Investigation of Aromatic Voltage Stabilizers for Enhancing High Voltage Stability of Epoxy for Power Electronics

Jiaxiong Li, Kathaperumal Mohanalingam, Omkar Gupte, Zhijian Sun, Kyoung-sik Moon and Ching-ping Wong

3D systems Packaging Research Center, Georgia Institute of Technology, Atlanta, GA, USA

cp.wong@mse.gatech.edu

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***Abstract*— Drive train electrification in automotive industry has become the general trend in recent years. As crucial components in the encapsulation and isolation of future wide-bandgap semiconductor-based power cards, epoxy resin and its composites face great challenges from the high voltage operation. This work provides an exploration into employing a group of polycyclic aromatic hydrocarbon molecules with varied number of aromatic rings, namely naphthalene, anthracene and pyrene, as voltage stabilizers in epoxy resin. The conjugated π system can be excited by the incoming high energy electrons, thus absorbing their kinetic energy which endangers the polymer integrity. The UV-Vis spectra of the compounds were recorded to illustrate the energy absorbing behavior, and the effects of these additives on epoxy curing, glass transition temperature and dielectric properties are presented. In the study, pyrene was found to enhance the breakdown voltage of the epoxy film.**

Keywords-Epoxy, Encapsulant, Voltage stabilizer, Dielectric, Aromatic Hydrocarbon

I. INTRODUCTION

We have evidenced the rapid advancements in wide-bandgap semiconductors in the past decade, with the demonstration of excellent performances of gallium nitride (GaN) for high frequency and silicon carbide (SiC) for high voltage power applications, greatly surpassing that of the current silicon (Si) technology and likely its very limit. Specifically in the high power end, SiC dies benefit from their high temperature, high voltage operation capability and low loss, are allowed to be pushing into more extreme voltage ratings that are becoming the trend for drive train electrification in automotive industry. In doing so, dramatic device miniaturizations have been achieved by relieving the bulky cooling accessories [1].

Though fascinating in theory, the adoption of high performance SiC has been held back by inadequate packaging technologies as well as materials. The harsh operation conditions (high temperature/high voltage) where SiC managed to survive and thrive remained grand challenges for interconnect, substrate as well as encapsulant materials [2, 3]. In terms of voltage, both the increasing voltage supply and the decreasing package thickness generate a more demanding dielectric field on the insulators, for example underfill and epoxy molding compound (EMC). The integrity of these polymeric composite materials under such high field stressing are critical to the reliability and safety of the electronic system [4]. Catastrophic failure occurs when the endured electric field exceeds the intrinsic material limit, that turns the insulator into electrical conductor, which in the encapsulant case, leads to not only mechanical and electrical failure of the package but also the die.

It is therefore crucial to enhance this specific value, known as breakdown voltage (BDV, or dielectric strength) of the epoxy based encapsulants, in order for the high voltage and compact power package to be realized. Typically, such epoxy composites consist of epoxy and hardener resin, high concentration of inorganic filler (80-90 wt% of silica in EMC and 60 wt% in underfill) and additives including flame retardant, adhesion promoter and so on. Polymers and ceramics, being good insulators, are rooted from the immobilized ground electrons around the nuclei. Unlike constitutive properties such as electrical or thermal conductivity, the dielectric strength of the composite does not follow rule of mixture but is rather limited by the weakest spots under field whose breakdown induces the catastrophic failure of the system. In the polymeric composite, these weak spots are normally the poor organic interface regions around the inorganic phases. The distorted and enlarged local electric field, due to the irregular geometry and possibly the dielectric constant difference, often initiate the local breakdown that in turn alters the field applied on the adjacent continuum. We first try to enhance the dielectric breakdown strength of the polymeric resin material as a whole.

Theories regarding the dielectric breakdown mechanisms in polymer materials have been proposed [5], including:

1. Electronic breakdown, intrinsic bond cleavage under electron collision, and the following current multiplication (avalanche) to transform the polymer into conductor, normally captured at low temperature.

2. Thermal breakdown, thermal failure of polymer, forming conductive or nonconductive char due to the enormous Joule heat from leakage current at breakdown point.

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3. Mechanical breakdown, electromechanical forces that become important in polymer softening (melting) stage.

Being complex in nature, the disordered structural configuration and dipole distribution of different polymers dictate that equally complicated mechanisms are involved in their breakdown process. Nevertheless, it is generally accepted that the mobile ions as a major troublemaker that conducts current and induces thermal breakdown. Much effort has been devoted to synthesis ultra-clean materials, and the application in high-density polyethylene (HDPE) or crosslinked polyethylene (XLPE) for high voltage cable applications have demonstrated over 600 kV/mm level BDV value through eliminating the mobile ionic species to an extreme level [6]. Further approaches toward increasing the BDV has advised researchers to visit the underlying electronic mechanism, whereby electrons are becoming the major charge carriers. Various types of voltage stabilizers, including benzophenone derivatives and polycyclic aromatic compounds have been adopted to absorb the kinetic energy of the injected "hot" electrons [7, 8]. In this work, we examine the effects of a group of polycyclic aromatic hydrocarbon, containing 2, 3 and 4 benzene rings (namely naphthalene, anthracene and pyrene) respectively with a planer π-conjugation structure in high purity epoxy/anhydride formulations on the dielectric properties and breakdown strength of the polymer.

II. Experimental

A. Materials

Electronic grade cycloaliphatic epoxy resin was obtained from Union Carbide Co. and anhydride hardener from Lindau Chemicals, Inc. Phosphine catalyst, naphthalene, anthracene and pyrene (structure shown in Fig. 1) were obtained from Alfa Aesar. All chemicals were used as received.

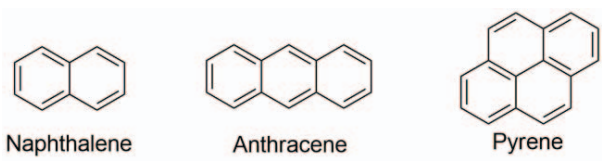

Fig.1. Chemical structure of Naphthalene, anthracene and pyrene.

B. Method

Epoxy and anhydride hardener are mixed at 100:90 weight ratio, into which 1 wt% of phosphine catalyst to the epoxy weight was added. The above mentioned polycyclic aromatic compound are then added to the mixture, at 10^{-5} mol/g resin concentration, as determined by analyzing the UV-Vis spectra in the following discussion, and dissolved by ultra-sonication. All of the well-dissolved epoxy solution presents a light orange color, originated from anhydride, as shown in Fig. 2.

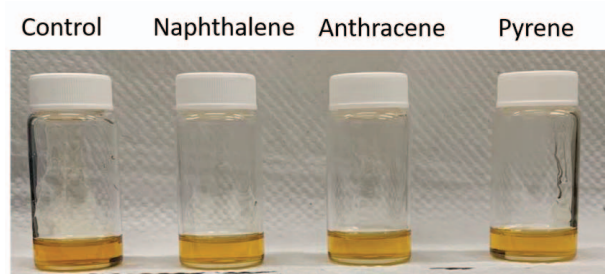

Fig.2. Picture of epoxy resin and that doped with naphthalene, anthracene and pyrene.

The epoxy were then blade coated on FR-4 Cu clad with polyimide tape (40 um) as thickness control. The entire structure was cured in oven at 150 ºC for 2 hrs and 200 ºC for an additional 1 hr. In order to create the arrayed top electrode (Fig. 3(a)), a stainless-steel shadow mask was used covering the top of epoxy and Cu/Ti were sputtered. A fabricated sample is shown in Fig. 3(b). Although fully wetted after blading, the de-wetting process of epoxy during cure occurred, and only the center parts of the substrate are left covered. From SEM, the thickness of the films ranged from 15-25 microns.

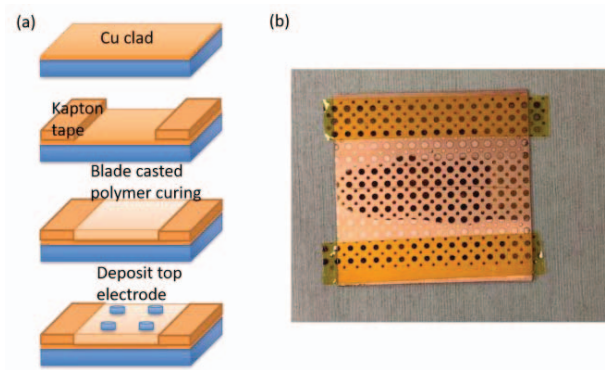

Fig.3. (a) Process flow of creating epoxy and top (sputtered Cu/Ti)/ bottom (Cu clad) electrode, and (b) picture of a fabricated sample.

C. Characterization

UV-Vis spectra of the polycyclic aromatic compounds were obtained using a Shimadzu UV-2450 spectrophotometer in ethanol solution, over the wavelength range of 800-400 nm. Curing profile and glass transition temperature of the epoxy formulations were studied using TA Instrument DSC Q2000 at 10 ºC/min ramping rate in nitrogen atmosphere. Frequency-dependent permittivity and loss tangent of the sample were measured with a probe station set up hooked to an Agilent 4284A LCR meter, scanned from 100 Hz to 1 MHz at 1 V rms. Dielectric breakdown measurements were performed again using probes put into contact with

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top and bottom electrode, which are attached to a 60 kV voltage supply, ramped at a rate of 500 V/s and breakdown criteria taken as 3 mA measured, where often a spark due to discharge into air was observe at the breakdown point. At least 10~15 peak breakdown voltage values were recorded, utilizing the many top electrodes on the surface and primarily focusing on the center part of the film.

III. RESULTS AND DISCUSSION

A. UV-Vis spectra of the polycyclic aromatic compounds

The delocalized π electron clouds in an aromatic hydrocarbon system can be excited upon photon or electron input. The UV-Vis spectroscopy probes the excitation energy of each specific molecules through light absorption, which is essential to understand the trapping of injected high energy electrons from the electrodes under applied field. Fig. 4 shows the UV-Vis spectra of the three compounds under investigation, with the wavelength of the input light converted to energy (unit in eV). At over 3 eV (cut-off frequency), all three compounds started to show absorptions. Originated from the molecular and the subsequent electronic structure, the system containing 2, 3 and 4 benzene rings presented drastic differences in the absorption profile. For example, the naphthalene showed an elevated plateau at 4.5-5.5 eV, followed by the strong absorption doublets. Adding another conjugated benzene ring resulted in the early response with the quadruplet peaks starting at around 3.3 eV for anthracene. The following major absorbance peak also shifted to lower energy below 5 eV, characterizing the strong light/electron absorption in anthracene, through π/σ electron excitation and resonance. Further, the four-benzene ring containing pyrene exhibited the gradually enhancing quadruplet, triplet and doublet absorbance peaks in order, with increasing input photon energy, that represents the designated resonances in the different number of benzenes upon excitation.

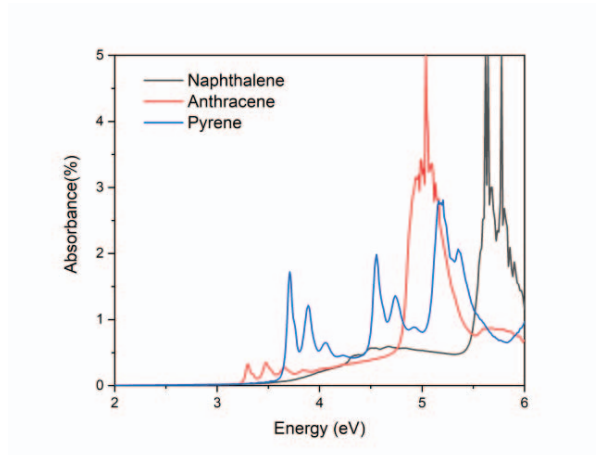

Fig. 4. UV-vis spectra of naphthalene, anthracene and pyrene.

All three of the examined compounds showed strong absorption of light, and therefore to the high-speed electrons during their collision, which is used to trap injected electrons under high electric field that will otherwise be breaking covalent bonds in the polymer to initiate avalanche breakdown. Aiming at this target, a simple calculation is shown below to determine the effective concentration of these molecules to be doped in the resin. Under an electric field of 60 kV/mm, an electron needs to be accelerated from a distance of 50 nm to obtain the kinetic energy of 3 eV, which from the UV-vis spectra is the bare minimum to trigger excitation of the π-conjugated molecules. To space the molecules with an average intermolecular distance of 50 nm, the equation ($d=N^{-1/3}$, N being the number of molecules in unit volume) giving a good estimate helps us determining the additive dosage of 10^{-5} mol/g of resin, assuming the resin density 1.25 g/cm^3. As such, the well dispersed polycyclic aromatic compounds could find and capture the accelerated electrons with high enough kinetic energy for ring excitation.

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B. *Effects of additives on curing and T_g of epoxy*

Although the dosage of additives is quite low, they have found profound effects on altering the curing profiles of the epoxy/anhydride formulation using phosphine catalyst. Fig. 5(a) presents the DSC thermogram of the epoxy with and without additives, where the total heat (ΔH), onset temperature (T_i) and peak temperature (T_p) of the curing peaks are listed in Table I.

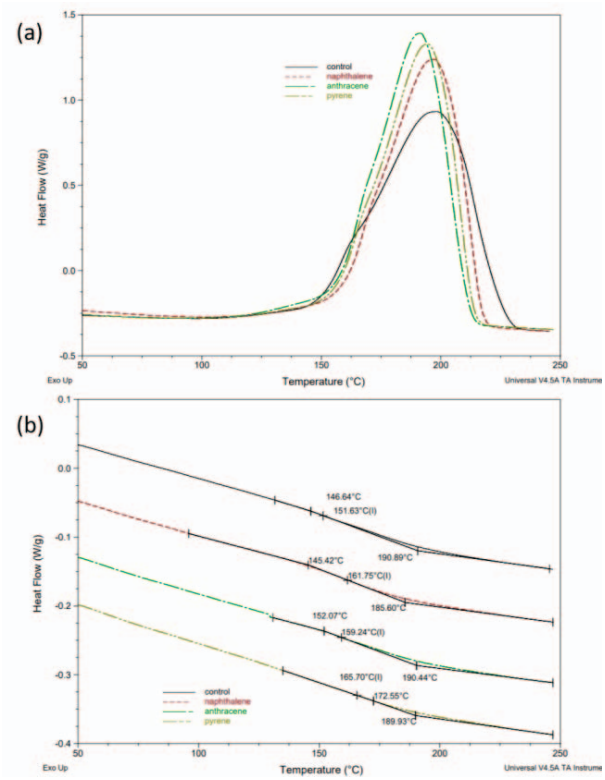

Fig. 5. (a) curing thermogram and (b) DSC glass transition temperature of epoxy control and epoxy with naphthalene, anthracene and pyrene additives

TABLE I. EXTRACTED DATA FROM DSC SCANS OF EPOXY CONTROL AND EPOXY WITH NAPHTHALENE, ANTHRACENE AND PYRENE ADDITIVES

	ΔH (J/g)	**T_i (ºC)**	**T_p (ºC)**	**T_g (ºC)**
Control	360.2	147.21	198.83	151.63
Naphthalene	350.7	154.96	197.48	161.75
Anthracene	362.5	157.17	191.67	159.24
Pyrene	356.9	156.28	194.80	165.70

The epoxy/anhydride system is known for its excellent high temperature properties and is therefore widely used in encapsulant applications. As most thermoset polymers, high glass transition temperature requires higher curing temperature in order to fully consume the reactive groups in the diffusion control stages, where the gradually built-up real time T_g of the system surpasses the curing temperature. The curing diagram in Fig. 5(a) presents a rather high temperature curing peak of around 150 ºC. Interestingly, upon adding the polycyclic aromatic hydrocarbons, though none bearing reactive groups, the curing peak shifted from the epoxy/anhydride control. An increased onset temperature and a decreased peak temperature was found in all the modified formulations, virtually brings the peak forward and narrowed it down while the area underneath were not affected. To be more specific, the shoulder peak in the original epoxy/anhydride diminished followed by a rapid grand curing reaction. The mechanism of phosphine catalyst in the epoxy/anhydride system is through its nucleophilic attack on epoxy ring to initiate cure, due to the lone pair electrons on phosphorus. The shoulder peak in the epoxy control sample is attributed to the ring opening reaction, while the following major peak the curing reactions related to hydroxyl groups reacting with anhydrides to form polyester structure. The effects of the aromatic hydrocarbons can therefore be characterized as delaying the phosphine attack reaction, possibly due to the interactions of the lone pair electrons on phosphorus with the π system. Further heat input frees the phosphine species which actively attacks the epoxides to initiate cure. The rapid heat release in these formulations compared to the control sample, once reaches the onset, may be related to the large population of active phosphines that are just recently unbounded. Furthermore, the additives increased the glass transition temperature of the cured epoxy, from around 150 ºC to up to 170 ºC, which could be related to the additional restrain based on π-π coordination of the additives and resin backbone. The high T_g of epoxy is favored for high temperature applications, whereas when visiting the thermal breakdown mechanism of a polymer dielectric, should also promote the breakdown strength of the film as to restrain the mobile ion transport which in turn resist the thermal degradation of the resin.

C. *Dielectric properties of the epoxy with additives*

The dielectric response of the polymer dielectric in packaging, namely dielectric constant (ε_r') and loss (ε_r''), are critical properties that affect the high-speed signal and power transmission in the surrounding circuit elements. Generally, lower values of these two are favored as following which both the signal delay time (t_d) and signal loss (α_d) would grow as can be seen from (1) and (2), where l being the length of the transmission line, ε_r' and μ_r' the real relative permittivity and permeability of the medium, c the speed of light and tanδ the loss tangent (ε_r''/ ε_r').

$$t_d = \frac{l\sqrt{\varepsilon_r'\mu_r'}}{c} \tag{1}$$

$$\alpha_d \propto \sqrt{\varepsilon_r'} \times \tan\delta \tag{2}$$

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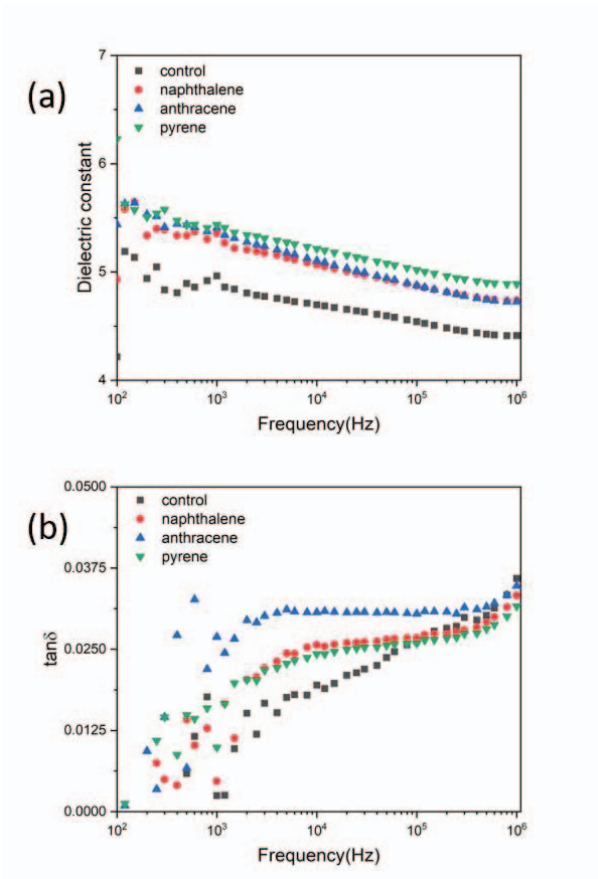

Fig. 6. (a) Dielectric constant and (b) tanδ of epoxy control and epoxy with naphthalene, anthracene and pyrene additives.

Fig. 6 shows the measured dielectric constant and tanδ of the prepared samples. From Fig. 6(a), all the samples present a descending trend of dielectric constant against frequency. This is commonly seen in all dielectrics as higher frequency electric field inevitably requires higher spatial freedom of the charge bearing mediums to be polarized as response, which is often limited in solid states. The dielectric constant of around 4.5 is typical in epoxy materials, while the additives slightly increased this value. Though intrinsically non-polar due to the high symmetry of their molecular structures, these aromatic hydrocarbons offers a large population of delocalized π electrons, whose density could be redistributed under applied field that renders the polarizability. In addition, though careful examinations are due, the possible additive aggregates in the system could significantly alter the dielectric properties through introducing interfacial polarization. With regard to the dielectric loss, the additives also slightly increased the polymer tanδ compared to the control sample but remained in the same level (~0.025). Accompanied with the permittivity drop with frequency, the tanδ increases due to the same reason, the reluctant internal response (re-distribution of space charges at such frequency range) that sacrifices polarization and generates heat. A larger contribution of the molecular level polarization mechanism in the polycyclic aromatic hydrocarbons doped epoxy may explain the relatively mild increase in the tanδ against frequency.

The direct correlation of dielectric constant and loss, to the dielectric breakdown strength is hard to be drawn, where one would need to differentiate the mechanism behind each from a chemical structure point of view. For example, in pure polymers bearing rich hydroxyl groups (say polyvinyl alcohol) that are quite polar with high dielectric constant compared to its more neutral hydrocarbon counterparts (such as polyethylene), evidence have been found that at low temperatures the intrinsic electronic breakdown was disrupted by these polar sites scattering injected electrons and breakdown voltage are therefore increased. However, considering the mobile ion transport and thermal breakdown mechanism built on the Joule heat from leakage current, more polar the resin, water as electrolytes are more prone to be drawn to the system leading to increased leakage current. Other than the population of polar groups, other factors in the polymers, and especially in the composites such as dipole mobility, free volume and space charge reside to affect and attenuate the dielectric constant of the system, each could have a different role when subjected to breakdown conditions. Loss, on the other hand, as it usually represents the conductive/leakage part and is directly linked to heat, is normally harmful in a DC and especially AC breakdown event. Below, the DC BDV of the polymers with polycyclic aromatic hydrocarbons will be presented.

D. Breakdown voltage of the epoxy with adidtives

Dielectric breakdown, being a catastrophic and destructive event, needs to be characterized statistically. Weibull analysis is often used to describe the failure events, and in the application for breakdown strength, (3) gives the probability of failure at voltage (field) V, F(V) as:

$$F(V)=1-\exp\left(-\frac{V}{\alpha}\right)^{\beta} \tag{3}$$

$$\ln\left(\ln\left(\frac{1}{1-F(V)}\right)\right)=\beta\ln V-\beta\ln\alpha \tag{4}$$

where α is the scale parameter, indicating the characteristic value at which a 63.2% probability of failure is found, and β is the shape parameter that describes the dispersion of the data around the Weibull fit. For linear plots, the rearrangement of (3) to (4) gives such convenient relationship.

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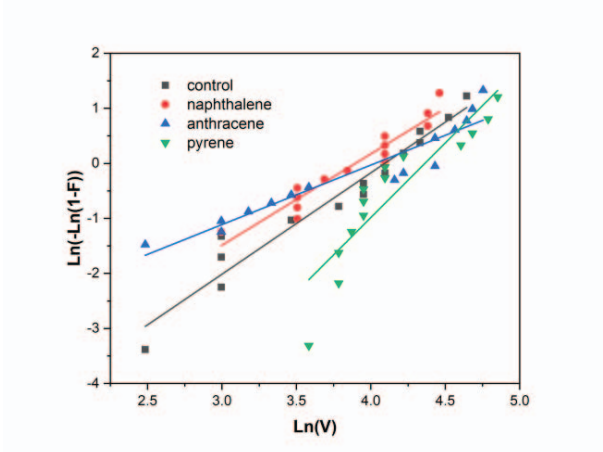

Fig. 7. Weibull plots of breakdown voltage (kV/mm) distributions in epoxy control and epoxy with naphthalene, anthracene and pyrene additives.

TABLE II PARAMETERS FROM WEIBULL PLOTS OF BREAKDOWN VOLTAGE IN EPOXY CONTROL AND EPOXY WITH NAPHTHALENE, ANTHRACENE AND PYRENE ADDITIVES

	α (kV/m)	β
Control	60.01	1.84
Naphthalene	49.25	1.66
Anthracene	56.19	1.08
Pyrene	78.36	2.71

Fig. 7. shows the Weibull plots of the samples, whereas the parameters are summarized in Table II. Judging from the α value, naphthalene noticeably decreased the breakdown strength of the film, while anthracene showed a rather slight decrease and going on to the four-member-ring containing pyrene, an almost 1/3 increase in α value was obtained. In addition, the Weibull parameter, β shows slight increase as well for the pyrene containing epoxy compared to even the control samples showing some promise to increased reliability of breakdown (which can be seen from the reduced spread of the measured breakdown data). The measured higher tanδ value in the former two may represent a slight increase in conductivity of the film upon adding these lower members of the polycyclic aromatic compound. The film quality may also have significant impacts on this value, but most likely the dispersion of the additives in the resin are good. Though the pyrene holds a relatively narrower band gap compared to its naphthalene and anthracene cousins, the measured higher values in BDV likely benefited from the higher glass transition temperature of its cured resin, the milder dielectric loss increase (meaning the resistivity might have not suffered too much), and the large area under the UV-Vis absorption peaks to absorb the kinetic energy of hot electrons have recommended it to be a suitable voltage stabilizer in epoxy formulations.

IV. SUMMARY

In this work, three polycyclic aromatic hydrocarbons, with increasing number of benzene rings have been explored in the application of enhancing dielectric breakdown strength of epoxy resin for packaging high power devices. The fundamental attribute lies in their conjugated π system to be excited and stabilize the colliding high energy electron, which would otherwise attack the polymer chain and initiate avalanche breakdown. The UV-Vis absorption spectra of of these materials were used to probe their capabilities of receive these collisions where all three molecules showed notable responses, and to determine the effective doping level of the additives. The effects of the additives on epoxy curing, dielectric properties and breakdown strength were evaluated. While epoxies with naphthalene and anthracene decreased the breakdown strength, pyrene presented a boost in the resin glass transition and breakdown voltage, right in the target of our needs, though slightly increasing the dielectric constant and loss.

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