

## Scientific report

Regarding the project implementation in the period October–December 2020

Project title: “**The behaviour of new multicomponent polymeric systems in simulated environmental conditions for flame retardant coating materials**” Code: **PN–III–P1–1.1–TE–2019–0604**

### Stage Summary

The first stage of the project (2020) comprises three activities. The first two activities consist of the scientific documentation (Activity 1.1) and the investigation of modern synthesis and characterization methods (Activity 1.2). The third activity (Activity 1.3) describes the synthesis and structural characterization of the precursor to the oligophosphonate (OP) and the OP. The OP will be used in the next stage for the obtaining of the proposed multicomponent materials. The OP is designed as an aromatic polyester for making the epoxy resin eco–friendly and non–corrosive compared to halogen based flame retardants. All proposed activities for this stage have been fully achieved and are presented below in this report.

### Scientific and technical description

**Activity 1.1. Scientific documentation:** - Creation of a database with recent information in the field of phosphorus based monomers and polymers, as well as epoxy resins (books, reviews and scientific articles, patents); - Analysis of informational data

Epoxy resins have been around from back in World War II and their application domains have been continuously increasing ever since. This is due to their numerous outstanding properties, such as excellent mechanical and electrical behaviour, very good adhesion to a wide variety of substrates, chemical, abrasion and corrosion resistance, moderate toughness, flexibility, low curing shrinkage<sup>1</sup>. Due to their valuable properties epoxy resins are present in construction and civil engineering, electronics, transportation, encapsulating structures in aeronautics, and used as various products: adhesives, coatings, paints, laminates, floorings, mortars, sealing and road antiskid systems and many others<sup>2</sup>. The high reactivity of the oxirane ring endows the epoxy resins with a versatile crosslinking capacity toward a large variety of functional groups (amines<sup>3</sup>, acids<sup>4</sup>, phenols<sup>5</sup>, amides<sup>6</sup>, thiols<sup>7</sup>) for the obtaining of different polymer matrices in various applications<sup>8</sup>. However, epoxy resins are constituted of carbon, oxygen and hydrogen atoms. As a consequence, they exhibit increased flammability and low thermal stability<sup>9</sup>. Therefore, the enhancement of flame resistant capacity, while maintaining their good features together with recycling and reducing environmental impact remains a main challenge in the production of advanced materials for different applications. The improving of epoxy resins flame resistance may be undertaken either by blending fire retardant additives followed by curing, or by chemical modification<sup>10</sup>. Although the adding of organohalogens into epoxy networks proved to be extremely efficient<sup>11</sup>, such compounds have been prohibited by global environmental legislation<sup>12</sup>. The combustion mechanism generates corrosive and extremely toxic gases and high smoke quantities<sup>13</sup>. Several modification strategies have been developed in order to improve the epoxy resins thermal stability and fire resistance, such as with phosphorus<sup>14</sup>, layered double hydroxides<sup>15</sup>, boron<sup>16</sup>, melamine<sup>17</sup>, silicon<sup>18</sup>, montmorillonite<sup>19</sup>, etc. Of all the mentioned modification pathways, the incorporation of organophosphorus compounds proved to be the most efficient, not only in considerably reducing flammability, but also in lowering the number and toxicity of the volatiles evolved during combustion. Depending on their structure, phosphorus flame retardants may act in the condensed or gas phase. In the condensed phase, the most common to phosphorus additives<sup>20</sup>, the flame retardant reduces the degradation rate and/or hinders the combustion mechanism pathway. The gas phase occurs through the scattering of the entities which maintain the flame. During burning or thermal degradation, the organophosphorus structure yields phosphoric acid. With increasing heat non–volatile polyphosphoric acid is formed. This further reacts with the decomposing structure through esterification and dehydration, generating char residue. The phosphorus content in the char residue increases with the phosphorus concentration in the initial polymer<sup>21</sup>. The residue behaves as a two–way barrier by: (i) inhibiting heat and oxygen from reaching the burning polymer and (ii) blocking the access of volatile fuels and molten polymer to the combustion area. This significantly increases combustion time or even extinguishes the fire. Increasing research efforts are undertaken in investigating and comprehending the effects of phosphorus content on the thermal degradation mechanisms and combustion behavior of such materials. It is also worth mentioning that volatile phosphorylated entities are some of the most efficient flame

retardants, since phosphorus-containing radicals are five and ten times more effective than bromine and chlorine ones, respectively. Also, they are far less toxic than both<sup>22</sup>. Bulky phosphorus based monomers containing the polar P=O group are known for improving fire resistance of different materials, amongst other properties. Of such compounds, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is widely used due to its versatility in functionalization possibilities<sup>23</sup>. DOPO contains an active hydrogen atom, making it susceptible to react with a wide range of electron deficient moieties forming a large and diverse number of phosphaphenanthrene based structures. The incorporation of different DOPO based oligomers into epoxy matrices not only enhanced their flame resistance, but also decreased production costs. Also, the bulky DOPO rings facilitate the introduction of their corresponding oligophosphonates into the epoxy matrices. The use of such additives in enhancing the flame retardant capacity of epoxy resins may either lead to a compromise or provide the optimal properties required in different applications. Aromatic polyphosphonates are known to be superior flame retardants compared to non-polymeric ones because of their lower volatility and extractability. They also generally induce enhanced compatibility within the polymer matrices<sup>24</sup>. Polyphosphonates are most commonly obtained via polycondensation reaction between bisphenols and alkyl(aryl)phosphonic dichlorides<sup>25</sup>.

### **Activity 1.2. Investigation of modern instrumental techniques and methods: - Selection based on literature information of investigation and characterization methods**

Structural investigations will be undertaken by using: Fourier transform infrared spectroscopy (**FTIR**), nuclear magnetic resonance (<sup>1</sup>**H-NMR**), scanning electron microscopy (**SEM**) and energy dispersive X-ray spectroscopy (**EDX**). Thermogravimetric analysis (**TGA**) in inert and oxidative atmospheres will be used for thermal degradation of the samples. The resulted gaseous products will be identified with **TGA-FTIR** and **Py-GC-MS** coupled devices. The flame retardant capacity will be tested by **cone calorimetry**. A medium pressure **mercury lamp** (100 W) at 365 nm will be used for the photoirradiation of the multicomponent materials. Colour modification studies during photoirradiation will be made with a **colorimeter**. **UV-Vis** spectroscopy with an integrated sphere will be used for reflectance measurements.

### **Activity 1.3. Synthesis and structural characterization of the precursor to the oligophosphonate; Synthesis and structural characterization of the synthesized oligophosphonate.**

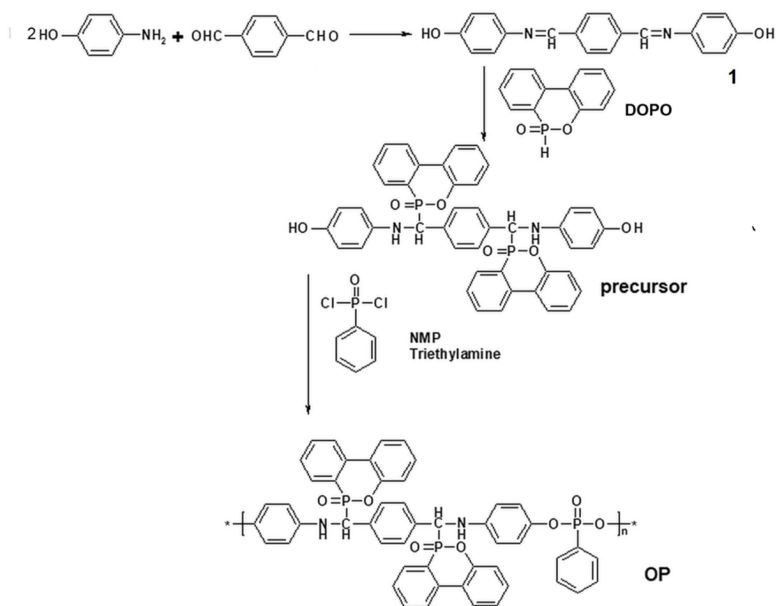
#### **1.3.1. Synthesis and structural characterization of the precursor to the oligophosphonate**

4,4'-Terephthalylidene-bis(*p*-hydroxyaniline) (compound 1), was synthesized by reacting 4-aminophenol (0.2 mol), terephthalaldehyde (0.1 mol) and a catalytic amount of 4-toluenesulfonic acid dissolved in 300 mL dry ethanol (Scheme 1). The mixture was refluxed for 3 h under stirring. After cooling at room temperature the product was separated by precipitation over a water-ice mixture, filtered, washed with distilled water and dried under vacuum. The final product was recrystallized from toluene.

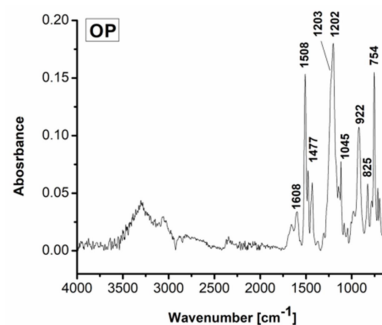
The synthesis of bis((6-oxido-6H-dibenz[*c,e*][1,2]oxaphosphorinyl)-(4-hydroxyaniline)-methylene)-1,4-phenylene (*the precursor to the oligophosphonate*), was achieved by reacting compound 1 with DOPO. Compound 1 (14.62 g, 0.0462 mol), DOPO (20 g, 0.0926 mol) and dried ethanol (103 mL) were introduced into a round flask equipped with a condenser and a magnetic stirrer. The mixture was stirred at 50 °C for 12 h under nitrogen atmosphere. The resulting precipitate was filtered, washed with ethanol and dried under vacuum (yield: 90%). **Characterization: FTIR** (KBr, cm<sup>-1</sup>): 3265 (NH), 3060 (C-H aromatic), 1477 (P-Ar), 1218 and 1142 (P=O), 1043 (P-O-C), 914 (P-O-Ar), 753. **<sup>1</sup>H-NMR** (400 MHz, DMSO-d<sub>6</sub>, d, ppm): 8.50 (m, 2H), 8.17 (m, 4H), 7.88 (m, 2H), 7.68 (m, 2H), 7.56 (m, 2H), 7.42 (m, 2H), 7.34 (m, 4H), 7.18 (m, 2H), 6.54 (m, 8H), 6.1 and 5.6 (m, 2H, N-H), 5.4 and 4.9 (m, 2H, CH-P).

#### **1.3.2. Synthesis and structural characterization of the the oligophosphonate (OP)**

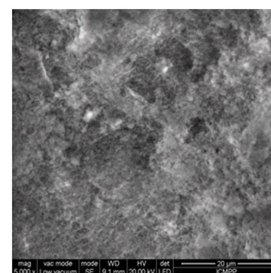
The OP was obtained by solution polycondensation reaction of equimolar amount of the precursor with phenylphosphonic dichloride (Scheme 1). In a flask equipped with a reflux condenser, magnetical stirrer and nitrogen inlet and outlet, were introduced and mixed the precursor (7.48 g, 0.01 mol), N-methyl-2-pyrrolidone (NMP) (30 mL) and triethylamine (3 mL). After a homogeneous solution was obtained phenylphosphonic dichloride (1.95 g, 0.01 mol) was added under stirring, during 0.5 h. The reaction flask was then immersed in an oil bath at 50 °C and the mixture was stirred vigorously for 8 h. The resulting solution was then cooled to room temperature and poured into methanol. The obtained solid was filtered and re-dissolved in NMP. The oligomer was isolated by precipitation in water, washed several times with water, and dried at 60 °C in a vacuum oven for 24 h to give a powdery solid (yield: 94%).



**Scheme 1.** The synthesis of the precursor to the OP and the OP.



**Figure 1.** FTIR spectrum of OP.



**Figure 2.** SEM micrograph of OP.

### Characterization of the OP

**Structural characterization** of the OP was investigated by FTIR spectroscopy (Figure 1). The OP component exhibited a sharp absorption band at  $1477\text{ cm}^{-1}$ , describing the aromatic P–C stretching vibrations. The bands from  $1202$  and  $922\text{ cm}^{-1}$  correspond to aromatic P–O–C stretching vibrations. The band at  $1045\text{ cm}^{-1}$  was attributed to the aliphatic P–O–C bond asymmetric stretching vibrations. The band at  $1203\text{ cm}^{-1}$  corresponds to aromatic P=O stretching. The deformation vibrations of 1,2-disubstituted aromatic DOPO rings generate the band at  $754\text{ cm}^{-1}$ , while the band at  $825\text{ cm}^{-1}$  is characteristic to the deformation vibrations of *p*-phenylene rings. The signals at  $1608$  and  $1508\text{ cm}^{-1}$  correspond to aromatic C=C stretching vibrations. **Morphological characterization** of the OP by SEM is shown in Figure 2. The OP possesses high solubility in polar aprotic solvents: dimethylformamide (DMF), *N,N*-dimethylacetamide and NMP. This good solubility is induced by the presence of bulky pendant DOPO entities in the diol increasing the free interchain volume and enhancing solvent diffusion in the macromolecules. Through the gel permeation chromatography (GPC) method the molecular weights and distribution were determined for the OP. The number average molecular weight ( $M_n$ ) was  $6184\text{ g mol}^{-1}$  and the weight average molecular weight ( $M_w$ ) was  $6501\text{ g mol}^{-1}$ . The polydispersity ( $M_w/M_n$ ) was 1.051. The GPC curve showed a narrow molecular weight distribution. The relatively low molecular weight values are a consequence of the bulky DOPO entities decreasing functional group reactivity and hindering polycondensation propagation. **The inherent viscosity** was determined at a concentration of 0.5 % (w/v) OP solution in 1-methyl-2-pyrrolidone (NMP) at  $25\text{ }^\circ\text{C}$  on an Ubbelohde viscometer and was found to be  $0.95\text{ cL g}^{-1}$ , characteristic to low molecular weight polymers.

### Conclusions

Documentation in modern synthesis and instrumental techniques for problem definition and elaboration of the experimental study were conducted and selected. Team members established monthly detailed activity plans. An effective and efficient communication of administrative, technical and financial research issues, both within the team and with the contracting authority was followed. The entire research team was involved in drafting the stage report. The synthesis and structural characterization of the precursor to the OP and the OP were successfully accomplished. **One article has been accepted for publication in an ISI journal and another article is in writing process.**

**The research team has met its objectives with a total degree of achievement.**

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## References

- [1] R. Thomas, P. Vijayan, S. Thomas, *Recycling of thermosetting polymers*, in: A. Fainleib, O. Grigoryeva (Eds.), *Recent Developments in Polymer Recycling, Transworld Research Network, Kerala*, **2011**, pp. 122; [2] M.H. Irfan, *Chemistry and Technology of Thermosetting Polymers in Construction Applications*, Springer Science and Business Media, Dodrecht, **1998**, pp. 78–96, 230–239; [3] C. Luo, J. Zuo, J. Zhao, *High Perform. Polym.* **25** (2013) 986–991; [4] T.V. Kosmidou, A.S. Vatalis, C.G. Delides, E. Logakis, P. Pissis, G.C. Papanicolaou, *EXPRESS Polym. Lett.* **2** (2008) 364–372; [5] A. Soulintzis, G. Kontos, P. Karahaliou, G.C. Psarras, S.N. Georga, C.A. Krontiras, *J. Polym. Sci. Part B: Polym. Phys.* **47** (2009) 445–454; [6] W. Zhang, X. Li, L. Li, R. Yang, *Polym. Degrad. Stab.* **97** (2012) 1041–1048; [7] F.–L. Jin, S.–J. Park, *Polym. Degrad. Stab.* **97** (2012) 2148–2153; [8] D. Rosu, C.–D. Varganici, L. Rosu, O.M. Mocanu, *Thermal degradation of thermosetting blends*, in: P.M. Visakh, Y. Arao (Eds.), *Thermal Degradation of Polymer Blends, Composites and Nanocomposites*, Springer, Cham, **2015**, pp. 17–21. [9] A. Toldy, A. Szabó, Cs. Novák, J. Madarász, A. Tóth, Gy. Marosi, *Polym. Degrad. Stab.* **93** (2008) 2007–2013; [10] J.A. Mikroyannidis, D.A. Kourtides, *J. Appl. Polym. Sci.* **29** (1984) 197–209; [11] C.H. Lin, S.L. Chang, T.P. Wei, S.H. Ding, W.C. Su, *Polym. Degrad. Stab.*, **95** (2010) 1167–1176. [12] S. Gaan, L. Mauclair, P. Rupper, V. Salimova, T.–T. Tran, M. Heuberger, *J. Anal. Appl. Pyrolysis* **90** (2011) 33–41; [13] L.W. Weber, H. Greim, *J. Toxicol. Environ. Health* **50** (1997) 195–215; [14] Y.–J. Xu, J. Wang, Y. Tan, M. Qi, L. Chen, Y.–Z. Wang, *Chem. Eng. J.* **337** (2018) 30–39; [15] C.–H. Tseng, H.–B. Hsueh, C.–Y. Chen, *Compos. Sci. Technol.* **67** (2007) 2350–2362; [16] C. Martín, G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, *J. Polym. Sci. Part A: Polym. Chem.* **44** (2006) 6332–6344; [17] S.M. Cakic, I.S. Ristic, V.M. Jašo, R.Ž. Radičević, O.Z. Ilíc, J.K.B. Simendic, *Prog. Org. Coat.* **73** (2012) 415–424; [18] Y. Zheng, K. Chonung, X. Jin, P. We, P. Jiang, *J. Appl. Polym. Sci.* **107** (2008) 3127–3136; [19] B. Guo, D. Jia, C. Cai, *Eur. Polym. J.* **40** (2004) 1743–1748; [20] V. Benin, S. Durganala, A.B. Morgan, *J. Mater. Chem.* **22** (2012) 1180–1190; [21] T.–S. Leu, C.–S. Wang, *J. Appl. Polym. Sci.* **92** (2004) 410–417; [22] Y. Qi, Z. Weng, Y. Kou, L. Song, J. Li, J. Wang, S. Zhang, C. Liu, X. Jian, *Chem. Eng. J.* **406** (2021) 126881; [23] D. Sun, Y. Yao, *Polym. Degrad. Stab.* **96** (2011) 1720–1724; [24] S. Roy, S. Maiti, *Polymer* **39** (1998) 3809–3813; [25] I.–D. Carja, D. Serbezeanu, T. Vlad–Bubulac, C. Hamciuc, A. Coroaba, G. Lisa, C.G. López, M.F. Soriano, V.F. Pérez, M.D.R. Sánchez, *J. Mater. Chem. A* **2** (2014) 16230–16241.