30	2.37	2.28	2.19	2.36	2.27	2.30

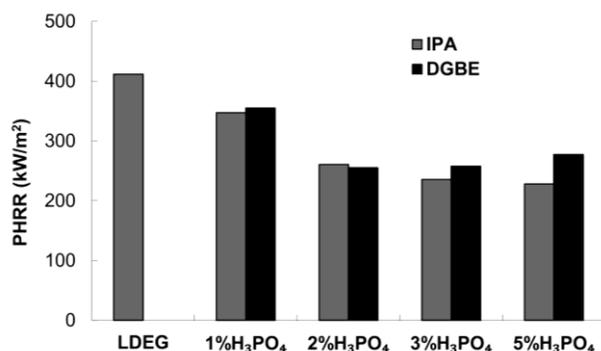


Figure 11 PHRR with increasing H<sub>3</sub>PO<sub>4</sub> concentration.

It could be seen that the TSR of the samples with IPA and DGBE coatings was higher than that of the samples with the reference coating. Also, the CO and CO<sub>2</sub> production of samples with IPA and DGBE coatings was higher (Table 4). In general, the flame retardancy of IPA coatings was higher than that of DGBE coatings, probably because of the presence of phosphate triesters and polyphosphate esters in IPA polyols. The 3% IPA coating had the lowest values of PHRR, ML, THR, mEHC and TSR.

#### 4 CONCLUSIONS

The results of this work showed that linseed oil can be epoxidized with the relative conversion to oxirane of 87.9%. As a result of the phosphorylation of epoxidized linseed oil in similar conditions but in the presence of two different solvents, the polyol synthesized in the presence of the less polar isopropyl alcohol, unlike the case of the more polar diethylene glycol butyl ether, had phosphate triester and polyphosphate in the polyol structure. Because of the presence of phosphate triester and polyphosphate in the polyols, IPA coatings had higher mechanical characteristics, char residue upon thermal decomposition and flame retardancy. These parameters were also higher than the characteristics of the reference LDEG coating. The PU coating based on the 3% IPA polyol had the highest flame retardancy.

#### ACKNOWLEDGMENT

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