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► **To cite this version:**

Servane Haller, Damien Bachellerie, Sébastien Pruvost, Loriane Desmars, Sophie Iglesias, et al.. Epoxy composite with hBN fillers compatible with industrial application in electrical equipment. 2020 IEEE 3rd International Conference on Dielectrics (ICD), Jul 2020, Valencia, France. pp.590-593, 10.1109/ICD46958.2020.9341949 . hal-04719070

HAL Id: hal-04719070

<https://hal.science/hal-04719070v1>

Submitted on 7 Oct 2024

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Epoxy composite with hBN fillers compatible with industrial application in electrical equipment

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Abstract- Hexagonal Boron Nitride (hBN) has been used as secondary filler in an epoxy formulation in gas insulated substation (GIS) demonstrating higher electrical performance under HVAC stress, while being compatible with industrial process and constraints. A synergetic effect between hBN and alumina has been observed regarding thermal and electrical properties. A 500% increase in the thermal conductivity could be achieved with a limited impact on viscosity increase. Breakdown strength has been measured in flat sheets in oil and with embedded electrodes under divergent field simulating a defect. The breakdown strengths resulting from these different experimental setups show an interesting barrier effect from hBN even at low ratio in the formulation. Both results can be correlated with increased lifetime under thermoelectrical stress.

I. INTRODUCTION

Gas insulated substations contain a large number of insulating spacers that are critical to support and insulate the high voltage conductor from the metallic enclosure at the ground voltage, and ensure gas tightness between the compartments. Insulation is mainly performed by the dielectric gas and its volume is optimized to achieve both insulation and thermal conduction of calories generated at the high voltage conductor. For high voltage equipment, the limiting parameter for the design becomes the electrical stress in the spacer. Therefore, there is an interest in using materials with superior electrical performances that would allow to reduce the size of the overall equipment. Such new material could result in decreasing the metal quantity in the equipment and the mass of the dielectric gas, which has predominantly a greenhouse effect gas: SF₆.

Decreasing the size of the spacer requires to prove superior electrical properties after ageing and in presence of defects since design criteria include degradation of the material and imperfect manufacturing.

The interface between fillers and matrix is known to be a weak point in composite materials due to difference in electrical permittivity building field enhancement known as Maxwell Wagner Sillars effect. Moreover, interfaces can be the place of delamination that would activate partial discharge and cause a premature failure of the system. Classical fillers for epoxy composites used as spacers in GIS are micro size alumina or silica which present strong mismatch in permittivity with the matrix. Recently, hexagonal boron nitride (hBN) have attracted significant research interest due to its high thermal conductivity, high electrical resistivity, low dielectric constant,

low density and excellent temperature resistance. In addition to the filler nature, the platelet geometry of hBN is known to have a positive impact on thermal properties [1]. A comparison of physical properties of epoxy matrix, alumina and hBN can be found in table A. Moreover, composites using hBN fillers have shown interesting increase in breakdown strength.

TABLE I

Physical properties of Epoxy matrix, alumina filler and hBN filler from [2], [3]

Raw materials	Epoxy	Alumina	hBN
Density	1.15-1.20	3.99	2.2-2.8
Thermal conductivity W/mK	0.2	30-40	X-Y plane 400, Z-3-6
Dielectric constant /1 MHz	4	9-10	4-5
Dissipation factor / 1 MHz	<0.02	<0.0004	0.0003
Electrical resistivity S/m	~10 ¹⁵	>10 ¹⁴	10 ¹⁵ -10 ¹⁶

A major counterpart of this filler at industrial level is that its platelet geometry tends to increase viscosity, making the manufacturing process challenging for volume content above 20% [4]. In this study, we present an optimized formulation containing both alumina and microsized hBN with increased performance and acceptable viscosity [5]. Similar strategies at filler content over 60% in volume or using nano hBN have demonstrated a synergetic effect of the fillers with no adverse impact on process properties [6], [7].

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. Alumina used in this study is an irregularly shaped micro alumina and Hexagonal boron nitride fillers are micron sized platelet particles (D60 6 μm, D90 20 μm) with sub-micrometric thickness.

Before use, as received fillers were dried at 80 °C under primary vacuum during 20 h. In order to facilitate dispersion, epoxy prepolymer/fillers and hardener/fillers premixtures were prepared. The dispersion of fillers in each reactant was performed using a planetary mixer SpeedMixer DAC-800 (10 minutes at 1300 rpm 10 mbar). Afterwards, the two premixtures were poured together in appropriate proportions and the reactive blend was mixed during 10 minutes at 1500 rpm and 10 mbar.

Three formulations have been investigated in this study: a reference formulation containing 37% in volume of alumina EP_37A, a formulation containing 18.5% in volume of hBN EP_18.5BN that is the maximal ratio that was possible to process and a mixture of both fillers at optimized ratio with a total volume fraction of 37% EP_37(A+BN).

Finally, prepolymer mixtures were cast into an aluminium mould treated with a release agent. The mould can be two flat aluminium sheets or a mould for embedded electrodes supporting two aluminium electrodes as presented in Fig. 5. The samples are cured 4 h at 100 °C and post-cured 8 h at 140 °C.

B. Experimental methods

Rheology has been performed on an ARES G2 rheometer from TA instrument operated with plate-plate geometry at 50°C and at increasing shear rate from 0.5 to 100 s⁻¹. Transient plane source method [8] was applied to measure thermal conductivity of the composites at room temperature using the TPS 2200S (HotDisk AB, Sweden) with a sensor that was located between two identical tested samples. Glass transition temperature has been measured using a MAIA 300 DSC from Netzsch at 10°C/min. Three samples were tested for reproducibility in each case.

C. Breakdown bench for embedded electrodes

Breakdown of embedded electrodes have been performed in an in-house developed test rig. Four samples can be activated using pistons and are connected to the high voltage electrode one at the time in an enclosure able to maintain 4 bars of SF₆. The test rig is connected to a 660 kV 50Hz AC transformer and voltage is applied with a 2 kV/s ramp up to breakdown value. A cross-section of the test rig and a picture of the experimental setup are shown in Fig. 1 and Fig. 2.

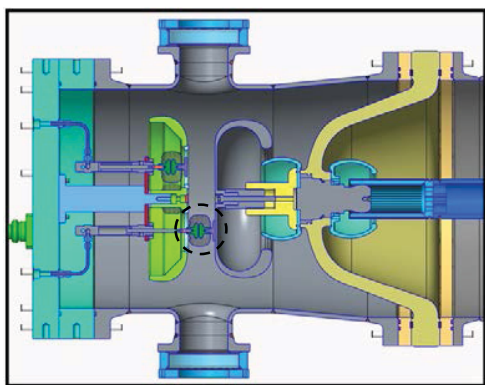


Fig. 2: Cross-section of the test rig for embedded electrodes breakdown. Embedded electrodes (one is highlighted with a dashed circle) are put in contact with high voltage (on the right) through the activation of an actuator. The test rig is filled with SF₆.



Fig. 3: Experimental setup for the connection of the breakdown test rig (front right) to an AC transformer.

III. RESULTS

Since the addition of hBN fillers has the major drawback to increase viscosity, which makes the manufacturing process difficult, the solution proposed is to mix hBN with a more standard filler, alumina, and to create a synergetic effect between the two fillers.

Glass transition onset temperature has been measured to be 115°C on all formulations, confirming that there is no impact of the filler on the polymerization and curing of the epoxy resin.

The viscosity of the reactive mixtures has been measured at 50°C for several formulations as shown in Fig. 3. As expected, the unfilled epoxy displays the lowest viscosity with a Newtonian behaviour on the full range of shear rate measurement. The addition of 37% in volume of alumina in the epoxy increases the viscosity by about one order of magnitude. At 18.5% in volume of hBN, a significant increase in the viscosity is observed at low shear rate. This formulation presents a shear thinning behaviour as already observed for hBN filled epoxy [9]. The formulation containing both alumina and hBN at 37% in volume presents a slightly higher viscosity at low shear rate compared to the one filled with only alumina. A limited shear thinning behaviour may explain that the viscosity drops at higher shear rate.

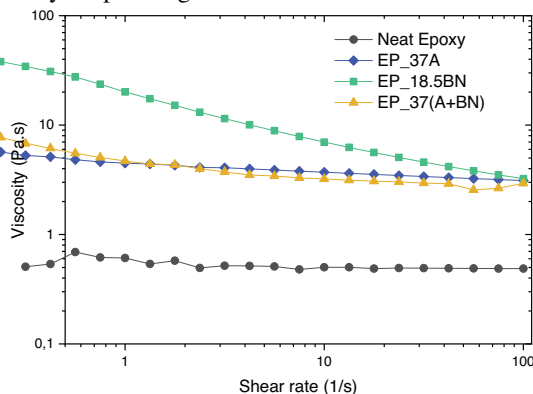


Fig. 4: Evolution of viscosity with shear rate at 50°C for unfilled epoxy matrix (Neat Epoxy), epoxy filled with 37% alumina in volume (EP_37A), epoxy filled with 18.5% hBN in volume (EP_18.5BN) and the optimized formulation containing both hBN and alumina with a total volume fraction of 37% (EP_37(A+BN)).

TABLE II
Thermal conductivities of all formulations

Formulation	Thermal conductivity (W/mK)	Increase compared to neat epoxy (%)	Increase compared to reference (%)
Neat Epoxy	0,20	-	-
EP_37A	0,88	340	-
EP_18.5BN	0,88	340	0
EP_37(A+BN)	1,22	500	40

Thermal conductivity of neat epoxy has been measured to be 0.20 W/mK that corresponds to what can be found in the literature using the same epoxy material [10]. The addition of 37% in volume of alumina increases the conductivity up to 0.88 W/mK. Using only hBN fillers at 18.5% in volume, the thermal conductivity is measured to be 0.88 W/mK, which corresponds to a 340% increase compared to the neat epoxy. We observe that the better intrinsic conductivity of hBN can only compensate for the lower volume content in the epoxy matrix. The optimized formulation with both alumina and hBN fillers however enables an increase up to 1.22 W/mK at the same filler volume content. Therefore, a 500% increase in the thermal conductivity can be achieved compared to the neat epoxy while keeping the filler volume up to 37% and the viscosity at an acceptable level, which corresponds to an about 40% increase compared to the alumina only filled formulation.

Dielectric spectroscopy has been performed on the epoxy matrix. The real permittivity at 20°C and 1 kHz is measured to be 3.64. The addition of 18.5% of hBN in volume increases this value up to 3.88, confirming that hBN fillers have a close yet higher permittivity compared to the one of the matrix. In contrast, the addition of alumina results an increase of the permittivity up to 6. Incorporating small amount of hBN at constant volume content of 37% enables to limit the permittivity increase to 5.26 as predicted by the theory of effective permittivity in dielectric mixtures.

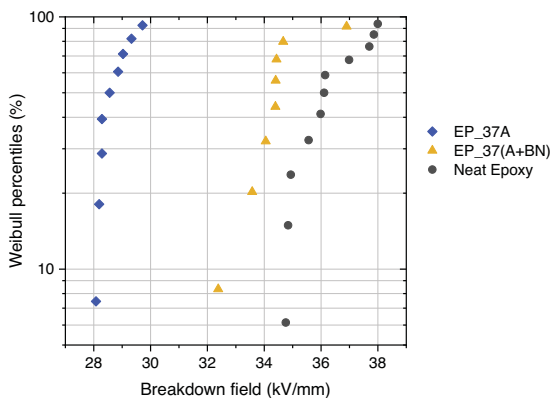


Fig. 5: Weibull representation of AC breakdown strength of 1 mm thick flat sheets in oil for neat epoxy, EP_37A and EP_37(A+BN) in a sphere-sphere electrode configuration.

Breakdown test has been performed on 1 mm thick flat samples with a 40 mm diameter in oil in a sphere-sphere configuration on several formulations. Weibull analysis displayed in Fig. 4 clearly shows that the breakdown strength decreases when alumina is added to neat epoxy resin. This well-known phenomenon can be attributed to the introduction of interfaces that act as defects, where field enhancement occurs and that the fillers do not effectively act as barrier to the propagation of the electrical arc as already observed by others [11]. On the opposite, the addition of hBN results in an increase of breakdown strength in such a way that surface flashover was systematically observed for Ep_18.5BN. A single sample with increase size of 70 mm in diameter was successfully perforated at 48 kV/mm. Since the real permittivity of hBN fillers is higher than the one of the epoxy matrix, this significant increase in breakdown strength is explained by a barrier effect from the fillers that shifts the breakdown to higher electrical field value. The addition of hBN at constant filler volume results in an increase of the breakdown strength of about 15% compared to the formulation containing only alumina fillers.

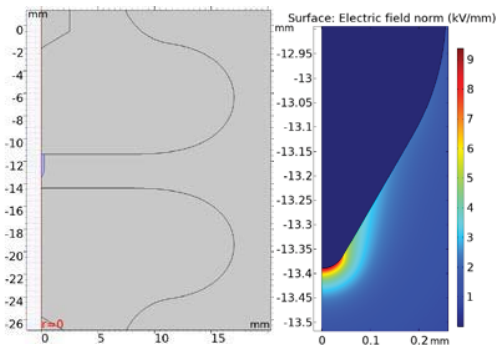


Fig. 6: Geometry of the embedded electrodes containing a needle (in blue) and simulation of the electrical field concentration at the tip of the needle.

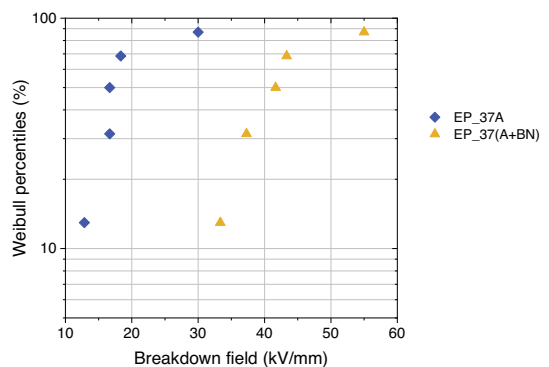


Fig. 7: Weibull representation of AC breakdown strength of embedded electrodes with needle defect for EP_37A and EP_37(A+BN).

The barrier effect of hBN fillers has been further investigated in a configuration of strong divergent field. This scenario corresponds to metallic particle of asperity at the interface with the metal core. A tungsten needle with radius of 50 μm is used to model such defect. The needle is put at the centre of a flat electrode with a Karlsson profile at its edges and sticks out of two millimetres in a manner that there is no influence of the electrode itself and that the distance between the tip of the needle and the ground electrode is 1 millimetre. The epoxy is then casted around the electrodes in order to get rid of the influence of the external medium and edge effects. Multiphysics computations with COMSOL show a tenfold field reinforcement at the tip of the needle as displayed in Fig. 5. The embedded electrodes are installed in the breakdown bench described in Fig. 1.

Weibull representations of epoxy formulation at 37% in volume content filler are displayed in Fig. 6. Despite a strong dispersion of the results, a significant increase in the breakdown field under divergent field can be observed with the addition of a small rate of hBN fillers. Average value of 19 kV/mm and 42 kV/mm can be achieved with only alumina fillers and an optimized ratio of alumina and hBN fillers respectively.

IV. DISCUSSION

The addition of hBN as a secondary filler in an epoxy formulation has resulted in an increase of the thermal conductivity, a limitation of the increase of the dielectric constant and superior breakdown strength under divergent field. The improvement of the electrical withstand in the presence of sharp defects simulated by a needle is an interesting property to guarantee long lifetime in real life conditions.

Moreover, the interfaces between the fillers and the matrix are known to be the weakest point of composite materials submitted to electrical stress. Due to the permittivity mismatch between the fillers and the epoxy known as Maxwell Wagner Sillars effect, the electrical field is concentrated in the epoxy close to the interface. The epoxy located at the interface with filler is therefore submitted to an electrical stress but also a thermal stress if the heat cannot be disperse effectively in the whole material. The addition of hBN at small volume content is supposed to create thermal bridges, helping to evacuate the heat and delaying the chemical degradation in the epoxy matrix. The increase of the thermal conductivity, although not critical for the design, may play an important role for the management of defects propagation at the micrometre scale.

Therefore, the improvement of thermal and electrical parameters due to the addition of hBN in the epoxy formulation is expected to increase lifetime subjected to thermoelectrical stress. Ageing tests will be performed to quantify the improvement and to confirm this hypothesis.

V. CONCLUSION

The combination of hBN with another filler such as alumina enables to benefit from its remarkable thermal, dielectric and electrical properties at low filler ratio and therefore with

limited impact on the process properties. An increase of 500% of the thermal conductivity could be achieved using the combination of both fillers compared to unfilled matrix. Moreover, an increase in the electric strength compared with formulation containing alumina filler only could be demonstrated. Up to 100% increase of the breakdown strength could be observed in embedded electrodes containing a needle to simulate a sharp defect. These material properties open the ways for increasing the thermoelectrical stress in normal operation conditions on GIS spacers and therefore designing more efficient very high voltage systems for both cost and ecological considerations.

ACKNOWLEDGMENT

This work was supported by a grant of the French National Research Agency (ANR) as part of the "Investissements d'Avenir" Program (ANE-ITE- 002-01).

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