High Voltage Electrical Properties of Epoxy / h-BN Microcomposites

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***Abstract* — Two high voltage properties – DC conductivity and AC breakdown strength – of epoxy composites filled with 30 wt% of micron sized hexagonal boron nitride (h-BN) are discussed in comparison to neat epoxy. The influence of h-BN upon the field dependence of DC conductivity has been studied up to 18 kV/mm. The addition of h-BN does not lead to a modification of limiting conduction mechanisms: the J-V characteristics show an ohmic behavior at low fields and a space charge limited current (SCLC) at higher fields for both neat epoxy and composite. However, the addition of 30 wt% h-BN reduces the overall electrical conductivity and increases the threshold voltage between ohmic and SCLC regions, leading to a significant modification of electrical conductivity within the field range compared to neat epoxy. AC breakdown strength is enhanced for epoxy – h-BN composites while generally speaking the addition of micro fillers in an epoxy matrix tends to decrease it.**

Keywords — epoxy composites; hexagonal boron nitride; AC breakdown strength; DC conductivity; electrical conduction mechanisms

I. Introduction

High voltage insulation requires materials that have high electrical resistivity and breakdown strength, low permittivity and dielectric loss together with high thermal conductivity and low coefficient of thermal expansion (CTE). Epoxy resins crosslinked with acid anhydride hardeners are widely used as they are easy to process and have excellent dielectric, electrical and mechanical properties up to relatively high temperatures. However, neat epoxy systems exhibit low thermal conductivity and unsuitable CTE when used with metallic materials such as high voltage conductors. A common solution to improve thermal properties of the polymer consists in adding high amounts of electrically insulating inorganic fillers with high thermal conductivity and low CTE. Hexagonal boron nitride (h-BN) is an attractive insulating filler because of the association of its excellent intrinsic properties (low relative permittivity ≈ 4, high thermal conductivity ≈ 400 W/mK in plane, good electrical insulator) and its platelet shape. Thermal properties of epoxy – h-BN composites have been extensively studied as obtained materials are very useful for thermal management when electrical insulation is required. However, high voltage behavior and more specifically electrical conductivity of such materials have been less explored. The aim of this work is to contribute to high voltage characterization of epoxy – h-BN microcomposites.

II. Experimental

A. Materials and sample preparation

The epoxy system consists in a diglycidyl ether of bisphenol A (DGEBA) prepolymer crosslinked with an anhydride hardener. Hexagonal boron nitride particles used in this study are micron sized platelet particles (D60 6 µm, D90 20 µm) with sub-micrometric thickness, provided by Momentive.

Before use, as received h-BN particles were dried at 80 °C under primary vacuum during 20 h. In order to facilitate dispersion, epoxy prepolymer/fillers and hardener/fillers pre-mixtures were prepared. The dispersion of h-BN in each reactant was performed using a planetary mixer SpeedMixer DAC400 (20 minutes at 2500 rpm). Afterwards, the two pre-mixtures were poured together in appropriate proportions and the reactive blend was mixed during 10 minutes at 2500 rpm. It was then degassed under vacuum at 80 °C during 1.5 hours. Finally, it was cast into an aluminum mold treated with a release agent, cured 4 h at 100 °C and post-cured 8 h at 140 °C. The composite filled with 30 wt% of h-BN will be named as Ep-30BN.

B. Experimental methods

DC conductivity measurements were carried out at 60 °C from 2 kV/mm to 18 kV/mm, by increasing electric field. The test apparatus has been designed following IEC standard 62631-3. Fig. 1 gives the simplified setup used for current measurement (protection components are not shown). The samples are disks with a diameter of 70 mm and a thickness of 1 mm. Gold electrodes were sputtered at the surface of the samples to allow good contact with high voltage, measurement and guard electrodes. Samples were conditioned 24 h at 80 °C under primary vacuum before the first measurement in order to eliminate absorbed water. They were short-circuited during conditioning to evacuate electrical charges resulting from processing. Measurements were carried out in a 5 bars dry nitrogen atmosphere to avoid partial discharges in the surrounding medium at high fields and to keep a low humidity level. For each measurement, voltage was applied to the sample during 10 h. Samples were then short-circuited at least during

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the same amount of time before next voltage application. Current values taken into consideration in this study are those at 10 h of polarization and were obtained by fitting the experimental data to remove measurement noise. Two different samples were tested in order to check the repeatability of the results.

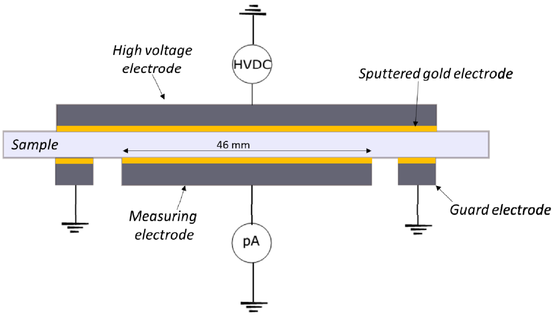

Fig. 1: Simplified setup for conductivity measurement

AC breakdown voltage measurements were performed at room temperature. Rapid ramp tests were carried out at 2 kV/s, 50 Hz according to IEC standard 60243-1. Electrode profile is given in Fig. 2, it has been adapted from the standard and can be considered close to the sphere-sphere profile. Samples are disks with a diameter of 40 mm and a thickness of 1 mm. They were immersed in transformer vegetal oil (Envirotemp® FR3® provided by Cooper) in order to avoid flashovers. At least 10 samples were tested for each formulation and a two-parameter Weibull distribution was used to analyze the results (1).

$$P(E_i) = 1 - e^{\left(-\frac{E_i}{\alpha}\right)^{\beta}} \quad (1)$$

The scale parameter α is the electric field at which the failure probability is 63.2 % and the shape parameter β characterizes the dispersion of the results (high values of β imply a narrow distribution).

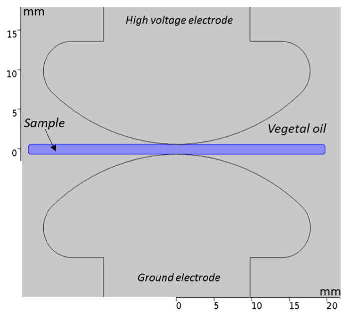

Fig. 2: Profile of the electrodes for AC breakdown strength measurement

III. Results

In addition to high voltage properties, which are the main focus of this work, information are given about thermal and dielectric properties of studied materials.

A. *Thermal and dielectric properties of studied materials*

The addition of 30 wt% of h-BN to the epoxy matrix leads to an improvement of thermal properties: thermal conductivity is increased by 340 % and CTE is decreased by 16 %. In the same time, permittivity and dielectric loss remain almost unaltered due to the small difference between h-BN and epoxy dielectric properties. Similar results were reported in [1], [2]. Note here that the glass transition temperature is not significantly affected by the addition of h-BN and that the temperatures at which high voltages characterizations were performed is far below it.

TABLE I. THERMAL AND DIELECTRIC PROPERTIES

Sample	**Relevant properties of studied materials**				
	Thermal properties			***Dielectric properties*** [d]	
	T_g [a] (°C)	λ [b] (W/mK)	$CTE_{T<Tg}$ [c] (µm/mK)	ε_r'	ε_r''
Neat epoxy	115	0.2	74	3.6	0.028
Ep-30BN	111	0.88	62	3.8	0.022

[a] Glass transition temperature, Differential Scanning Calorimetry, 10 °C/min, onset
[b] Thermal conductivity, Transient Plane Source Hot Disk method, 20 °C
[c] Coefficient of thermal expansion, Thermo-Mechanical Analyzer, 3 °C/min, 0.005 N
[d] Broadband Dielectric Spectroscopy, 100 kHz, 60 °C

B. *DC conductivity measurements*

The influence of electric field E upon electrical conductivity σ_{DC} of neat epoxy and Ep-30BN at 60 °C is given in Fig. 3. Both materials exhibit a region of constant low conductivity at low field, followed by an increase in conductivity at higher fields. The addition of h-BN leads to a significant decrease in the overall conductivity values. In order to evaluate the agreement between experimental data and several interface or bulk limited conduction mechanisms, results will be shown using different representations using applied fields E and current densities J.

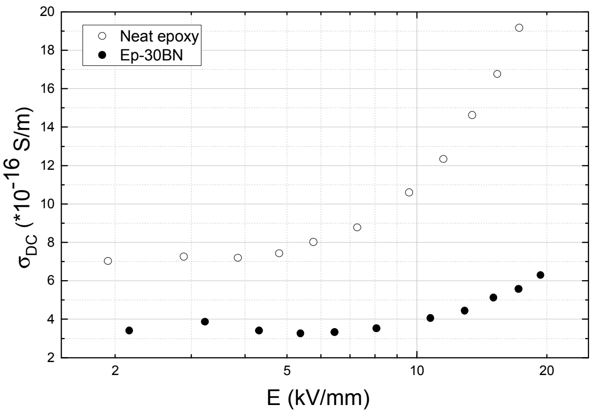

Fig. 3: Influence of electric field E upon conductivity σ_{DC}

1) *Electrode-limited conduction*

Fowler-Nordheim mechanism is, in first approximation, temperature independent and J-E relationship is given by

$$J = AE^2 \exp\left(-\frac{B}{E}\right) \quad (2)$$

where A and B are constants. It is mostly observed at very low temperatures or very high voltages. In this study, experimental current values are not controlled by this mechanism, as the characteristic plot ln(J/E²) versus 1/E (not shown here) does not give a straight line whatever the electric field range is. This mechanism has already been discarded for other epoxy systems [7], [10].

In the Schottky mechanism, injection is assisted by the electric field and by the temperature as they respectively contribute to lower the potential barrier at the interface and to enhance the energy of charge carriers. The J-E relationship is given by

$$J = AT^2 \exp\left(-\frac{\varphi_0 - \beta_S\sqrt{E}}{kT}\right) with\ \beta_S = \sqrt{\frac{e^3}{4\pi\varepsilon_r\varepsilon_0}} \quad (3)$$

where A is the Richardson-Dushman constant, ϕ_0 is the potential barrier at E = 0 V, k is the Boltzmann constant, β_S is the Schottky constant, e is the elementary charge, ε_r is the high frequency relative permittivity of the material and ε_0 is the vacuum permittivity. Experimental results for both materials show a straight line with slope β_S/kT in the characteristic plot of Schottky mechanism (Fig. 4). Calculation of permittivity from the experimental Schottky constant gives $\varepsilon_r' = 1.33$ for neat epoxy and $\varepsilon_r' = 2$ for Ep-30BN. These values are much lower than measured values at relatively high frequency (100 kHz) given in Table I. This significant difference could be attributed to an electric field modification at the interface due to space charge accumulation. The electric field to consider would then be modified by a factor k in comparison to the average field in the volume of the sample. In order to obtain realistic values of permittivity from Schottky constant, the field at the interface has to be increased by a factor 2.71 for neat epoxy and 1.85 for Ep-30BN. This value seems to be in contradiction with the expected homocharge formation at the electrode due to charge carrier injection [3].

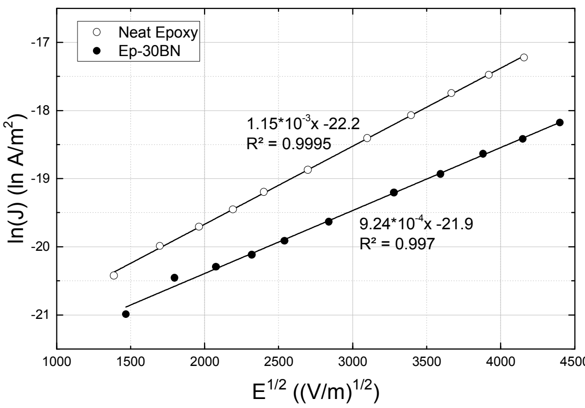

Fig. 4: ln(J) versus E1/2 – Indentification of Schottky mechanism

2) *Bulk-limited conduction*

a) Ohmic conduction

At low electric fields, both J-E characteristics follow the Ohm's law (Fig. 5):

$$J = n_0 e\mu E\ or\ \sigma = n_0 e\mu \quad (4)$$

where n_0 is the number of thermally generated free carriers and μ is the mobility of charge carriers. It should be kept in mind that ohmic conduction is trap-limited in insulators [4]. The addition of h-BN leads to a decrease in ohmic conductivity: $\sigma_{neat\ epoxy}/\sigma_{Ep\text{-}30BN} = 2$ at low fields.

b) Space Charge Limited Current (SCLC)

The SCLC model takes into account local modification of electric field in the material due to injected charge carriers. In the simplest case, i.e. mobility of charge carriers independent from the electric field, trap-free materials, good injecting electrodes and single type of charge carriers, space charge build up in the materials leads to the well-known Mott-Gurney law:

$$J = \frac{9}{8}\cdot\frac{\varepsilon_r\varepsilon_0\mu}{d}E^2 \quad (5)$$

where d is the sample thickness. If traps are present in the material the same law can be verified as long as the traps remain shallow [5]. The current is then multiplied by a factor ϑ equal to the ratio of free injected carriers to total injected carriers. The space charge limited current dominates the ohmic current when the number of free injected carriers is at least equal to the number of thermally generated free carriers. Both tested materials follow the Mott-Gurney law at high fields, however, the departure from Ohm's law occurs at different electric fields for neat epoxy and Ep-30BN (6.8 kV/mm and 10.5 kV/mm respectively). Injected charge carriers apparent mobilities calculated from (5) are $\mu_{neat\ epoxy} = 3.9 \times 10^{-11}$ cm²/(Vs) and $\mu_{Ep\text{-}30BN} = 1 \times 10^{-11}$ cm²/(Vs).

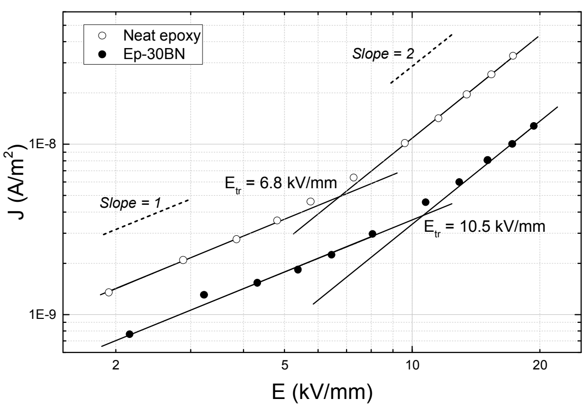

Fig. 5: J versus E in a log-log representation

c) Poole-Frenkel

Poole Frenkel transport mechanism describes a charge de-trapping process assisted by temperature and electric field.

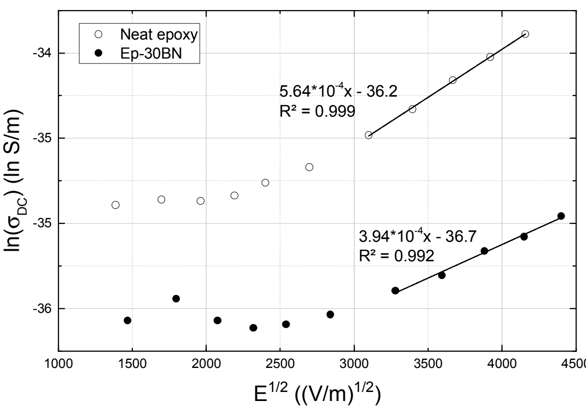

Fig. 6: ln(σ_{DC}) versus $E^{1/2}$ - Poole Frenkel mechanism identification

The space charge limited current could be modified by Poole Frenkel mechanism because it would induce a field dependent apparent mobility. However this would imply a departure from the $J \propto E^2$ behavior [6] which is not observed experimentally. When the current is fully controlled by the Poole Frenkel mechanism, the conductivity follows:

$$\sigma = \sigma_0 \exp\left(\frac{\beta_{PF}\sqrt{E}}{kT}\right) with\ \beta_S \leq \beta_{PF} \leq 2\beta_S \qquad (6)$$

The expression of β_{PF} depends on charge compensation [7]. As for Schottky mechanism, even if experimental data exhibit a straight line in the characteristic plot (Fig. 6), the slopes do not provide realistic values for ε_r' (e.g. between 11 and 45 for Ep-30BN).

C. AC breakdown strength measurements

The measured breakdown strength for neat epoxy is 37 kV/mm (Fig. 7), which corresponds to literature values for neat epoxy systems measured with more classical sphere-sphere electrode setups [8], [9]. No Weibull plot is shown for Ep-30BN because all tested 40 mm samples underwent surface flashovers without volume breakdown at average applied field of 41 kV/mm. One 70 mm sample was tested in order to decrease surface flashover risks and the obtained volume breakdown strength was 48 kV/mm, which is much higher than for neat epoxy.

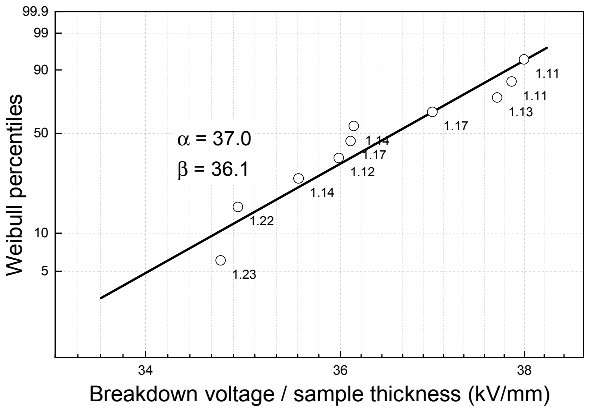

Fig. 7: Weibull probability plot for AC breakdown strength of neat epoxy. Thickness in mm is given for each sample.

IV. Discussion

At low fields, studied materials exhibit a bulk-limited ohmic behavior. At higher fields, conductivities are well fitted by the SCLC model, which appears to be the most probable mechanism for both materials. Similar conclusions about limiting conduction mechanisms have already been drawn for epoxy systems below their glass transition temperature [7], [10], [11]. Further measurements as a function of sample thickness and electrode material would be interesting data to confirm the limiting mechanisms (e.g. SCLC depends on sample thickness, Schottky interface limited current depends on electrode material).

The addition of h-BN significantly affects the DC behavior of studied epoxy networks. The ohmic conductivity of Ep-30BN is divided by two compared to neat epoxy. This could be either interpreted as a reduction by a factor of two of free carriers apparent mobility, or of the amount of thermally generated free carriers [4]. The decrease in conductivity could be attributed to a modification of traps density and/or depth induced by h-BN particles and matrix/filler interfaces. Furthermore, the departure from Ohm's law is shifted to higher fields for Ep-30BN compared to neat epoxy, leading to an increase in threshold voltage from ohmic to SCLC region and to a decrease in apparent mobility in SCLC region. The latter is divided by four, hence the decrease in apparent mobility with the addition of h-BN is doubled in SCLC region compared to ohmic region. Considering that injected charge carriers are in the same thermal equilibrium as thermally generated carriers [5], the increase in threshold voltage could be due to an actual increase in onset field for space charge accumulation [12] and/or to a reduction of the amount of injected carriers. A reduction of accumulated space charge in epoxy – h-BN nanocomposites has been observed in [13], with or without modification of onset field for space charge accumulation depending on filler loading. Space charge measurements on studied materials would be necessary to understand the SCLC behavior.

Epoxy-inorganic fillers microcomposites usually show a reduced breakdown strength compared to neat epoxy. However Ep-30BN appears to have a higher breakdown strength than neat epoxy. An increase in breakdown strength with micron sized h-BN particles addition has already been observed [14], [15], though a slight decrease has been reported in [8]. The significant beneficial effect of h-BN upon breakdown strength can be explained by several factors. First, the small difference of permittivity between the epoxy matrix and h-BN particles may reduce field distortion in the bulk of the composite compared to widely used micro fillers in high voltage insulation, such as alumina [16]. The high shape factor of h-BN may also play a role by increasing electrical treeing pathway. Moreover, modification of space charge behavior by h-BN particles might have a positive influence on breakdown properties. Indeed, less charge accumulation in the material could lead to reduced AC field distortion at the electrode-sample interface and then to a higher breakdown voltage [17], [18].

V. Conclusion

Properties of epoxy composite filled with 30 wt% of micron sized h-BN were compared to neat epoxy. The addition of micro h-BN to the epoxy matrix leads to an improvement of many properties amongst the one required for high voltage insulation. Thermal properties are improved while dielectric breakdown strength is enhanced and dielectric properties remain almost unaltered. Ep-30BN shows an overall reduction of apparent charge carriers mobility compared to neat epoxy. For both materials, the current is ohmic at low field and a SCLC mechanism has been proposed at high fields. Ep-30BN has a higher threshold field from ohmic to SCLC regions, which could lead to a better withstand of electrical stress.

Space charge measurements would be useful complementary information to better interpret obtained results.

ACKNOWLEDGMENT

This project benefited from a state support in conformance with the program of Investments of the Future carrying the reference (ANE-ITE-002-01).

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