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A phosphazene compound multipurpose application -Composite material precursor and reactive flame retardant for epoxy resin materials

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Abstract

Cyclotriphosphazene containing the epoxy group hexaglycidyl cyclotriphosphazene (HGCP) was synthesized in one step. The reaction was a nucleophilic substitution of cyclophosphazene chlorine by the epoxy function of 2,3-Epoxy-1-propanol in presence of triethylamine. The purified compound of the reaction was characterized by FTIR, ^{31}P, ^{1}H, and ^{13}C -NMR nuclear magnetic resonance spectroscopy. This reactive monomer that is inherently flamed retarding contain P and N, can be used on their own as composite material precursor or added to current bulk commercial polymer diglycidylether of bisphenol A (DGEBA) to enhance flame retardancy. The thermal stability and flame retardancy of HGCP thermoset with MDA curing agent and its blend as flame retardant with DGEBA were checked by thermal gravimetric analysis coupled with infrared spectoscopy and the UL-94 vertical test. The correlation between these properties (thermal stability and flame retardancy) and the HGCP contents (phosphorus content) were discussed. The results show that HGCP as composite material precursor lead a good material with thermal stability at elevated temperature compared with DGEBA thermoset with MDA curing agent.

HGCP as flame retardant presents a good dispersion in DGEBA, and the blend thermoset with 4,4'-methylene-dianiline (MDA) curing agent leads to a significant improvement of the thermal stability at elevated temperature with higher char yields compared with pure DGEBA thermoset with the same curing agent. HGCP acts with an intumescent char-forming and gas action by CO_2 gas emission which its act to dilute the combustible gas. Improvement has also been observed in the fire behaviour of blend.

Keywords: Synthesis; epoxy resin; flame retardant; thermal stability.

1. Introduction

Epoxy resins are widely applied as advanced composite matrices in electronic/electrical industries where a remarkable flame-retardant grade is required, but the fire risk is a major drawback of these materials [1].

There are two approaches to achieve flame retardancy for polymers generally known as the “addition” and the “reaction”, and the latter is given much attention to recently [2]. Traditionally, brominated reactive compounds [3] are used as co-monomers with epoxy resins to obtain fire-retardant materials. However, flame-retardant epoxy resins containing bromine can produce corrosive and obscuring smoke and may give super-toxic halogenated dibenzodixines and dibazofurans with deleterious effects on the environment and human health. Recently, in consideration of environmental problems, researches for halogen-free fire-retardant epoxy resins have received a great deal of attention [4,5]. Phosphorylation is considered to be one of the most efficient methods to confer flame retardancy on epoxy resins [6-8], whereas phosphate-based epoxy resins could possess excellent flame retardancy only when using amine curing agents. Some studies indicated that the flame-retardant efficiency significantly improved when phosphorus and nitrogen existed simultaneously in the curing system of epoxy resin. Therefore, the phosphorus-nitrogen synergistic effect on flame retardancy is very interesting [9].

In recent years, there has been considerable interest in the phosphazene-based family of materials because they not only have a wide range of thermal and chemical stabilities, but also can provide improved thermal and flame-retardant properties to polymers and their composites [10-15]. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers. The chlorine groups attached to the phosphorus atoms are easily substituted by various nucleophiles to form reactive cyclotriphosphazenes.

Cyclotriphosphazene, as a ring compound consisting of alternating phosphorus and nitrogen atoms with two substituents attached to the phosphorus atoms, exhibits unusual thermal properties such as flame retardancy and self-extinguishability [16,17]. Cyclotriphosphazene has several advantages as a reactive flame-retardant functional oligomer. First, the flexible synthetic methodology can be developed for preparation of cyclotriphosphazene-based copolymer with various substituents, which allows us to obtain multifunctional initiators or terminators with ease. Second, thermal and nonflammable properties of the cyclotriphosphazene moieties can be conferred to the resulting polymers, especially, of low molecular weights [12,13,18-20].

Therefore, when cyclotriphosphazenes are incorporated into the network of thermoset polymers, they can increase the thermal property and flame retardancy of the polymers because of phosphorous and nitrogen flame-retardant synergy. The reason is that the thermal decomposition of the phosphazene-based polymers is an endothermic process, and 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; meanwhile, the inflammable gases released such as CO_2, NH_3 and N_2 cut off the supply of oxygen so as to achieve the aims of synergistic flame retardancy [21-24]. The phosphazene-based polymers have more effective flame retardancy than any other flame-retardants, making them a new focus [25-29]. However, the phosphazene-based polymers used as a flame-retardant component with epoxy resins are seldom reported [28].

In this report, we developed a novel nonflammable halogen-free epoxy resin by incorporating the cyclotriphosphazene group, and investigated the thermal property and flame-retardancy of this thermoset resin with MDA curing agent.

The synthesized phosphazene-containing epoxy group (HGCP) is a phosphazene compound multipurpose, it can be used both as composite material precursor and as flame retardant in epoxy resins.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene, 4,4'-methylene-dianiline (MDA) (Aldrich chemical company) and 2,3-epoxy-1-propanol (ACROS chemical company, 99%) stored at temperature of 4°C to 6 °C, DGEBA (Epon828). All these materials were used without any further purification.

2.2. Instrumentation

Infrared spectra were recorded on a Vertex 70 FT-IR spectrophotometer using KBr technique. ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) Spectra were obtained on a Bruker AVANCE 300 NMR Spectrometer using $CDCl_3$ as solvent. Chemical shifts (δ-scale) are quoted in parts per million and following abbreviations are used: s = singlet; m = multiplet.

Thermogravimetric analysis (TGA and DTA) were carried out on an SETARAM thermogravimetric analyzer (The SETSYS evolution) with a heating rate of 10°C/min from room temperature to 1000 °C under air atmosphere.

The DSC measurements were carried out using a PYRIS6 DSC in nitrogen atmosphere, with a heating rate of 10°C/min under N_2 from 40 to 300°C. UL 94 standard test carried out in terms of the method proposed by Underwriter laboratory. It was used to evaluate the fire retardancy properties of the materials.

The microstructures of samples and the chars were recorded using "MEB ENVIRONNEMENTAL" scanning electron microscope (SEM) coupled with (EDX) elementary analysis.

2.3. Synthesis of hexaglycidyl cyclotriphosphazene (HGCP)

Hexaglycidyl cyclotriphosphazene (HGCP) was synthesized in one step, according to the procedure literature [30,33]. The reaction was a nucleophilic substitution of cyclophosphazene chlorine by the epoxy function of 2,3-epoxy-1-propanol in presence of triethylamine (Figure 1). The purified compound of the reaction was characterized by FTIR, ^{31}P, ^{1}H, and ^{13}C -NMR nuclear magnetic resonance spectroscopy.

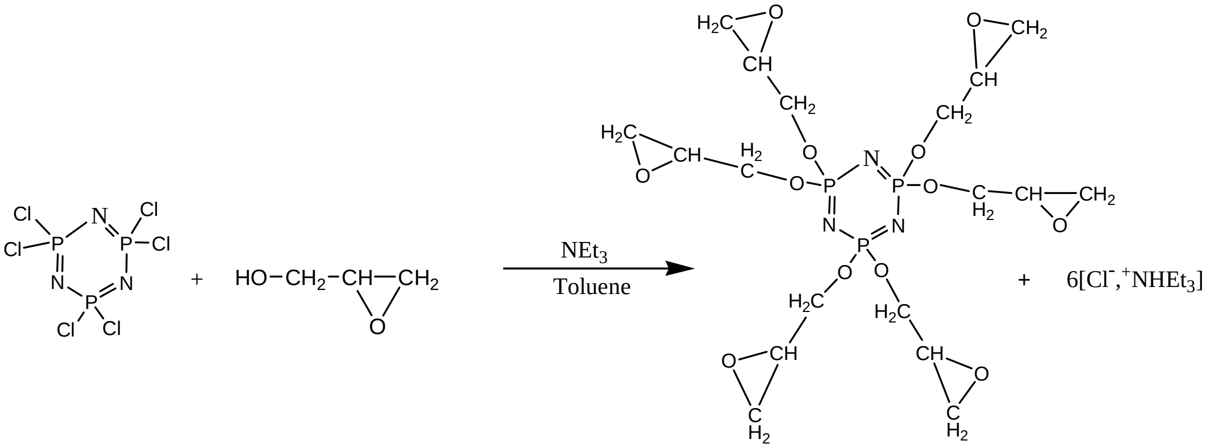


Figure 1. Synthesis of hexaglycidyl Cyclotriphosphazene (HGCP)

2.4. Sample preparation

Epoxies (HGCP, DGEBA and there blend) were warmed to melt and the curing agent (Scheme 1) added and mixed until homogeneous. The resin-hardener mixture was then poured into preheated molds and cured in a forced convection oven to make samples (Figure 2).

The mixture of the epoxy resin with 4,4'-methylene-dianiline (MDA) curing agent before the crosslinking is carried out according to the protocol adopted by Levan [34]. The formulations and cure schedules were as follows:

*The samples were prepared by mixing stoichiometric amount of MDA and epoxy resins HGCP, DGEBA and there blend.

*The samples thus prepared were underwent the cycle of heating: one night with 70°C, three hours with l00°C, two hours with 120°C, one hour with 140°C and 30 minutes with 150°C.

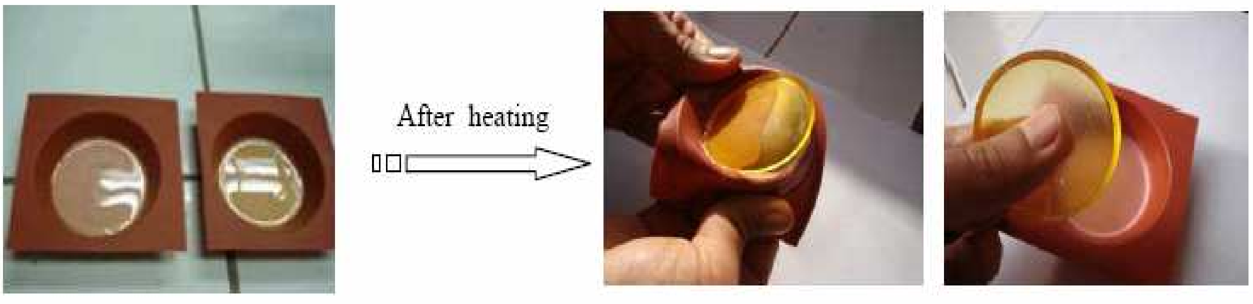


Figure 2. Technical of samples preparation

Table 1. Formulations prepared of (DGEBA/HGCP) thermosets with MDA curing agent

Samples	%DGEBA per 100g of blend	% HGCP per 100g of blend	Parts of MDA to thermoset 100g of (DGEBA/HGCP) blend (g)
1	100	0	29
2	95	5	29
3	90	10	30
4	85	15	32
5	80	20	33

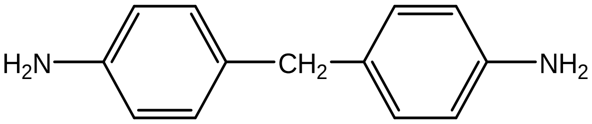
3. Results and discussions

3.1. Composite material precursor application

HGCP have been examined for its application as composite material precursor [33]. Compared to DGEBA, the thermal stability and flame retardancy of HGCP thermoset with MDA curing agent were checked by thermal gravimetric analysis coupled with infrared spectoscopy and the UL-94 vertical test. The correlation between these properties (thermal stability and flame retardancy) were discussed.

3.1.1. Reactivity of HGCP and DGEBA toward the MDA Curing Agent

MDA is a reactive agent (the free NH_2 groups make it capable to react with epoxy groups), it was expected to act as crosslinking agent (Scheme 1).



Scheme 1. Chemical structures of 4,4’-methylene-dianiline (MDA) using as curing epoxy resins.

In order to evaluate the effect of structure of HGCP resin compared to that of DGEBA on curing behavior with MDA, studies were carried out using stoichiometric ratio of (HGCP and MDA), (DGEBA and MDA). The characteristic curing temperatures are summarized in table II.

Therefore, onset temperature T_0 of exotherm may be used as a criterion for evaluating the relative reactivity of various resins.

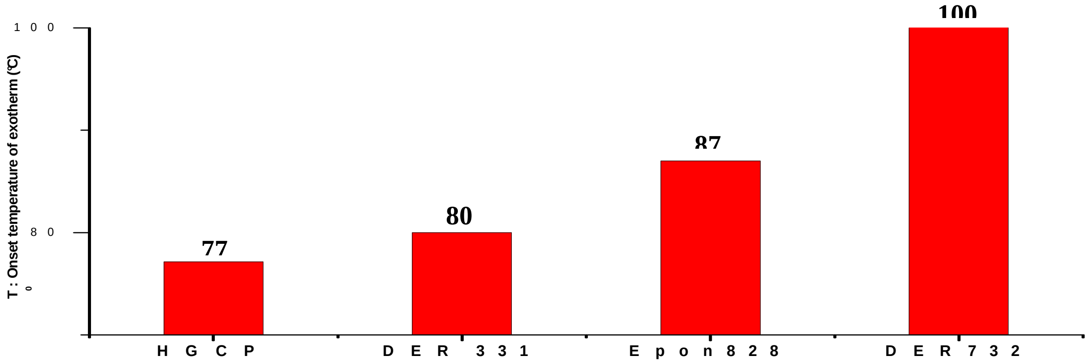


Figure 3. The Initial Curing Temperature of HGCP and DGEBA Epoxy resins cured by the MDA curing agent.

The exothermic peaks were observed in the system (HGCP/MDA): the onset temperature of exothermic peak was observed at 77.13 °C, while the systems (DGEBA/MDA) such as (DER 331/MDA), (Epon828/MDA) and (DER732/MDA) according to other studies [28] the onset temperature of exothermic peak was higher than that observed in (HGCP/MDA) system (Figure 3).

We can conclude that the HGCP is more reactive toward MDA than the DGEBA epoxy resin, because the amine–epoxy cross-linking reactions of (HGCP/MDA) was faster than that of (DGEBA/MDA). This may be ascribed to the electronic effect. The polymerization of an epoxy resin with an amine is considered to occur via a nucleophilic attack of the amine nitrogen on the methylene carbon atom of the epoxy group. The electron withdrawing cyclotriphosphazene ring in the HGCP reduces the electron density of the methylene carbon atom and makes the reaction between the oxirane ring and the amine easier.

On the other hand, in a densely cross-linked structure, the HGCP hydroxyls and residual epoxy groups were likely to remain immobilized and unable to react together easily, lead the end of the exotherm until 231 °C.

3.1.2. Thermal behaviour and mechanism degradation

The thermal properties of the cured epoxy polymers were evaluated by TGA under air.

Figure 4 shows the TGA thermograms of the cured HGCP/MDA and Epon828/MDA polymers. The Epon828/MDA polymer exhibited a 5% weight loss at 311 °C and a rapid weight loss around 362 °C. Unlike the one-stage weight-loss behaviour of the Epon828/MDA polymer, the HGCP/MDA polymer showed two stages weight loss (figure 5). The first maximum weight-loss temperature (T_{max1}) around 258 °C indicates that the thermal stability of the HGCP/MDA polymer was less than that of the Epon828/MDA polymer. This is attributed to the less stable P-O-C bond linkage. This result is the same with that reported in the previous study [35].

This degradation as we can see in DTA curve (figure 6) has an endothermic effect. Nevertheless, the percentage of the weight loss of HGCP/MDA before reaching 257 °C was less than 5%. This weight loss could be ascribed to the decomposition of the phosphate groups that caused the formation of the phosphorus-rich residues to inhibit further decomposition of the polymer. Consequently, the second maximum weight-loss temperature (T_{max2}) of the HGCP/MDA polymer was higher than the T_{max} of the Epon828/MDA polymer (as listed in table 2), implying that the thermal stability of the resin at a high temperature was improved as the phosphate and the cyclotriphosphazene moieties were covalently incorporated into the epoxy resins. This phenomenon, in agreement with other studies [36], played an important role in improving the flame-retardant properties of the resins. The second degradation as we can see in DTA curve (figure 6) is exothermic which might be ascribed to the generation of P-O-P. The appearance of P-O-P group can be considered as a crosslinker linking to different species, resulting in the formation of complex phosphorus structures [37].

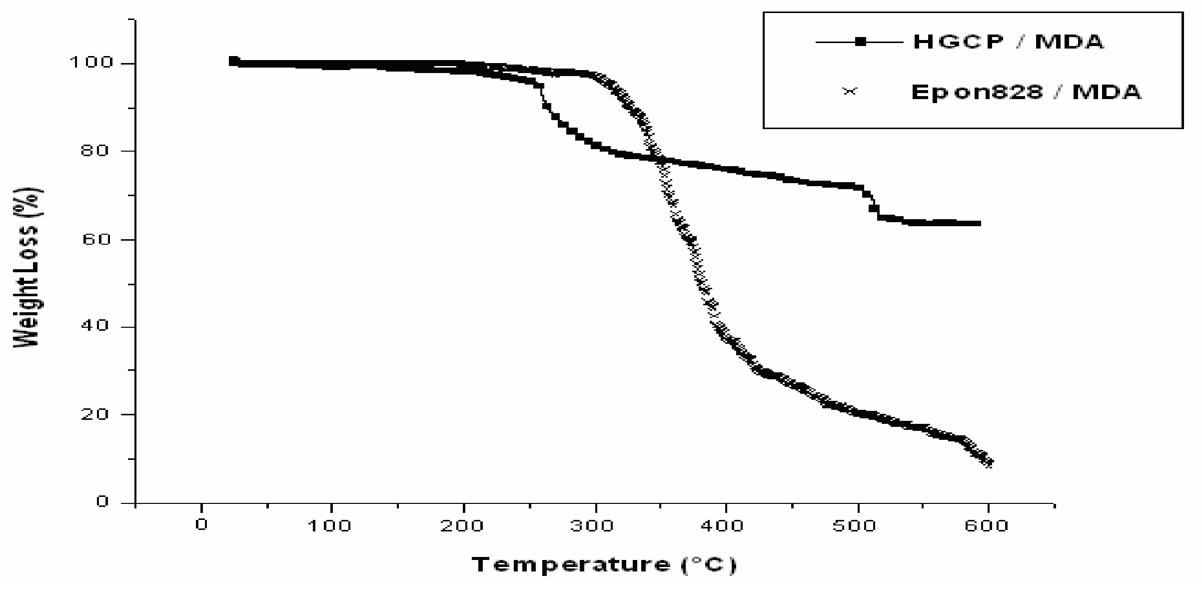


Figure 4. Thermogravimetric analysis of samples (HGCP/MDA) and (DGEBA/MDA) in air atmosphere at 10°C min^{-1} heating rate

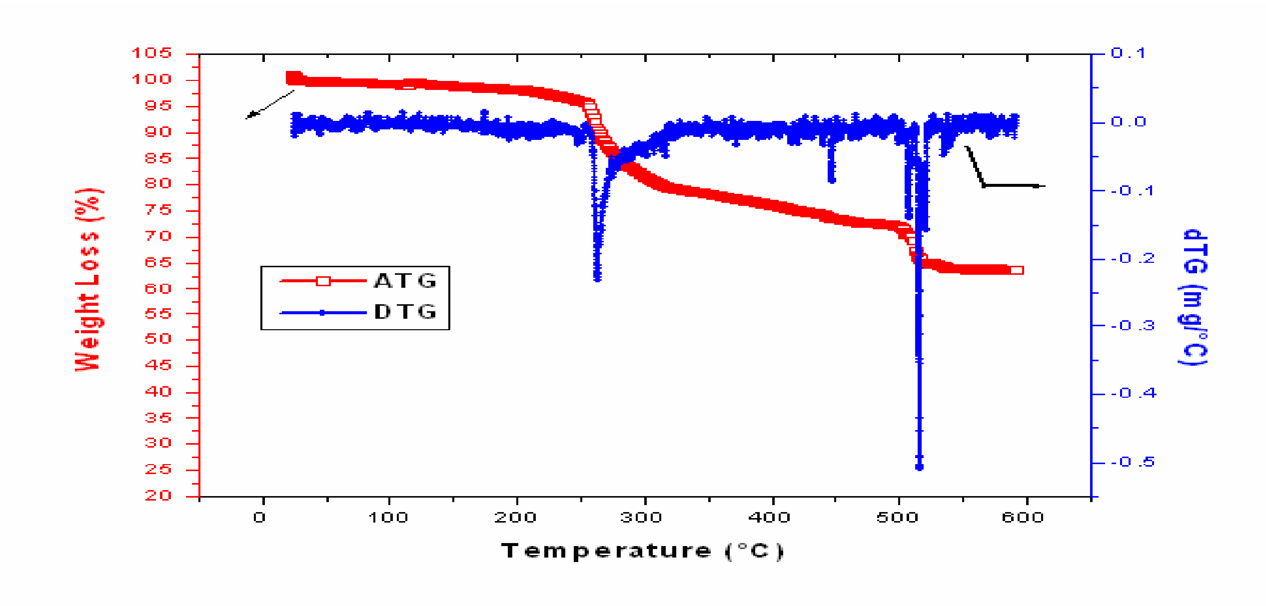


Figure 5. Thermogravimetric analysis of sample (HGCP/MDA) and first derivative under air atmosphere and with 10°C min^{-1} heating rate.

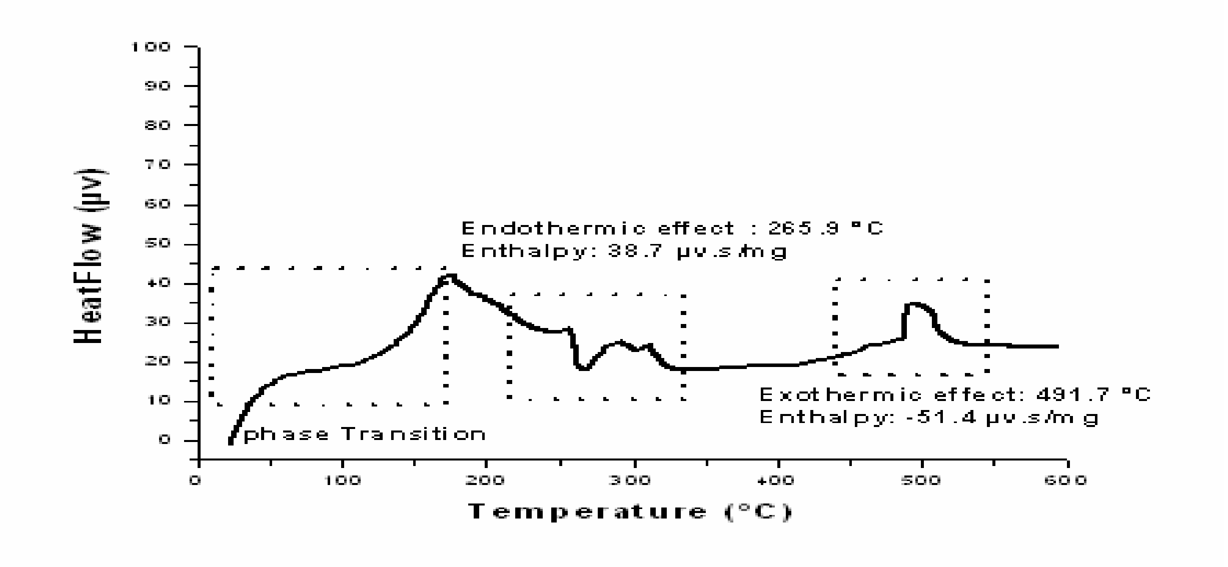


Figure 6. DTA analysis of sample (HGCP/MDA) in air atmosphere at a 10°C min^{-1}

Table 2. Thermogravimetric data of the HGCP.

Samples	**Temperatures of weight loss from TGA (°C) (in Air)**				**Char (%) at 500°C**	**HeatFlow DTA**	
	5%	**10%**	**Tmax 1**	**Tmax 2**			
HGCP/MDA	257	263	258	512	71.9	Tmax$_1$: 265.9°C Endothermic effect	Tmax$_2$:491.7°C Exothermic effect
						Enthalpy 38.7 µV.s/mg	Enthalpy -51.4 µV.s/mg
Epon 828 /MDA	311	325	-	362	20	-	

Figure 7 shows the FTIR spectra of residual products of HGCP/MDA degraded at different temperatures. The absorption of cyclophosphazene (1183 cm^{-1} and 1249 cm^{-1}) is still rather strong at 250 °C. However, in the FTIR spectra of HGCP/MDA , the absorption peak at 1013 cm^{-1} due to P-O-C bond decrease with the increasing temperature and disappear at 500 °C. The characteristic absorption peaks for P=N at about 1209 cm^{-1} and for ester group at 1183 cm^{-1} also disappear at 500 °C.

Moreover, a new peak at 1079 cm^{-1}, which might be ascribed to the generation of P-O-P, and appear at 500 °C. This is in agreement also with the TGA, DTG and DTA data for our sample (HGCP/MDA).

The formation of phosphorus-rich char in the decomposition of cyclotriphosphazene-containing epoxy resins not only increased the weight-loss temperature in the high-temperature region but also resulted in a high char yield (figure 8).

This category of flame retarding mechanism is that known as ‘intumescent’, in which materials swell when exposed to fire or heat to form a porous foamed mass, usually carbonaceous, which acts in the condensed phase promoting char formation on the surface as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air. This act is an agreement with the result of study of gases evolved during TGA trials in air atmosphere by means of thermogravimetry coupled with Fourier transform infrared spectroscopy (TG–FTIR) (figure 9), which indicate the reduction of gaseous products in the case of HGCP/MDA compared with DGEBA/MDA sample. But we can observe the CO_2 emission (2250 cm^{-1}) which persist in gas phase’s; such a gas can plays an important role in autoextinguiblity of sample.

In general, phosphazenes give high char yields at elevate temperatures and also undergo a high degree of cross-linking to form a dense ultrastructure [38-41].

An increase in char formation limit the production of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, and decrease the thermal conductivity of the surface of a burning material. Therefore, the flammability of the material is reduced. UL-94 test results are also given in table 3. V-0 rating was obtained for HGCP/MDA. By way of comparison with DGEBA, HGCP exhibited self-extinguishing characteristics in the UL94 V test.

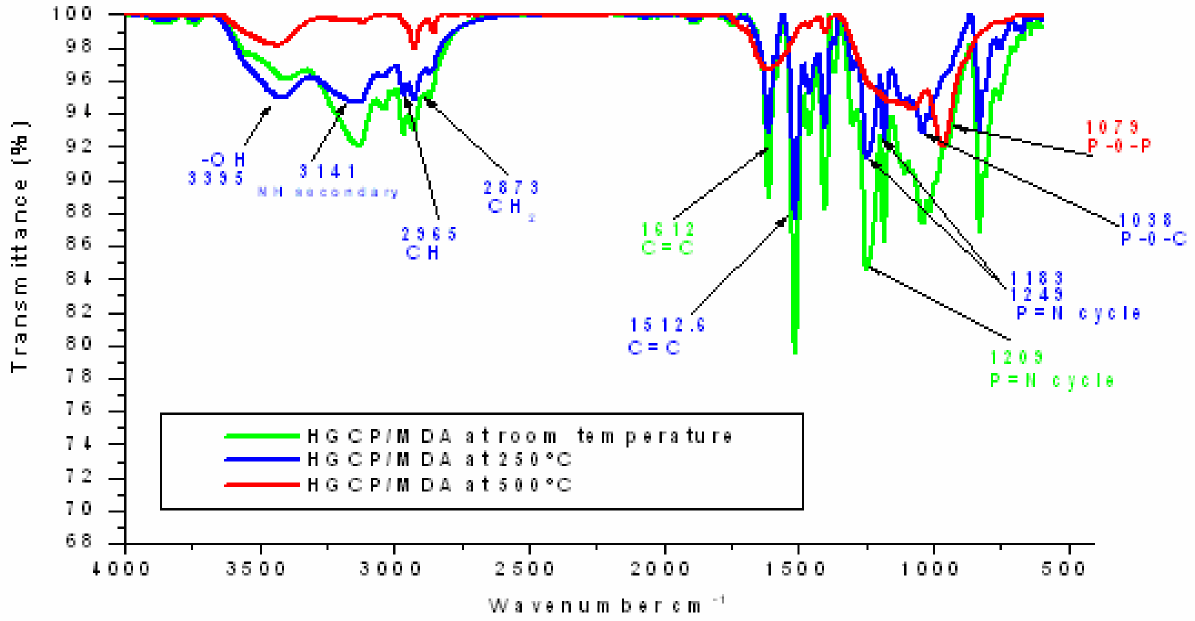


Figure 7. FTIR spectra the thermal degradation of HGCP/MDA sample in room temperature, 250 and 500 °C.

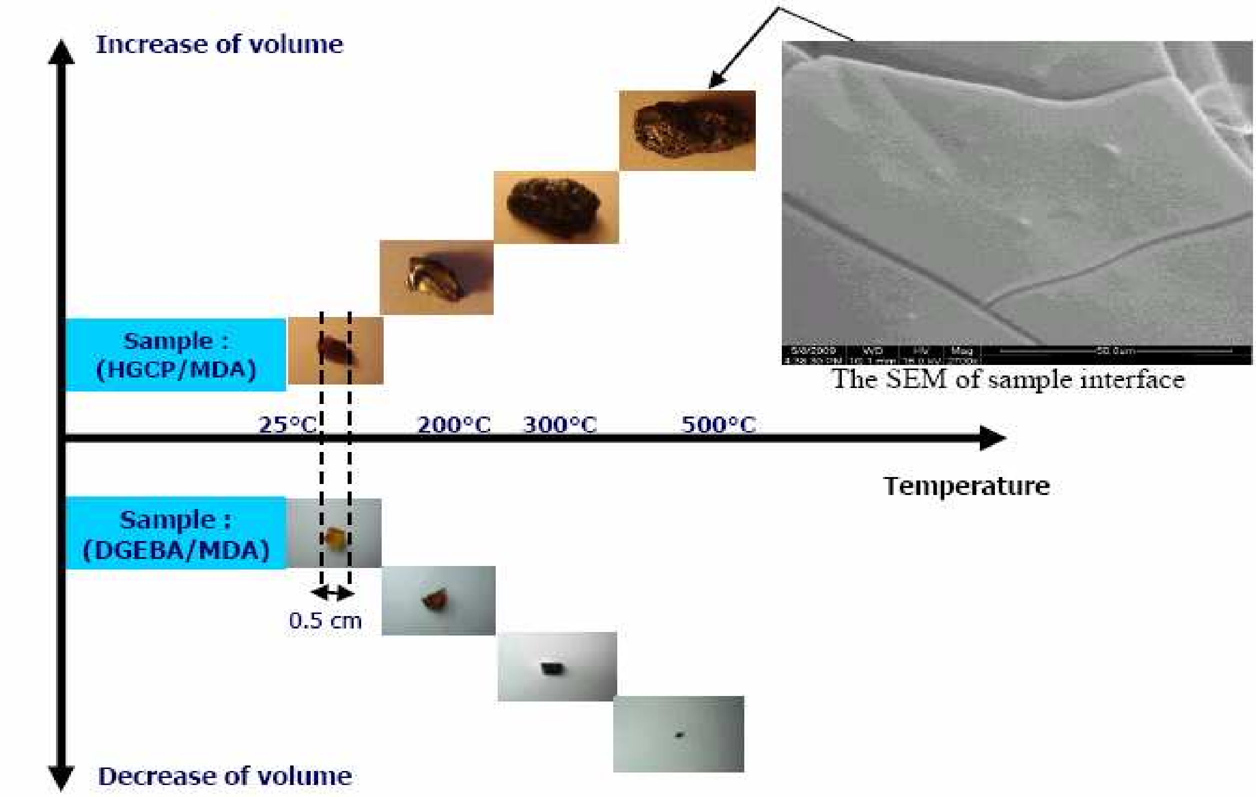


Figure 8. Evolution of samples volume of (HGCP /MDA) and (DGEBA / MDA) at different temperature heating in the range of RT—500 °C.

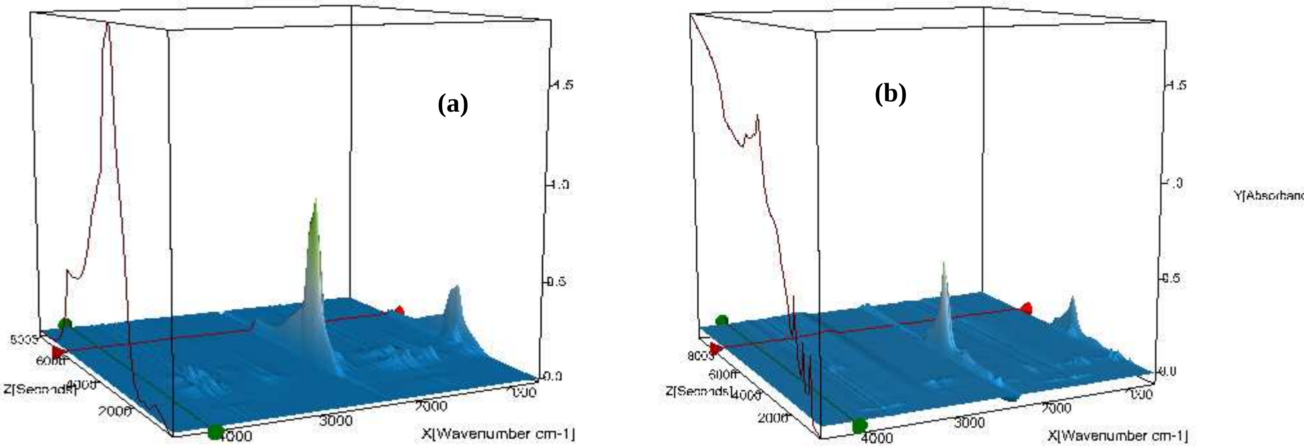


Figure 9. FT-IR spectrum of gas evolved during TGA of DGEBA/MDA (a) and HGCP/MDA (b)

Table 3. Flammability data

Epoxy resin/MDA	Dripping	UL94 rating (*)	Remarks
HGCP/MDA	No	V0	Very light smoke
DGEBA/MDA	No	Burning	Very strong black smoke

(*) V-0 (vertical burn classification): Burning stops within 10 seconds. No flaming drips are allowed. Flaming drips, widely recognized as a main source for the spread of flames, distinguish V1 from V2.

3.2. Reactive flame retardant application

HGCP have been examined for its application as flame retardant for composite material based on DGEBA epoxy resin [30]. The thermal stability and flame retardancy of DGEBA flame retarded with different amount of HGCP were thermoset with MDA curing agent and were checked by thermal gravimetric analysis coupled with infrared spectoscopy and the UL-94 vertical test. The correlation between these properties (thermal stability and flame retardancy) were discussed.

3.2.1. Dispersion of flame retardant with base polymer matrix

- Physical mixing of DGEBA and HGCP

It is important for the flame retardant additive to be dispersed in polymer matrix for improved flame retardancy properties. Since the HGCP is coated with organic groups such as epoxy groups and DGEBA is an organic prepolymer epoxy resin, well dispersion was expected. Due to compatibility occurring between two species, flame retardant additive disperse in prepolymer DGEBA and no agglomerates are observed (Figure 10). In the opposite, this result compared with the mixture of DGEBA and $[NPCl_2]_3$ we can observe the agglomeration of this last which indicates the no compatibility of this inorganic compound in the organic matrix of DGEBA. This is an argument for our compound HGCP of its well dispersion in DGEBA due to the organic groups of epoxy functions attached in cyclophosphazene

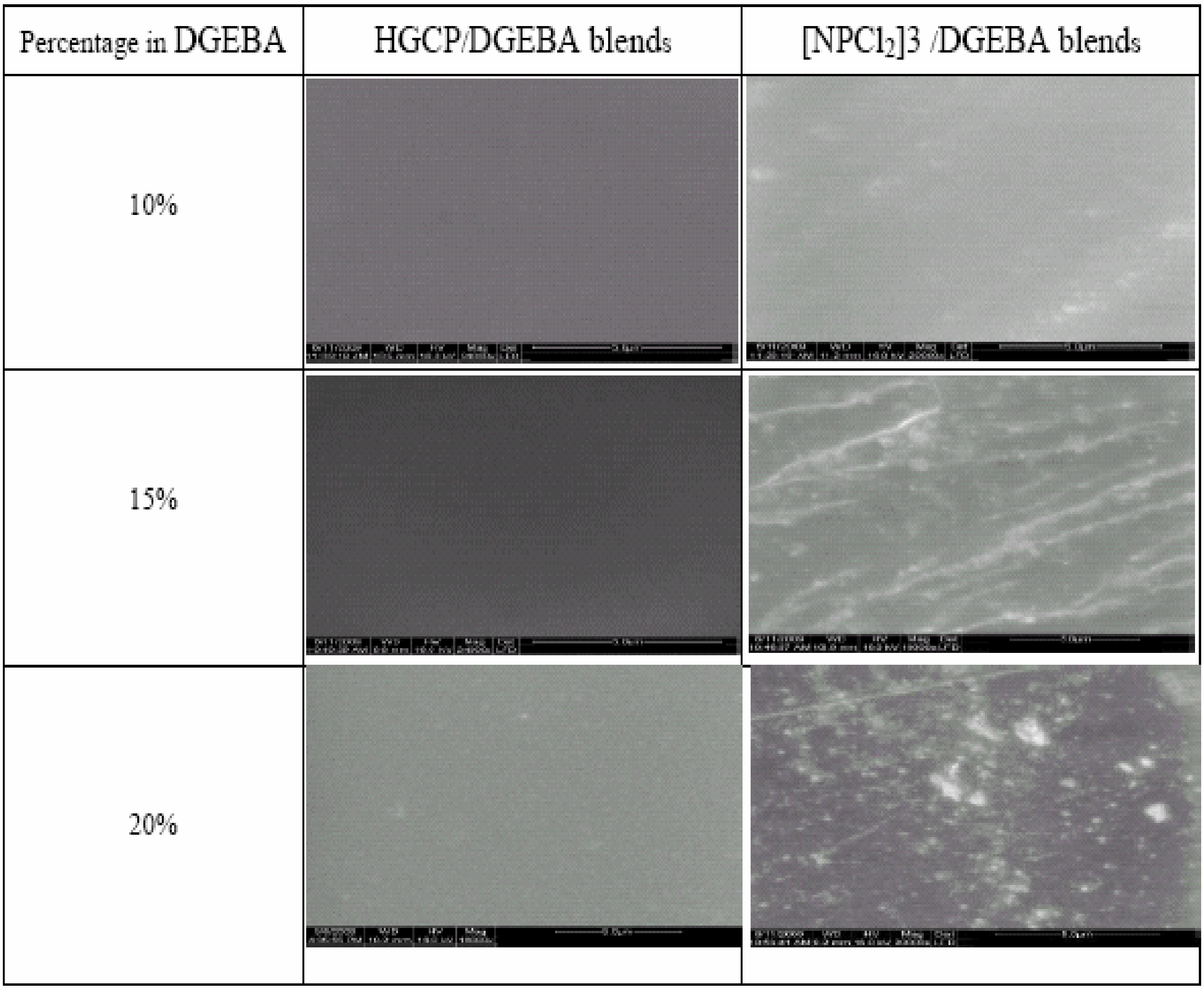


Figure 10. The SEM results of the physically blended DGEBA and flame retardant “HGCP” compound in melt blender, DGEBA/$[NPCl_2]3$ blends. [30]

3.2.2. Reactivity of (DGEBA/HGCP) blend toward the MDA curing agent

MDA is a reactive agent (the free NH_2 groups make it capable to react with epoxy groups), it was expected to act as crosslinking agent.

In order to evaluate the effect of (HGCP/DGEBA) blend on curing behavior with MDA, studies were carried out using a DSC stoichiometric ratio of (DGEBA/20%HGCP) and MDA, with a heating rate of 10 °C/min under nitrogen atmosphere from 40 to 300 °C.

The characteristic curing temperatures are summarized in table 4.

Table 4. The Initial Curing Temperature of HGCP and DGEBA Epoxy resins cured by the MDA curing agent. [30]

Epoxy Resin/ MDA	**T_0: Onset temperature of exotherm (°C)**
HGCP	77
DGEBA	95
DGEBA/20%HGCP	93

Therefore, the exothermic onset temperature (T_0) may be used as a criterion for evaluating the relative reactivity of resins.

In the case of (HGCP/MDA) system, the onset temperature of exothermic peak was observed at 77 °C, while the (DGEBA/ 20%HGCP/MDA) and (DGEBA/MDA) systems, the onset temperature of exothermic peak was higher than that observed in (HGCP/MDA) system, around the 95°C (Table 4). But the addition of HGCP in DGEBA gives a large exothermic peak and no significant effect on the onset temperature of DGEBA epoxy resin. And it evident that all blends witch HGCP is less than 20% can gives no effect on the onset temperature of DGEBA epoxy resin.

We can conclude also that the HGCP is more reactive toward MDA when it is only mixed with the curing agent because the epoxy groups of HGCP are in direct contact with amine of MDA and it makes the amine–epoxy cross-linking reactions of (HGCP/MDA) faster than that of blend (DGEBA/20%HGCP/MDA).

3.2.3. Thermal behavior

The thermal stability of a polymeric material is very important while used as a flame retardant which mainly concerns the release of decomposition products and the formation of a char. Thermal stability of HGCP an its blend with DGEBA cured by MDA were characterized using TGA as illustrated in below figures. Char yields were investigated to obtain information the fire resistance of samples. Figure 11 shows the TGA and DTG curves for the DGEBA, HGCP and there blends cured by MDA. The pure DGEBA sample began to lose its weight at about 300 °C and degraded in the range of 300–450 °C with around 50% weight loss and little residue remained at above 600 °C.

The HGCP/DGEBA blends have a lower initial decomposition temperature of around 247 °C, and they have the same degradation behaviour in the range of 247–342 °C. This is attributed to the less stable P-O-C bond linkage and to the easy decomposition of organic network and the highest phosphorus content in HGCP molecule. This result is the same with that reported in the previous study [42]. For DGEBA sample, the weight loss at 370 °C reached to 60% due to its more volatile side organic group. The char yield of (DGEBA/HGCP/MDA) at elevated temperature increase with the increasing of HGCP amount in sample because the phosphorus content increase gradually. So, the TGA curves for (DGEBA/MDA) and (DGEBA/HGCP/MDA) samples show significant difference over 600 °C. The (DGEBA/HGCP/MDA) samples present a slower mass loss rate and a highest char yield due to the phosphorus content of HGCP and the organic content in DGEBA.

DGEBA without flame retardant (HGCP) begins to decompose first at 300°C, and second phase of weight loss was at 486°C and totally degraded at 650°C. When HGCP is added to DGEBA matrix, thermal stability of compound increases as expected. From the first derivative it is observed that existence of HGCP decreases amount of exothermic reactions. Addition of HGCP pulled first decomposition of (DGEBA/HGCP/MDA) blends around 245°C. However, the stability increased up to 800°C. DGEBA with HGCP preserves 20% of its original weight at 800°C in contrast with neat DGEBA compound was totally disappeared.

3.2.4. Degradation mechanism

- Condensed phase action

The TGA results indicated that cyclophosphazenes play important roles to increase the thermal stability of DGEBA at elevated temperatures. However, its stability at lower temperatures decreases. To further investigate their influence, in-situ FTIR was used to monitor the thermal degradation of DGEBA, HGCP and the blend from room temperature (RT) to 500 °C.

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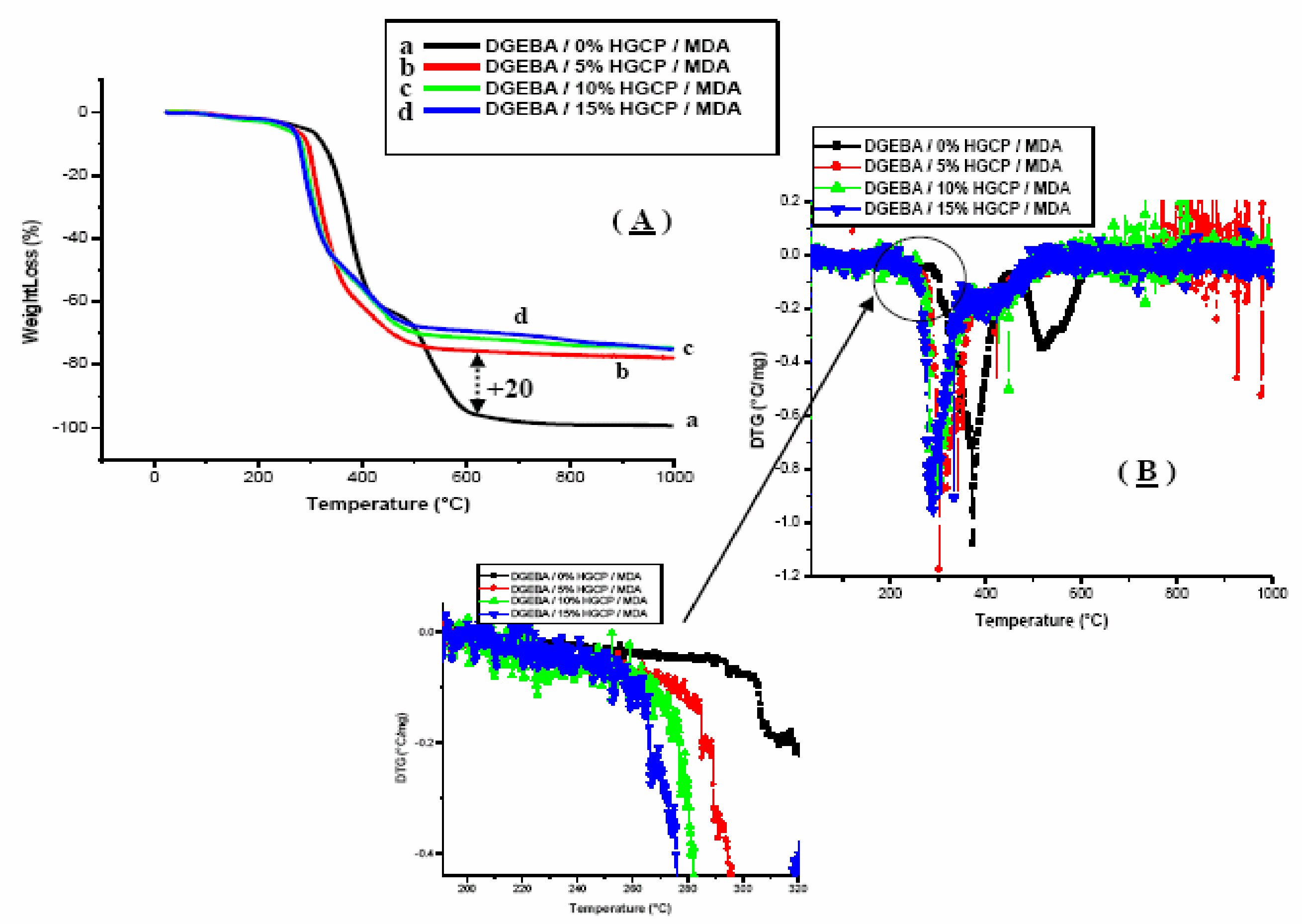

Figure 11. Thermogravimetric analysis (A) and first derivative (B) of samples (HGCP/MDA), (DGEBA/MDA) and (DGEBA/HGCP/MDA) under nitrogen atmosphere at a 10°C min^{-1} heating rate.

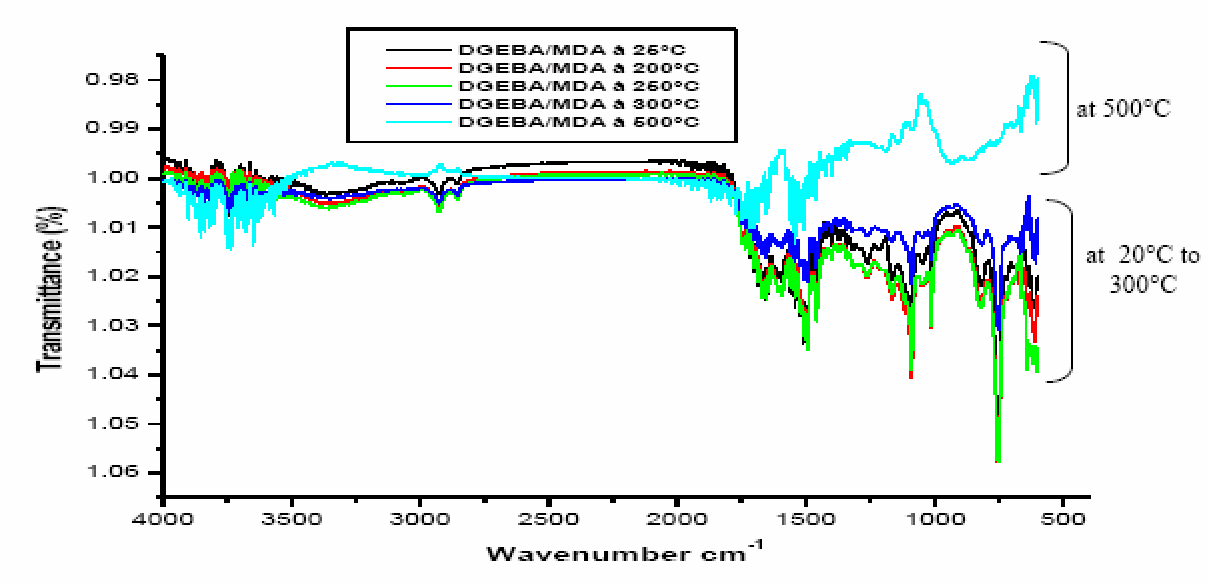

Figure 12. FTIR spectra the thermal degradation of DGEBA/MDA sample in room temperature to 500 °C.

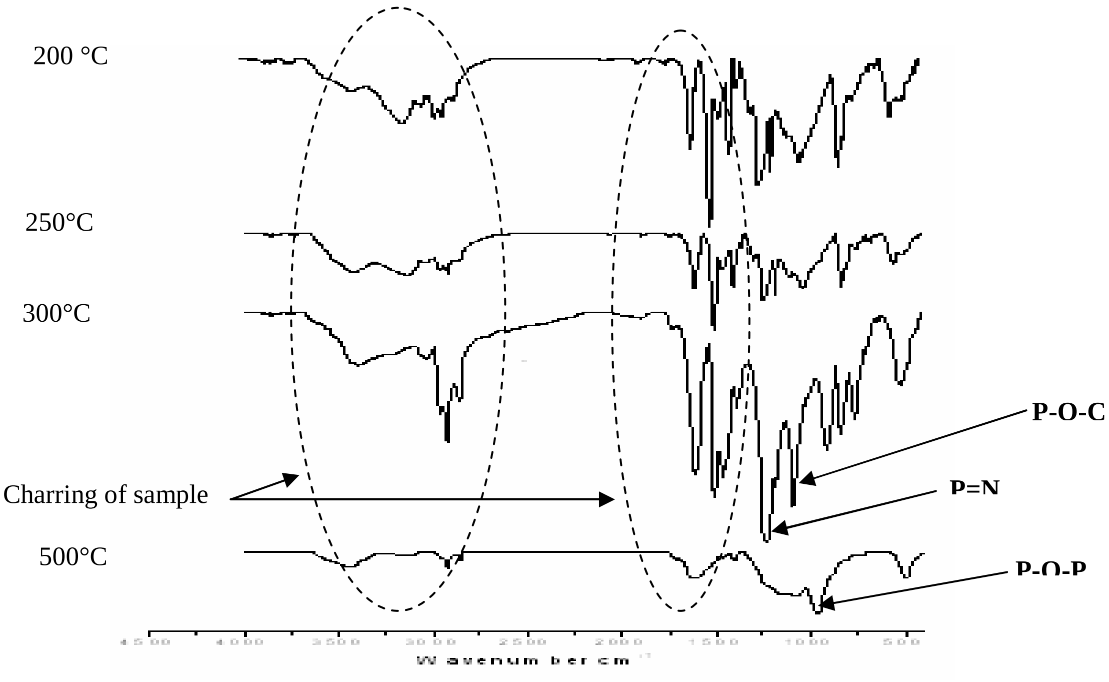

Figure 13. FTIR spectra the thermal degradation of DGEBA/HGCP/MDA sample in room temperature to 500 °C.

The residual products of (DGEBA/MDA) sample degraded at different temperatures were analysed by FTIR (Figure 12). There was little change in the absorption peaks of the FTIR spectra before 300 °C, which is consistence with the TGA result. The absorption of ether group (1089 cm^{-1} and 1012 cm^{-1}) is still rather strong at 300 °C. No new absorption bands have been found during the thermal degradation period. However, in the FTIR spectra of (DGEBA/20%HGCP/MDA) sample (Figure 13), the absorption peaks at 1013 cm^{-1} and 903 cm^{-1} due to P-O-C bond decrease with the increasing temperature and disappear at 250 °C. The characteristic absorption peaks for P=N at about 1240 cm^{-1} and for ether group at 1170 cm^{-1}, 1240 cm^{-1} also disappear at elevated temperatures. Compared with those in (DGEBA/MDA) sample, the absorption peaks at 2850–2980 cm^{-1} (C–H) in the spectra of (DGEBA/20%HGCP/MDA) sample decrease more quickly with the increasing temperature.

Moreover, a few new peaks at 1079 cm^{-1}, which might be ascribed to the generation of P-O-P, and appear at 500 °C. This is in agreement also with the TGA and DTG data for our samples. Similar to the mechanism which has been reported [43,44], one possible reason for the result is that cyclophoshazenes could experience the reactions as follows while heating (Figure 14):

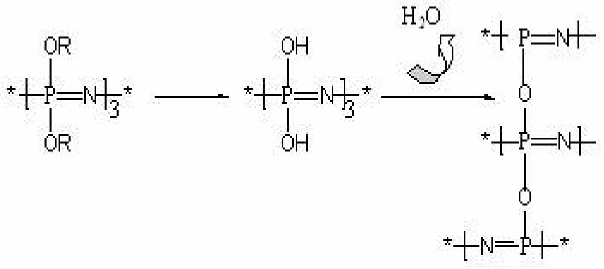

Figure 14. Mechanism decomposition of HGCP in DGEBA matrix.

The obtained structure could act as an acid catalyst, which would accelerate the cleavage of side groups and the breaking of ether groups (P-O-C) in HGCP and its blend with DGEBA. Then, the degradation products reacted with the residue of (DGEBA/20%HGCP/MDA) and formed more stable structures. The appearance of P-O-P group is considered a crosslinker linking to different species, resulting in the formation of complex phosphorus structures [42]. This is why the thermal degradation of the blend containing cyclophosphazenes is much slower than DGEBA at above 400 °C (Figure 11).

The formation of phosphorus-rich char (Figure 15) in the decomposition of blend was observed with high char in high-temperature region.

We can conclude that HGCP has an intumescent action in condensed phase of blend.

- *Gas phase action*

The cyclotriphosphazene moieties can release the inflammable gases such as CO_2, NH_3 and N_2 during burning to dilute the hot atmosphere and cool the pyrolysis zone at the combustion surface. These mentioned inflammable gases can cut off the supply of oxygen.

This act is an agreement with the results of the study of gases evolved during TGA trials in air atmosphere by means of thermogravimetry coupled with Fourier transform infrared spectroscopy (TG–FTIR) (Figure 16) [45].

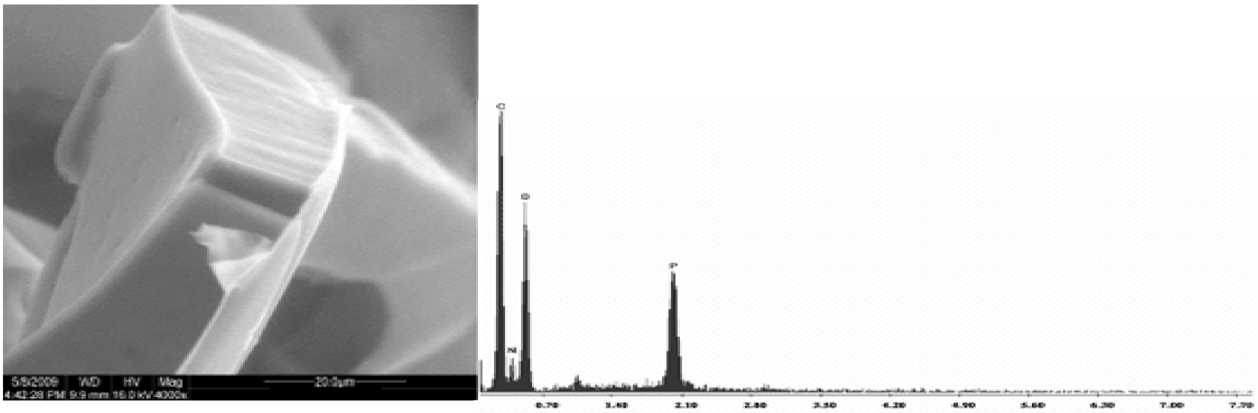

Figure 15. The SEM results and EDX analysis of the barrier formed on the surface of (DGEBA/HGCP/MDA) sample at 600°C.

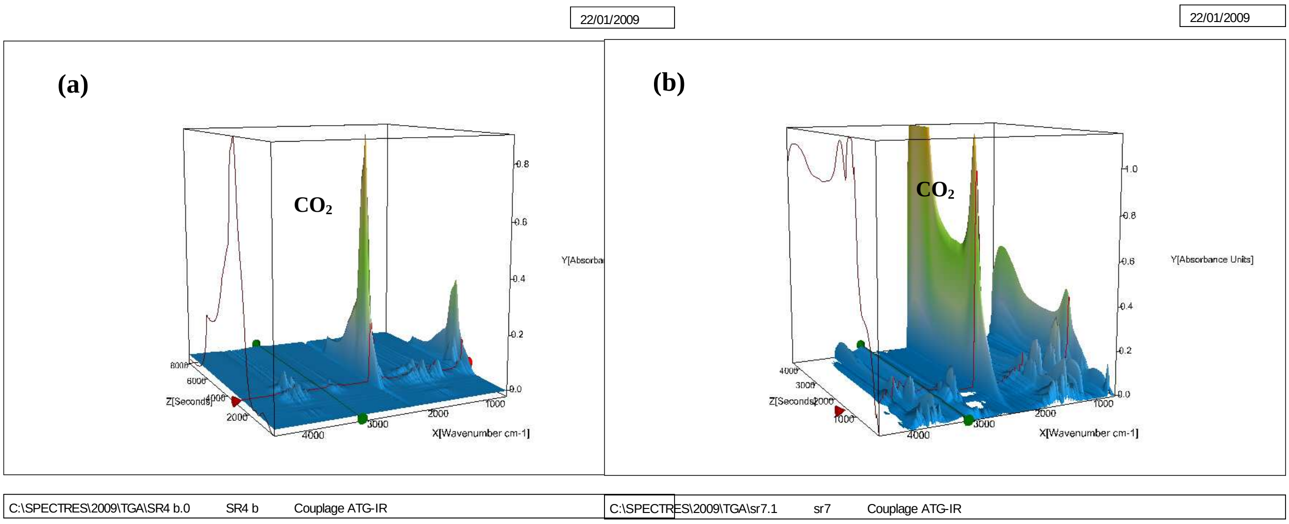

Figure 16. IR of Gases involved during the TGA analysis of DGEBA/MDA sample: (a) and DGEBA/HGCP/MDA sample(b)

The incorporation of HGCP to DGEBA epoxy resin decreases the time and the temperature of CO_2 emission, compared to the pure (DGEBA/MDA) sample. This act can play a very important role to the auto extinguibility of the sample.

We can also observe the H_2O emission, which can be due to the condensation between P-O-H, resulting from the degradation of HGCP. This can be in agreement with the mechanism giving in figure 14.

3.2.5. SEM-EDX and TGA-IR analysis of flame retarded DGEBA with HGCP

SEM pictures of chars of DGEBA/HGCP/MDA are shown in Figure 17. We can see from the pictures that there are formation of bubbles at interior surface starting the fist degradation in the range of 247–342 °C. From this period, HGCP began to release non-flammable gases such as CO_2, NH_3 and N_2 [45].

These mentioned inflammable gases inside bubbles can create gullys on the surface of sample which are considered channels to dilute the hot atmosphere and cool the pyrolysis zone at the combustion surface.

These mentioned inflammable gases can cut off the supply of oxygen. This act is an agreement with the results of the study of gases evolved during TGA trials in air atmosphere by means of thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR), which indicate the continues emission of non-flammable gases such as CO_2 during thermal degradation of sample (Figure 16).

The pores formed during charring are evident in Figure 3. However, HGCP is also able to limit the char porosity, forming extensive glass-like surfaces and closing some pores at higher temperatures (Figure 17), and so limiting the access of oxygen to the undegraded polymer and the expulsion of pyrolysis gases. These results indicate that when char formation was promoted, the flame retardancy of cured DGEBA epoxy resin with HGCP linked in the network was significantly increased.

This kind of structure is helpful for heat insulation and hindering of mass transfer. Thus, this kind of char can effectively lower the temperature of polymer substrate under it and hinder gas exchange between upperlayer and downlayer of it, and as a consequence improve the flame retardancy of the material.

The phosphorus contents of blends at various temperatures were measured with EDX analysis, and are listed in Figure 17. While heating the blends from room temperature to 500 °C, the phosphorus contents in blends increased steadily.

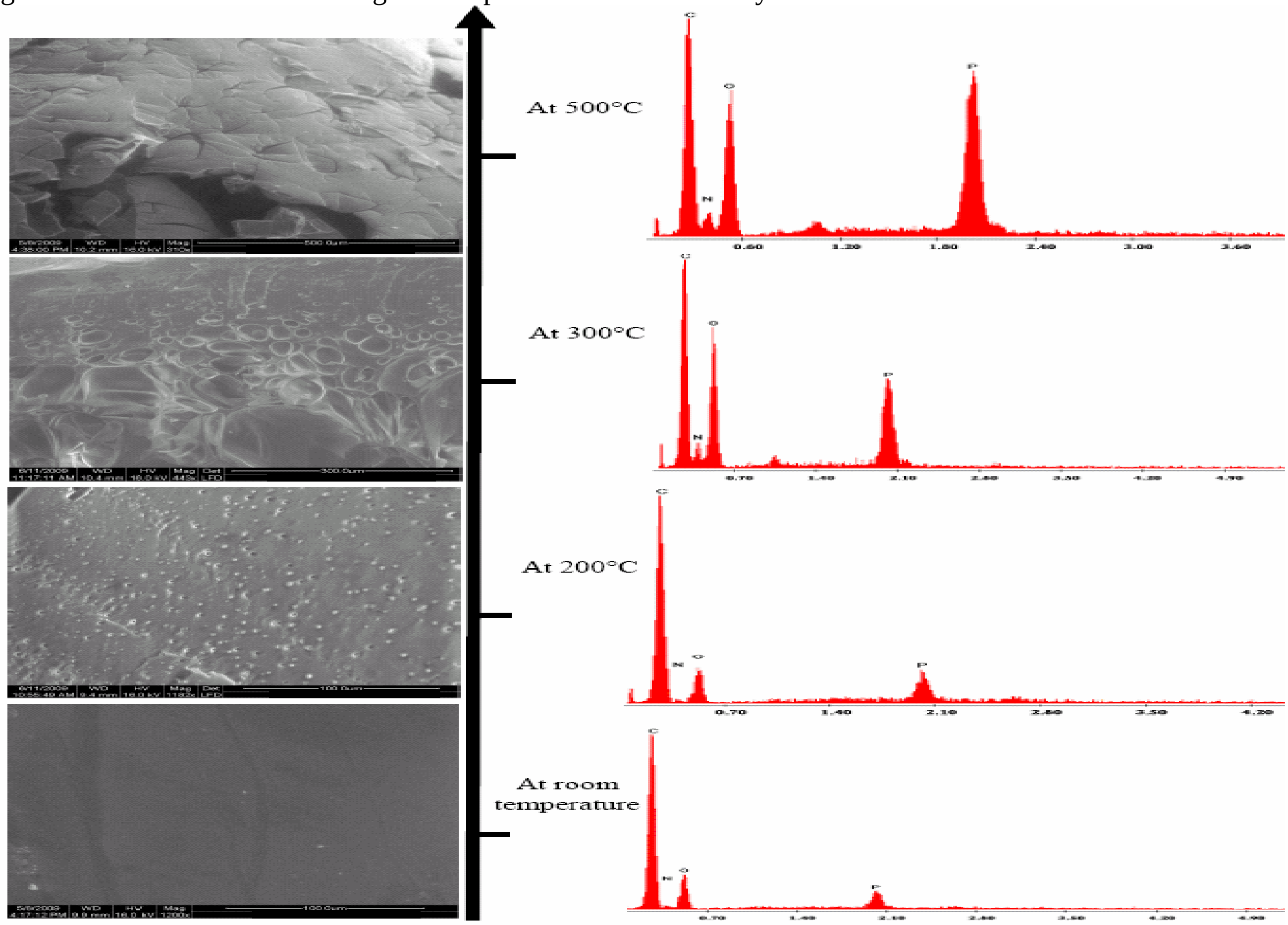

Figure 17. SEM images of inflammable gas evolution and char formation process for intumescent protection of burned specimen of (DGEBA/HGCP/MDA) and its EDX analysis [45].

The results indicate that phosphorus element could remain exclusively in the residue during the thermal degradation. Combined with the results from FTIR analysis, the formation of new structures with rich phosphorus in the blends is crucial, which are more stable and act as a protective layer at elevated temperature.

3.4. Flame-retardant properties

Flame-retardant properties of the (DGEBA/HGCP) blends thermoset with MDA curing agent were further evaluated by UL94 vertical flammability test, and the results were listed in table 5. It is clear that the incorporation of HGCP in DGEBA thermosets with MDA curing agent gains excellent flame retardancy in comparison with the flammable DGEBA curing system reported in lots of literatures [46]. The samples successfully achieved the flammability rating of UL94. It's reached the V-0 class in UL94 vertical test.

By way of comparison with DGEBA, the incorporation of HGCP to DGEBA exhibited self-extinguishing characteristics in the UL94 vertical test.

The formation of the important char during the flammability test of (DGEBA/HGCP/MDA) blends compared with the (DGEBA/MDA) sample, improves and is in agreement also with the previous results. In addition, a loading of 5%, a V-0 grade of UL94 can be reached.

In view of flame retardant efficiency and economic, the optimum addition amount of HGCP is from 5%.

Table 5. Flammability data

Formulations	Curing agent	Dripping	UL94 rating (*)	Remarks
DGEBA/0%HGCP	MDA	No	V1	Very strong black smoke
DGEBA/ 5%HGCP	MDA	No	V0	Light smoke
DGEBA/10%HGCP	MDA	No	V0	Light smoke
DGEBA/15%HGCP	MDA	No	V0	Light smoke
DGEBA/20%HGCP	MDA	No	V0	Light smoke

(*) V-0 (vertical burn classification): Burning stops within 10 seconds. No flaming drips are allowed. Flaming drips, widely recognized as a main source for the spread of flames, distinguish V1 from V2.

4. Conclusion

This research constitutes the report of the multipurpose application of cyclotriphosphazene-containing epoxy group (HGCP). It have been examined for their application as composite material precursor and reactive flame retardant. The comparison of the thermal behaviours of the epoxy resins revealed an improvement of thermal inertia of the HGCP compared to the DGEBA (Epon828), which is mainly due to the difference in their chemical structures incarnated by the presence of phosphorus and by the more compact structure in the case of the HGCP.

The observed characteristics of the polymer, namely good thermal stability, solubility in practical solvents, make this polymer a suitable candidate for the development of flame-retardant materials, composite systems and advanced materials.

In the second application of HGCP as a reactive flame retardant, the addition of HGCP can effectively improve the thermal stability of DGEBA blend at elevated temperatures. However, the initial decomposition temperature of the blend decreased due to the breakage of P-O-C bonding.

The presence of HGCP in the blend had positive effect on overall flammability. At the levels of 20% HGCP in the blend, there was evidence of significant flame retardancy. It was believed to result from the production of a protective char layer which inhibited the overall combustion of the blend. No obviously improved flammability was found in the blend containing HGCP.

The result is attributed to the condensed and gas phase mechanism and homogeneous distribution of HGCP in DGEBA matrix.

The halogen-free flame retardant synthesized in this study using for epoxy resin, has potential applications in electric and electronic fields in consideration of the environment and human health.

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