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Physico-chemical study of DGEBA epoxy resin flame retarded with an ecological flame retardant based on cyclotriphosphazene

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Abstract

In the present research, we have investigated the analysis of gases generated under thermal decomposition of neat and flame retarded DGEBA epoxy resin based on HGCP (Hexaglycidyl cyclotriphosphazene). The use of thermogravimetry coupled with Fourier transform infrared spectroscopy (TG–FTIR) has allowed the continuous detection of a number of the most important fire gases. The morphology of samples during thermal degradation have been observed by way of scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray (EDX) analysis. We have shown that 5% add-on of HGCP can impart DGEBA UL94 V-0 rating. IR data and thermal decomposition data show that HGCP accelerates the emission of the inflammable gas and char forming of DGEBA. In addition, SEM pictures indicate that HGCP promotes foaming and char expansion, and improve gullys on char surface as well. All these fact were helpful to combine the gas action and the condensed phase action (intumescent) for HGCP flame retardancy.

Keywords: flame retardant, HGCP, cyclotriphosphazene, epoxy resin, intumescent

1. Introduction

DGEBA is a commonly used composite material precursor and has many excellent properties, such as high electrical resistance, good mechanical properties and high workability under various processing conditions. However, since DGEBA degrades easily at high temperatures, the use of additives to improve thermal stabilization and flame retardant properties is an area of great interest.

Furthermore the increasing focus on the health and environmental compatibility of flame retardants has drawn the attention to the halogen-free additives and especially to the organophosphorous reactive flame retardants [1].

Flame retardant agent based on cyclophosphazene has excellent fire-retardant properties, halogen free and thermal stability due to the high content of nitrogen and phosphorus [2]. At present, a wide range of phosphazene flame retardant agents which contain hydroxyl, amino, carbon carbonyl groups and other functional groups were synthesized and were studied as fire-retardant materials [1-6].

We reported that thermal stabilization and flame retarded of DGEBA could be improved by a reactive flame retardant such as hexaglycidyl cyclotriphosphazene (HGCP) [4].

It have been incorporated into DGEBA epoxy resin by blending. Improvement in the thermal stability of blended with 20% of HGCP has been reported [4].

The work in this area, interest in the kinetic analysis of gas evolving and the formation of char during thermal degradation of (DGEBA/HGCP) blends, and its effect on both of gas action and condensed phase action of flame retardancy and self-extinguishability. The flame retardant efficiency of HGCP with a low amount in DGEBA epoxy resin is also discussed.

2. Experimental

2.1. Materials

Hexaglycidyl cyclotriphosphazene (HGCP) (Figure 1) was synthesized according to the procedure literature [4], 4,4'-methylene-dianiline (MDA) (Aldrich chemical company) and DGEBA (Epon828).

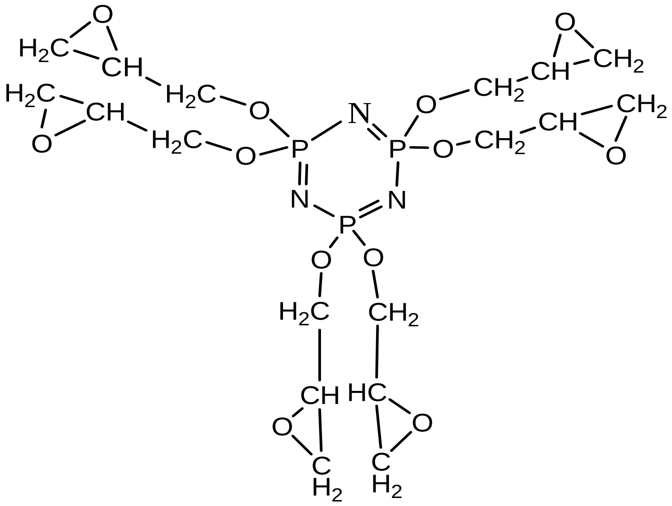

Figure 1: Chemical structure of Hexaglycidyl cyclotriphosphazene (HGCP).

2.2. Instrumentation

Thermogravimetric analysis (TGA) were carried out on an SETARAM thermogravimetric analyzer (The SETSYS evolution) with a heating rate of 10°C/min between room temperature to 1000 °C under N_2 atmosphere. Fourier transform infrared (FTIR) spectra were obtained using Vertex70 FTIR spectrometer. 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 blends and the chars were recorded using "MEB ENVIRONNEMENTAL" scanning electron microscope (SEM). And Energy Dispersive X-ray (EDX) analysis was used in order to assess the presence of phosphorus in residues.

2.3. Samples preparation

(HGCP/DGEBA) blends were warmed to melt and the curing agent 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 (Table 1). 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 [7].

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 discussion

3.1. Thermal proprieties of formulations of flame retarded DGEBA with HGCP.

The addition of the HGCP stabilizes DGEBA at higher temperature whatever its percentage in the formulation (Figure 2). The stage of major degradation of the formulations takes place between 233°C and 343°C. This first stage corresponds to partial degradation of the HGCP and DGEBA with a weight loss of 43%. The second stage which proceeds between 343°C and 475°C is allotted to the degradation of the residue formed at the first stage and with that of the DGEBA.

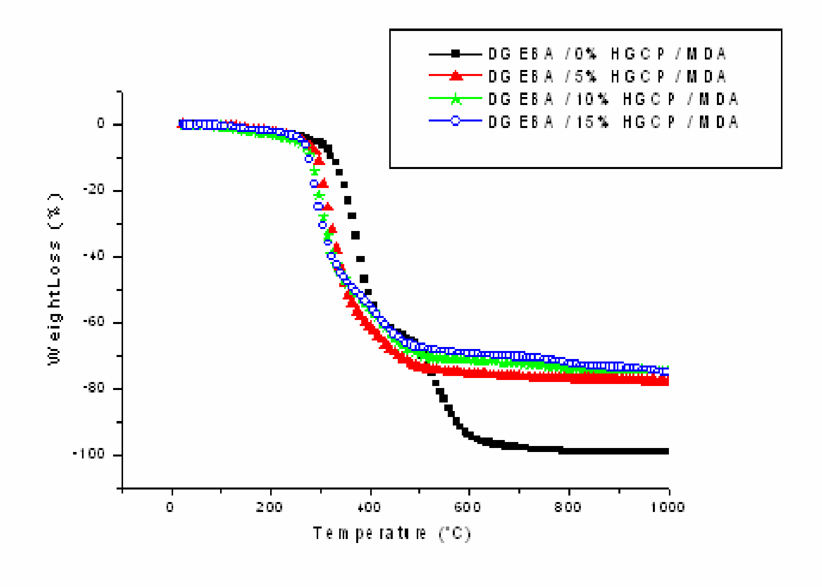

Figure 2: TGA thermogram of samples: (DGEBA/0%HGCP/MDA), (DGEBA/5%HGCP/MDA), (DGEBA/10%HGCP/MDA) et (DGEBA/15%HGCP/MDA). Analysis under in N_2 atmosphere at a 10°C min^{-1} heating rate.

These two stages of degradation, lead to the formation of a significant amount of residue thermically stable about 20% over 600°C for (DGEBA/5%HGCP/MDA) sample. The reduction in the initial degradation temperature, can be explained by the low stability of the P-O-C bond and the release of the compounds birds.

Indeed, The IR spectra of char formed in the second stage of degradation for all formulations are similar and showed 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 data for our samples and the previous study [4, 8, 9].

The appearance of P-O-P group is considered a crosslinker linking to different species, resulting in the formation of complex phosphorus structures with good thermal stability [10].

We can conclude that the addition of HGCP into DGEBA had an effect on thermal stability of the blends until the loading reached to 5%.

With only 5% of HGCP in blend we can observe an increase of the weight-loss temperature in the high-temperature region. The result of a high char yield and the formation of phosphorus-rich char in the decomposition of sample 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 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 [11-17].

3.2 Flame retardancy properties of formulations (DGEBA/HGCP/MDA)

It can be seen from Table 2 that HGCP is effective in flame retarding DGEBA. With the addition amount increasing, the formation of thermally stable residues of DGEBA increases notably. At a loading of 5%, the residue reaches 20% above 600°C, which is far higher than that of pure DGEBA. 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 2: Flammability data of the formulations samples by way UL-94 test.

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.

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

SEM pictures of chars of DGEBA/HGCP/MDA are shown in Figure 3. We can see from the pictures that there is 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.

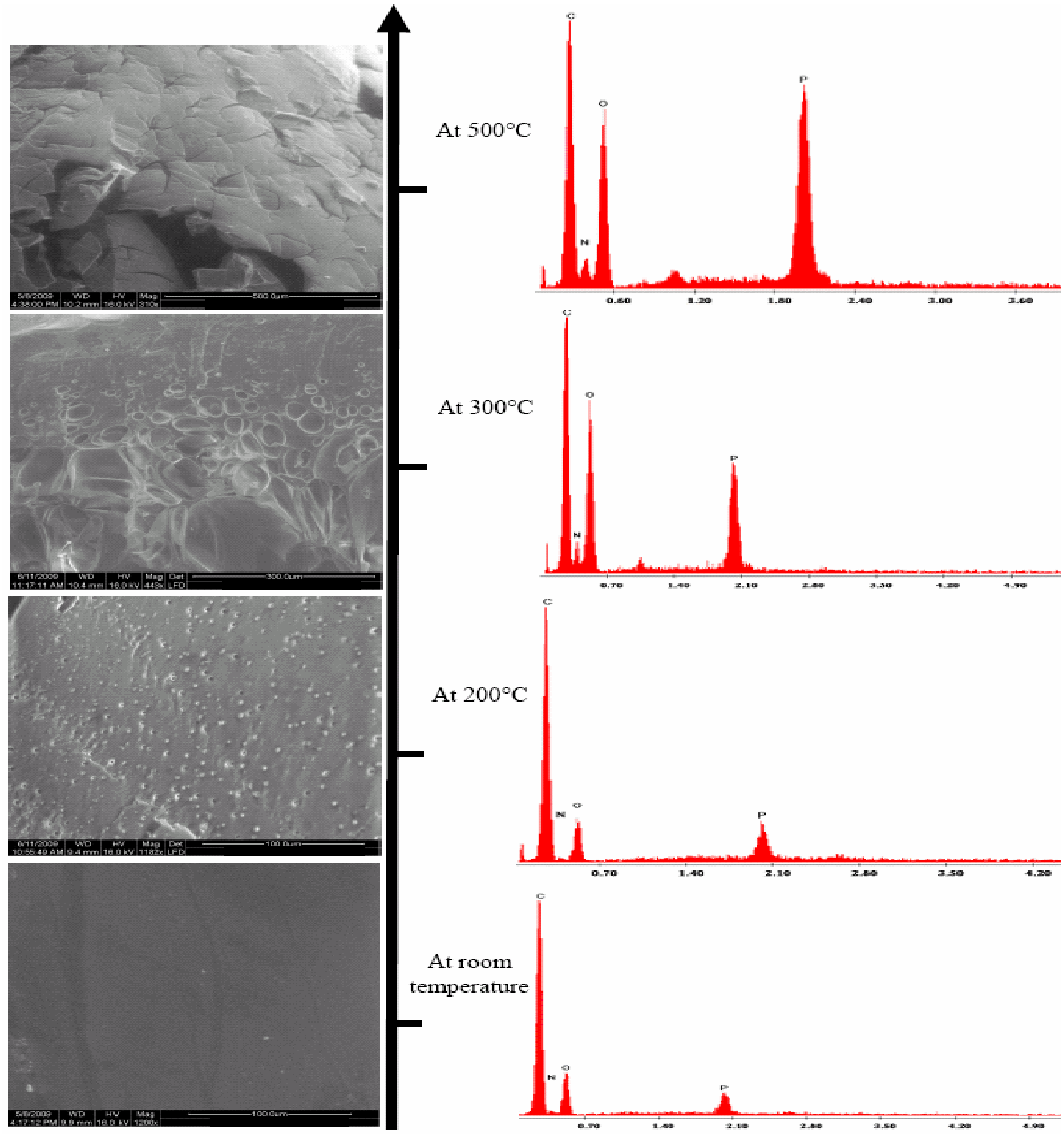

Figure 3: SEM images of inflammable gas evolution and char formation process for intumescent protection of burned specimen of (DGEBA/HGCP/MDA) and its EDX analysis.

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 [18-27]. 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 4).

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 3), 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.

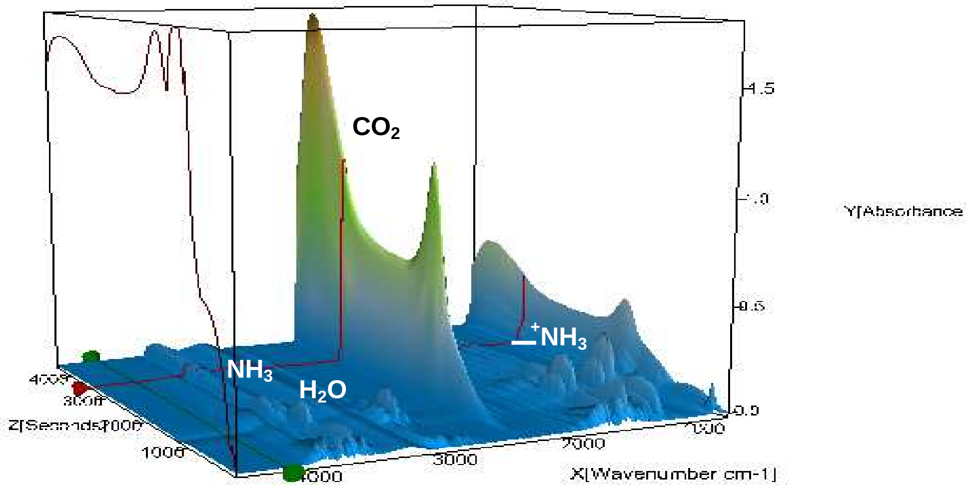

Figure 4: FT-IR spectrum of gas evolved during TGA of sample (DGEBA/HGCP/MDA) in air atmosphere at a 10 °C min^{-1} heating rate.

The phosphorus contents of blends at various temperatures were measured with EDX analysis, and are listed in Figure 3. While heating the blends from room temperature to 500 °C, the phosphorus contents in blends increased steadily.

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.

4. Conclusion

When HGCP amount was added to DGEBA, the formation of thermally stable residues were increased and even UL-94 V-0 ratings were obtained at reasonable amount of loading about 5%, indicating that HGCP can be an efficient additive-type flame retardant with an intumescent char-forming. And no or little change in the amount of charred residue was observed with the addition of HGCP. A gas-phase flame-retarding mode of action is believed to work for this compound. By creating the gullys on char surface, the regular emission of inflammable gas CO_2 and NH_3 may be responsible for gas-phase action which its act to dilute the combustible gas.

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