

Green Synthesis and Characterization of Phosphorus Flame Retardant Crosslinking Agents for Epoxy Resins

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ABSTRACT: The flame-retardant efficacy of phosphorus-containing reactive amine hardeners for epoxy resins is well-known; however their synthesis often applies hazardous, objectionable reagents. The aim of this work is to develop an effective synthesis method for the preparation of P-containing amines, which can act as flame-retardant crosslinking agent in epoxy resins. The syntheses and testing of an aliphatic and two aromatic amines are described: curing properties, glass transition temperature, thermal stability, and flame-retardant performance of the amines are studied. On the basis of these results, the scaling-up and the optimization of the synthesis of the phosphorus-containing aliphatic amine hardener in ReactIRTM *in situ* FTIR apparatus is discussed. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40105.

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INTRODUCTION

Many organophosphorus additives have low molecular weight and are therefore somewhat volatile, leading to the possibility of their loss from the polymer by migration. Clearly, there is a need to increase the permanence of the additive within the polymer; therefore, the incorporation of the organophosphorus functionality within the polymeric structure is a reasonable progression of this field. Reactive organophosphorus monomers built chemically into polymers can render the macromolecules inherently flame retardant. In the case of epoxy resins either the epoxy component, or the crosslinking agent or both can hold the phosphorus-containing chemical unit.

As for the crosslinking agent, aliphatic and aromatic diamines are the most widely used curing agents for epoxy resins. Phosphorus containing reactive amines have potential applicability not only in epoxy resins but also in some other engineering plastics. However, most of the currently applied synthesis methods mean multistep, complex reaction ways, often applying expensive and/or halogen-containing reagents. The methods described in the literature for the synthesis of phosphorus-containing amines can be categorized into the following main groups:

Reaction of Phosphorus Oxychlorides with Aminophenols or Aminoalcohols, or with Nitrophenols Followed by Reduction to Obtain the Amino Group

An immediately extinguishing resin system with 3.9% phosphorus-content was developed, by curing tetraglycidylether of 4,4 diaminodiphenyl methane (TGDDM) with bis(4-aminophenyl)methylphosphonate.¹ This component was synthesized by reduction of the product of the reaction of *p*-nitrophenol with methylphosphonic dichloride. The same method was applied for synthesizing bis(4-aminophenyl)phenylphosphonate (BAPP).² This new component was applied in diglycidyl ether of bisphenol A (DGEBA) and TGDDM epoxy resins. A reduction of 30% of the maximum of heat release could be achieved when curing DGEBA (2.82% P-content), while in case of TGDDM the reduction was more than 50%.³ DGEBA mixed with siliconized DGEBA in different ratios was also cured with BAPP.⁴ The LOI could be increased by 10 V/V% when the mixing ratio of the two epoxies was 100:15 (DGEBA:Si-DGEBA).

Reaction of Phosphorus Oxychlorides with Amines

By the reaction between phosphoryl chloride derivatives and commercially available polyetheramines, ethylenediamine and *N*-phenyl-1,4-phenylenediamine, series of P-containing poly(alkylene) amines with or without aromatic groups were

synthesized.⁵ DGEBA was cured with the prepared amines. The highest P-content (i.e., 4.07%) could be reached when applying the reaction product of ethylenediamine and phenylphosphonic dichloride as hardener. As expected, this formulation showed the best results: an LOI of 31, and 12.2% char yield in air at 850°C. These values could not be significantly increased despite the application of a phosphorus-containing epoxy component.⁶ The synthesis of a cyclophosphazene-based aromatic diamine was also carried out, and showed high thermal stability with a char yield of 55.6% at 600°C in nitrogen.⁷

Transesterification of Phosphate Esters with Aminophenols or Aminoalcohols

Triphenyl phosphate can easily be transesterified with 3-aminophenol to form tris-(3-aminophenyl)-phosphate (TAPP).⁸ Similarly effective by-products (incompletely replaced compounds and oligomers) can also be found in the reaction mixture, but they decrease the crosslink-density. The laminates made of novolac type epoxy resin cured with TAPP reached V-1 rating according to the vertical UL-94 test.

Nitration of Aromatic Phosphine Oxides Followed by Reduction to Obtain the Amino Group

A comparative research was carried out by Braun et al.⁹ about the effect of different oxidation state of phosphorus on the flame retardancy. According to their results, the best flame-retardant performance can be reached with the application of aromatic phosphinate-type FRs. By nitrating then reducing diphenylmethylphosphine oxide, bis(4-aminophenyl)methylphosphine oxide can be prepared.¹⁰ TGDDM was cured with this new P-containing amine. The P content of this composition was 4 mass%, which resulted in an immediately extinguishing resin, with 23% char yield at 800°C in N₂.

Reaction of 9,10-Dihydro-9-oxa-10-Phosphaphenanthrene-10-oxide (DOPO) with Reagents Containing Amine Groups

Due to the active proton of the DOPO molecule, it can easily react in additional reactions with different amine-containing substituents. The addition can occur on oxo¹¹ or imine groups.¹² When applying the reaction product of DOPO and 4,4'-diaminobenzophenone (2DOPO-A) in siliconized DGEBA, an LOI value of 35% could be reached with 2.35% P- and 4.57% Si-content.¹³ DOPO can also react with an aromatic diimine, resulting in a symmetric diamine which can be used as co-curing agent in DGEBA – 4,4'-diaminodiphenyl methane (DDM) system. At 1.5% P-content, V-0 rating could be reached, while the LOI was 37. By the nitration and then reduction of the aromatic rings of DOPO, a P-containing curing agent can be gained, which can increase the LOI by 13 V/V%.¹⁴ New organophosphorus oligomer, poly(DOPO-substituted hydroxyphenyl methanol pentaerythritol diphosphonate) was synthesized by Wang et al.¹⁵ Incorporating it into epoxy resin cured by DDM, significantly enhanced char yield could be achieved comparing to the reference resin, accompanied with increased glass transition temperature.

Although the additive types of flame retardants are still dominating the market their many disadvantages facilitate the progress of the reactive approach. However the available reactive solutions are mostly too complicated and expensive. In the followings an alternative, halogen-free route for producing

phosphorus-containing reactive amine curing agents is presented, which can be used instead of the ways described above: “reaction of phosphorus oxychlorides with amines”.

According to the work published by O. Mauerer,⁸ which gives an example for transesterification of phosphate esters with aminophenols or aminoalcohols, the reaction between a tertiary ester and amine function does not take place: according to his experience, in the reaction of a tertiary ester of phosphoric acid and an aminophenol, only transesterification reaction between the triester and phenol functions occurred, resulting in variously substituted esters, however the amine group remained intact. The reaction between tertiary phosphoric ester and diamines has not yet been described, although an article of A. Michaelis from 1903 contains a hint that if monoamide-diester of phosphoric acid (C₆H₅CH₂NHP(O)(OC₆H₅)₂) is heated together with benzylamine for a long time it will be converted into phosphine oxide, however the reaction condition are not defined and the product is not characterized by any means of analytics (also the exact name and chemical formula of the compound is missing)¹⁶.

The concept of the present work was to develop a simple, cost-effective and environmentally friendly method for the synthesis of both aliphatic and aromatic phosphorylated amines with high phosphorus-content. The authors also aimed at finding an alternative route to produce the phosphorus-containing reactive amine curing agents previously synthesized,¹⁷ in particular *N,N,N'*-tris(2-aminoethyl)phosphoric triamide (TEDAP), which found its use not only as flame retardant,^{18,19} but also as base material for pH-reversible supramolecular hydrogels²⁰ and for preparation and stabilization of gold nano- and microcrystals.²¹

EXPERIMENTAL

Materials

Reagents Used in Organic Syntheses. Triethyl phosphate (TEP, M: 182.2 g/mol, ρ : 1.071 g/cm³, bp: 215°C), ethylene diamine (EDA, M: 60.1 g/mol, ρ : 0.899 g/cm³, bp: 118°C), *o*-phenylene diamine (OPDA, M: 108.14 g/mol, ρ : 0.899 g/cm³, mp: 99–102°C) and *m*-phenylene diamine (MPDA, M: 108.14 g/mol, ρ : 0.899 g/cm³, mp: 64–66°C), supplied by Sigma Aldrich, were used as received, without further purification. Toluene (M: 92.1 g/mol, ρ : 0.87 g/cm³, bp: 111°C) was received from Molar Chemicals Kft., and was used after distillation.

Polymer Components. The applied epoxy resin matrix consisted of epoxy component type MR 3016 (non modified, resin-like reactive diluent, epoxy equivalent: 156–170; viscosity at

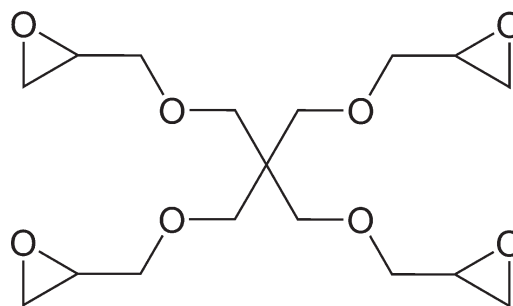


Figure 1. Main component of MR 3016.

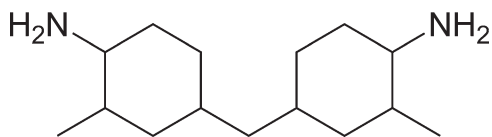


Figure 2. Main component of MH 3122.

25°C: 850–1200 mPa.s; density at 25°C: 1.24 g/cm³) (Figure 1) cured with MH 3122 hardener (amine number: 464–490 mg KOH/g; viscosity at 25°C: 80–120 mPa.s; density at 20°C: 0.944 g/cm³) (Figure 2) supplied by IPOX Chemicals Kft., Hungary.

Analytical Methods

The ³¹P-NMR spectra of the synthesized amines were recorded in a Bruker-300 NMR spectrometer at 25 MHz.

Infrared spectra (4000–400 cm⁻¹ or 4000–650 cm⁻¹, depending on the physical state) of the synthesized phosphorus-containing amines were recorded using a Bruker Tensor 37 type Fourier transform infrared (FTIR) spectrometer with resolution of 4 cm⁻¹, and equipped with DTGS detector.

Mass spectroscopic measurements applying fast atom bombardment ionization technique (MS FAB) were performed on ZAB-2SEQ spectrometer.

Mass spectroscopic measurements applying matrix assisted laser desorption/ionization technique (MALDI TOF) measurements were taken on Bruker BiFlex III MALDI-TOF apparatus and evaluated with XMASS 5.0 software.

The curing process was monitored with TA instruments DSC Q2000 type DSC equipment in 50 mL/min nitrogen flow. Tzero type aluminium pans were used, the sample size was between 5 and 10 mg. In order to determine the total reaction enthalpy, simple heating/cooling/heating program was used, the first heating cycle consisted of a linear ramp from 25 to 175°C to ensure the proper curing, while the second one of a ramp from 0 to 150°C. The first heating cycle was carried out with 2°C/min heating rate, while the second one with 10°C/min. From the first ramp the curing enthalpy was determined, while from the second one the glass transition temperature of the different systems was received.

The thermal stability of the different compositions was determined by TGA measurements using Setaram Labsys TG DTA/DSC instrument in the temperature range of 25–500°C at a heating rate of 10°C/min under nitrogen gas flow rate of 30 mL/min. About 15–20 mg of sample was used in each test.

The flame retardant performance was characterized by limiting oxygen index (LOI) measurements according to the ASTM D 2863 standard. The LOI value expresses the lowest oxygen to nitrogen ratio where specimen combustion is still self-supporting.

Standard UL-94 flammability tests (ASTM 1356-90 and ANSI/ASTM D-635/77) were also performed. UL-94 classification is used to determine the ignitability, dripping and flame spreading rates. The increasing values of UL-94 ratings are as follows: HB, V-2, V-1, V-0.

Synthesis of Reactive Flame Retardant Monomers

As TEDAP proved to be an efficient flame retardant curing agent for epoxy resin, the authors aimed at finding an alterna-

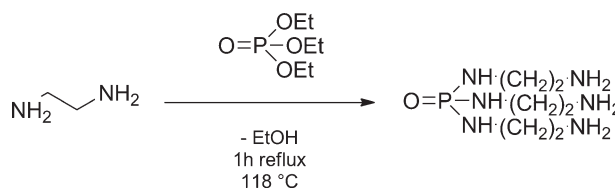
tive route, possibly suitable for industrial scale-up, to produce the phosphorus-containing reactive amine curing agents, which were previously synthesized in the reaction of phosphorus oxychloride and diamines.¹⁷ The reaction between the phosphorus oxychloride and amine functional group is a well-described method.²² However, the reaction of POCl₃ and H₂NCH₂CH₂NH₂ is highly exothermic and needs effective cooling even at laboratory scale, which renders the up-scaling of the reaction extremely difficult. Besides, POCl₃ is an expensive, halogen-containing reagent. Generally phosphorus oxychlorides are used when the more environmental-friendly, less toxic, less expensive, and easier to handle phosphoric esters and phosphoric acid is not reactive enough due to the different chemical moiety around the phosphorus atom.

Considering the former publications cited in the introduction,^{8,16} even if it is not trivial that the reaction between a tertiary phosphoric ester and diamines would take place, triethyl phosphate (P(O)(OEt)₃) was chosen as new phosphorylation agent. It is a cheap, commercially available reagent, also used as flame retardant agent in polymer chemistry. Reaction of triethyl phosphate with an aliphatic diamine, ethylene diamine and two aromatic diamines, *o*- and *m*-phenylenediamine was attempted. Concerning the choice of amine reagents, it can be noted that short chained aliphatic amines are widely applied as crosslinking agents in epoxy resins and are produced in large quantities, and choosing them as a reactant in this synthesis, high phosphorus content of the hardener and the epoxy resin system can be achieved. As the phosphorus-content is proportional to the flame retardant effect, this was an important aspect. On the other hand although the phosphorus-content which can be achieved using aromatic amines is lower than in case of short chained aliphatic amines, the aromatic backbone offers numerous advantages as high char yield, higher thermal stability, more rigid structure leading to higher glass transition temperature.

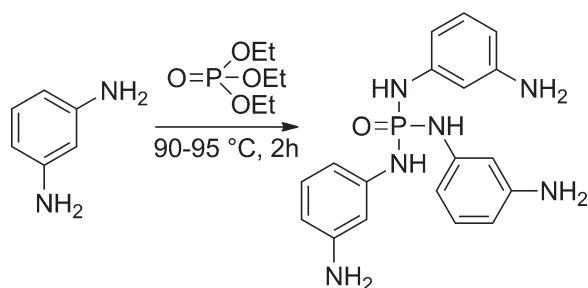
Synthesis of *N,N',N''*-tris(2-aminoethyl) Phosphoric Triamide (TEDAP) from Triethyl Phosphate

As first trial, the transamidation of triethyl phosphate (TEP) was attempted with ethylene diamine (EDA), according to the Scheme 1.

To 36.7 mL (0.55 mol) of EDA 9.3 mL (0.055 mol) of TEP was added dropwise and the mixture was stirred at the boiling point of EDA, at 118°C for 1 h. Instead of the necessary 3 equivalents of EDA 10 equivalents were used in order to shift the equilibrium in the direction of the required trisubstituted product. The excess of EDA was removed by vacuum distillation to give the liquid, yellowish brown product in 93% yield. The crude mixture was analyzed by ³¹P-NMR chemical shifts, mass



Scheme 1. Synthesis of TEDAP from P(O)(OEt)₃.



Scheme 2. Synthesis of TMPDAP.

spectroscopical data obtained from MS FAB and MALDI-TOF and FTIR spectra. The FTIR spectra confirmed the formation of P-N-C bonds.²³ According to the MALDI-TOF spectra the product mainly contained monomers, but possible fragments of dimers, trimers, and tetramers were also detected.

³¹P NMR (DMSO-*d*₆ δ): 6.64

MS, *m/z*: 225 (monomer, M+)

FTIR (cm⁻¹): 738 (P-N), 1054 (P-N-C), 1216 (P=O), 3351 (N-H)

amine number: 500 ± 5 mg KOH/g

Synthesis of *N,N,N'*-tris(3-Aminophenyl) Phosphoric Triamide (TMPDAP) from Triethyl Phosphate

An aromatic diamine, *m*-phenylenediamine was used in the transamidation reaction according to the Scheme 2.

7.136 g (0.066 mol) of *m*-phenylenediamine was heated in a round flask until melting (64–66°C). When the amine was completely melted, 3.72 mL (0.022 mol) of P(O)(OEt)₃ was added dropwise, then stirred at 90–95°C for 2 h. The forming ethanol was removed from the reaction mixture by vacuum evaporation to give the liquid, dark green product in 90% yield. The crude mixture was analyzed by ³¹P-NMR chemical shifts, mass spectroscopical data obtained from MS FAB and FTIR spectra.

³¹P NMR (CDCl₃ δ): -1.05

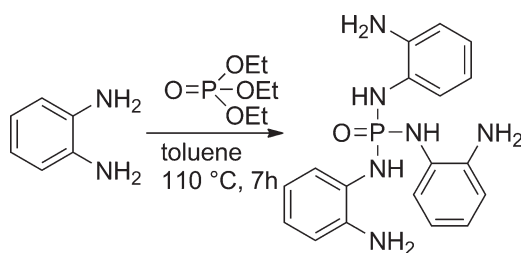
MS, *m/z*: 369 (M+) (trisubstituted product)

FTIR (cm⁻¹): 764 (P-N-C), 976 (P-N-C), 1195 (O=P-N), 1258 (P=O), 3377 (N-H)

amine number: 655 ± 5 mg KOH/g

Synthesis of *N,N,N'*-tris(2-Aminophenyl) Phosphoric Triamide (TOPDAP) from Triethyl Phosphate

The transamidation reaction was also carried out with another aromatic diamine, *o*-phenylenediamine according to the Scheme 3.



Scheme 3. Synthesis of TOPDAP.

To the solution of 70 mL toluene and 7.136 g (0.066 mol) of H₂NC₆H₄NH₂ 3.72 mL (0.022 mol) of P(O)(OEt)₃ was added and the mixture was stirred at the boiling point of toluene, at 110°C for 7 h. After cooling, the dark violet solid product was filtered out, with a yield of 90%. The crude mixture was analyzed by ³¹P-NMR chemical shifts, mass spectroscopical data obtained from MS FAB and FTIR spectra.

³¹P NMR (CDCl₃ δ): -1.25

MS, *m/z*: 307 (M+) (disubstituted product)

FTIR (cm⁻¹): 748 (P-N-C), 927 (P-N-C), 1273 (P=O), 3363 (N-H)

amine number: 307 ± 5 mg KOH/g

RESULTS AND DISCUSSION

Curing Properties of the Synthesized Amines

For investigating the applicability of the synthesized phosphorus-containing amines as curing agents for epoxy resins, DSC measurements were carried out. The pentaerythritol-based model epoxy component (MR 3016) and the corresponding amines were mixed in appropriate ratio for the maximal crosslink density, i.e., according to their epoxy equivalent and the amine number, respectively. For a better comparison, the results of the P-containing amines are compared to that of the reference cycloaliphatic diamine (MH 3122).

From the first heating ramp, the curing enthalpies of the different epoxy resin systems were determined (Table I). The highest enthalpy was measured in the case of the reference cycloaliphatic diamine (MH 3122), which means that the curing of this system is the most exothermic among the investigated ones. The difference between the measured values of the two P-containing aromatic amines (TMPDAP and TOPDAP) is negligible; however, the peak of curing appears at somewhat higher temperature in the case of the *o*-phenylene diamine-based molecule. This phenomenon can be explained by steric hindrance of the amine groups in *ortho* position compared to that of the *meta* one. The aliphatic phosphorus-containing TEDAP showed the lowest curing enthalpy, so the less exothermic reaction. In the case of high-scale curing, the low exothermity can be beneficial for the processing of the resin and for controlling the sample preparation.

The glass transition temperature (*T*_g) of the four different systems was also determined from the second heating ramp in the DSC. The *T*_g was assigned to the inflection point of the DSC curve. The highest value was measured in the case of the cycloaliphatic reference hardener, as expected. The rigidity of the

Table I. Curing Behavior of the Different Amines

Curing agent	Onset point (°C)	Peak of curing (°C)	Enthalpy of curing (J/g)	Glass transition temperature (°C)
Reference	65.5	99.7	402.5	97.7
TEDAP	43.6	77.2	283.3	40.4
TMPDAP	55.7	84.5	337.5	79.5
TOPDAP	70.7	92.8	337.3	77.5

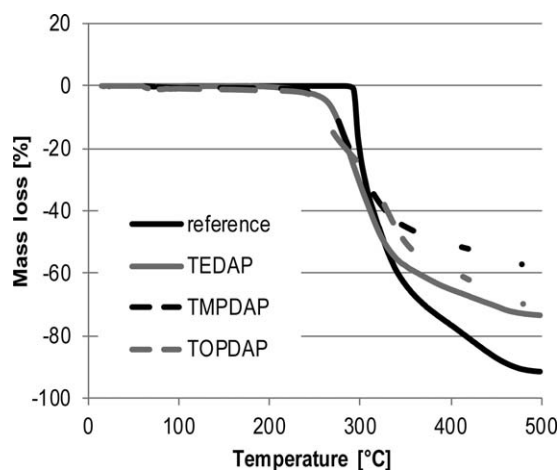


Figure 3. TGA curves of the cured resins.

cycloaliphatic rings hinders the segmental movements in the cross-linked resin, so high temperature is needed for the glassy transition. In the case of the two aromatic, phosphorus-containing amines, the T_g is somewhat lower, as the rings are bound together via the more flexible N-P-N bonds compared to the one atom distance between the cycloaliphatic rings (Figure 2). TEDAP showed the lowest glass transition temperature among the investigated resin systems, as expected. Both the epoxy and the hardener have flexible aliphatic chains, which allows easy segmental movements and thus relatively low T_g .

Thermal Stability

The thermal stability of the resins cured with the three synthesized P-containing hardeners and with the reference cycloaliphatic one was investigated with TGA measurements (Figure 3).

The degradation of the reference cycloaliphatic hardener starts with a sharp mass decrease at 295°C, and a very high decomposition rate (Table II). The residue at 500°C is less than 10%, as expected, as no charring agent is present in the system. When the P-containing hardeners are applied, the decomposition starts at lower temperatures. According to our previous study on the flame retardancy mechanism of TEDAP,¹⁸ this can be explained by the evolved PO radicals at the early stage of degradation slowing down the further degradation steps. The degradation of the *o*-phenylene diamine-based TOPDAP-cured resin shows a two-step curve, with almost the same decomposition rates (Table II). This double degradation can be explained by the lower stability of the

amine starting material itself even at room temperature due to the $-NH_2$ groups in *o*-position. Furthermore, the residue of the TOPDAP-cured resin is less than that of its stereoisomer, TMPDAP: 28.9% compared with 41.8% for the latter one. The TMPDAP-cured system shows elongated and relatively slow degradation. The highest decomposition rate appears at 280°C, between the values of the two steps of TOPDAP. The amount of charred residue for the aliphatic P-containing hardener (26.6%) is somewhat lower than that for the aromatic ones, which is related to the beneficial effect of the aromatic rings in char formation. Also the rate of decomposition is higher in the case of TEDAP; however this maximum is reached at higher temperature (Table II).

Flame Retardancy Results

For the comparison of the flame retardant efficiency of the synthesized phosphorus-containing amines, standard LOI and UL-94 measurements were carried out. The obtained ratings are summarized in Table III. It can be stated, that the application of all the P-containing hardeners results in decreased flammability compared to the reference system. The phosphorus-content of the samples is also presented. The difference between the P-content of the two aromatic amines is caused by the difference of their amine values requiring different mixing ratios for achieving the same level of crosslinking. However, the measured LOI values are above 30 V/V% in all cases, which indicates the beneficial effect of the phosphorus in terms of decreasing the ignitability of the resins.

The flame retardant efficacy of the synthesized amines is more pronounced in the case of the UL-94 tests. The reference system reached only HB classification with a relatively high flame spreading rate (32 mm/min), while the P-containing resins passed the horizontal test, so no flame spreading rates could be measured. The significance of the phosphorus-content is doubtless: the TMPDAP-cured resin contains less than 2 mass% P and reaches only V-1 classification, while the samples with more than 2 mass% P-content could reach the best, V-0 classification.

These results are even more considerable, when comparing to the results of conventional FR additives. In this reference epoxy resin system, with the application of ammonium polyphosphate (APP) as additive flame retardant, the V-0 could be reached only at 5 mass% P-content, while DOPO proved to be incompatible with the pentaerythritol-based epoxy component as even at 4 mass% of P-loading, the UL-94 classification remained HB.²⁴

Table II. Thermal Degradation of the Different Resins

Curing agent	$T_{-5\text{mass}\%}$ (°C)	$T_{-50\text{mass}\%}$ (°C)	dTG_{max} (%/min)	$T_{dTG_{\text{max}}}$ (°C)	Char yield (%)
Reference	294.5	326.5	-24.75	296	8.6
TEDAP	263.5	326.5	-8.78	289	26.6
TMPDAP	265.6	390.6	-7.49	280	41.8
TOPDAP	256.4	349.8	-6.98-6.83	263/325	28.9

$T_{-5\text{mass}\%}$, temperature at 5 mass% loss; $T_{-50\text{mass}\%}$, temperature at 50 mass% loss; dTG_{max} , maximum mass loss rate; $T_{dTG_{\text{max}}}$, temperature belonging to dTG_{max} .

Table III. Comparison of LOI and UL-94 Results of Reference and FR Epoxy Resin Matrices

Hardener	P-content (%)	LOI (V/V%)	UL-94 ^a
cycloaliphatic reference	0	23	HB(32 mm/min)
TEDAP	2.8	33	V-0
TMPDAP	1.7	31	V-1
TOPDAP	3.0	30	V-0

^aIn parenthesis the horizontal burning rate is showed, where measurable.

Optimization and Scale-Up of the Synthesis of TEDAP in ReactIR-Apparatus

Based on the comparison of LOI and UL-94 results (Table III) and previous flame-retardancy results on TEDAP,^{17–19} optimization and scale-up of the synthesis of TEDAP was carried out.

First, spectroscopic monitoring of the synthesis was performed in order to study the chemical reactions in depth. Since there is no Raman-active change during the reaction, the on-line monitoring by Raman-spectroscopy was not possible. In case of IR-spectroscopy the problem was that the spectrum of EDA in excess overwhelmed the spectra of the other components in the samples taken from the reaction mixture. The feasible solution proved to be the utilization of the ReactIRTM *in situ* FTIR apparatus (type Mettler-Toledo). This instrument allows *in-situ* real-time FTIR analysis of a reaction mixture in the mid-IR region using a multi-reflection diamond ATR insertion sensor, which can withstand reaction conditions over a wide temperature range (−80 to 250°C) under pressures up to 100 bar. The spectral range for this instrument is 450 cm^{−1} to 4800 cm^{−1}. The technology is well-suited to perform kinetics research because the data can be collected very rapidly (resulting in accurate determination of reaction rates), the diamond sensor is compatible with chemical environments, and *in-situ* characterization of component allows detection of unstable species (that may not be measurable by chromatographic or other off-line techniques).

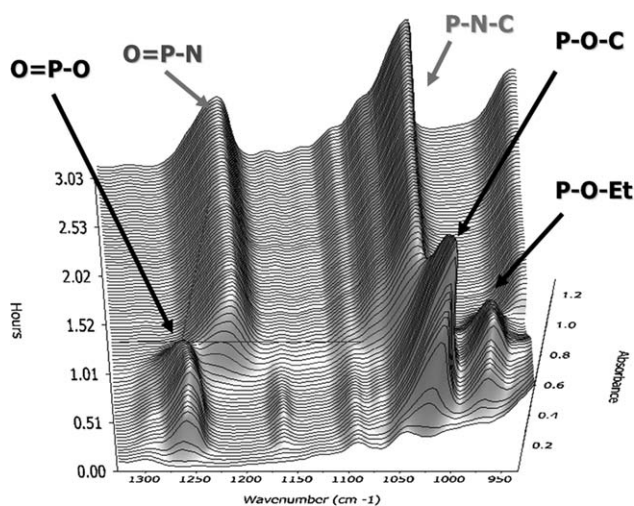


Figure 4. Joint IR spectra of components in the function of time.

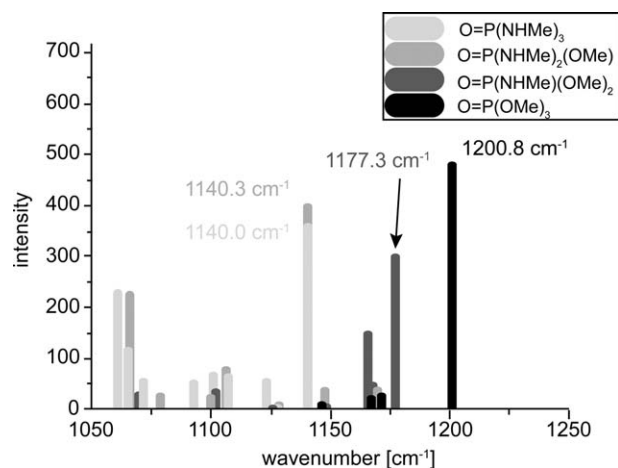


Figure 5. B3LYP/6-31++G(d,p)//PCM (Polarizable Continuous Media) calculations.

The scaled-up synthesis of TEDAP was carried out in the ReactIR instrument: To 99 g of EDA (1.65 mol, 10 equivalents) 30 g of TEP (0.165 mol, 3 equivalents) were added in ~25 min, with controlled feed speed. The reaction mixture was heated up to the boiling point of the EDA (118°C) in ~30 min and kept refluxing and mixing with magnetic stirrer until the end of the reaction.

According to the 3D joint IR spectrum of the components in the function of time (Figure 4) it can be concluded that by feeding the TEP the intensity of (RO)₃P=O peak at 1266 cm^{−1}, P-O-C peak at 1027 cm^{−1} and P-OEt peak at 970 cm^{−1} is gradually increasing. On the base of the B3LYP/6-31++G(d,p)//PCM (Polarizable Continuous Media) calculations (Figure 5) it can be expected that due to the occurring transamidation the signal of P=O is going to be gradually shifted to lower wavenumbers. After starting the heating-up of the reaction mixture the intensity of the peaks characteristics for TEP starts to decrease with a parallel increase of the peaks characteristics for TEDAP: (RNH)₃P=O at 1224 cm^{−1} and P-N-C at 1054 cm^{−1}. After a transition time where both the starting material, mono-,

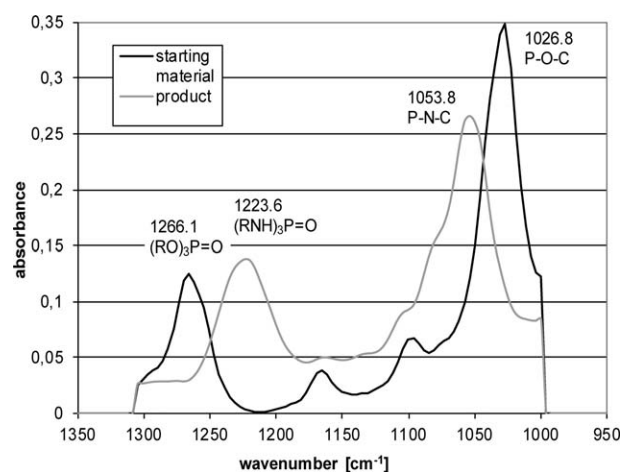


Figure 6. IR spectra of the starting material and the product after the deconvolution of the joint IR spectrum of the components.

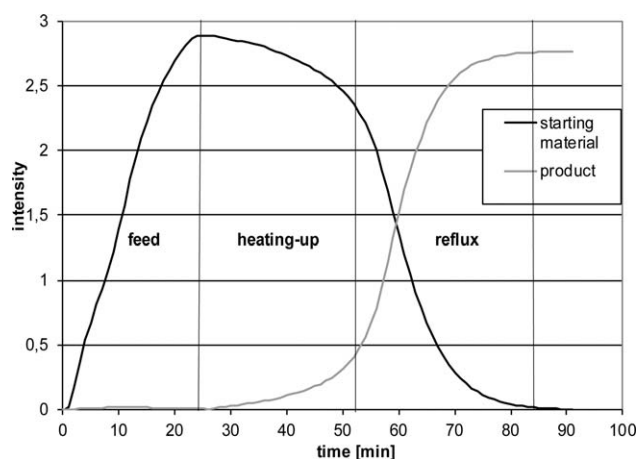


Figure 7. Calculated concentration profiles.

di-, and trisubstituted products are present, the overall transamidation occurs.

From the joint 3D IR spectrum the 2D IR spectrum of the starting material and the product can be obtained by deconvolution (Figure 6) and based on the selected characteristic peaks a concentration profile can be obtained (Figure 7).

The concentration profile allows the determination of the reaction time: after ~30 min of reflux no more starting material is available in the reaction mixture and the concentration of the product reaches its maximum. If the reaction time is longer than the determined, it leads to the oligomerization of TEDAP. The differences between the monomeric and oligomeric form of TEDAP can be summarized as follows (Table IV).

Therefore, it can be concluded that the optimal reaction time depends on the required product: if a liquid product is needed with better crosslinking properties and a bit lower P-content, than less reaction time is enough however, if an oligomeric product with higher P-content but weaker crosslinking properties is necessary, than longer reaction time is needed.

CONCLUSIONS

A new, environmental-friendly and cost-effective one-pot synthesis method was developed for the synthesis of phosphorus-containing amines. The starting material, triethyl phosphate is commercially available and produced in large quantities for other purposes, is not harmful to the environment and during the reaction no harmful by-products are formed. In the case of the aliphatic amine, the excess of ethylenediamine serves also as solvent in the reaction, and helps to shift the equilibrium in the direction of the desired product; furthermore it can be recycled during the production. When the aromatic *o*-phenylene diamine is used as starting material, the formed product is crystalline, which can be easily filtered out from the toluene solution. The *m*-phenylene diamine can react with the phosphorylating agent even in molten phase, so the application of solvents can be avoided. The potential applicability of the synthesized P-containing amines as hardeners and so reactive flame retardants for epoxy resins was investigated by DSC measurements. Based on the results, it can be stated that all the tested molecules can cure the resins, and thus, can be used as crosslinking agents. The flame-retardant efficacy was also tested. The resins with more than 2 mass% P-content could reach the best, V-0 classification in the UL-94 test, while all the investigated FR systems have > 30 V/V% LOI values.

On the basis of the FR results, the scaling-up of the aliphatic P-containing amine was carried out. The optimal circumstances of the reaction could be identified by in-situ ReactIR measurements, where the formation of the product was followed by IR spectrometry. The optimal reaction time was found to be 30 min for the formation of the monomeric form of TEDAP.

The moisture sensitivity of the P-N is a known issue, and it largely depends on the moiety of the P-N bond as well. For example bulky aromatic groups around the sensitive groups significantly increase the stability under wet conditions. The performed reactions intended to demonstrate that this new reaction way is feasible and the synthesized amines are suitable for curing epoxy resins. In case of a real application, where

Table IV. Comparison of the Characteristics of Monomeric and Oligomeric Form of TEDAP

	Monomeric form	Oligomeric form
Structure		
Physical appearance	 brownish yellow, liquid	 yellow, solid
Melting point	-	45°C
Amine number	500 ± 5 mg KOH/g	< 500 ± 5 mg KOH/g
P-content	13.84 mass%	n=2: 15.98 - n=4: 17.32 mass%
Reaction time	30 min	> 30 min

moisture sensitivity is a crucial issue, tailor-made amines with bulky apolar groups can be the solution. In many application areas epoxy resin composites are used together with a coating layer e.g. paint, which hinders the access of moisture to the epoxy resin matrix.

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