Electrical Study of a Composite Material Based on an Epoxy Polymer Containing Cyclotriphosphazene

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Abstract

In this work, we have prepared, studied, formulated and characterized the electrical behavior of a composite material based on an epoxy resin Diglycidyl Ether of Bisphenol A (DGEBA) reinforced with hexaglycidyl cyclotriphosphazene (HGCP). The hardener used is 4,4'-methylene dianiline (MDA). DGEBA-HGCP-MDA epoxy composite materials with reinforced HGCP which varied from 5 to 10% by weight were prepared by mixing in the molten state. The cured composites have been characterized by the electrical characterization, this is done with a frequency variation range from 0.1 Hz to 100 KHz at room temperature. These measurements revealed that the electrical behaviors strongly depend on the quantity of HGCP in the DGEBA matrix. The capacitance-frequency measurements suggest a distribution of the states located in the forbidden band of the mixtures. Materials as prepared appear to be promising applications in electronic compounds.

Keywords: *Epoxy resin, HGCP, Formulation, composite and electrical behavior.*

1- INTRODUCTION

Epoxy resins are thermosetting polymers that have been extensively employed in various areas such as aerospace, coatings, adhesives, electronic devices, laminates and encapsulations due to the characteristics of outstanding mechanical and electrical properties, relatively low curing shrinkage, superior adhesion to substrates as well as good thermal, chemical and corrosion resistance [1].
Hexachlorocyclotriphosphazene is a procured oligomer usually used for the synthesis of phosphazene-based polymers [2]. The groups like chlorine which are attached to the phosphorus atoms are usually treated as good leaving groups which are easily replaced by various nucleophiles to form cyclotriphosphazene reagents. incorporation of cyclotriphosphazene in a thermosetting polymer network could add several advantages to the polymer like for instance, it enhances the network thermal, mechanical and electrochemical properties. This could be attributed to the synergy of phosphorus and nitrogen [3]. 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 cyclotriphosphazene, the compatibility is supported between the inorganic layer of cyclotriphosphazene 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 [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.
In this work the three epoxy components (DGEBA-HGCP-MDA) was reinforced by various amount of hexaglycidyl of cyclotriphosphazene (HGCP). The amounts of HGCP ranged from 5% to 10%. The epoxy system was cured with the MDA. Produced thermosetting network was characterized by system and electrical study by Keithley 3330LCZ impedance meter.

2- EXPERIMENTAL MATERIAL AND PROCEDURES

2.1. Materials and Methods

The chemical structures of the materials studied in this work are represented in Figure 1. The material was diglycidyl ether of bisphenol A (DGEBA) type Epon 828, the curing agent 4,4′-methylene dianiline (MDA) and hexaglycidyl of cyclotriphosphazene (HGCP). The synthesis of HGCP resin was carried out according to a published procedure [5].

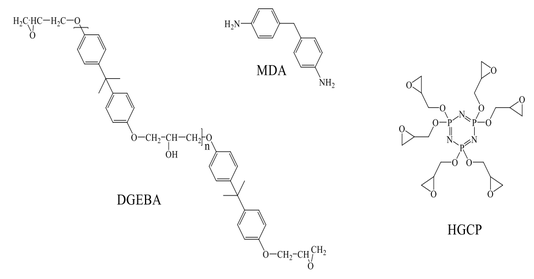

Figure 1. Chemical structures of the epoxy materials and the curing agent.

2.2. Sample Preparation

Mixing the polyepoxide and the hardener (curing agent) produced a bridged three-dimensional network as shown in Figure 2. The curing process was exothermic, the crosslinked materials were hard. They could therefore respond to use in a wide temperature range. The procedures of mixing epoxy resin with hardener before crosslinking was followed by Levin [6]. MDA was crystallized at room temperature, then placed in an oven at 120 °C (more than melting point) and the resin was brought to 70 °C. After melting, the was mixed to form a single phase which was at 70 °C. The samples thus prepared were sealed in Teflon molds and underwent the following cooking cycle:
One night at 70 °C, 3 h at 100 °C, 2 h at 120 °C, 1 h at 140 °C and 30 min at 150 °C

Figure 2. Sample preparation technique.

2.3. HGCP Dispersion Approach in a Polymer Matrix

Numerous studies have already demonstrated that the physical properties largely depend on the degree of dispersion of the nanoparticles in the polymer matrices. Mainly, the influence of the degree of dispersion on the rheological and mechanical properties is well known. The absence of chemical bonds and compatibility between the polymer and the particle, which has a link with the dispersion, can influence the mechanical properties of the composites because a strong interfacial bond can effectively transfer the load from the matrix to the reinforcement. Often used are the chemical surface modification of the inorganic nanoparticle, the modification of the deposition reaction, the chemical modification of mechanical force, the modification by high energy and the modification by polymer surface grafting and intercalation. These changes resolve the heterogeneous aggregation issues. The interactions between the reactive groups of the polymer and the nanoparticles depend on the chemical structure of the polymer and the surface charge of the nanoparticles. Good dispersion was expected due to the organic group on the HGCP and since DGEBA is epoxy resin. Due to the compatibility between two species, the flame retardant additive dispersed in the DGEBA resin and no agglomerate was observed (Figure 3).

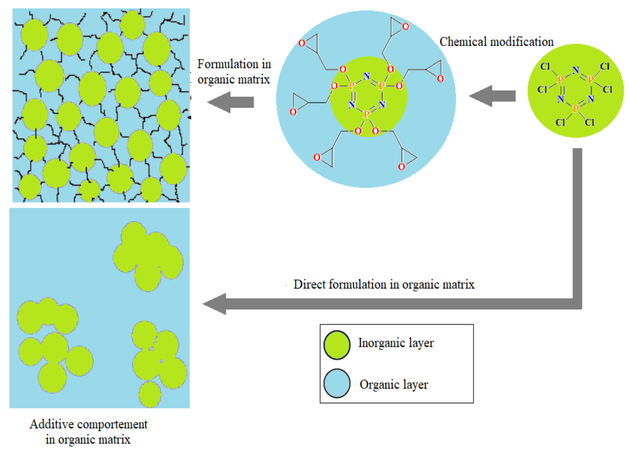

Figure 3. Dispersed hexaglycidyl of cyclotriphosphazene (HGCP) in an organic matrix diglycidyl ether of bisphenol A (DGEBA).

Compared to the composite ($[NPCl_2]_3$-DGEBA), the aggregations were observed in the latter composite. This suggests that the modified chlorocyclophosphazene may be well dispersed in DGEBA, which resulted from improved compatibility with DGEBA resin and the crosslinked structure of cyclophosphazene. In this work, while HGCP had good dispersion in DGEBA epoxy resin, the study will focus on the effect of HGCP in the physical behavior of materials based on DGEBA epoxy resin.

2.4. Electrical Measurements

The electrical measurements were carried out at room temperature on samples. The impedance measurements (capacitance-frequency) were carried out using a Keithley 3330LCZ impedance meter (Oceanside, CA, US). All instruments are controlled by a computer via a GPIB card.

3. RESULTS AND DISCUSSION

3.1. Electric Properties

Figure 4 shows the capacity-frequency characteristics of (DGEBA/HGCP/MDA) in the frequency range 1–100 kHz. The capacity decreased by a factor of two when the frequency was increased to 100 kHz. This dispersion of capacity can be explained by the distribution of the localized states in the band gaps of HGCP network , barrier inhomogeneities and series resistance. At high frequency (1 kHz), the deep states could not follow the barrier modulation and the capacitance must be replaced by the dielectric capacitance of the matrix. In addition, for 5% and 10% of the quantity of HGCP, the capacity of the samples increased. This could be due to the increase in nods in the samples.

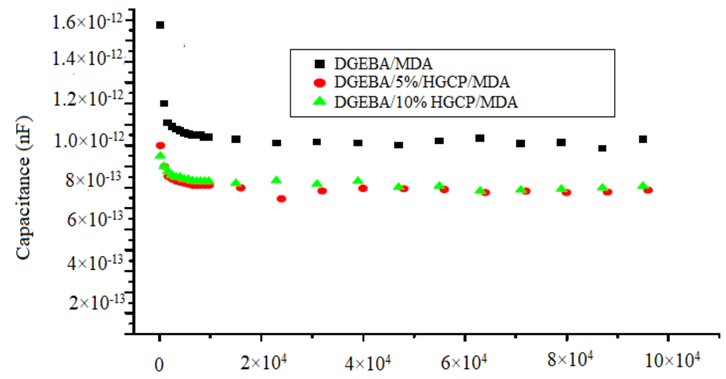

Figure 4. Capacity-frequency characteristics for DGEBA samples with different quantities of HGCP (0%, 5% and 10%).

4. CONCLUSION

Various composite materials based on the epoxy resin DGEBA, MDA as hardener and the epoxy resin HGCP as an additive were prepared and formulated. The chemical modification of cyclophosphazene facilitated better dispersion by optimizing the compatibility between the organic matrix and the cyclophosphazene. In addition, for 5% and 10% of the quantity of HGCP in the DGEBA, the capacity of the samples increases. This could be due to the increase in nods in the samples.

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