Abstract—Metal oxide nanoparticles have been shown to improve the dielectric breakdown strength of insulating polymers. Polyamideimide is a material of practical use for high temperature insulation, and nanoparticle fillers show promise in improving the high temperature stability and dielectric breakdown strength. This work demonstrates the effect of 40-50 nm alumina nanoparticles on the improvement in AC breakdown strength of polyamideimide at elevated temperature and characterizes related electrical properties to gain insight into the mechanisms leading to this improvement. Breakdown tests were performed at temperatures up to 300 °C. The buildup and movement of space charge as a function of filler loading was measured at room temperature using pulsed electroacoustic analysis. Dielectric spectroscopy was used to measure the permittivity at temperatures up to 300 °C. In addition to improving the dielectric breakdown strength, alumina nanoparticles also improved the resistance to thermal degradation, which should allow operation of the composites at temperatures above the operating temperature of the base resin.

Keywords—Dielectric spectroscopy; dielectric strength; high temperature; polyamide-imide; nanocomposite

I. INTRODUCTION

The addition of ceramic nanoparticles can improve the dielectric breakdown strength and voltage endurance of polymers [1,2,3]. These improvements have been attributed to the large interfacial area present in nanocomposites. The large interfacial area can alter charge trapping behavior and local conductivity and can act as sites for polarization. These sites can affect bulk charge distribution, permittivity and breakdown characteristics [2,4].

Most nanodielectric literature focuses on polymers with limited use at high temperature, such as XLPE and epoxies. In this work both room temperature and high temperature (300 °C) characterization of alumina-PAI nanocomposites is presented. Data on nanosilica filled PAI was presented previously [5]. Polyamideimide (PAI) is a polymer which can withstand high operating temperatures (220 °C extended use), and is of interest for its use for high temperature wire insulation.

II. EXPERIMENTAL

A. Sample Preparation

Tritherm B 981-N-42 polyamideimide resin (Elantas PDG) was used for the matrix. Nanotek alumina nanoparticles (Nanophase) with an average diameter of 50 nm were used as filler. The nanoparticles were dispersed in the resin using a Dual Asymmetric Mixer (FlackTek). Alumina balls were added during mixing to improve dispersion.

Samples for breakdown testing, dielectric spectroscopy and thermally stimulated current were prepared by spin coating resin onto electropolished copper plates. The samples were cured in a three step process with increasing temperature to maximize solvent removal and prevent bubble formation.

Samples for pulsed electroacoustic analysis were prepared by spin coating multiple layers onto a Kapton sheet. Solvent was driven off at elevated temperature between each coating. After the desired thickness was achieved, the film was removed from the Kapton and cured as above.

B. Breakdown Testing

AC breakdown testing in oil was carried out at room temperature (Dow Corning 561 silicone transformer fluid) and at 300 °C (Krytox XHT-1000 PFPE oil). Carbon paint was applied to the area of the film to be tested in order to provide intimate contact between the polished aluminum electrode and the PAI film. During testing, a nominal ramp rate of 200 V/s (RMS) was used.

C. Dielectric Spectroscopy

Dielectric spectroscopy between 30 and 300 °C was performed using a Novocontrol dielectric spectrometer. The PAI films were removed from the copper substrate to prevent copper oxidation from influencing the results. Both sides of the sample were sputter coated to provide intimate contact between the sample and the electrode. Tests were carried out between a frequency of $10^3$ Hz and $10^5$ Hz. Prior to testing, the materials were dried in a vacuum oven at 150 °C for 2 hr.

D. Pulsed electroacoustic analysis (PEA)

PEA was carried out at room temperature. A semiconductor contact was used at the cathode and an aluminum contact at the
anode. Tests were carried out on unfilled PAI and 7.5 wt % alumina composites at DC electric fields between 10 and 25 kV/mm. The electric field was applied for 2 hr, the sample grounded and measurements continued for an additional 2 hr.

E. Thermogravimetric Analysis

TGA on composites was carried out using a TA Instruments Q50 TGA. Tests to quantify the degradation temperature were carried out in air using a heating rate of 20 °C/min from room temperature to 1000 °C.

III. RESULTS AND DISCUSSION

A. Breakdown Testing

Weibull plots of the breakdown testing results in air at room temperature and at 300 °C are shown in Fig. 1 and Fig. 2. The nanoparticles are effective at increasing the breakdown strength through 7.5 wt % alumina at both of these temperatures.

The AC breakdown data was fitted to a two-parameter Weibull distribution to quantify the changes in breakdown strength [6]. The characteristic value, \( \eta \), for each test is shown in Fig. 3. For both temperatures, a plateau in breakdown strength is seen at 5 and 7.5 wt % alumina. For 10 wt % alumina nanocomposites the breakdown strength drops approximately 11 %.

Studies on nanoparticle filled polymer composites indicate that the nanoparticles can improve the electrical breakdown strength in some cases and reduce the electrical breakdown strength in others [7,8]. Work on other systems has also shown peaks in the breakdown strength as a function of filler loading [9,10]. It is likely that the agglomeration state of the particles in the nanocomposites is of importance in determining the final electrical breakdown properties at these high loadings. In this work, scanning electron microscopy indicates the presence of agglomerates at 10 wt % loading.

B. Dielectric Spectroscopy

The real and imaginary permittivity of PAI-alumina nanocomposites are shown in Fig. 4 and Fig. 5. With increasing temperature, the permittivity of the resin and composites increases, similar to increases seen in polyimides [11].

At both temperatures the real permittivity (\( \varepsilon' \)) is increased with the addition of alumina nanoparticles through 7.5 wt % alumina. At room temperature the increase is about 80 % over the range of frequencies measured, with the base resin permittivity ranging between 2.5 and 2.8. At 300 °C the increase is between 65 and 70 %, with the base resin permittivity ranging between 8 and 10. At 300 °C, no difference in permittivity can be measured between 2.5 wt % and unfilled PAI. In contrast to the effects on real permittivity, the imaginary permittivity (\( \varepsilon'' \)) shows no discernable trend with the addition of nanofiller at these loadings and frequencies.

Additional data was taken at 100 and 200 °C. Plots of the real and imaginary permittivity at 10^1 and 10^4 Hz as a function of temperature are shown in Fig. 6 and Fig. 7. Over the range of temperatures measured the real permittivity increases with increasing loading at both frequencies. The increase in permittivity is approximately the same magnitude at each temperature. The imaginary permittivity shows no discernable change with alumina nanoparticle loading over the range of temperatures and frequencies measured. The jump in the imaginary permittivity from 200 to 300 °C in all cases can be attributed to the glass transition temperature of the resin, which occurs near 280 °C.
Literature data has shown that the real permittivity can increase or decrease with the addition of nanofillers, above or below that which would be expected according to volumetric arguments. Increases in the dielectric constant have been seen in polyimide-BaTiO$_3$ and alumina nanocomposites [12,13]. The interfacial zone between the particle and the matrix is believed to have a different dielectric response than the matrix, and the difference in measured permittivity and that expected from volumetric effects has been correlated with the particle surface area [14]. In this system, the real permittivity in the nanocomposites is above that which would be expected from the Maxwell-Garnett mixing rule. Based on the interfacial arguments, the interphase region for the system should have a higher permittivity than the matrix.

C. PEA

PEA data was collected at room temperature on unfilled PAI and PAI filled with 7.5 wt % alumina. Examples of the PEA data generated are given in Fig. 8 and Fig. 9. These plots show data collected at 15 and 25 kV/mm at the start of the test and after application of the field for 2 hr. Charge injection at the cathode can be seen, with a decrease in the image charge peak magnitude and buildup of charge adjacent to the cathode. No charge injection is apparent at the anode.

Previous work has shown that the addition of nanoparticles can increase the field required for charge injection and limit space charge buildup in the composite [2,10]. In the current work, this phenomenon is not apparent, with the unfilled and composite materials exhibiting similar space charge profiles at the fields and times applied. It should be noted that in order to produce material thick enough to test, between 15 and 20 layers of material were needed. The layers are expected to be well bonded, but it is possible that interfaces are present in the materials which may alter charge transport or accumulation.
D. TGA

Thermogravimetric analysis on the base resin and alumina composites shows that the degradation temperature increases with the addition of alumina to the system. The data are shown in Table 1. The increase in degradation temperature is practically useful for application in high temperature wire insulation, as it potentially raises the useful operating temperature of the composites above that already provided by the base resin.

IV. SUMMARY

The addition of alumina nanoparticles to PAI resin can improve the dielectric breakdown strength at both room temperature and up to 300 °C. At high loadings, in this case 10 wt % alumina, agglomeration can become significant and lead to a reduction in the breakdown strength. Alumina nanoparticles are also able to increase the real permittivity of the nanocomposites due to a combination of the nanoparticles higher permittivity and the interfacial region between the particles and the matrix. In addition to improving the dielectric breakdown strength at elevated temperature, the nanoparticles are also effective at increasing the degradation temperature of the resin, improving the suitability for use in high temperature applications.

TABLE I. DEGRADATION TEMPERATURES AS DETERMINED BY TGA.

<table>
<thead>
<tr>
<th>Loading (wt %)</th>
<th>Peak Loss Rate Temp (°C)</th>
<th>10 % Mass Loss Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>605</td>
<td>520</td>
</tr>
<tr>
<td>5</td>
<td>610</td>
<td>570</td>
</tr>
<tr>
<td>10</td>
<td>620</td>
<td>540</td>
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</tbody>
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REFERENCES


Figure 9. PEA data at 25 kV/mm 0 min and after 2 hr. The arrow shows the progression of the measured charge.