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Polymer Degradation and Stability 91 (2006) 585–592

Polymer Degradation and Stability

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Synthesis of phosphorus-based flame retardant systems and their use in an epoxy resin

A. Toldy*, N. Tóth, P. Anna, G. Marosi

Department of Organic Chemical Technology, Budapest University of Technology and Economics, PO Box 91, 1521 Budapest, Hungary

Received 11 November 2004; received in revised form 14 January 2005; accepted 14 February 2005
Available online 10 October 2005

Abstract

Methods are proposed to synthesize efficient organophosphorous compounds and combine them with montmorillonite nanoparticles. The chemical–physical structure and mechanism of action of the new systems were studied in epoxy resin. Best results were achieved using the fully phosphorylated calixresorcinarene derivative: the heat release rate peak could be decreased by 61% and the LOI value was increased from 21 to 28. The salt form of additives in case of phosphorylated phloroglucine derivatives was not advantageous in epoxy resin, because the additives could not participate in the crosslinking process effectively due to their inhomogenous distribution in the matrix. The incorporation of the nanoparticles did not create the desired flame retardant effect which can be explained by the increased heat conductivity and lower mobility of the nanoparticles due to the crosslinked structure.

Keywords: Organophosphorous flame retardant; Epoxy resin; Intercalated montmorillonite; Cone calorimetry

1. Introduction

The fire retardant properties of organophosphorus compounds have been recognized and developed over a number of years and they have thus found use as additives in a variety of polymeric materials [1,2]. Many organophosphorus additives are of low molecular weight and are therefore somewhat volatile, causing their partial loss from the polymer during either high temperature processing by migration to the surface or in the early stages of combustion. Additionally, their transition to the gaseous phase may cause the smoke of the burning material to become loaded with toxic phosphorus-containing compounds. Clearly, there is a need to increase the permanence of the additive within the polymer in order to maximize the fire retardancy and to reduce the evolution of toxic species. The incorporation of the organophosphorus functionality within the polymeric structure, increasing the molecular weight of the additive or their combination with nanoparticles may offer solutions to this problem.

Our aim was to synthesize various reactive and additive type aromatic organophosphorus compounds and to incorporate them into epoxy resin. The effect of combining the organophosphorus compounds with nanoparticles was also studied.

2. Experimental

2.1. Materials

Materials used in organic synthesis were the following: Phosphorus pentoxide (MW 141.94; from Reanal, Hungary), phloroglucinol·$2H_2O$ (MW 162.14; mp 218–221 °C; from Aldrich Chemical Co.), toluene (MW 92.14; 0.865 g/ml; from Aldrich Chemical Co.), melamine (MW 126.12; from Merck), triethylamine (MW 101.19; 0.726 g/ml; from Reanal, Hungary), tetrahydrofuran (MW 72.11; 0.889 g/ml; from

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* Corresponding author. Fax: +36 1 436 1150.
E-mail address: gmarosi@mail.bme.hu (G. Marosi).

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doi:10.1016/j.polymdegradstab.2005.02.025

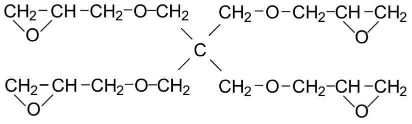


Fig. 1. Main component of Eporezit AH-16.

Table 1
Characteristics of the epoxy resin

Type of epoxy resin	Epoxy equivalent	Viscosity at 25 °C (mPa s)	Density at 25 °C (g/cm^3)	General description
Eporezit AH-16	160–175	800–1800	1.24	Non-modified, resin-like reactive diluent

Aldrich Chemical Co.), diethyl chlorophosphate ($C_4H_{10}ClO_3P$) (MW 172.55; 1.194 g/ml; from Aldrich Chemical Co.).

The polymer matrix was epoxy resin (ER) type Eporezit AH-16 used with Eporezit T-58 curing agent (P+M Polimer Kémia Kft., Hungary). Figs. 1 and 2 show the main components of Eporezit AH-16 and Eporezit T-58. The characteristics of the epoxy resin and curing agent are shown in Tables 1 and 2, respectively.

Mono- and diphosphorylated phloroglucine derivatives and the partially and fully phosphorylated calixresorcinarenes were used as flame retardant additives. Bentone SD-1 (bentonite based organoclay product of Rheox Inc.) type montmorillonite nanoparticles (MMT) were also used in two forms: (a) 1–2% additive of well dispersed nanoparticles, (b) intercalated nanoparticles. The MMT was intercalated with K8P in the following way: K8P was added into the diluted dispersion of Bentone SD-1 in toluene. Then, the toluene was removed by distillation and drying. This way flame retarded ER samples containing 1% MMT were prepared.

2.2. Methods

The ^{31}P NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4 MHz. Chemical shifts are downfield relative to 85% H_3PO_4. The Raman spectroscopic measurements were made on a Labram type Raman instrument (Jobin Ivon France). The Raman spectra were processed using LabSpec 4.02 software.

The epoxy components and the appropriate flame retardant additives were mixed by hand in a glass beaker in order to obtain a homogenous mixture. A mould 120 mm long, 15 mm wide and 3 mm thick was used for preparing the cured samples. Thermogravimetry (TG) was performed using Setaram Labsys equipment, sample weight: 10 mg, heating rate: 10 °C/min in nitrogen atmosphere. Differential scanning calorimetry (DSC) was used to follow the curing of the thermosetting matrix. The DSC measurements were carried out using Setaram DSC 92 apparatus, sample weight: 10 mg, in nitrogen atmosphere, the temperature program consisted of a 1 min isotherm at 30 °C and a subsequent linear part with a heating rate of 10 °C/min from 30 to 500 °C. Measurements were carried out immediately after mixing the appropriate components. The fire resistance was characterized by Cone Calorimeter (Stanton Redcroft, heat flux of 50 kW/m^2), UL-94 test (according to ASTM 1356-90 and ANSI/ASTM D-635/77, respectively) and Limiting Oxygen Index measurement (LOI, according to ASTMD 2863).

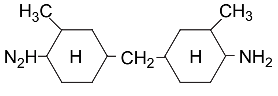


Fig. 2. Main component of Eporezit T-58.

3. Results and discussion

The concept of the work was, on the one hand, to synthesize partially and fully phosphorylated polyols by a more simple method than reported earlier [3,4] and, on the other hand, to extend this earlier published phosphorylation method to hydroxyphenols with higher molecular weight and better compatibility with polymers. The applicability of the new additives in an epoxy resin was evaluated by varying their concentration and by combining them with nanoclay in the forms of mixture and intercalated structure.

3.1. Synthesis of organophosphorus compounds

3.1.1. Synthesis of phosphorylated phloroglucinol derivatives

Phosphorous pentoxide was added to a suspension of phloroglucinol in toluene at 80 °C. The amount of phosphorous pentoxide to be added was calculated according to the number of OH groups to be esterified (1, 2 or 3 OH groups). The mixture was left to react for 2 h. Afterwards melamine was added to the mixture to neutralize the OH groups of phosphoric acid functionality. Toluene was removed by distillation. This way solid state mono- (MPP), di- (DPP) and trisubstituted phloroglucinol derivatives (TPP) were synthesized (Figs. 3–5). The reactions were followed by Raman spectroscopic measurements. The signature of the OH groups (3100–3650 cm^{-1}) in the Raman spectra decreased proportionally to the degree of substitution.

Table 2
Characteristics of the curing agent

Type of curing agent	Amine number	Viscosity at 20 °C (mPa s)	Density at 20 °C (g/cm^3)	General description
Eporezit T-58	460–470	100–200	0.944	Curing agent

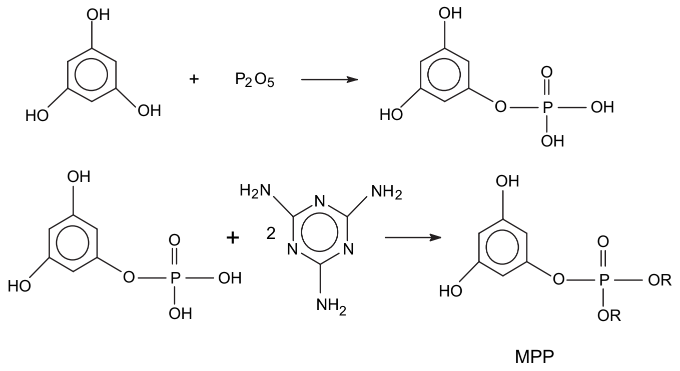


Fig. 3. Monophosphorylation of phloroglucinol.

3.1.2. Phosphorylation of C-methylcalix[4]resorcinarene

The partial and overall phosphorylation of *C*-methylcalix[4]resorcinarene was carried out by integrating a general phosphorylation method for polyhydroxy compounds published elsewhere [3] and a method for functionalisation of *C*-methylcalix[4]resorcinarene described in literature [5].

According to this newly developed procedure *C*-methylcalix[4]resorcinarene (synthesized according to the literature [6]) and 5 equivalents of triethylamine were dissolved in tetrahydrofuran, and 5 equivalents of diethyl chlorophosphate were added to the solution. The mixture was stirred at room temperature for 48 h. The precipitate was filtered off, washed with water and dried at 100 °C for 5 h to give a light yellow powder, the tetraphosphorylated product, K4P4OH (Fig. 6). ^{31}P NMR ($CDCl_3$) δ −3.5.

The full phosphorylation was carried out the same way described above using 10 equivalents of the appropriate reagents to give a brown, viscous liquid, the octaphosphorylated product, K8P (Fig. 7). ^{31}P NMR ($CDCl_3$) δ −11.3.

3.2. Incorporation into ER matrix

3.2.1. Phloroglucine derivatives in ER

The phloroglucine derivatives are reactive additives (their free NH_2 groups make them able to react with epoxy groups), which were expected to act both as flame retardant and crosslinking agent.

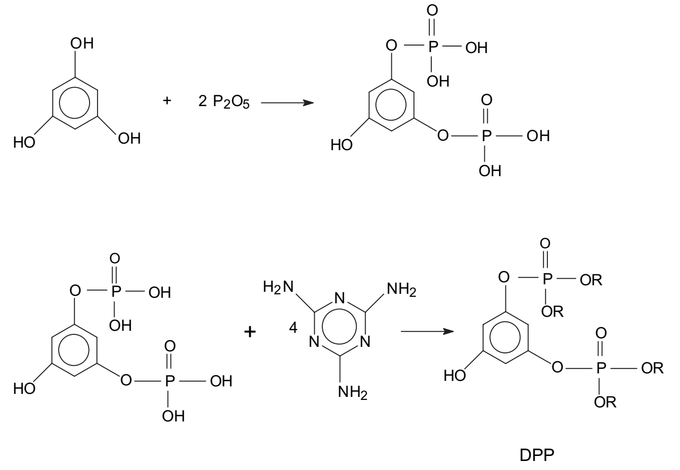


Fig. 4. Diphosphorylation of phloroglucinol.

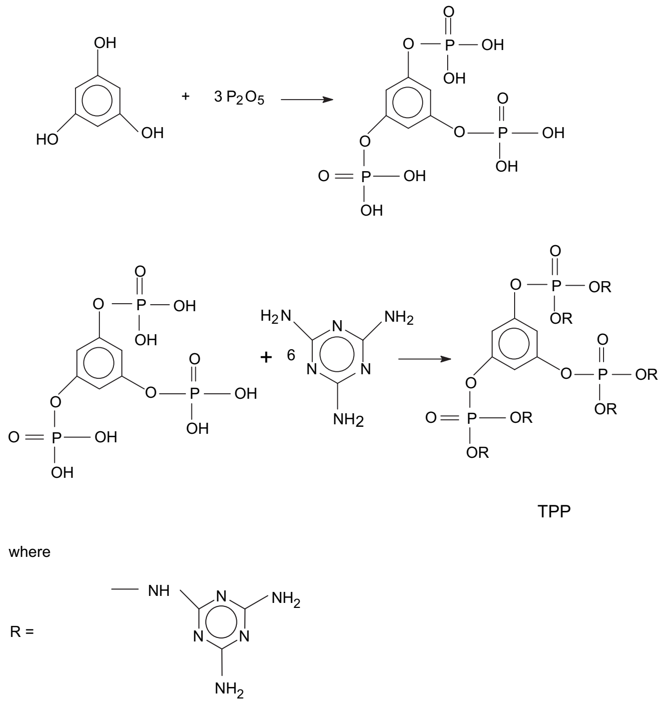


Fig. 5. Triphosphorylation of phloroglucinol.

The fire retardancy of these samples was evaluated by LOI measurements. The results are given in Fig. 8.

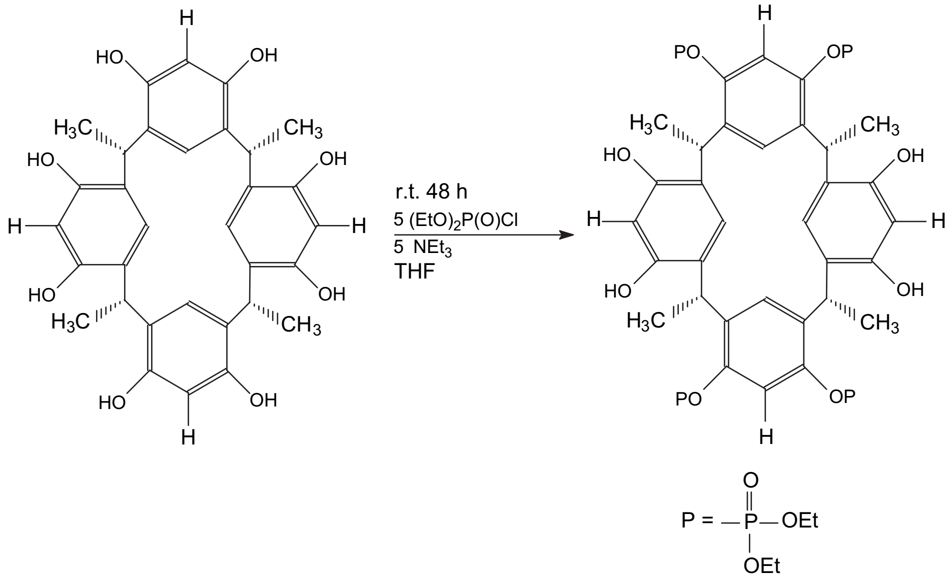
Increasing the P concentration in the system a clear increase of the flame retardancy can be seen, the achieved values are, however, moderate if less than 1% or 2% P is introduced by MPP or DPP, respectively.

The effect of the additive on the network structure of the epoxy resin can be determined by measuring the enthalpy of crosslinking. The DSC results determined during the crosslinking process are given in Table 3.

The enthlapy values clearly show that by increasing the amount of the phosphorylated phloroglucine derivatives the enthalpy of the curing decreased, thus the additives could not participate effectively in the crosslinking process. The reason behind this may be the inhomogenous distribution of the phloroglucinol-based additives in the resin. Indeed it could be seen even in preparation of the samples that these salt-type components could not be distributed molecularly in the matrix. It could be concluded that the salt form of additives is not advantageous in epoxy resin.

3.2.2. Calixresorcinarene derivatives in ER

The phosphorylated calixresorcinarenes cannot function as crosslinking agents, but due to their higher molecular weight they are technically compatible — not migrating within the polymer matrix. Their high phosphorus content and the



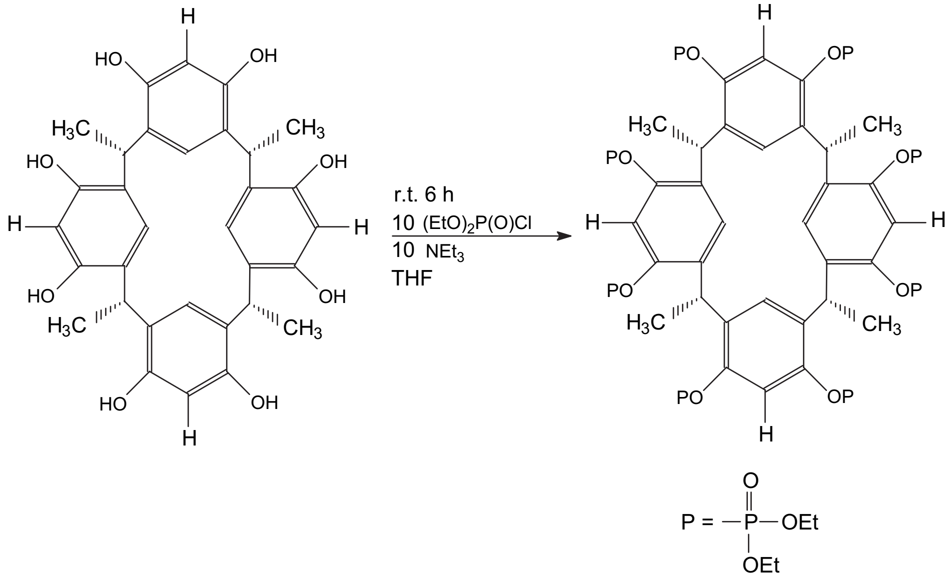
K4P4OH

Fig. 6. Partial phosphorylation of *C*-methylcalix[4]resorcinarene.

existence of aromatic rings in the molecules are promising for flame retardant efficiency.

The flame retardancy of ER samples containing partially and fully phosphorylated calixresorcinarenes (indicated as K4P4OH and K8P, respectively) in various concentrations was evaluated in the Cone Calorimeter applying heat flux of 50 kW/m^2. The results of Cone Calorimetry are given in Figs. 9–11.

The peak of heat release rate (HRR) is decreased by increasing the quantity of the additive, implying that the heat release rate is a function of the quantity of the phosphorus in the sample. In the case of the sample where 2.5% P was incorporated using K8P, the HRR peak could be decreased by 61%. Furthermore, in the case of the sample containing 2.5% of phosphorus as K4P4OH there is a shift in the time of the HRR peak, which is also advantageous.



K8P

Fig. 7. Full phosphorylation of *C*-methylcalix[4]resorcinarene.

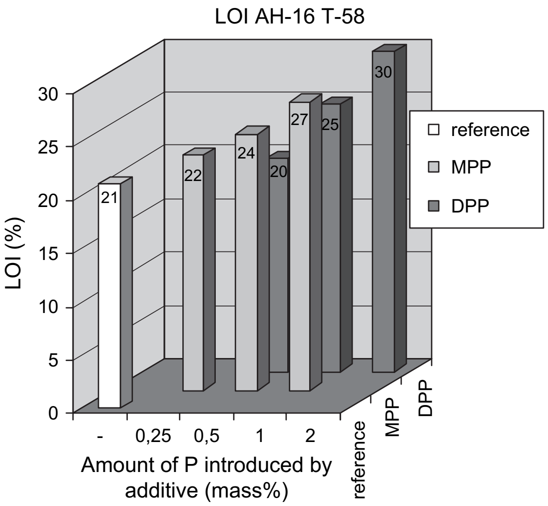


Fig. 8. LOI as the function of the amount of P introduced by MPP or DPP in case of AH-16 T-58 samples.

The amount of CO_2 evolved during the burning as a function of time is in accordance with the heat release rate: by increasing the quantity of phosphorus in the sample, the quantity of evolved CO_2 is decreased, showing that the burning is successfully retarded. The amount of evolved CO as a function of time shows that in the case of the samples containing 1.25% P of the additive the burning is retarded, and due to the more incomplete combustion, more CO is evolved than in case of the reference sample. In the case of the samples containing 2.5% P the burning is also retarded, but the barrier layer, formed on the surface of the samples, does not allow the evolved gases to emerge, therefore the CO peak decreased.

Having no reaction with the epoxy matrix, the phosphorylated calixresorcinarenes were expected to influence the crosslinking of the ER. The DSC runs taken during the crosslinking process of ER containing K4P4OH and K8P in various concentrations are shown in Figs. 12 and 13, respectively. A considerable shift of the exothermic peak occurs when the phosphorous additives are introduced. This shift is more concentration dependent in the case of partially phosphorylated calixresorcinarene (K4P4OH). The enthalpies of crosslinking and the LOI values are summarised in Table 4.

Table 3
DSC results of epoxy resin samples containing phosphorylated phloroglucine derivatives

Resin	Curing agent	Additive	Amount of P (mass%)	Exothermic peak (°C)	Enthalpy (J/g)
AH-16	T-58	–	–	80.4	−288.9
AH-16	T-58	MPP	0.25	78.0	−233.5
AH-16	T-58	MPP	0.5	80.8	−149.8
AH-16	T-58	MPP	1	81.2	−125.1
AH-16	T-58	DPP	0.5	78.3	−190.6
AH-16	T-58	DPP	1	79.4	−144.4
AH-16	T-58	DPP	2	80.1	−121.7

By increasing the ratio of K4P4OH or K8P incorporated in epoxy resin, the exothermic effect of the curing is decreased, which implies to lower network density; however, the decrease is less than in case of phosphorylated polyols. Considering the LOI values, one would expect better fire resistance from increasing the phosphorus content. However, it should be taken into account that increasing the amount of the additive decreases the crosslink density of the crosslinked network, which has an opposite effect on the fire resistance. Therefore, in case of K4P4OH the LOI increased only by 4–5, while in case of K8P by 3–7. The best result was achieved with the sample where 2.5% P was incorporated using K8P. Further increase is expected to be achieved by incorporation of reactive function in the phosphorylated calixresorcinarene molecules.

3.2.3. Combination of nanoclay additive with calixresorcinarenes

There were two reasons for combining the synthesized phosphorous compounds with nanoparticles:

1. Montmorillonite (MMT) nanoplatelets were expected to compensate the softening effect of the flame retardants.
2. Phosphorous flame retardants intercalated between the nanolayers were recently found to be very efficient in polypropylene and it was reasonable to try utilizing the same effect in ER.

K8P type phosphorylated calixresorcinarene was selected for combination with MMT. The organophilised MMT was introduced into ER in two forms: as a well dispersed, partially exfoliated additive and as an intercalated structure containing K8P between the MMT galleries (prepared according to the method described in Section 2). The results of the combined systems are given in Table 5.

It can be concluded that the incorporation of the nanoparticles did not give the desired effect concerning the flame retardancy: they did not influence the LOI values, but they degraded the UL-94 classification from V-0 to HB if we compare to the sample containing only K8P. This different effect of nanoparticles in thermoplastic and thermosetting matrix can most probably be explained by the differences in the degradation of the polymer matrix. In thermoplastic polymers flame retarded with MMT intercalated with phosphorylated polyol, the action of flame retardant starts with gas formation between layers of MMT separating the layers from each other and the formed gas bubbles tend to move out from the bulk driving the nanoparticles to the surface. The polymer matrix is protected this way in a very early phase [7]. In contrast, the crosslinked structure of thermosetting matrix hinders the migration of the nanoparticles to the surface and thus the rapid formation of the protective layer. Furthermore the mineral additive increasing the

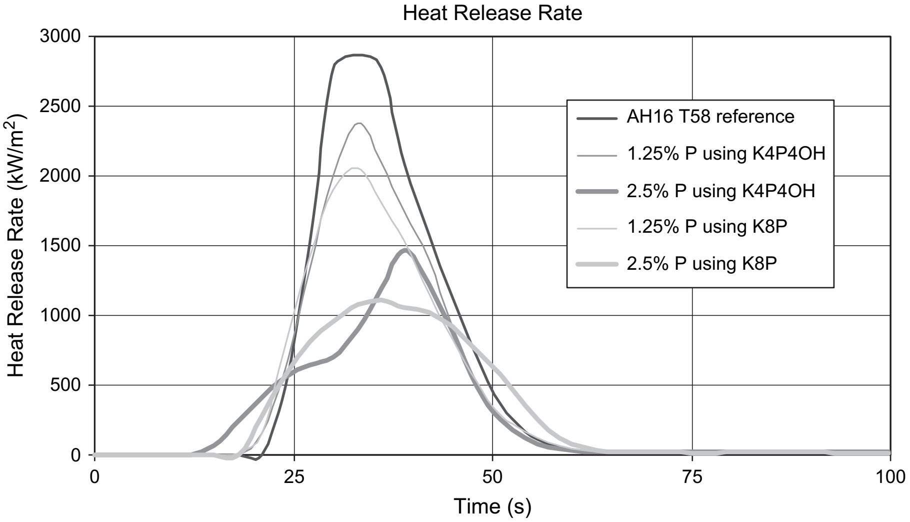


Fig. 9. Heat release rate of epoxy resins containing calixresorcinarenes.

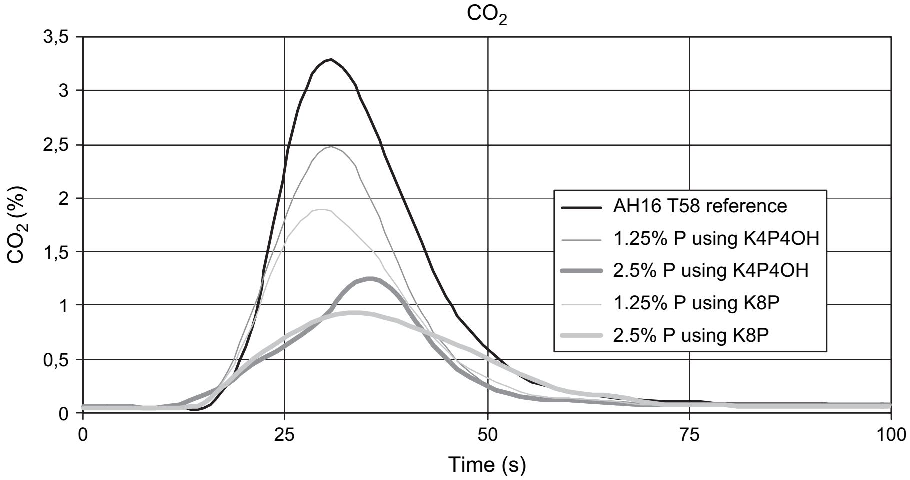


Fig. 10. Quantity of evolved CO_2 as a function of time during burning process.

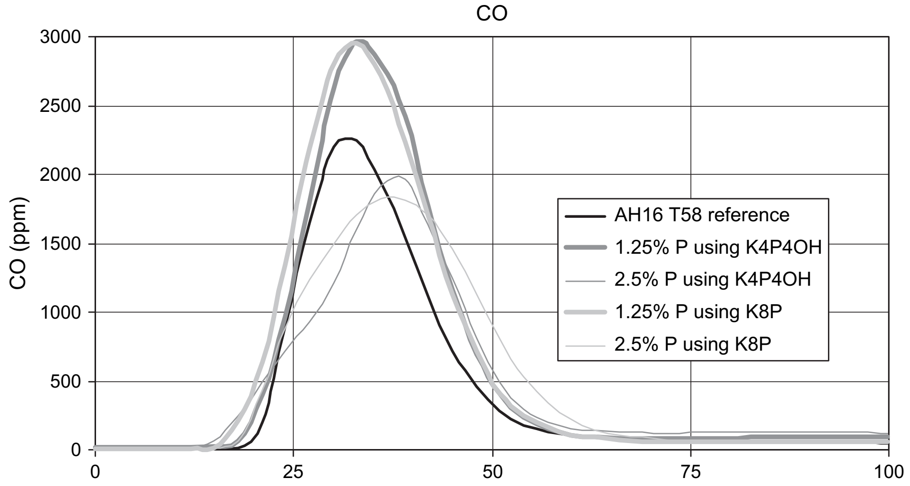


Fig. 11. Quantity of the evolved CO as a function of time during burning process.

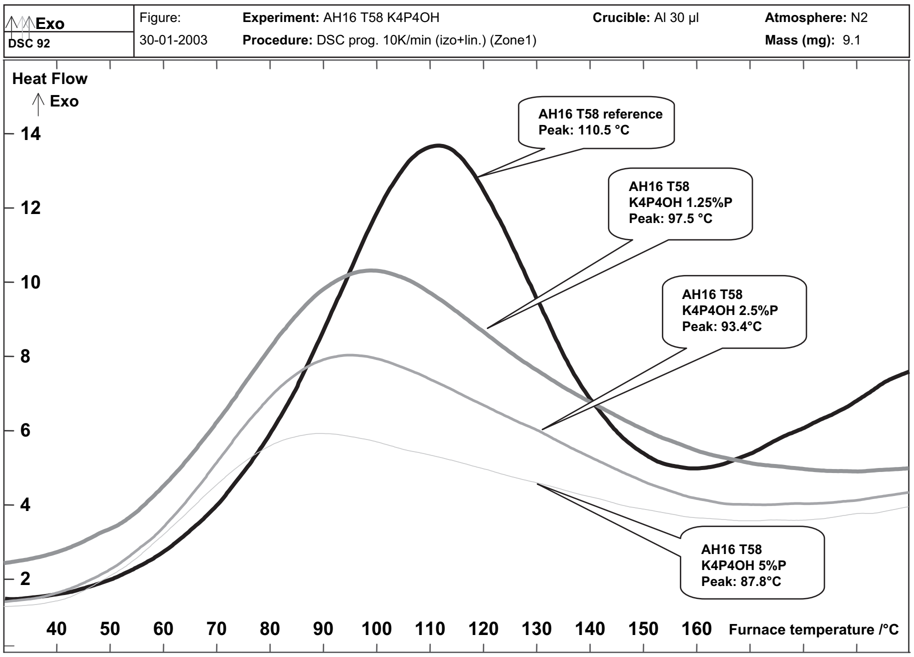


Fig. 12. Enthalpy of curing of ER samples containing K4P4OH.

heat conductivity of the samples decreases the UL-94 rating.

4. Conclusions

A simple method is proposed for the synthesis of partially and fully phosphorylated polyols, and a phosphorylation method reported earlier is extended to hydroxyphenols with higher molecular weight and better compatibility with polymers. The salt form of the additives is not advantageous in epoxy resin because the additives do not participate effectively in the crosslinking process. Using the fully phosphorylated calixresorcinarene derivative LOI value could be increased from 21 to 28 and V-0 UL-94 rating was achieved. Further

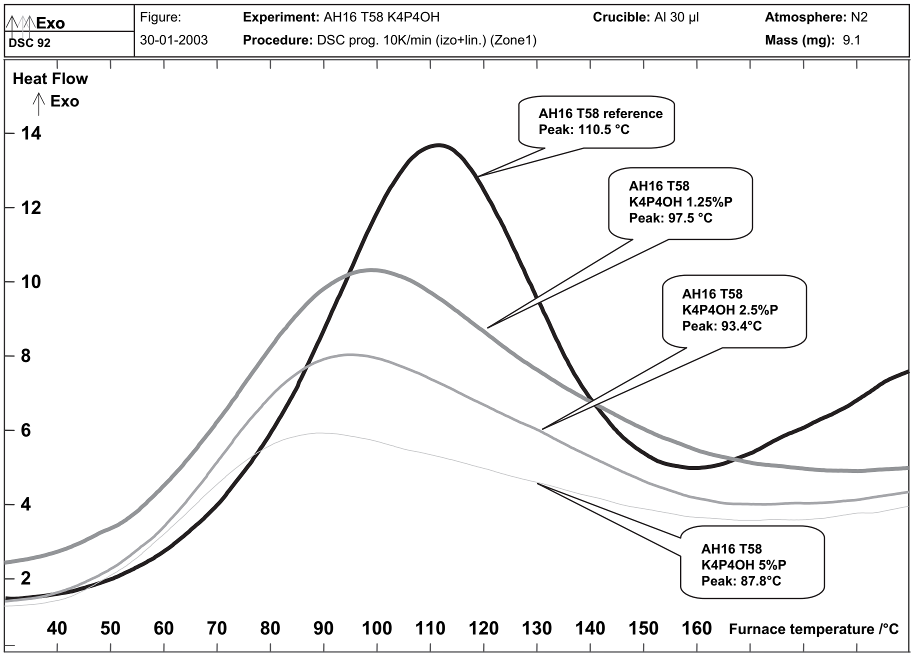


Fig. 13. Enthalpy of curing of ER samples containing K8P.

Table 4
DSC and LOI results of epoxy resin samples containing phosphorylated calixresorcinarene derivatives

Resin	Curing agent	Additive	Amount of P (mass%)	Enthalpy (J/g)	Limiting oxygen index (LOI) (%)
AH-16	T-58	–	–	−288.9	21
AH-16	T-58	K4P4OH	1.25	−281.5	25
AH-16	T-58	K4P4OH	2.5	−195.3	26
AH-16	T-58	K4P4OH	5	−153.3	26
AH-16	T-58	K8P	1.25	−242.4	24
AH-16	T-58	K8P	2.5	−221.3	28
AH-16	T-58	K8P	5	−70.5	–[a]

[a] No curing was observed, so the LOI could not be measured.

Table 5
LOI and UL-94 results of the ER systems containing nanoparticles

Resin	Curing agent	Additive	Amount of P (mass%)	Amount of MMT (mass%)	Form of MMT	Limiting oxygen index (LOI)	UL-94 level
AH-16	T-58	–	–	–	–	21	HB
AH-16	T-58	K8P	2.5	–	–	28	V-0
AH-16	T-58	K8P	2.5	1	Additive	28	HB
AH-16	T-58	K8P	2.5	2	Additive	28	HB
AH-16	T-58	K8P	2.5	1	Intercalated	28	HB

improvement is expected by incorporation of reactive function in the phosphorylated calixresorcinarene molecules. Introduction of montmorillonite nanoparticles either in disperse or intercalated form resulted in much less flame retardancy performance than (earlier) in thermoplastic matrixes. The lower mobility of the nanoparticles (due to the cross-linked structure) and the increased heat conductivity may be the reason behind the poorer performance of MMT in epoxy resin.

Acknowledgements

The authors acknowledge advices received from Prof. István Bitter concerning the synthesis of calixresorcinarenes and the financial supports received through the No 505637 EU-6 framework program (NMP3-CT-2004-505637), Széchényi OM-3A/0036/2002 project of Ministry of Education Hungary.

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