

University of Pardubice

Faculty of Chemical Technology

CURING AGENTS BASED ON DERIVATIVES HEXACHLORO-CYCLO-TRIPHOSPHAZENE FOR EPOXY RESINS

Ing. Mgr. Lucie Zárybnická



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UNIVERSITY OF PARDUBICE
FACULTY OF CHEMICAL TECHNOLOGY
INSTITUTE OF CHEMISTRY AND TECHNOLOGY OF
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**CURING AGENTS BASED ON DERIVATIVES
HEXACHLORO-CYCLO-TRIPHOSPHAZENE FOR EPOXY
RESINS**

Annotation of Ph.D. Thesis

Author: Ing. Mgr. Lucie Zárbybnická

Study programme: Chemistry and Technology of Materials

Surface Engineering

Supervisor: prof. Ing. Petr Kalenda, CSc.

Co-supervisor: Ing. Miroslav Večeřa, CSc.

Consultant: Ing. Eliška Stránská

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SUMMARY

The presented dissertation deals with the topic of phosphazenes and their subsequent use as flame retardants and curing agents for the thermosets. The theoretical part is focused on phosphazenes, their history, hexachloro-*cyclo*-triphosphazene, its properties and synthesis. The next part is devoted to epoxy resins, their preparation and curing. In the last part, the search was focused on flame retardants, the use of hexachloro-*cyclo*-triphosphazene derivatives as curing agents and flame retardants for bisphenol type epoxy resins, which have been commonly used in industry.

The experimental part of the dissertation is devoted to the synthesis of hexachloro-*cyclo*-triphosphazene derivatives, curing of a selected epoxy resin with prepared hexachloro-*cyclo*-triphosphazene derivatives and the comparison of a selected amine which is commonly used as a hardener for epoxy resins. It summarizes the methods used for the characterization of prepared materials with the emphasis on the effect of hexachloro-*cyclo*-triphosphazene derivatives on fire retardancy.

KEY WORDS: phosphazene
hexachloro-*cyclo*-triphosphazene
curing
epoxy resin
flame retardant

1 INTRODUCTION

One of the most widespread type of polymers is epoxy resin. Epoxy resins are viscous liquids which, after curing and therefore the formation of a 3D network, exhibit a variety of application possibilities and excellent properties, including excellent chemical resistance, adhesion, thermal and electroinsulating properties [1]. The basic principle of curing epoxy resins with a hardener containing multiple amino groups is the crosslinking reaction between active hydrogen atoms in the hardener and the oxirane groups in the epoxy resin. The field of epoxy resin utilization is quite extensive. Epoxy resins are used as adhesives, sealing compounds, binders of composite materials, or as powder coatings. The disadvantage of cured epoxy resins is their behavior during burning (smoke evolution, high burning rate, oxygen consumption) [2].

Cyclophosphazenes can be used as flame retardants for epoxy resins. The most prominent representatives of these compounds containing the phosphorus and nitrogen atoms are phosphazenes, namely hexachloro-*cyclo*-triphosphazene (HCCTP). Chlorine atoms of HCCTP are very reactive, allowing for the preparation of a large number of substitution derivatives that are used in many industries. Phosphazenes can generally be applied, for example, as flame retardants [3-6], antioxidants [7], pesticides [8] or in medicine [9].

The typical reaction of hexahalogeno-*cyclo*-triphosphazene is a nucleophilic substitution where the nucleophile is able to pass its free electron towards attacking electrophilic phosphorus atoms. Amines, alcoholates, alcohols or thiols are among the most common compounds used in the nucleophilic substitution. Phosphazene derivatives which contain in their structure active hydrogen atoms can be used as hardeners for epoxy resins.

Hexahalogeno-*cyclo*-triphosphazene contains alternating phosphorus and nitrogen atoms in the cycle with two substituents attached to the phosphorus atoms. This compound exhibits unusual thermal properties such as flame retardancy and self-extinguish ability [10-11]. The reason is that the thermal decomposition of the phosphazene-based polymers is an endothermic process. Phosphate, metaphosphate, polyphosphate generated in the thermal decomposition form a nonvolatile protective film on the surface of the polymer to isolate it from the air. This film can cut off the supply of oxygen so as to achieve the synergistic flame retardancy [12-13].

The mechanism of action during burning of cyclophosphazenes is related to the synergistic effect between phosphorus and nitrogen, which are contained in the phosphazene structure. Polyphosphazene-containing polymers cause thermal

decomposition of phosphazenes during combustion to form phosphates, metaphosphates and polyphosphates, with a nonvolatile protective film being formed on the surface of the polymer. At the same time, gases such as CO_2 , NH_3 and N_2 are produced, and oxygen is restricted [14-17]. Cyclophosphazene can also produce phosphinylidene radicals ($\text{PO}\bullet$) that slow down the process of burning polymeric material [4]. The mechanism of action of cyclophosphazenes during combustion is still a topic for discussion.

2 AIM OF THE THESIS

- Preparation of new hexachloro-*cyclo*-triphosphazene derivatives by nucleophilic substitution with selected amines (isophorone diamine, allylamine, cyclohexylamine, *N*-[3-(trimethoxysilyl)propyl]ethylenediamine).
- Characterization of prepared hexachloro-*cyclo*-triphosphazene derivatives by means of elemental analysis, determination of chlorine content by incineration, determination of refractive index, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), ³¹P nuclear magnetic resonance (NMR), and mass spectrometry (MS).
- Use of the prepared hexachloro-*cyclo*-triphosphazene derivatives as curing agents for the commercially available CHS-EPOXY E520 epoxy resin.
- Characterization of the cured epoxy resins in terms of structure and burnig behavior using a dual cone calorimeter.
- Comparison of the epoxy resin curing using the prepared hexachloro-*cyclo*-triphosphazene derivatives with curing by isophorone diamine which is a commonly utilized epoxy resin hardener.

3 EXPERIMENTAL PART

3.1 MATERIALS

- isophorone diamine (IPDA), 3-(aminomethyl)-3,5,5-trimethylcyclohexanamine, (Vestamin IPD, Evonik, purity 99.7%)
- CHS Epoxy 520 (Spolchemie, CZ)
- tetrahydrofuran (THF), (Penta Chemicals, CZ, purity 99.8%)
- triethylamine (TEA), (Sigma-Aldrich, CZ, purity $\geq 99\%$)
- cyclohexylamine (Sigma-Aldrich, CZ, purity $\geq 99\%$)
- allylamine (Sigma-Aldrich, CZ, purity $\geq 99\%$)
- *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (Sigma-Aldrich, CZ, purity 97%)
- acetonitrile (ACN), (Penta Chemical, CZ, purity $\geq 99\%$)
- diaminotetrachlorocyclotriphosphazene (prepared at the Institute of Chemistry, Masaryk University, Brno)
- glacial acetic acid (Penta Chemical, CZ, purity 99.8%)
- potassium hydroxide (Penta Chemical, CZ, purity $\geq 99\%$)
- hexadecyltrimethylammonium bromide (Penta Chemical, CZ, purity $\geq 98\%$)
- chloroform (Penta Chemical, CZ, purity $\geq 99\%$)
- perchloric acid (Penta Chemical, CZ, purity 65%)
- ammonium chloride (Penta Chemical, CZ, purity $\geq 99\%$)
- phosphorus pentachloride (Penta Chemical, CZ, purity $\geq 98\%$)
- anhydrous calcium chloride (Penta Chemical, CZ, purity $\geq 99\%$)
- phosphorylate trichloride (Penta Chemical, CZ, purity $\geq 99\%$)
- trichloropropane (Sigma-Aldrich, CZ, purity $\geq 99\%$)

3.2 INSTRUMENTS

The elemental analysis was performed on a FLASH Organic 2000 Elemental Analyzer (ThermoFisher Scientific), which can detect carbon, hydrogen, nitrogen and sulfur. Determination of chlorine was carried out by burning in oxygen atmosphere followed by titration with sulfuric acid according to Schöniger [18]. The method was tested on *o*-chlorobenzoic acid standard containing 21.915 % of chlorine. Determination of amine number, extractable fraction, epoxy groups according to Jay was performed by titration methods [19].

³¹P NMR spectra (δ , ppm; J, Hz) were recorded using a BRUKE AVANCE DRX 300 instrument at the frequency of ³¹P: 202.46 MHz and 85 % H₃PO₄ (as the external standard). The samples were sealed in Simax tubes (diameter 4 mm), inserted in NMR cuvettes (diameter 5 mm) filled with D₂O (external lock). The spectra were measured in the coaxial NMR cuvette system.

The FT-IR spectroscopy of the samples was performed on a Nicolet IS50 with an integrated diamond ATR FT-Raman module. The FT-IR spectrometer with the integrated module and ATR fully reflective optics has a broadband DLaTGS detector to make measurements in the area 5000-100 cm⁻¹. The spectral resolution of the device is 0.09 cm⁻¹.

MS was performed on an Agilent Technologies instrument (MSD Model 5975B) with a probe for direct entry. The mass selective detector operated in the electron impact ionization mode (ie. EI ionization) with the ionization energy of 70 eV. The samples were prepared as 0.01% solution in methanol for the analysis.

For the elemental determination of cured epoxy resin samples, a high resolution X-ray energy-dispersion spectrometer (EDS) was used; operation without liquid nitrogen; element detection at least Z = 5, detector energy resolution min. 129 eV Mn Ka. EDAX TEAM Basic EDS with Octane Pro (Octane Pro Silicon Drift Detector (SDD), active area 30 mm², resolution 129 eV (Mn)) in combination with SEM Quanta FEG 250.

Optical microscope images of cured samples were taken on white paper and white paper with comparative text. The pictures were magnified 200x. Cured samples were evaluated in terms

of their gloss, transparency, color. The images were taken using a Dino-Lite semi-professional set Premium 4.0. consisting of the AM4113T microscope with measurement and the MS35B tripod that allows precise and high-quality image focusing.

DSC analysis was performed according to ISO 11357-2 using a Perkin-Elmer DSC with a control and evaluation software Universal Analysis 2000 QSeries. Measurements were performed in a nitrogen atmosphere at a heating rate of 20 °C/min with a temperature range of 25-400 °C. The sample weight ranged from 1 to 5 mg.

TGA was performed on the device consisting of the computer, oven and Sartorius balance BP210E S. It was measured in a quartz ampoule in the temperature range of 25-950 °C at a heating rate of 5 °C /min under air.

Brinell hardness test method-test specimens were prepared with a thickness of 4 mm. Measurement was carried out according to standard EN ISO 6506-1. Value was determined for hardness HB/15.6/10 and HB/15.6/60 using instrument HP 250 VEB Leipzig, Germany.

The resistance to the impedance of the prescribed shape (Shore D) to the test material is measured. Hardness is inversely proportional to the penetration of the steel tip into the test material. It is expressed in Shore D units. The measurements were made 10 times. By determining the Shore D hardness, cured samples of epoxy resin were characterized.

Samples of cured epoxy resin were also tested for their water absorption by means of two tests. First, swelling at room temperature was monitored for 1 month, and secondly, water absorption in boiling water was determined [19].

Testing of materials (7x7x5 cm) against burning was carried out in the dual cone calorimeter that is a product of Fire Testing Technology Ltd., England. The sample was placed into the adopted sample holder suitable for testing of thermally thin materials. The centre of the samples was situated 6 cm from the lowest part of the cone heater. The heat release rate was calibrated by burning methane. The cone radiancy 25 kWm⁻² used corresponds to a cone temperature 680 °C. It was set from the calibration diagram for a distance of the sample from the cone edge 6 cm.

3.3 SYNTHESIS

Synthesis of hexachloro-*cyclo*-triphosphazene (HCCTP)

Hexachloro-*cyclo*-triphosphazene was prepared as follows (Fig. 1) [20]. To a 2 L flask placed in a silicone oil bath was charged with 750 mL of trichloropropane, 1.12 mol of phosphorus pentachloride and 1.11 mol of ammonium chloride with addition of 0.095 mol of phosphoryl trichloride. The reaction was carried out in the presence of inert (in particular nitrogen) at the boiling point of the solvent (146 °C) for 8 hours. After completion of the reaction, the solvent was vacuum distilled at 70 °C, the mixture containing both cyclic and linear phosphazene. The product was subsequently distilled off with water vapor, followed by vacuum sublimation at 50 °C and recrystallization from n-heptane.

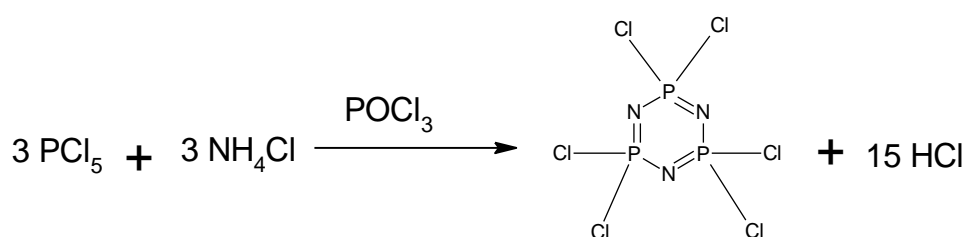


Fig. 1: Simplified scheme of HCCTP synthesis.

Synthesis of hexaisophorone diamino-*cyclo*-triphosphazene (HICTP)

The hexaisophorone diamine-*cyclo*-triphosphazene derivative was prepared as follows (Fig. 2). 0.753 mol of isophorone diamine and the corresponding amount of tetrahydrofuran under an inert atmosphere were placed in a Schlenk flask. With constant stirring of the reaction mixture, 0.037 mol of hexachloro-*cyclo*-triphosphazene in tetrahydrofuran was slowly added at the boiling point of the solvent. The reaction was terminated after 24 hours by subsequent filtration of the resulting salt, 3 times washing with tetrahydrofuran followed by vacuum distillation and isolation of the product. The product was checked during the synthesis by a thin-layer chromatography and the resulting derivative was also confirmed by the refractive index measurement. The reaction was terminated after 24 hours. Then the resulting salt was filtrated and 3 times washed with tetrahydrofuran. Subsequently, the product was isolated by a vacuum distillation and was characterized by ³¹P NMR, elemental analysis, mass spectrometry, FT-IR spectroscopy and thermogravimetric analysis.

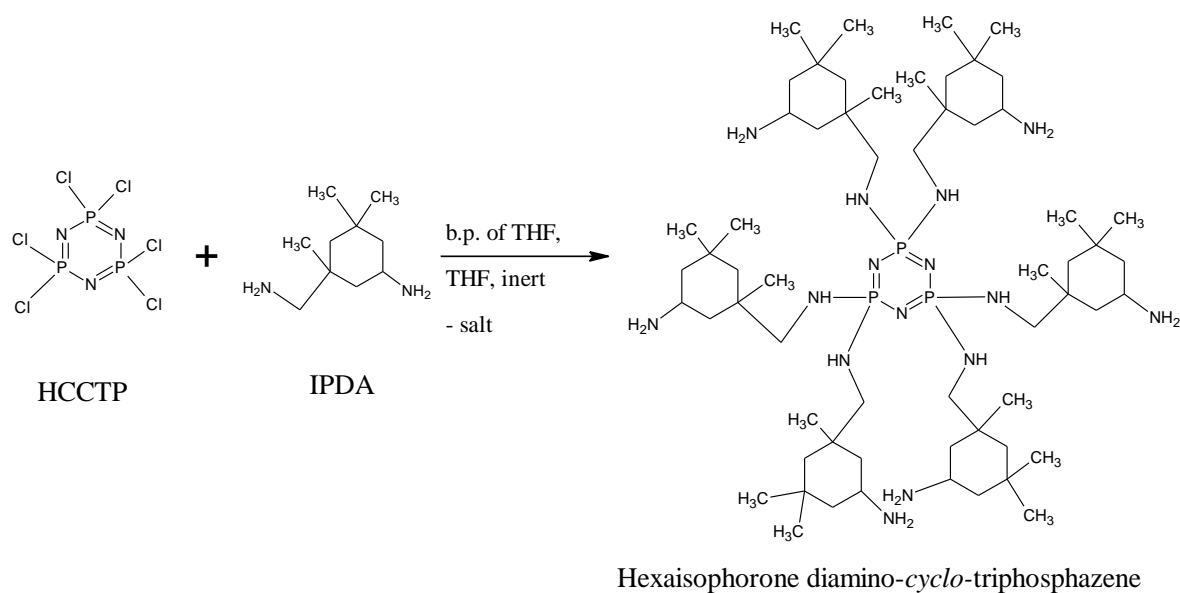


Fig. 2: Scheme of HICTP synthesis.

Synthesis of hexaallylamino-cyclo-triphosphazene (HACTP)

Preparation of HACTP is based on the following synthesis (Fig. 3). 0.289 mol of hexachloro-cyclo-triphosphazene dissolved in 300 mL of tetrahydrofuran was charged into the Schlenk flask under an inert atmosphere. The flask was heated to 50 °C. A mixture of 3.51 mol of allylamine with dried tetrahydrofuran was then slowly dosed, followed by an increase in the reaction temperature to 55-60 °C. The reaction was terminated after 2 days. The resulting salt was filtrated and 3 times washed with tetrahydrofuran. Filtration of the resulting salt was followed by 3 times washing with THF. The product itself was precipitated with distilled water, after isolation of the product followed by drying in a vacuum oven at 50 °C. The resulting product was characterized by ³¹P NMR, elemental analysis, mass spectrometry and FT-IR spectroscopy, thermogravimetric analysis.

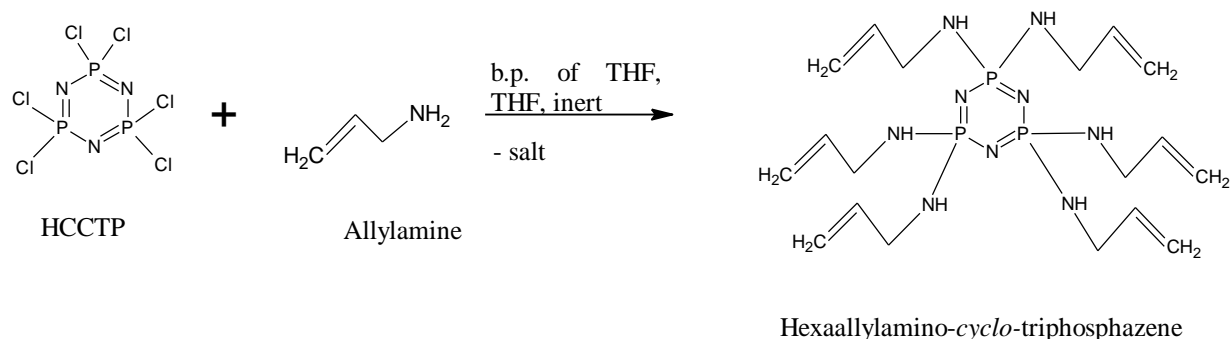


Fig. 3: Scheme of HACTP synthesis.

Synthesis of hexacyclohexylamino-*cyclo*-triphosphazene (HCACTP)

Hexacyclohexylamino-*cyclo*-triphosphazene was prepared by the following synthesis (Fig. 4). In the Schlenk flask, 0.009 mol of hexachloro-*cyclo*-triphosphazene dissolved in dried THF was charged under an inert atmosphere. With stirring, a mixture of 0.173 mol of cyclohexylamine dissolved in dried THF was slowly added dropwise. The reaction was complete in 3 days, followed by the filtration of the resulting salt, washing 3 times using THF and the subsequent precipitation of the product with distilled water. The precipitated HCACTP product was dried under vacuum. The resulting product was characterized by ^{31}P NMR, elemental analysis, mass spectrometry, FT-IR spectroscopy and thermogravimetric analysis.

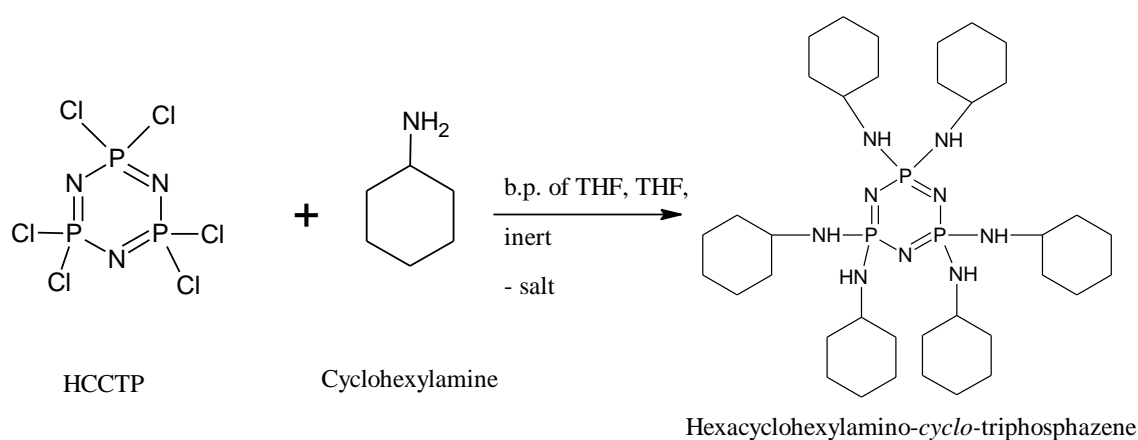


Fig. 4: Scheme of HCACTP synthesis.

Synthesis of diaminotetracyclohexylamino-*cyclo*-triphosphazene (DTCATP)

Diaminotetracyclohexylamino-*cyclo*-triphosphazene was prepared using Schlenk vessels in the presence of nitrogen inert gas. Diaminotetrachloro-*cyclo*-triphosphazene was prepared according to the reference [21]. The actual synthesis (Fig. 5) of DTCATP consisted of reacting 0.0008 mol of diaminotetrachloro-*cyclo*-triphosphazene dissolved in dried toluene with 0.0097 mol of cyclohexylamine which was dissolved in dry toluene and added dropwise to the reaction Schlenk vessel heated at 95 °C. The reaction was complete after 3 days, followed by the filtration of the resulting salt, 3 times washing with toluene and the subsequent precipitation of the product with distilled water. Further, the product was filtered and dried in a vacuum oven at 50 °C. The final product was characterized by ^{31}P NMR, elemental analysis, MS, FT-IR spectroscopy, TGA, chlorine and amine content determination.

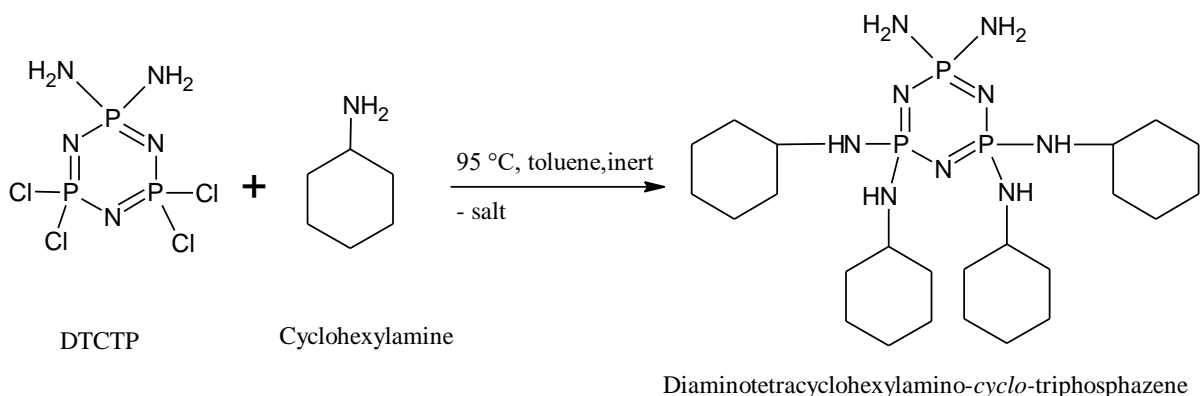


Fig. 5: Scheme of DTCATP synthesis.

Synthesis of hexa(trimethoxysilyl)propylethylenediamino-cyclo-triphosphazene (HSDATP)

The derivative was prepared by the following reaction (Fig. 6). 0,0049 mol HCCTP dissolved in dry acetonitrile was introduced into the Schlenk flask under an inert atmosphere. A mixture of 0.021 mol of triethylamine and 0.029 mol of *N*-[3-(trimethoxysilyl)propyl] ethylenediamine dissolved in dry acetonitrile was dosed dropwise into the reaction vessel. The reaction proceeded at the boiling point of acetonitrile under nitrogen atmosphere. The reaction was complete in 2 days. The resulting salt was filtrated, 3 times washed with ACN followed by vacuum isolation of the product. The final product was characterized by ^{31}P NMR, elemental analysis, MS, FT-IR spectroscopy, TGA, chlorine and amine content determination.

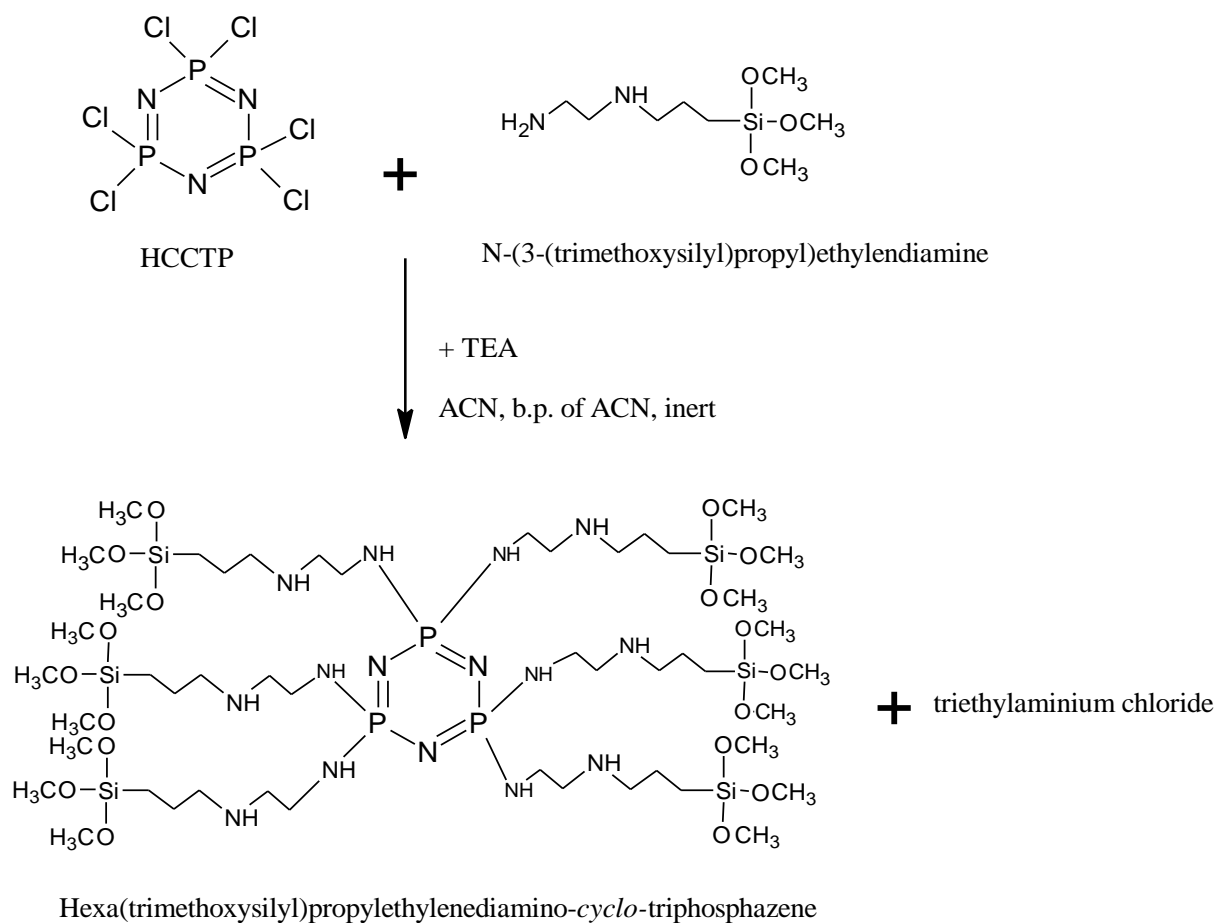


Fig. 6: Scheme of HSDATP synthesis.

3.4 CURING OF EPOXY RESIN

The curing of epoxy resin consisted in mixing CHS-EPOXY E520 epoxy resin with the prepared HCCTP derivatives in the amount calculated according to the equation (1):

$$\text{g of the curing agent/ kg of the epoxy resin} = (\text{EE/kg}) \times H_{\text{ekv.}} \times 1.1 \quad (1)$$

where EE/kg is the epoxy equivalent of CHS-EPOXY E520 (5,266 EE/kg) and $H_{\text{ekv.}}$ [g/mol] is the hydrogen equivalent of the particular HCCTP derivative, 10 % excess of the HCCTP derivatives was always used. Hydrogen equivalents for the prepared phosphazene derivatives are shown in Tab. 1.

The curing process differed for each derivative with the curing temperature and curing time. These optimal conditions were determined by DSC, where the kinetics of the curing process was monitored for each system cured at various curing temperatures and curing time periods. During curing, active hydrogen atoms of the prepared derivative were reacted with epoxide groups of the selected epoxy resin.

In general, the calculated amounts of a selected phosphazene derivative and the epoxy resin were mixed properly, then they were put into the cartridge and further centrifuged at 3000 rpm for 3 minutes. After removing air the contents of the cartridge was poured into a silicone mold and cured at the selected optimal conditions (see Table 1) followed by hardening at 120 °C for 3 hours.

Table 1: Hydrogen equivalents ($H_{\text{ekv.}}$) for IPDA and the prepared derivatives HCCTP.

Curing agent	$H_{\text{ekv.}}$ [g/mol]	Amount of curing agent [g] to 1000 g CHS-Epoxy E520	Parameters of curing
HICTP	63.93	370.3	70 °C - 100 min
HACTP	73.03	423.0	70 °C - 120 min
HCACTP	120.65	698.9	100 °C - 300 min
DTCATP	69.95	405.2	70 °C - 450 min
HSDATP	121.92	706.2	45 °C - 100 min
IPDA	42.58	246.6	40 °C - 180 min

Samples of epoxy resins cured by the HCCTP derivatives were further characterized by FT-IR spectroscopy, DSC and TGA. The number of reacted epoxy groups present in the cured samples was determined using the titration method. Further, the cured materials

were characterized by EDX and optical microscopy. The flammability of cured epoxy materials with respect to the utilized phosphazene hardener was evaluated by means of a dual cone calorimeter.

4 RESULTS AND DISCUSSION

Characterization of the prepared HCCTP derivatives

HCCTP derivatives were prepared by nucleophilic substitutions of selected amines with the pre-prepared hexachloro-*cyclo*-triphosphazene and diaminotetrachloro-*cyclo*-triphosphazene, respectively. The reactions were always carried out in an nitrogen atmosphere using Schlenk's technique. The prepared products were characterized by elemental analysis, amine determination, chlorine content, FT-IR spectroscopy, MS, ^{31}P NMR and TGA.

The characterization of epoxy resin curing with the prepared HCCTP derivatives

Differential scanning calorimetry was monitored for each system. The CHS Epoxy E520 sample was first prepared and the hardener mixed in the desired weights and placed in the DSC instrument, followed by heating the sample to a temperature at 10 °C/min. Upon completion of the temperature program, the curing temperature was taken from the recording and the samples were loaded at the selected temperature at specified time intervals, and the enthalpy of the curing process was then read. Tab. 2 summarizes the determined optimal curing temperatures and time intervals for the individual curing systems followed by hardening at 120 °C for 3 hours. It can be seen clearly that the lowest curing temperatures (around 40 °C) were required in the case of hardening with HSDATP and IPDA, while the highest curing temperature (100 °C) was needed for curing with the HCACTP derivative. This curing agent was shown to require the second longest curing time as well. The most time-demanding curing was found in the case of DTCATP hardener, curing proceeded for 450 min at 70 °C.

Tab. 2: Summarized results of optimal curing temperatures and curing time intervals for the individual phosphazene derivatives and IPDA.

Curing agent	Temperature of curing [°C]	Time of curing [min.]
HICTP	70	100
HACTP	70	120
HCACTP	100	300
DTCATP	70	450
HSDATP	45	100
IPDA	40	180

Characterization of the cured epoxy materials

In terms of optical properties, CHS Epoxy E520 based cured samples were first visually evaluated using an optical microscope at a magnification of 200x. For comparison, pictures were taken on a white paper basis and on a white paper with text. Color change can be observed for the samples cured using HACTP and DTCATP, whereas curing with HICTP and HCACTP provided non-transparent samples. The best transparency was found in the case of IPDA-cured sample.

Further, the cure efficiency using hexachloro-*cyclo*-triphosphazene derivatives was evaluated and compared with the conventional IPDA amine hardener (see Table 3). It was shown that HICTP, HACTP and HSDATP derivatives in the role of epoxy curing agents provided highly cured epoxy materials comparable to IPDA hardener.

Tab. 3: Efficiency of CHS Epoxy E520 hardening with different curing agents in terms of the number of reacted epoxide groups.

Curing agent	Content of reacted epoxide groups [%]
HICTP	96.54
HACTP	95.38
HCACTP	79.88
DTCATP	89.69
HSDATP	96.95
IPDA	97.98

The FT-IR spectroscopy was used to verify the structure of the cured samples. In all cases, the peak at the wavelength of 910 cm^{-1} disappeared, confirming the hardening of the epoxy resin with the phosphazene-based hardener.

Samples of epoxy resin cured with the prepared derivatives were also tested for their glass transition temperature by means of DSC (see Table 4) and for their thermal behavior using TGA (see Table 5). The highest T_g of $171.9\text{ }^\circ\text{C}$ can be seen in the case of the sample cured with HSDATP derivative, followed by the IPDA-cured sample having a T_g value of $153.9\text{ }^\circ\text{C}$ and the sample cured with HICTP derivative having T_g of $137.6\text{ }^\circ\text{C}$. The other systems exhibited T_g below $100\text{ }^\circ\text{C}$, the lowest T_g value ($89.6\text{ }^\circ\text{C}$) can be observed in the case of DTCATP curing.

Tab. 4: Determination of glass temperature for the cured samples.

Curing agent	T _g [°C]
HICTP	137.6
HACTP	99.6
HCACTP	93.6
DTCATP	89.6
HSDATP	171.9
IPDA	153.9

Tab. 5: Results TGA for the cured epoxy samples.

Curing agent	T _{onset} [°C]	T _{max} [°C]	Weight loss [%]
HICTP	319.7	352.4	85.3 % (540 °C)
HACTP	307.2	348.2	2.1 % (267.3 °C) 77.2 % (565 °C)
HCACTP	312.8	344.2	2.5 % (272.5 °C) 84.7 % (540 °C)
DTCATP	307.5	339.1	88.1 % (550 °C)
HSDATP	299.7	398.1	79.42 % (400 °C)
IPDA	359.6	386.1	78.3 % (500 °C)

The cured samples were also tested for their water absorption at room temperature for 30 days and water absorption in boiling water. The lowest water absorption after 30 days in water at room temperature was shown in the case of the sample cured with 1.1 % of IPDA, the worst result was obtained for the sample cured with 13.9 % of DTCATP. The best results of boiling water absorption were achieved in the case of samples cured with IPDA, HACTP and DTCATP. From the point of view of the best stability in the water environment, it can be seen that the best results were obtained in the case of HICTP-cured sample (water uptake of 0.44%), followed by IPDA-cured sample (water uptake 0.72 %.) The least stable sample in the water environment was the sample cured with DTCATP with a water absorption of 11.93 %.

In terms of hardness, the samples were tested using Shore D and Brinell testing methods. From the Table 6 it can be seen that the highest hardness values after 10s-long testing according to the Brinell method were reached in the case of the sample cured

with HICTP, for 60s-long testing the highest hardness was shown in the case of the sample cured by IPDA. The HCACTP-cured sample with the lowest content of epoxide reacted groups was assumed to exhibit the lowest hardness which was confirmed conclusively.

Tab. 6: Hardness results obtained using Brinell a Shore D testing methods.

Curing agent	Brinell		Resistance [Shore D]
	HK [10s]	HK [60s]	
HICTP	275.47	240.65	85.9
HACTP	216.89	224.11	83.8
HCACTP	118.08	101.69	78.0
DTCATP	271.52	234.75	84.5
HSDATP	242.56	200.47	81.9
IPDA	291.83	268.10	85.9

As mentioned above, P-N atoms act retarding during burning and the content of the Si element, is retarded during burning. Another important influence is the burning rate of cured epoxy resin, moisture, thermal stability. An important factor in terms of flammability is the determination of the firing time, ie the start time of the combustion process. The best results in terms of initiation time were achieved by the system cured with IPDA and HICTP with 185 s, on the other hand the worst results achieved by the system cured with HSDATP with 110 s.

Several parameters were monitored and evaluated during the testing of cured samples in the combustion process. The important quantity is heat release rate (HRR), this indicator tells us how much and how fast the burning proceeds. Other tested parameters are total heat release (THR), total oxygen consumed (TOC), mass loss rate (MLR), specific extinction area (SEA), effective combustion heat (EHC, Effective Heat of Combustion) and maximum average rate of heat emission (MARHE). The results of these significant parameters of the burning process can be seen in Table 7.

Tab. 7: Results of flammability measurements using dual cone calorimeter.

Parameters	Using curing agent for curing of CHS Epoxy E520					
	HICTP	HACTP	HCACTP	DTCATP	HSDATP	IPDA
mean HRR [kW/m ²]	284.03	180.96	186.51	243.09	366.01	487.06
mean EHC [MJ/kg]	25.93	26.75	27.24	23.59	25.43	25.78
mean MLR [g/s]	0.07	0.03	0.03	0.04	0.092	0.121
mean SEA [m ² /kg]	755.94	631.38	785.17	936.26	711.42	796.44
Total heat release [MJ/m ²]	99.41	41.83	79.07	88.73	112.73	137.37
Total oxygen consumed [g]	39.30	10.37	19.39	21.75	45.05	54.68
Mass lost [g]	24.55	6.22	11.45	15.04	28.37	34.09
Average specific MLR [g/s·m ²]	27.40	59.27	22.67	31.67	31.66	34.94
Total smoke release [m ² /m ²]	2900.07	996.33	2303.89	3521.06	3154.42	4248.56
Total smoke production [m ²]	18.56	3.99	9.22	14.08	20.19	27.19
MARHE [kW/m ²]	348.20	371.15	434.70	390.51	482.62	344.20

5 CONCLUSION

- In total, five cyclophosphazene derivatives were prepared, which were characterized by analytical methods, and their structure was confirmed.
- The prepared derivatives were successfully used both as curing agents and as flame retardants for the commercially available CHS Epoxy E520 epoxy resin. The prepared samples of cured resins were tested from the point of view of thermal and, most importantly, from the point of view of burning behavior.
- The most important result of this dissertation is the finding of a significantly positive effect of hexachloro-*cyclo*-triphosphazene derivatives as curing agents based on prepared to reduce the flammability of cured epoxy resin. All samples of commercial epoxy resin cured with the prepared hexachloro-*cyclo*-triphosphazene derivatives showed an improved overall burning performance compared to the sample cured with the conventional IPDA curing agent.

6 REFERENCES

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