Synthesis and application of reactive organophosphorous flame retardants

Theses of PhD dissertation

Toldy Andrea

Tutor:

Prof. Marosi György

Budapest University of Technology and Economics

Department of Organic Chemistry and Technology

2007

I Introduction and aims

Epoxy resins have been commercially available for 60 years and have found use mainly in industrial applications where their exceptional characteristics as good adhesion to many substrates; moisture, solvent and chemical resistance; low shrinkage on cure; outstanding mechanical and electronic resistant properties justify their higher costs compared to other thermosets. They are widely used as adhesives, surface coatings, laminates and matrix materials in electronic, transport and aerospace industries, however their thermal and fire resistance needs to be improved in many application areas. The increasing focus on the health and environmental compatibility of flame retardants has drawn the attention to the organophosphorous reactive flame retardants. The new European Directive 2002/95/EC, requiring the substitution of some widely used brominated flame retardants (polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)) in new electrical and electronic equipment put on the market from 1 July 2006, also facilitates the headway of phosphorous flame retardants. In case of epoxy resins the phosphorus-containing chemical unit, providing the flame retardant effect, can be incorporated into the epoxy component, the crosslinking agent or into both of them.

Our aim was to synthesize phosphorus-containing phenolic and amine type flame retardants with high phosphorus-content and high functionality to be reactively incorporated into the epoxy resin matrix providing improved flame retardant performance compared to additive flame retardants in economic and environmental-friendly way. According to preliminary flame retardancy results the best performing phosphorus-containing compound was chosen for further investigation: its effect on curing process, thermal stability and fire performance of the epoxy resin was studied.

The effect of montmorillonite and sepiolite type clay particles was studied both alone in epoxy resin and combined with phosphorus-containing flame retardants. Optimal amount of clay additives was determined on the basis of their effect on crosslinking density of the epoxy resins and fire performance.

The mode of action and degradation pathway of the reference and flame retarded epoxy resin was investigated by complex structural and mechanical characterization of the formed intumescent char; solid residue analysis by infrared spectroscopic methods and x-ray photoelectron spectroscopy and analysis of the gases evolved during the degradation by thermogravimetric measurements coupled with infrared and mass spectroscopy.

Finally, the scale-up and optimization of the synthesis of the chosen best-performing compound was carried out both in reactor calorimeter and ReactIR apparatus. Catalytic effect of clay particles on the synthesis was also studied. Optimization of phosphorus-content of the flame retarded epoxy resin was done on the bases of crosslinking density, mechanical and fire performance properties of the resin compositions. Glow wire flammability index test served to determine if the new flame retardant epoxy resins meet the strict requirements of the electronic and electrical industry, where they are mostly supposed to find an application. Last but not least, estimation of the environmental effects and costs was performed.

II Applied methods

The synthesized organic compounds were characterized by mass spectroscopic measurements applying fast atom bombardment ionization technique **(MS FAB)** and matrix assisted laser desorption/ionization technique **(MALDI TOF)**, **^{31}P NMR** and **infrared (FTIR) spectroscopic measurements** and **amine number** determination.

Thermal characterization of the synthesized compounds and epoxy resin samples was done by **thermogravimetric (TG)** and **differential scanning calorimetry (DSC)**

measurements. DSC was also used to monitor the curing process of the thermosetting matrix beside **rheological measurements**.

The **fire resistance** was characterized by limiting oxygen index measurement **(LOI), UL-94 test**, **mass loss calorimeter (MLC)** and **glow wire flammability index (GWFI) test**. The MLC measures mass loss rate, time to ignition and heat release rate during the burning of specimens. The coupling of MLC with FTIR IR spectrometer (MLC-IR) was established in order to detect the evolved gases. The **GWFI test** is used to simulate the effect of heat as may arise in malfunctioning electrical equipment comparing the ability of materials to extinguish flames and not to produce particles capable of spreading fire.

A complex method for mechanical and structural characterization of the char was developed using rheometer. After the **thermal treatment** of the cured epoxy resin samples done in the furnace of rheometer the solid residues were characterized by **attenuated total reflection infrared (ATR-IR) spectroscopy.** The elemental analysis of the pyrolysis residues was carried out by **x-ray photoelectron spectroscopy (XPS)**. The average bubble diameter of the intumescent chars was determined using **scanning electron microscopy (SEM)**. The gases evolved during thermal degradation of epoxy resin were analysed using coupled **TG/DTA-MS** and **TG-FTIR** techniques.

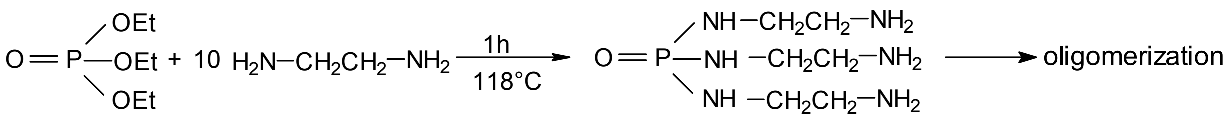
3 New scientific achievements

1 **New synthesis methods** were elaborated for the synthesis of phosphorus-containing phenolic and amine type flame retardants:

1.1 Chosen simple model hydroxyphenols, **hydroquinone** and **phloroglucinol** were phosphorylated: By choice of appropriate reaction conditions, the phosphorylation of hydroquinone by diethyl chlorophosphate gave predominantly the monophosphate, while the similar reaction of phloroglucinol led to the mixture of mono-, di- and triphosphorylated products.

1.2 The developed phosphorylation method was extended to **calixresorcinarenes**, polyhydroxyphenols with higher molecular weight and better compatibility with polymers. The synthesized partially and fully phosphorylated calixresorcinares were applied as flame retardants in epoxy resin matrix.

1.3 A new, environmental-friendly and cost-effective one-pot synthesis method was developed for the synthesis of **phosphorus-containing amines**. The starting materials, triethyl phosphate and ethylenediamine are commercially available and produced in large quantities for other purposes, they are not harmful to the environment and during the reaction no harmful by-products are formed. The excess of ethylenediamine serves also as solvent in the reaction, which can be recycled during the production. A new, not yet described compound called **TEDAP** was synthesized this way, which serves both as crosslinking agent and flame retardant in epoxy resins.



TEDAP

2 The best performing **newly synthesized phosphorus-containing compound, TEDAP** was subject to detailed fire performance analysis and optimization:

2.1 The synthesized phosphorus-containing amine, **TEDAP** is suitable for the **substitution of traditional epoxy resin curing agents** providing additionally **excellent flame retardancy**: the epoxy resins flame retarded this way reach 960°C glow wire flammability index (GWFI) value, 33 limiting oxygen index (LOI) value and self-extinguishing, V-0 UL-94 rating - compared to the 550°C GWFI value, 21 LOI value and HB UL-94 rating of the reference AH-16 – T-58 epoxy resin. The peak of heat release was reduced from 960 to

110 kW/m^2 compared to non flame retarded epoxy resin, furthermore the time to ignition increased from 49 s to 98 s, which increases the time to escape in case of fire event.

2.2. It was determined that the **optimum of crosslinking density, mechanical properties and fire retardant performance** needs 4.5 mass% of phosphorus incorporated by TEDAP instead of the 3.5 mass% originally determined on the base of the amine number of TEDAP. This optimized amount of TEDAP provides the highest crosslinking density without reaching the level where the unreacted crosslinking agent acts as plasticizing agent deteriorating the mechanical properties and therefore the fire retardant performance as well. This way the oxygen index of the epoxy resin could be increased from 21 of the reference epoxy resin system to 39 and the strictest safety regulations of the electronic industry can be fulfilled.

2.3 Concerning the **optimization of TEDAP-synthesis** it was determined that the actual reaction time depends on the required product: if a liquid product is needed with better crosslinking properties and lower phosphorus-content is adequate, than less reaction time is enough and good quality vacuum is needed for the vacuum-distillation; if, however, an oligomeric product with higher phosphorus-content but weaker crosslinking properties is necessary, than longer reaction time is needed and there is no strong restriction on the quality of the applied vacuum. The **clay additives** perform **catalytic effect** on the oligomerization of TEDAP during the synthesis and also during the thermal degradation. This fact offers the advantage of not having to remove the catalyst from TEDAP and using it as flame retardant additive again.

3 The effect of **montmorillonite and sepiolite type clay particles** on the crosslinking process and fire performance of epoxy resin was studied both alone and combined with phosphorus-containing flame retardants:

3.1 It was stated that in the **reference, non flame retarded system** the application of up to 5% clay particles does not modify significantly the crosslinking process and the clay particles **catalyze the beginning of the degradation**, but they decrease the mass loss rate and **shift to higher temperatures the degradation process**. The best flame retardancy result was achieved using 5 mass% untreated sepiolite, because it results in a percolating protecting structure on the surface due to its fibrous structure.

3.2 In the **flame retarded epoxy resin system** the application of clays decreased the crosslinking density due to the adsorption of polar TEDAP on the surface of the clays, especially in case of untreated clays. It was stated that due to the applied clay particles the **thermal degradation starts at higher temperatures** but reaches its maximum intensity faster producing **more residue than the flame retarded reference**. Best fire retardant performance was reached applying 1 mass% of clay. **Montmorillonite**, due to its layered structure provides **better gas barrier properties**, therefore more oxygen is needed for combustion, which explains the higher oxygen index values; while the fibrous **sepiolite** facilitates the formation of **heat insulating char structure**, which results in lower heat release rate values.

4 A new method was developed for the **complex mechanical and structural characterization of the intumescent char** allowing the numerical description of char volume, char strength and diameter of the formed bubbles.

4.1 Comparing the AH-16 – T-58 reference and AH-16 – TEDAP flame retarded systems it was determined that the flame retarded system forms significantly more char than the reference and the char of the reference is a more rigid char, with bigger average bubble diameter, while the **flame retarded system** provides a stronger, **more uniform char with smaller average bubble size**.

4.2 It was determined that incorporation of **clay particles decreased the average bubble size** resulting in a **more uniform char**, especially in the reference system. No significant difference was observed in the function of clay amount proving the dominance of the **bubble nucleating effect** of clays. The decrease in average bubble size was proved by SEM images.

5 The **degradation** of the reference aliphatic epoxy resin and the flame retarded epoxy resin was compared to each other and to aromatic epoxy reins and the **mode of action of phosphorus-containing flame retardants** was clarified:

5.1 It was determined that the main difference in the degradation of the reference and the flame retardant system is that the degradation of the TEDAP-containing epoxy resin begins at a temperature which is about 100°C lower than that of unmodified one, mainly with the emission of degradation products of TEDAP (PO radicals and $O=PNH_3$), which was proved by TG-MS coupled technique. The **evolved phosphorus-containing gases** act as flame retardant in the gas phase slowing down the further degradation steps: the maximum value of derivative mass loss is 5x lower than in case of the reference system.

5.2 It was stated that at high temperature degradation stage the solid phase effect of the phosphorus prevails: the amount of emitted phosphorous-containing gases is negligible, while the formation of **phosphorocarbonaceous intumescent char** results in a mass residue of 23.4%, while in case of the reference system amount of residue is basically omissible. The enrichment of the intumescent char in carbon and phosphorus was proved by XPS measurements.

5.3 Based on the mass loss and XPS results of the solid residue it was determined that ~25 mass% of the originally introduced phosphorus acts in gas phase, while the other 75 mass% stays in the solid phase. It can be concluded that the outstanding flame retardancy results can be explained by the **combined effect of phosphorus**: **at the beginning** the **gas phase action of phosphorus** is crucial for the slowing down the degradation before ignition and thus increasing the time to ignition to the double of the original value; while at **high temperature degradation** the **solid phase action** results in reduction of the peak of heat release rate to the 1/10 of the original value and an increased mass residue.

IV Application related activities

Considering the **material and production costs**, the price level of the newly synthesized TEDAP can be kept still around the price of the commercially available T-58 hardener, however TEDAP plays both the role of crosslinking agent and flame retardant providing a highly economic solution for fire retardancy.

Concerning the **environmental effects**, the starting materials of the synthesis are not harmful to the environment and during the reaction no harmful by-products are formed. The excess ethylenediamine not only shifts the equilibrium in the direction of the required trisubstituted product, but it serves also as solvent in the reaction. The excess ethylenediamine removed by vacuum distillation can be recycled during the production.

The so synthesized TEDAP is a **reactive flame retardant**, therefore smaller concentrations are required to reach the appropriate effect and the migration to the polymer surface is also hindered as the flame retardant is chemically incorporated into the epoxy resin matrix.

Glow wire flammability index (GWFI) measurements were done in order to estimate the industrial applicability of this new flame retarded epoxy resin system in electrical and electronic equipments. With the application of TEDAP the best, 960˘C GWFI level can be reached, which means that it can be used without restrictions in all kind of electrical and electronic equipments.

Publications:

1. Marosi, G.; Toldy, A.; Parlagh, G.; Nagy, Z.; Ludányi, K.; Anna, P.; Keglevich, G., A study on the selective phosphorylation and phosphinylation of hydroxyphenols. *Heteroatom Chemistry* **2002,** 13, (2), 126-130.

2. Marosi, G.; Keglevich, G.; Toldy, A.; Anna, P., Phosphorylated and phosphinylated hydroxy phenols as flame retardant components. *Phosphorus Sulfur and Silicon and the Related Elements* **2002,** 177, (8-9), 1993-1993.

3. Toldy, A.; Keglevich, G.; Marosi, G.; Anna, P., Parlagh, G.; Nagy, Z.; Ludányi, K., Hidroxi-fenolok szelektív foszforilezése és foszfinilezése. *Magyar Kémiai Folyóirat*, **2002**, 108 (12), 543-546.

4. Toldy, A.; Anna, P.; Marosi, G.; Keglevich, G.; Almeras, X.; Le Bras, M., Selective phosphorylation of hydroxyphenols for forming reactive flame retardants. *Polymer Degradation and Stability* **2003,** 82, (2), 317-323.

5. Marosi, G.; Toldy, A.; Anna, P., Zimonyi, E.; Keszei, S.; Krause, W.; Hörold, S., Flame Retardant Mechanism and Application of Synergistic Combinations of Phosphinates. in *Recent Advances in Flame Retardancy of Polymeric Materials* XVI., ed. M. Lewin, BCC. Inc., Stamford, USA, **2004**; 79-87.

6. Toldy, A., Synthesis of New Organophosphorous Flame Retardant Compounds and their Use for Reactive Modification of Polymers. *Periodica Polytechnica Chemical Engineering*, **2005**; 49/1, 82-83.

7. Toldy, A.; Tóth, N.; Anna, P.; Marosi, G., Synthesis of phosphorus-based flame retardant systems and their use in an epoxy resin. *Polymer Degradation and Stability* **2006,** 91, (3), 585-592.

8. Marosfői, B. B.; Szabó, A.; Toldy, A.; Anna, P., Marosi, G.; Tabuani, D.; Camino, G., Modeling of Combustion Process with Laser Pyrolysis Raman Microscope System. in *Recent Advances in Flame Retardancy of Polymeric Materials* XVIII., ed. M. Lewin, BCC. Inc., Stamford, USA, **2006**

9. Toldy, A.; Tóth, N.; Anna, P.; Keglevich, G.; Kiss, K.; Marosi, G., Flame retardancy of epoxy resin with phosphorus-containing reactive amine and clay minerals. *Polymers for Advanced Technologies* **2006,** 17, (9-10), 778-781.

10. Toldy, A.; Anna, P.; Csontos, I.; Szabó, A.; Marosi, G., Intrinsically flame retardant epoxy resin - fire performance and background, *Polymer Degradation and Stability,* **2007**, in print

11. Farkas, E.; Meszéna, Z. G.; Toldy, A.; Matkó, S.; Marosfői, B. B.; Marosi, G., Modelling of transport processes in a developing char. *Polymer Degradation and Stability,* **2007**, submitted

12. Toldy, A.; Anna, P.; Novák, Cs.; Madarász, J.; Tóth, A.; Marosi, G., Intrinsically flame retardant epoxy resin - fire performance and background – Part 2, *Polymer Degradation and Stability,* **2007**, submitted

Other publications:

13. Matko, S.; Toldy, A.; Keszei, S.; Anna, P.; Bertalan, G.; Marosi, G., Flame retardancy of biodegradable polymers and biocomposites. *Polymer Degradation and Stability* **2005,** 88, (1), 138-145.

14. Bertalan, G.; Marosi, G.; Toldy, A., Polymers for Advanced Technologies, *CHEMISTRY International* May-June **2006**, 28-31.

15. Marosi, G.; Toldy, A., 8th International Conference on Polymers for Advanced Technologies - PAT 2005. *Journal of Thermal Analysis and Calorimetry* **2006,** 86, (3), 661-661.

Presentations:

A. Toldy, Gy. Marosi, P. Anna, Intrinsically flame retardant epoxy resin – fire performance and background, 11th European Meeting on Fire Retardancy and Protection of Materials, Bolton, United Kingdom, 2007

A. Toldy, Gy. Marosi, P. Anna, N. Tóth, K. Kolos, Mechanism of thermal degradation of flame retarded epoxy resin systems, 4th International Conference on Modification, Degradation and Stability, San Sebastián, Spain, 2006

A. Toldy, Gy. Marosi, P. Anna, N. Tóth, B. Marosfői, Comparison of the Flame Retardant Mechanism of Nanocomposites in Thermoplastic and Thermosetting Matrices, 10th European Meeting on Fire Retardancy and Protection of Materials, Berlin, Germany, 2005

A. Toldy, P. Anna, S. Keszei,G. Bertalan, E. Zimonyi, Gy. Marosi: Synthesis of phosphorus-based flame retardant systems and their use in various polymers, 3rd International Conference on Modification, Degradation and Stability, Lyon, Franciaország, 2004

A. Toldy: Selective Synthesis of New Organophosphorus Flame Retardant Compunds and their Use for Reactive Modification of Polymers, V. Winter School Nanocomposites with Special Properties organized by BUTE Department of Physical Chemistry Laboratory of Soft Matters, Keszthely, Hungary, 2004

A. Toldy: Epoxigyanták égésgátlása foszfortartalmú reaktív adalékkal és nanorészecskékkel, 3rdConference of PhD Students at Faculty of Chemical Engineering, Budapest, Hungary, 2006

A. Toldy: Új szerves foszfortartalmú égésgátló vegyületek szintézise és felhasználása polimerek reaktív módosítására, 2nd Conference of PhD Students at Faculty of Chemical Engineering, Budapest, Hungary, 2004

Posters:

K. Kiss, A. Toldy, Gy. Marosi, Reactive flame retardant modification of polymer, 1st European Chemistry Congress, Budapest, Hungary, 2006

A. Toldy, P. Anna, Gy. Marosi, Gy. Keglevich, X. Almeras, M. Le Bras: Synthesis and Use of New Organophosphorus Flame Retardant Compounds, International Conference on Phosphorus Chemistry, Birmingham, England, 2004