Synthesis of a New Flame Retardant Curing Agent with Phosphorus and Their Application to Epoxy Resins

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Abstract. The synthesis has been made on a new kind of phosphorus-containing compound 2-(phenylphosphoryl)-1,4-benzenediol, which is defined as PPBDO. Besides, it is utilized as a flame retardant and meanwhile a curing agent of epoxy resins (EP). The description of the chemical structure was made in virtue of Fourier transform infrared (FTIR) spectroscopy, 1H, together with 13C nuclear magnetic resonance. Investigation on the flame retardant properties, cured epoxy resins’ combusting performances, and thermal degradation behaviors in virtue of restricting oxygen index (LOI) and vertical burning tests (UL-94) as well as cone calorimeter and thermogravimetric analysis (TGA) experiments. According to the results from the cone tests, the PPBDO integration could efficiently decreased the combustion parameters featured by epoxy resins thermosets, including Heat release rate (HRR), Total heat release (THR), etc. The TGA results displayed the PPBDO introduction managed to enhance epoxy resins matrix under the decomposition in advance, in comparison to the one pure EP, thus giving rise to a more concentration of char yield as well as thermal stability on the condition of high temperature.

Keywords: Curing agent; Flame retardant; Epoxy resin; Synthesis.

1. Introduction
In addition to the area of coating, casting, adhesive, epoxy resins are also enjoyed a welcomed application composite, encapsulant for semiconductors as well as insulating materials, used in the electric facilities and laminates for the reason of to the superior toughness, water resistance, solvent resistance, low shrinkage on cure, wonderful properties of electrical and mechanical resistance. Conventionally, Halogen compounds are commonly used to prepare flame retardant materials. Despite that the halogenated compounds which can express excellent flame retardancy for epoxy resins with widespread several-decade utilization, considering their toxicity as well as erode fumes in combustion, a number of countries have cut down the application frequency, Thereby, epoxy resins has been undergoing an extensive exploration and investigation on its growth and utilization road as halogen-free flame retardant. Also the last decades have been also witnessing the explorations on the improvement in flame retardancy. A wider varieties of halogen-free flame retardants have been put into use, which contain silicon, phosphorus, nitrogen, and so forth.

Of all the contents above, the addition of phosphorus containing flame retardant have been regarded as a most effective way of flame retardant epoxy resins. The reason is that is they can promote epoxy resins to form a carbonaceous char. It works as a physical obstacle to heat transfer, ranging from the flame, the polymer to the diffusion out of combustible gases and smokes. For instance, Wang and Shieh announced that epoxy resins under the cure of by bis (3-hydroxyphenyl) phenyl phosphate presented finer flame...
retardancy. Besides, the thermosets managed to pass UL-94 V-0 rate, as the phosphorus content was as low as 1.5 wt% within the cured resin.\(^{[16]}\) Synthesis was made on DAPO and then was reported. The cured epoxy resins arrived at the UL-94 V-0 rating as the phosphorus contents were 1.6 wt%\(^{[17]}\). Paul M. Hergenrother and some other scholars conducted \(^{[18]}\) synthesis on a new compound (bis(4-aminophenyl) methylphosphonate) containing phosphorus; and then it was employed as curing agent for the preparations of flame retardant thermosets. The thermosets’ LOI value amounted to 31% ; and the phosphorus contents were 3.9 wt%.

This thesis illustrated the synthesis on a new phosphorus-including compound with P-C bonds diphenyl-(2,5 dihydroxyphenyl)-phosphonate, with the definition of PPBDO. It was employed as flame retardant curing agents for the preparations of flame retardant epoxy resins. Moreover, coupled with the description and disclosure on the flame retardant properties and thermal degradation behavior, description and disclosure of flame retardant mechanism and water resistance and combustion behavior were made in virtue of the cured epoxy resins.

2. Experiment Contents

The attainment of materials of Diphenylphosphine oxide was provided by the Fusilin Co., Ltd (Qingdao, China). The purchase of 1,4-Benzquinone, m-phenylenediamine, ethanol and methylbenzene was made out of the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). The application of Epoxy resins (E-44, epoxide equivalent weights=213g/epoxide) was offered by Fude Chemicals Industry (Guangzhou, China).

2.1. Synthesis of 2-(phenylphosphoryl)-1,4-benzenediol (PPBDO)

Scheme 1 illustrates the synthetic route of PPBDO. 20.2 g (0.1 mol) DPO, 13.0 g (0.12 mol) Benzoquinone and 120 mL dried toluene got added in 250 mL flask of four necks which was outfitted with a reflux condenser, a thermometer as well as mechanical stirrer under the atmosphere of dry nitrogen. Then the heat was made on the mixture for refluxing temperature and 20-hour maintaining and stirring. Then came the cool-down of the reaction mixture, reaching the room temperature until masses of dark yellow precipitant was appearing the solution. Next, the filtering and washing of the precipitant was made with ethanol three times, and then was dissolved in potassium hydroxide solution, hydrochloric acid was dripped into the solution and white precipitant was produced. Finally, the white solid particles were obtained from filtering, washing with ethanol as well as the 8-hour vacuum drought on the condition of 60 °C. Yield of target product is 88.1% and melting range is 212.5~213.6 °C.

Scheme 1. Synthetic route of PPBDO.

2.2. Preparations for the Cured Epoxy Resins

The achievement of those epoxy resins thermosets was made in virtue of thermally curing based on various mass ratios PPBDO curing agents and PDA (0/100, 10/90, 20/80, 30/70, 40/60, 50/50). The homogeneous mixture of curing agents as well as epoxy resins in stoichiometric amounts was made based on mechanical stirrer on the condition of 120 °C. Table 1 lists the content of PPBDO and phosphorus in epoxy resins thermosets.
Table 1. Formulations and flame retardancy of epoxy resin system.

| Sample | Curing Agent Compositions(PPBDO/PDA) | P % | LOI (%) | UL-94 rating | Dripping |
|--------|-------------------------------------|-----|---------|--------------|----------|
| EP-0   | 0/100                               | 0.00| 17.8    | No rating    | Yes      |
| EP-1   | 10/90                               | 0.60| 26.5    | No rating    | No       |
| EP-2   | 20/80                               | 1.15| 30.2    | No rating    | No       |
| EP-3   | 30/70                               | 1.66| 31.4    | V-1          | No       |
| EP-4   | 40/60                               | 2.11| 31.9    | V-0          | No       |
| EP-5   | 50/50                               | 2.53| 32.1    | V-0          | No       |

2.3. Characterization of PPBDO
The attainment of FTIR spectra was conducted in virtue of potassium bromide discs and Perkin Elmer 400 spectrometer (USA). The attainment of NMR spectra was made in virtue of 10-25% deuteron dimethyl sulfoxide (DMSO-d6) and Bruker 300 NMR (300 MHz) spectrometer (Germany). The report of Proton and carbon chemical shifts was made, considering TMS was used for an internal reference. The reported phosphorus chemical conversion was made, considering aqueous phosphoric acid solution contributes 85% for external reference.

2.4. Flame Retardancy Tests
The measurement to vertical burning ratings (UL-94) was made on a CZF-2 instrument (Jiangning, China), based on sheet dimensions of 125 mm ×12.5 mm ×3 mm in light with the American National Standard ANSI/UL 94-2010. The measurement to limiting oxygen index (LOI) was made to a JF-3 limiting oxygen index chamber (Jiangning, China) on the basis of 130 mm ×6.5 mm ×3 mm sheet dimensions in accordance with ISO 4589-2:1996.

2.5. Cone Calorimeter Tests
The measurement to the combustion behavior subject to ventilated conditions was made in accordance with a Fire Testing Technology cone calorimeter (West Sussex, UK), conforming to ISO 5660-1 Criteria. The exposures of samples with 100 × 100 × 3 mm³ size was made to cone at a 50 kW·m⁻² heat flux; a test on specimen was made oriented with each of the samples.

2.6. Thermogravimetric Analysis
The implementation on thermogravimetric analysis (TGA) was made in virtue of a Perkin Elmer Pyris 1 Thermal Gravimetric Analyzer (Massachusetts, USA) on the condition of 10 °C min⁻¹ as the heating rate, heating from 50 °C to 800 °C in nitrogen atmosphere. The achievement of the thermal degradation data was based on the TGA as well as derivative thermal gravimetric analysis (DTG) curves.

3. Findings and Discussion
Description of PPBDO. The description of chemical structure featured by the synthesized PPBDO was respectively conducted via FTIR, ¹H, and ¹³C NMR Figure 1(a) expresses FTIR spectrum harbored by the reactant DPO. The culmination at 3051 cm⁻¹ corresponds to the aromatic C-H stretching vibration and 2374 cm⁻¹ got distributed to the P-H stretching. These culminations appear at 1589 and 1483 cm⁻¹, which are distributed to the stretching of benzene ring, 1439 cm⁻¹ for the P-C stretching vibration; 1188 cm⁻¹ assigned to the P=O stretching vibration. Figure 1(b) presents FTIR spectrum of PPBDO. Observation was made on the characteristic absorption peak at 2374 cm⁻¹ distributing to the P-H bonds disappears; the strong absorption peaks at 3143 cm⁻¹ distributing to O-H bonds in comparison to DPO’s FTIR spectrum. The findings reveal that the P-H bonds on DPO has been reacted with 1,4-Benzquinone.
Figure 1. FTIR spectrum of DPO (a) and PPBDO (b).

Figure 2 showed the $^1$H NMR spectrum harbored by PPBDO. The peaks appear at 7.507 to 7.586 ppm got derived from protons (1, 2, 3) within the benzene ring. Signals appear at 7.619 to 7.683 ppm corresponded to the proton (4) in the benzene ring. The peaks at 6.736, 6.973 and 6.894 ppm were attributed to protons (5), (7) and (8), respectively. The peaks appear at 9.134 and 9.785 ppm came out of the protons (6, 9) of –OH. Figure 3 display $^{13}$C NMR spectrum featured by PPBDO. The peaks at 131.71, 128.44, 131.38 and 132.65 ppm come from the carbon atoms (1~3) within the benzene ring, respectively. The peaks at 121.38, 152.39, 118.50, 117.56, 149.84 and 115.55 ppm is consistent with the carbon atoms (5~10) in the benzene ring.

Figure 2. $^1$H NMR spectral data of PPBDO.

Figure 3. $^{13}$C NMR spectral data of PPBDO.

The confirmation of the construction of PPBDO was firmly established FTIR, $^1$H NMR, as well as $^{13}$C NMR. According to the results, a successful synthesis was conducted on the commodity.

3.1. Flame Retardancy of Thermosets

In order for a good evaluation on PPBDO’s effects upon the flame retardancy featured by epoxy resins, the tests of LOI and UL-94 vertical burning tests were implemented. Table 1 illustrates the relative data. The LOI value featured by the EP/PDA system represented merely 17.8%. The vertical burning tests expressed no rating, which indicated the high combustibility of the pure epoxy resins. The LOI values were dramatically increased when the curing agent PPBDO was integrated with the epoxy resins. An increase in the LOI value featured by the EP/10 wt% PPBDO/90 wt% PDA thermosets came from
17.8% oriented with pure EP thermostets to 26.5% when 0.6% stood for the phosphorus content. A gradual increase of the LOI values featured by the EP thermostets was taking place as PPBDO content is increasing. The EP/40 wt% PPBDO/60 wt% PDA thermostets based on the 2.11% of phosphorus content managed to pass UL-94 V-0 flammability rating. The LOI value reached the highest ratio to 31.9%. The previous reports witnessed the improvement of numerous phosphorus compounds in the flame retardancy oriented with epoxy resins. For example, 30.0% stood for the LOI value of the EP thermostets cured with hyperbranched (3-hydroxyphenyl) phosphate (HHPP). No report was made on the vertical burning tests. 33% represented the LOI ratio of the epoxy resins cured with bis(4-amino phenoxy) phenylphosphine oxide as the phosphorus content arrived at 4.2%; however, no rating fell on the thermostets within the UL-94 test. In comparison to the reported findings, the synthesized PPBDO curing agent provided an effective flame retardancy oriented with epoxy resins. In reality, the phosphorus-containing curing agent upon degradation produced phosphoric, polyphosphoric acid after the addition of PPBDO, together with the created acids managed to accelerate the epoxy resins’ decomposition of and meanwhile establishing an insulating protective char layer. As a result, it managed to prevent the heat and oxygen removing materials’ surface and meanwhile enhancing the flame retardancy featured by the epoxy resins. The vertical burning test and limiting oxygen index test are known to be effectual approaches to ranking the flammability of the material kind on the occurrence of a small fire, when cone calorimeter has been considered as a most effectual approaches to measuring a number of crucial parameter of the real breakout of fire. Table 2 and Figure 4 illustrate the data attainment and curves featured by EP/PDA; EP/40 wt% PPBDO/60 wt% PDA thermostets was achieved out of the cone calorimeter test on the condition that a 50 kW·m⁻² heat flux TTI was applied to determining the impact of a flame retardant upon the ignitability, the measurement to which started at the onset of an HRR curve. Table 2 reveals that a decrease in the TTI of EP/40 wt% PPBDO/60 wt% PDA thermostets started at 63 s for pure EP till 51 s. The decomposition of PPBDO flame retardant additive did not occur in advance. However, it also enhanced the epoxy resins matrix, which aimed at a lower-based temperature. To some extent, the degradation conducts in advance was attributed to the charring formerly in the duration of the combustion and favored a finer flame retardancy featured by the EP thermostets.

The HRR has been known as the most critical parameter for quantifying fire size; an efficient flame retardant system is inclined to express a smaller HRR value. Figure 4(a) shows the HRR (heat release rate) curves harbored by EP/PDA as well as EP/40 wt% PPBDO/60 wt% PDA thermostets. The cured EP/PDA thermostets are observed to be burned quickly following ignition and two HRR culminations occurred in the duration of the combustion. The first HRR culmination appeared at 185 s at a PHRR (peak heat release rate) of 732.8 kW m⁻² as a result of combustion occurring to cured EP. The second HRR culmination under observation at 250 s and a PHRR of 316.9 kW m⁻² came out of the formed char layer’s crack based on the combined poor strength with low thermal stability. Figure 4(a) shows that, the observation on the HRR curve of the EP/40 wt% PPBDO/60 wt% PDA thermostets took on two culminations. The peaks appear earlier than those for the EP/PDA thermostets. The first HRR culmination of EP/40 wt% PPBDO/60 wt% PDA thermostets at 80 s featured by a PHRR of 256.3 kW m⁻² presents the consistence with the decomposition of the PPBDO additive during the former phase on heating and that exerts stimulation on the epoxy resins matrix to lower and char during an early phase. The matrix surface was the place for char layer’s insulation. Namely, the heat insulating char gave rise to abrupt enhancement of the surface temperature as well as speeding up the decomposition of EP matrix for EP composites’ surface. 170 is for the observation on the second HRR culmination of EP/40 wt% PPBDO/60 wt% PDA thermostets, which is consistent with EP thermostets’ combustion. An obvious decrease in PHRR begins to occur at 383.7 kW m⁻² for pure EP to 732.8 kW m⁻². PPBDO is conformed to upgrade the EP thermostets for the char formation as a result of the charring capacity harbored by epoxy resins themselves as well as the high-quality char from the degradation formation of PPBDO. It can prevent the heat transmission in the process of the ignition, thus lowering intensity of the combustion pyrolysis reactions and meanwhile decreasing heat release. According to Figure 4(b) and Table 2, the incorporation of PPBDO with epoxy resins, a decrease will occur to heat release from 103.1MJ m⁻² oriented with pure EP to 68.1MJ m⁻². The less THR value is signaling that partial EP/40
wt% PPBDO/60 wt% PDA thermosets, which was not undergoing complete combustibility, was likely to undergo a char-forming procedure. Lower HRR and THR are believed to be associated with the condensed stage, thus contributing to a finer flame retardancy for the epoxy resins thermosets.

**Table 2.** Cone calorimeter data of EP/PDA system, EP/40 wt% PPBDO/60 wt% PDA System.

| Properties          | Samples                |
|---------------------|------------------------|
|                     | EP/PDA | EP/40 wt% PPBDO/60 wt% PDA |
| TTI (s)             | 63     | 51             |
| Peak1-HRR (kW·m⁻²) | 732.8  | 256.3          |
| t_peak1-HRR (s)     | 185    | 80             |
| Peak2-HRR (kW·m⁻²) | 316.9  | 383.7          |
| t_peak2-HRR (s)     | 250    | 170            |
| THR (MJ·m⁻²)        | 103.1  | 68.1           |
| AMLR (g·s⁻¹)        | 0.11   | 0.09           |

![Figure 4](image-url) **Figure 4.** HRR (a) and THR (b) curves of EP/PDA system and EP/40 wt% PPBDO/60 wt% PDA system.

### 3.2. Thermal Degradation Behavior

TGA (Thermogravimetric analysis) can provide direct data on the thermal stability and char formation as well as degradation behaviors, which are featured by the samples. In addition, it can also offer the indirect data on the latent flame retardancy harbored by cured epoxy resins which are in large association with a char residue formation during pyrogenation. The starting decomposition temperature refers to the temperature where 1 wt% weight loss happens; the **Tmax** gets interpreted as the temperature at loss rate of a maximum weight. Figure 5 expresses the TGA as well as derivative thermogravimetric (DTG) curves featured by the thermosets (sample EP-0) and EP/40 wt% PPBDO/60 wt% PDA thermosts (Sample EP-4) on the condition of nitrogen atmosphere; Table 3 summarizes the concerned thermal degradation data. The decomposition of EP/PDA thermosts occurs on the condition of 333.4 °C; the char yield is merely 1.5 wt% on the condition of 800 °C. The thermal degradation duration is made up of two phases, as Figure 5(b) reveals, Step One’s highest maximum thermal decomposition ratio turns up on the condition of 386.3 °C at a 11.72 % min⁻¹ of weight loss rate as a result of integration of the decomposition with char-forming on epoxy resins. The second decomposition phase takes place in the range of 500 °C -800 °C; the 634.0 °C witnesses the peak and that can be put under the shaped char-residues-based decomposition at a lower thermal stability. Furthermore, the initial decomposition temperature at the EP/30 wt% PPBDO/70 wt% PDA system which started the decrease at the starting 333.4 °C EP/PDA system up to 310.7 °C, the increase of the residual char started at 1.5 , upgrading to 13.6% on the condition of 800 °C. When an increase of phosphorus content occurred to the cured epoxy resin system, the **T_initial** and **T_max** of the EP/40 wt% PPBDO/60 wt% PDA composites were respectively 304.4 and then 380.6 °C ; the **T_initial** presented a lower value compared to the one of the EP/30 wt% PPBDO/70 wt% PDA system. However, the char
residue got upgraded to 18.6% at the condition of 800 °C. Evidently, the char yield had an increase and \( T_{\text{initial}} \) was on the decrease based on an increase in the PPBDO content within the epoxy resins. The result was primarily stemmed out of the Phosphorus Groups within EP thermosets, and the first decomposition occurred to shape phosphorus abundant residue like polyphosphoric acid as well as the established acid reaction with epoxy resins. This reaction, which stimulated the epoxy resins degradation at an early stage on heat, led to lowered initial thermal decomposition temperature as well as thermosets’ charring formation in advance. This higher char yield is to upgrade the flame retardancy featured by the EP thermosets. The thermal degradation results are conforming to the aforementioned test of flame retardance. Accordingly, it can be concluded that PPBDO might exert stimulation on EP’s thermal degradation of during an prior degradation for the formation of a compact char. That presents the EP thermosets’ thermal decomposition higher-degree on the condition of high temperatures.

Table 3. Thermogravimetric Properties of EP/ PDA, EP/30 wt% PPBDO/70 wt% PDA and EP/40 wt% PPBDO/60 wt% PDA system.

| Samples                      | \( T_{\text{initial}} \) (°C) | \( R_{\text{1peak/T1peak}} \) (% min\(^{-1}\)/°C) | \( R_{\text{2peak/T2peak}} \) (% min\(^{-1}\)/°C) | Char residues at 800°C (wt%) |
|------------------------------|--------------------------------|------------------------------------------------|------------------------------------------------|----------------------------|
| EP/ PDA                      | 333.4                         | 11.72/386.3                                   | 1.76/634.0                                    | 1.5                        |
| EP/30 wt% PPBDO /70 wt% PDA  | 310.7                         | 10.9/387.6                                    | —                                              | 13.6                       |
| EP/40 wt% PPBDO /60 wt% PDA  | 304.4                         | 16.5/380.6                                    | —                                              | 18.6                       |

Figure 5. TGA (a) and DTG (b) curves of EP/ PDA, EP/40 wt% PPBDO/60 wt% PDA and EP/40 wt% PPBDO/60 wt% PDA system.

4. Conclusions

To sum up, a new phosphorus-including curing agent PPBDO with P-C bonds was successfully synthesized, and the obtained PPBDO combined with PDA with different mass fractions was employed to curing agent for preparing flame retardant epoxy resins. The EP/40 wt% PPBDO/60 wt% PDA composites managed to pass the UL-94 V-0 flammability rating, which harbor as high an LOI value as 32.1%. The integration of PPBDO with EP stimulated epoxy resins matrix to be decomposed as well as char forming in advance, enhancing the char yield and EP thermosets’ thermal stability on the condition to higher temperatures. PPBDO introduction manage to promote epoxy resins thermosets which help establish lasting and compact char layer, is able to inhibit smoke and combustible volatiles emission by reducing the heat transmission and heat release ratio in combustion duration. That contributes to an effectively functional flame retardancy to cured epoxy resins thermosets.

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References

[1] Lu, S.Y., and Hamerton, I., Recent developments in the chemistry of halogen-free flame retardant polymers, Prog. Polym. Sci., 27(2002)1661-1712.

[2] Zhang, H. K., Xu, M. J., and Li, B., Synthesis of a novel phosphorus-containing curing agent and its effects on the flame retardancy, thermal degradation and moisture resistance of epoxy resins, Polym. Adv. Technol., 27(2015)860-871.

[3] Brehme S, Schartel B, Goebbels J, Fischer O, Pospiech D, Bykov Y, Döring M, Phosphorus polyester versus aluminium phosphinate in poly(butylene terephthalate) (PBT): Flame retardancy performance and mechanisms, Polymer Degradation and Stability, 96(2011) 875-884.

[4] Liu, X.Q., Wang, D.Y., Wang, X.L., Chen, L., & Wang, Y.Z., Synthesis of organo-modified α-zirconium phosphate and its effect on the flame retardancy of IFR poly(lactic acid) systems, Polym. Degrad. Stab., 96(2011). 771-777.

[5] Spontón, M., Ronda, J. C., Galià, M., and Cádiz, V., Cone calorimetry studies of benzoxazine-epoxy systems flame retarded by chemically bonded phosphorus or silicon, Polym. Degrad. Stab., 94(2009) 102-106.

[6] Mercado, L. A., Reina, J. A., and Galià, M., Flame retardant epoxy resins based on diglycidylmethylenephethylsiane, J. Polym. Sci., Part A: Polym. Chem., 44(2006) 5580-5587.

[7] Canadell, J., Mantecon, A., and Càdiz, V., Copolymerization of a silicon-containing spiroorthoester with a phosphorus-containing diglycidyl compound: Influence on flame retardancy and shrinkage, Polym. Degrad. Stab., 92(2007) 1934-1941.

[8] Li, X., Ou, Y., & Shi, Y., Combustion behavior and thermal degradation properties of epoxy resins with a curing agent containing a caged bicyclic phosphate, Polym. Degrad. Stab., 77(2002) 383-390.

[9] Wang, X., Hu, Y., Song, L., Xing, W., & Lu, H., Preparation, mechanical properties, and thermal degradation of flame retarded epoxy resins with an organophosphorus oligomer, Polym. Bull., 67(2011) 859-873.

[10] Lisheng Zhou L. S., Zhang G. C., Li J. T.,Jing Z. X.,Qin J. B., and Feng Y. J., The flame retardancy and thermal stability properties of flame-retarded epoxy resins based on α-hydroxyphosphonate cyclotriphosphazene, J. Therm. Anal. Calorim., 129(2017) 1667-1678.

[11] Wu, C. S., Liu, Y. L., Chiu, Y. C., and Chiu, Y. S., Thermal stability of epoxy resins containing flame retardant components: an evaluation with thermogravimetric analysis, Polym. Degrad. Stab., 78(2002) 41-48.

[12] Lin, C. H., Wu, C. Y., and Wang, C. S., Synthesis and properties of phosphorus-containing advanced epoxy resins, II. J. Appl. Polym. Sci., 78(2000) 228-235.

[13] Wang, C. S., and Lin, C. H., Synthesis and properties of phosphorus containing advanced epoxy resins, J. Appl. Polym. Sci., 75(2000) 429-436.

[14] Ribera, G., Mercado, L. A., Galià, M., and Càdiz, V., Flame retardant epoxy resins based on diglycidyl ether of isobutyl bis(hydroxypropyl)phosphine oxide, J. Appl. Polym. Sci., 99(2005) 1367-1373.

[15] Lisheng Zhou L. S., Zhang G. C., Li J. T.,Jing Z. X.,Qin J. B., and Feng Y. J., The flame retardancy and thermal stability properties of flame-retarded epoxy resins based on α-hydroxyphosphonate cyclotriphosphazene, J. Therm. Anal. Calorim., 129(2017) 1667-1678.

[16] C.S. Wang and J. Y. Shieh, Synthesis and properties of epoxy resins containing bis(3-hydroxyphenyl) phenyl phosphate, Eur. Polym. J. 36(2000) 443-452

[17] M. Rakotomalala, M. Ciesielski, T. Zevaco and M. Doering, ChemInform Abstract: Synthesis and Reactivity of 6H - Dibenzo[c,e][1,2]oxaphosphine 6 - Sulfide, a Novel Thiophosphacyclic Molecule, Phosphorus, Sulfur Silicon Relat. Elem. 186 (2011) 989-998.

[18] P. M. Hergenrother, C. M. Thompson, J. G. Smith, J. W. Connell, J. A. Hinkley and R. E. Lyon, Flame retardant aircraft epoxy resins containing phosphorus, Polym. 46(2005) 5012 -5024.