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# Physical behaviour of epoxy resin material flame retarded with a reactive flame retardant based on cyclophosphazene

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## Abstract

Flame retarded epoxy materials were prepared by blend of HGCP (Hexaglycidyl cyclotriphosphazene) in an organic matrix based on DGEBA epoxy resin. The blends thermoset with 4,4'-methylene-dianiline (MDA) curing agent were characterized by various techniques which consist in thermal by DSC, the morphology by SEM. In electrical characterization it's done with frequency variation range from 100Hz to 100 KHz at room temperature. The rheological behaviour was investigated using small-deformation rheology. These measurements revealed that the reological and electrical behaviours depend strongly on the HGCP amount in DGEBA matrix. The Capacitance-Frequency and conductance-Frequency measurements suggest a distribution of free volume in the blends and select the samples as dielectric materials. The study of linear viscoelastic properties shows that the storage modulus G' is very sensitive to HGCP amount in DGEBA epoxy resin. The as prepared materials seem to be promising materials for electronic compounds.

*Keywords*: Epoxy resin, Flame retardant, morphology, dispersion, rheology, electrical behaviour.

## 1. Introduction

Like other thermoset resins, epoxy resins can be rendered fire-retardant either by incorporating fire-retardant additives or by copolymerization with reactive fire retardants.

Hexachlorocyclophosphazene have been widely studied because they have an excellent flame retardancy and environmental safety [1,2]. However, they have poor compatibility with epoxy resin which leads to reduce mechanical properties of composites and limit their application.

This problem might be solved by the technique of chemical modification. By grafting the organic group on cyclophosphazene, the compatibility is supported between the inorganic layer of cyclophosphazene and organic layer of the epoxy resin matrix. This technique is similar with that concerning the enveloping microscopic amounts of matter (solid particles, droplets of liquids, or gas bubbles) in a thin film of polymer which forms a solid wall [ 3,4]. This core/shell structure allows the isolation of the encapsulated substance from the immediate surroundings and thus protects it from any degrading factors such as temperature and improves the dispersion.

Preparation of modified chlorophosphazene has already been reported in previous works [5-7], but there are few works to report the effect of cyclophosphazene on physical behaviour of material as reactive flame retardant additive. The addition of HGCP can effectively improve fire retardation and the thermal stability of DGEBA blend at elevated temperatures. Nevertheless, this addition must be controlled, in order to avoid the risk of deterioration of physical properties. So here, modified chlorocyclophosphazene such as Hexaglycidyl cyclotriphosphazene (HGCP) was prepared and DGEBA flame retarded with HGCP were prepared and their mechanical and electrical properties were studied.

## 2. Materials and methods

### 2.1. Materials

Hexachlorocyclotriphosphazene [PNCl2]3, 4,4'-methylene-dianiline (MDA) (Aldrich chemical company) and DGEBA (Epon828). Hexaglycidyl cyclotriphosphazene (HGCP) was synthesized in one step, according to the procedure literature [5,8]. The reaction was a nucleophilic substitution of cyclophosphazene chlorine by the epoxy function of 2,3-epoxy-1-propanol in presence of triethylamine (Fig. 1).

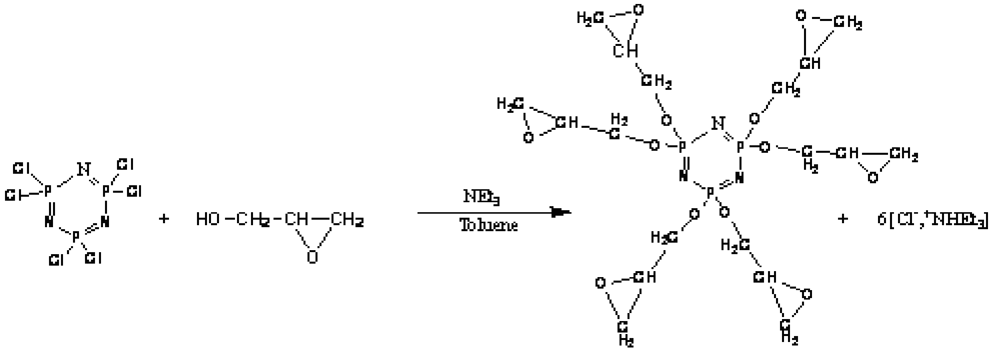


**Figure 1:** Synthesis of hexaglycidyl Cyclotriphosphazene (HGCP)

### 2.2. Differential scanning calorimetry

The differential scanning calorimetry (DSC) analysis was performed on a on an SETARAM thermogravimetric analyzer (The SETSYS evolution). The glass transition temperatures (Tg) of the systems were evaluated by DSC first heating scan at 10 °C/min up to 210 °C in nitrogen atmosphere.

The microstructures of samples were recorded using "MEB ENVIRONNEMENTAL" scanning electron microscope (SEM).

### 2.3. Sample preparation

Epoxies (HGCP, DGEBA and there blend) 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 (Fig. 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 [9]. The formulations and cure schedules were as follows:

The samples were prepared by mixing stoichiometric amount of MDA and [HGCP/DGEBA] blend.

**Figure 2:** Technical of samples preparation

### 2.4. Electrical measurements

The electrical measurements were performed at room temperature on (DGEBA/HGCP) samples with 0%, 5%, 10% and 15% amount of HGCP in DGEBA epoxy resin. The impedance measurements (capacitance – frequency) were carried out using a Keithley 3330LCZ impedance meter. All the instruments are controlled by a computer via a GPIB card.

### 2.5. Rheological measurements

Dynamic rheological measurements were performed using an Haake Mars, Modular advanced rheometer system (Thermo-Scientific) with the plane-plane geometry (the diameter of plateau is 25 mm and gap 1,8 mm).

The dynamic oscillatory measurements were performed using a frequency sweep (0.01 to 100 Hz) with a constant applied strain of 0.1% which is within the linear viscoelastic region. All the measurements were performed at least in duplicate at a constant temperature of 100°C.

### *2.6. Methods for dispersion evaluation*

In recent years the structural heterogeneity of polymers and their phase separation on a nanoscale length have been approached by several experimental techniques and methods based on mathematical or statistical principals. Among the most used experimental techniques for dispersion evaluation is scanning electron microscopy (SEM). It has a very large depth of focus yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample [10].

## 3. Results and discussions

### *3.1. Approach to disperse the inorganic nanoparticle such as cyclophosphazene in organic matrix*

It has been already proven by many researches that physical properties are largely dependent of the degree of nanoparticles dispersion in polymer matrices. Mainly, the influence of dispersion degree on mechanical and rheological properties is known. The absence of chemical bonding and compatibility between the polymer and the particle, that has a connection with dispersion, can influence the mechanical properties of composites because a strong interfacial bonding can effectively transfer the load from the matrix to the reinforcement.

Often used are surface chemical modification of the inorganic nanoparticle, deposition reaction modification, mechanical force chemical modification, modification by high energy and modification by polymer surface grafting and intercalation. These modifications solve the problems of heterogeneous aggregation. The interactions between the reacting groups of the polymer and the nanoparticles depend on the chemical structure of the polymer and the nanoparticle surface charge.

In case of HGCP, since it 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 (Fig. 3) [5,11].

Comparing with ([NPCl$_2$]3-DGEBA) composite, the aggregations are observed in the latter composite. It suggests that modified chlorocyclophosphazene can be well-dispersed in DGEBA, which results from the improvement of compatibility with DGEBA and cross-linked structure of cyclophosphazene.

In this work, while HGCP presents the good dispersion in DGEBA epoxy resin, the study will focused to the effect of HGCP in physical beihavior of material based on DGEBA epoxy resin.

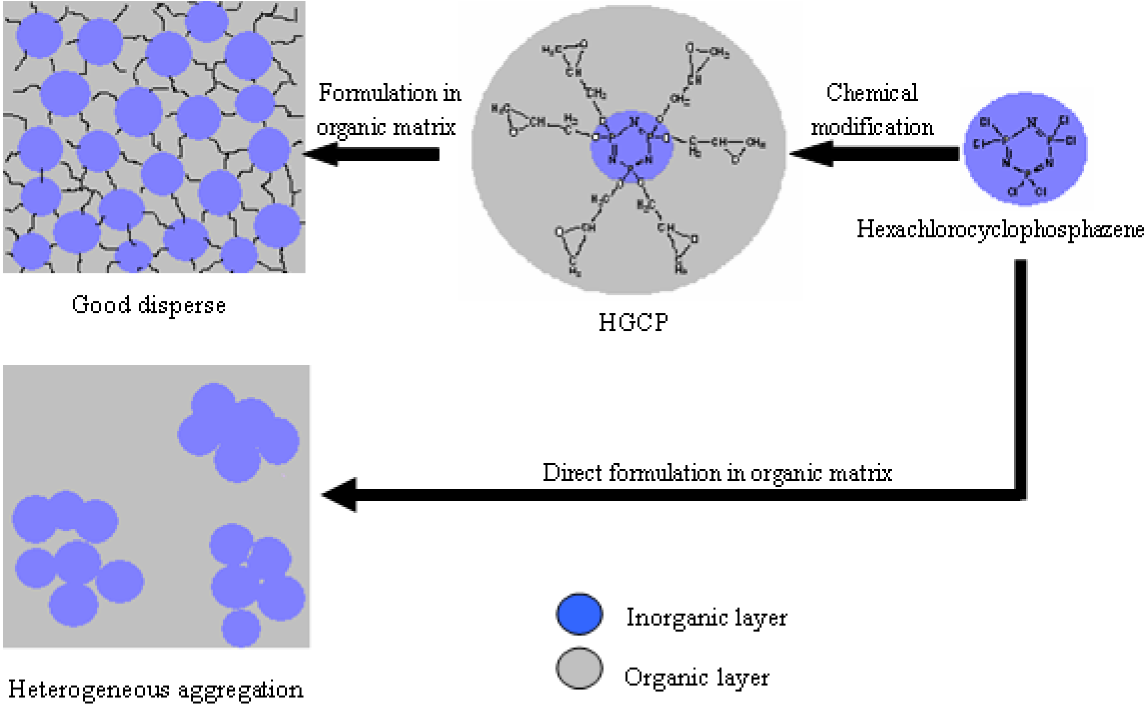


**Figure 3:** Disperse of cyclophosphazene in organic matrix.

### *3.2. Morphology study*

Figure 4 shows the SEM micrographs of DGEBA samples flame retarded with HGCP. For all amount of HGCP (5%, 10% and 15%), the samples were uniform and the examination of their surface morphology did not reveal the presence of any pinholes or porosity.

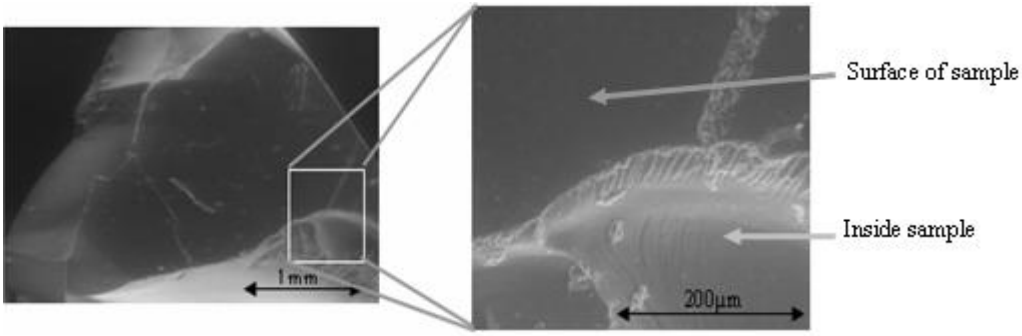


**Figure 4**: SEM micrograph of DGEBA samples morphology blended with HGCP.

### *3.3. DSC analysis*

A stack plot of DSC thermograms of the products is depicted in Figure 5. Clear single endothermic transitions appeared at the thermograms are corresponded to the Tg transitions. The samples : (DGEBA/ 5%HGCP), (DGEBA/ 10%HGCP) and (DGEBA/ 15%HGCP) have Tg of 62°C, 60°C and 70°C respectively.

The lower of the Tg values is attributed to the presence of glycidyl-pendant groups, which increase the free volume and consequently Tg dropped. However, presence of six reactive groups (epoxy) in the backbone of HGCP increase the nodes in matrix somewhat increased the Tg with the increasing of HGCP amount in DGEBA.

So, it can be concluded that the changes in Tg are the result of complicated balance between the free volume exhibited by the HGCP itself and the nodes resulting from (HGCP-MDA-DGEBA) crosslinking, affected by amount of HGCP.

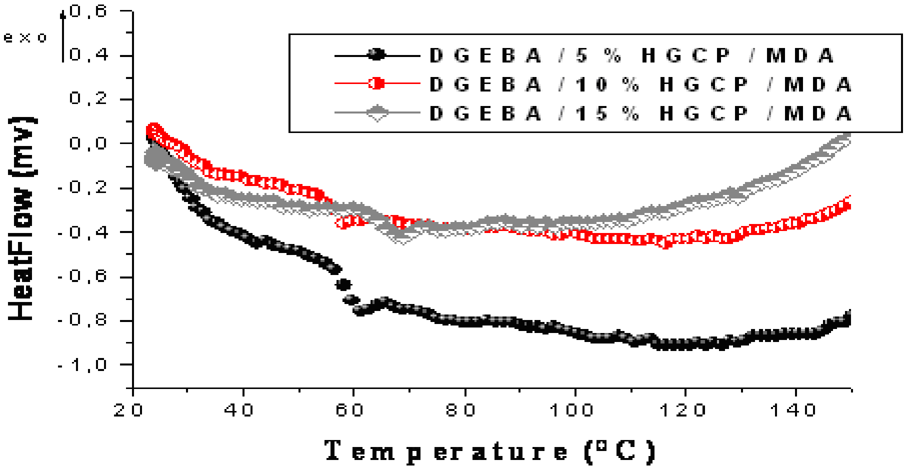


**Figure 5:** Comparison of DSC curves for formulations: [DGEBA/5%HGCP/MDA], [DGEBA/10%HGCP/MDA] and [DGEBA/15%HGCP/MDA].

### *3.4. Dynamic Viscoelastic Analyses of DGEBA Epoxy Resin with various amount of HGCP.*

The rheological properties of material are very sensitive to the chemical structure, reactive or not reactive of the flame retardant additive.

Dynamic viscoelastic analysis by way of Dynamic rheometry can gives information on the microstructure of cured epoxy resins.

We first measured the elastic modulus G' as a function of strain, to locate the linear zone of samples. Figure 6 shows the evolution of the elastic modulus as a function of strain at a frequency of 1 Hz for samples made with several amounts of HGCP (0% - 5% - 10% and 15%) in DGEBA epoxy resin.

For all samples, the linear zone is observed, but it decreases with the increase of HGCP amounts, which can be a sign that the samples obtained have a difference in physical behaviors even if HGCP is well-dispersed in DGEBA. Deformation subsequently used to study the rheological behavior is between 0,1% and 13%, depending on the HGCP amounts.

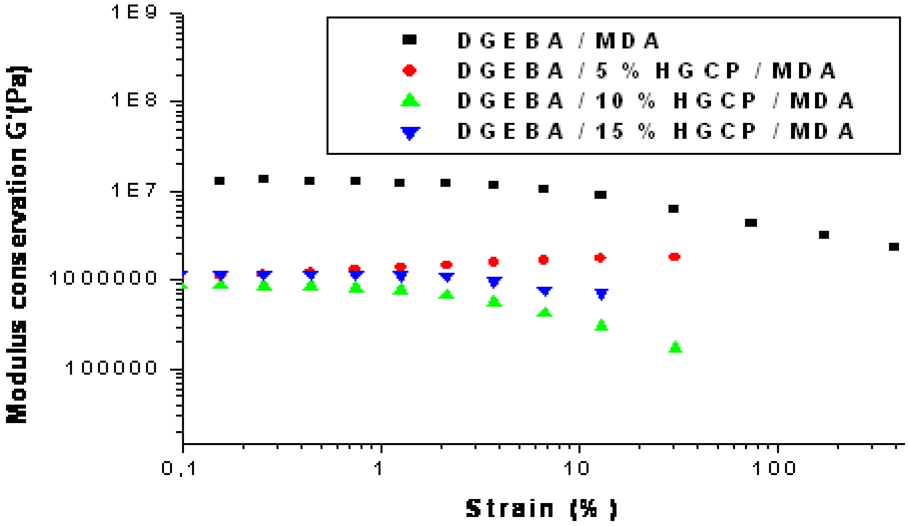


**Figure 6**: Modulus conservation G' as a function of stain for the DGEBA samples with different rates of HGCP (0%, 5%, 10% and 15%).

The elastic modulus G' and loss modulus G" as a function of frequency for DGEBA at various amount of HGCP are shown in figure 7. These measurements were obtained by applying a constant strain of 0.1%, which is within the linear viscoelastic region.

Thus, it is important to recognize that the frequency dependent moduli G’ and G’’ probe the behaviour of a material in an undisturbed state, where the applied strain deformations are sufficiently small so as not to affect the material properties.

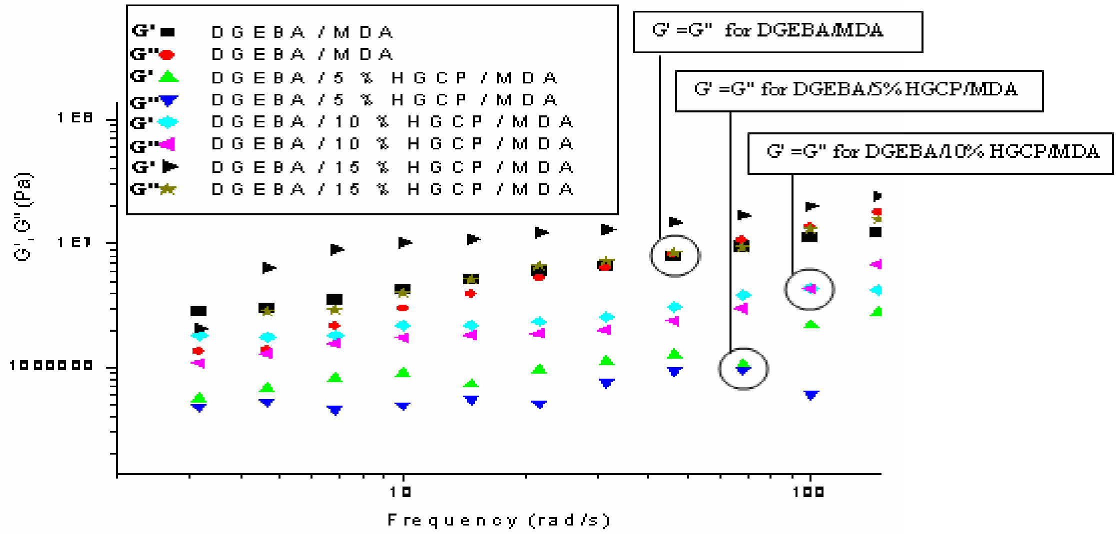


**Figure 7**: Elastic modulus G' and loss modulus G" as a function of frequency for (DGEBA/HGCP/MDA) blends. HGCP amounts are: 0%, 5%, 10% and 15%.

The results show that all blends of 0%, 5%, 10% and 15% HGCP amount behave as a solid, with both G' and G" nearly frequency independent and G' > G". The value of G' and G" increased with the increase of HGCP amounts from 10% in DGEBA epoxy resin. At high frequency we can observe the frequency of crossing when G'=G". This last decreases with 5% of HGCP and increases from 10% HGCP amount, which translate the hardness behaviour of samples attributed to the increase of nodes causing by the crosslinking of six reactive groups of HGCP in DGEBA/MDA matrix.

The appearance of plates on the G' module and G' was announced by many authors [12,13], including for composites containing $Mg(OH)_2$ [14]. The plate on G' is often connected to the formation of a percolate network.

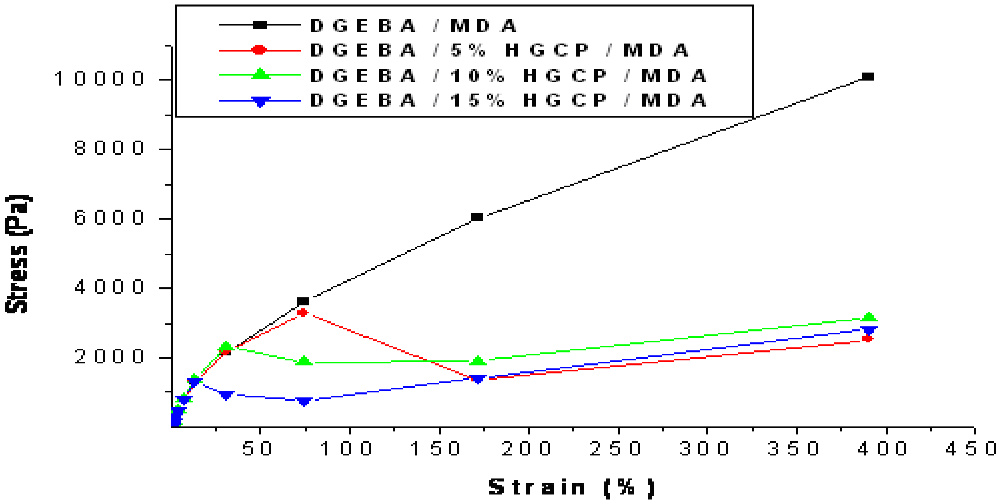


**Figure 8**: The stress-strain curves of DGEBA samples with different rates of HGCP (0% - 5% - 10% and 15%).

Figure 8 shows stress-strain curves for samples (DGEBA/MDA), (DGEBA / 5% HGCP / MDA), (DGEBA / 10% HGCP / MDA) and (DGEBA / 15 % HGCP / MDA).

Mechanical properties of DGEBA material are highly modified by HGCP flame retardant (Fig. 8). The presence of HGCP in DGEBA leads the appearance of plastic deformation zone from 20% of deformation. However, from 5% to 15% of HGCP amount, the Young modulus increased by a factor 2 which may be attributed to the increase of nodes in matrix.

In other had, the result indicates that the introduction of HGCP into DGEBA makes samples more pliable. This increased flexibility of samples may be attributed to free volume exhibited by the HGCP-MDA-DGEBA network.

### *3.5. Electrical proprieties*

Figure 9 shows the capacitance-frequency characteristics of (DGEBA/HGCP) in the frequency range 100 Hz to 100 kHz. The capacitance decreased by factor of two when the frequency is increased to 100 kHz. This dispersion in capacitance can be explained on the basis of distribution of localized states in the band gaps due to the free volume created by DGEBA/HGCPMDA network [15].

In addition, for 5% and 10% of HGCP amount, the capacitance of samples decreases and increases from 15%. This could be due to the increase of nods in samples.

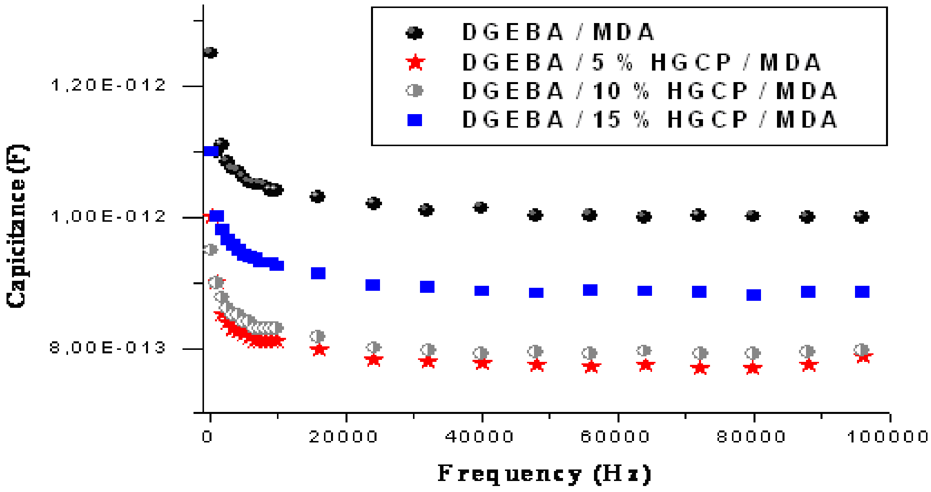
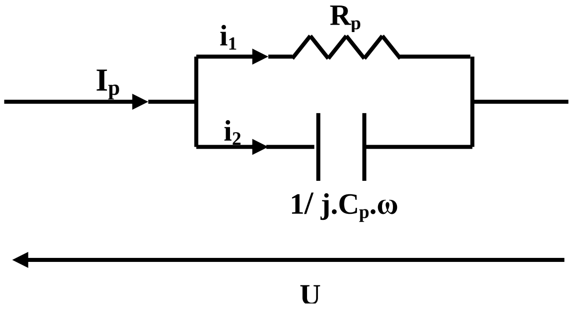


**Figure 9**: Capacitance-Frequency characteristics of samples: [DGEBA/MDA], [DGEBA/5%HGCP/MDA], [DGEBA/10%HGCP/MDA] and [DGEBA/15% HGCP/MDA]

Analysis of impedance spectra can be modeled based on an equivalent electric circuit consisting of a resistor (R) and capacitance (C) elements. It is can be used to represent the charge transfer/relaxation process in the material. The circuit consists of a resistor and capacitor joined together in parallel (Fig.10), and the conductance of the circuit can be represented by: $G = [1/Rp] + i.Cp.\omega$ .
Where: $G = 1/Z = I/U = [i_1+i_2]/U = i_1/U + i_2/U = [1/R_p] + j.Cp.\omega$



$Z = 1 / [ (1/Rp) + j.Cp.\omega]$

**Figure 10**: Parallel model of the equivalent impedance of material.

The limiting values at ω→0 and ω→∞ are as given below:
$G|_{\omega\to 0} = 1/R_p$ ; $Z'|_{\omega\to\infty} = \infty$

So, according to our results concerning conductance measurements (Fig.11), we can identify the characteristics of our materials which could be selected as dielectric materials.

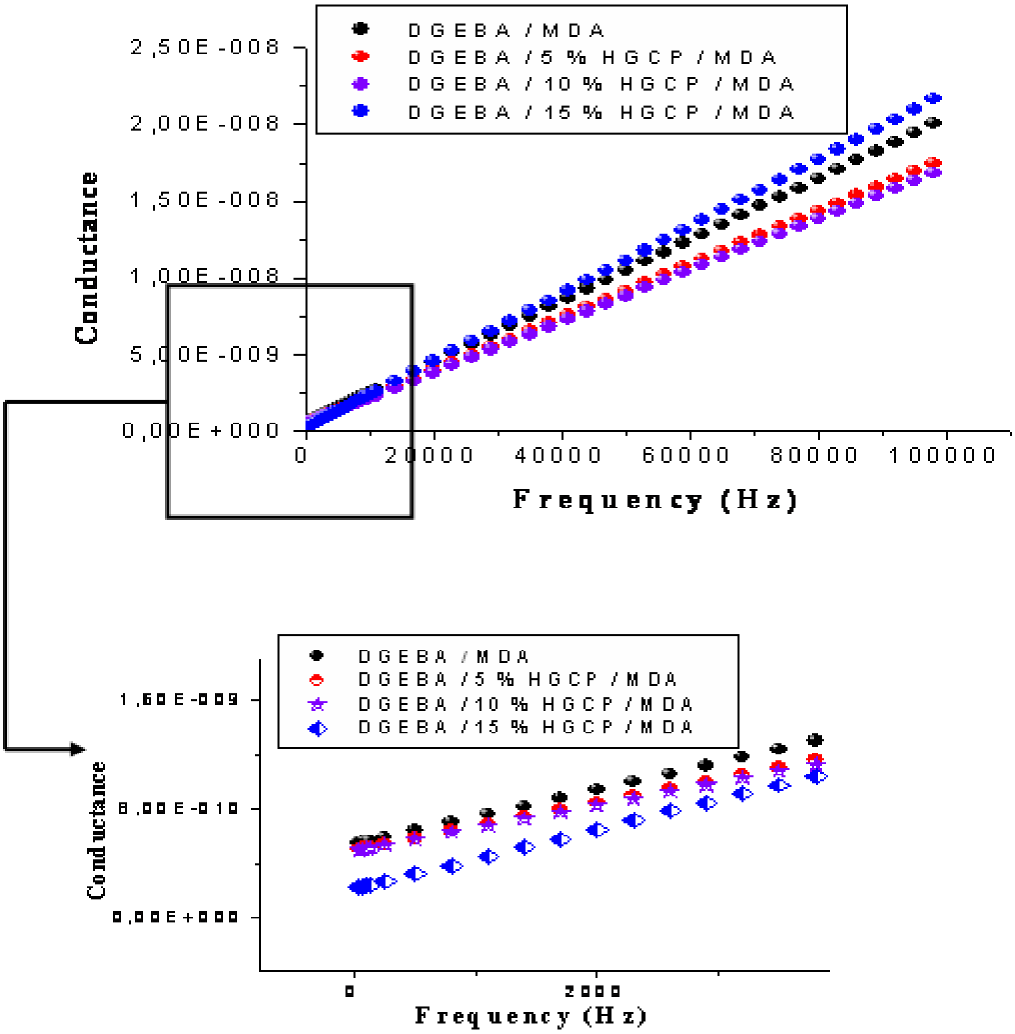


**Figure 11**: Conductance-Frequency characteristics of samples: [DGEBA/MDA], [DGEBA/5% HGCP/MDA], [DGEBA/ 10% HGCP/MDA] and [DGEBA/ 15% HGCP/MDA]

**Table 1**: Values of various electrical parameters for DGEBA/HGCP/MDA samples determined from the Conductance-Frequency measurements:

| Samples | Resistance Rp(Ω).$10^{9}$ | Capacitance Cp(F).$10^{-14}$ | Conductivity σ($10^{-12}$Ω/$cm^{-1}$) |
|---|---|---|---|
| DGEBA/MDA | 1,84 | 3,16 | 336 |
| DGEBA/5%HGCP/MDA | 1,99 | 2,75 | 311 |
| DGEBA/10%HGCP/MDA | 2,02 | 2,65 | 306 |
| DGEBA/15%HGCP/MDA | 4,67 | 3,48 | 132 |

With the increase of HGCP amount in DGEBA we can observe the increase of resistance $R_p$ about 4,67.$10^{9}$ Ω in DC mode (Table.1), but in height frequency (AC mode), 15% of HGCP becomes more conductor compared to other less amount (Fig.11). This response can be resulting from the increase of nods in sample; which facilitates the charge transfer in material.

## Conclusions

Addition of HGCP amounts as reactive flame retardant additive brought improvement in mechanical and electrical properties of epoxy material based on DGEBA. The chemical modification of cyclophosphazene facilitated better dispersion by optimizing compatibility between organic matrix and cyclophosphazene. The blends cured with MDA curing agent showed significant enhancement in flexural modulus and hardness, which is attributed to flexibility of HGCP inside a stretched matrix via the free volume exhibited by the HGCP-MDA-DGEBA network. Furthermore, the C-F measurements suggest a distribution of free volume in the matrix. Thus increase the electrical resistance of material and selects it as a dielectric material.

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