Assessing thermal and dielectric characteristics of healable, low-field illuminating optoelectronic stretchable material for electrical insulating purposes

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Abstract—An intrinsic self-healing material composed of polyvinylidene-fluoride (PVDF) based fluoroelastomer with the addition of a small amount of non-ionic fluorinated surfactant was studied as a candidate material for electrical insulating purposes. Structural and thermal properties were analyzed with Fourier transform infrared spectroscopy and simultaneous thermal analysis. Broadband dielectric spectroscopy, volume and surface resistivity, and dielectric strength measurements provided a comprehensive overview of the dielectric properties. The material has a relatively high thermal stability (200 °C), a low dielectric strength of 13 kV/mm, and volume and surface resistivities of 1.07E+09 Ω·cm and 1.94E+09 Ω, respectively. Due to various polarization effects, relative permittivity values are generally higher and increase with the loss factor at temperatures above 30 °C and at low frequencies (50 Hz). It was also found from high voltage testing that decomposition of the self-healing material was initiated by carbonization of the melt phase generated in the ignition area. Although a self-healing layer arises shortly after the destructive breakdown, the channel recovery activity is not consistent because of the material's low viscosity. These initial results obtained on a novel dipole-dipole based self-healing material composite can serve as a reference point for further development – to reduce the overall polarity of the system and improve the dielectric properties, while maintaining its self-healing ability.

Keywords—Healable optoelectronic materials; dielectric strength; electrical insulation; thermal measurement; volume and surface resistivity.

I. INTRODUCTION

Technological advancements in industry and academia related to polymer processing usher new possibilities and solutions in soft robotics and wearable electronics – applications that may become part of our daily lives [1-3]. As an example, the elastomer, especially those with enhanced chemical-mechanical properties (for instance, intrinsic self-healing) is indeed attractive for investigating its dielectric possibilities for high-voltage (HV) applications such as power plants and rotation machines.

One of the latest achievements in materials science development, and a promising material for HV applications, is the HELIOS material. HELIOS is a transparent, self-healing and high-ε dielectric for low-field-emission stretchable optoelectronics, where ε refers to dielectric permittivity. The researchers introduced the material as an intrinsic self-healing material composed of a poly-vinylidene-fluoride (PVDF) [4] based fluoroelastomer with a small amount of non-ionic fluorinated surfactant.

Characterization of the dielectric properties of the healable HELIOS material was carried out according to IEC-60243. Furthermore, the self-healing process of conductive channels arising during HV testing, thermal properties, volume and surface resistivities, dielectric strength, polarity, and flammability were observed. This paper gives a brief overview of the optimization of the HELIOS self-healing material and how further development could achieve enhanced reliability and longer service life.

The assessment was carried out using the following general parameter sets for a high-voltage insulator: the highest
temperature classes of maximal hot spot temperature (250 °C) [5], the minimal electrical resistivity of 1E16 Ω·cm (for natural elastomers) [6], 52 kV as maximal equipment's voltage [7], relative permittivity in the order of ones [8] and loss factor lower than 0.01 [9].

II. EXPERIMENTAL

A. Test sample definition

The self-healable, low-field illuminating optoelectronic material HELIOS was provided by the Department of Materials Science and Engineering (MSE), National University of Singapore. The development and fabrication processes were described in the literature [4]. For the experiment, square-shaped samples were used with dimensions of 50 × 50 mm and a mean thickness of 0.71 mm. It is a soft, transparent, and mechanically resistant elastomer.

B. Material structure characterization

This investigation covered the analysis of thermal properties, the material's melting and degradation behaviour, range of working temperature, and physical changes of HELIOS material. The simultaneous thermal analysis (STA) by SDT Q600 (TA Instruments) was carried out for this purpose. The STA was conducted in an air atmosphere in the temperature interval from ambient temperature to 800 °C with a constant heating rate of 10 °C/min. The weight of the HELIOS sample was approximately 9 mg.

C. Broadband dielectric spectroscopy (BDS)

BDS was used to determine the complex relative permittivity, more specifically, the values of the real part (dielectric constant, \( \varepsilon' \)) and the imaginary part (loss factor, \( \varepsilon'' \)) at selected frequencies. The measurements were conducted in temperature interval from -30 °C to 60 °C. The HELIOS sample was initially cooled from 25 °C to -30 °C, then heated to 60 °C, and finally cooled to the laboratory environment temperature of 25 °C. The Alpha A analyzer with an active ZGS electrode system manufactured by Novocontrol Technologies was used for BDS at the testing voltage of 1 Vrms.

D. Volume and surface resistivity

The values of volume and surface resistivity for the tested material were calculated using the following equations:

Equation (1) for the volume resistivity

\[
\rho_v = \frac{\pi(d+g)^2 \cdot V}{4h \cdot I} \text{ (} \Omega \cdot \text{cm) ,} \tag{1}
\]

and Equation (2) for the surface resistivity

\[
\rho_s = \frac{\pi(d+g)^2 \cdot V}{g \cdot I} \text{ (} \Omega \text{)} , \tag{2}
\]

where \( V \) is the applied voltage from the Keithley 248 electrometer (50 V), \( I \) is the current reading from the Keithley 6514 source, \( \pi \) is the mathematical constant, approximately equal to 3.14159, \( d \) is the effective diameter of the guarded electrode (20 mm), \( g \) is the distance between the electrodes (1 mm), and \( h \) is the thickness of the sample. At room temperature, with a source voltage of 50 V, the current through the specimen was measured. The mean value of measured current flow was taken for the time interval of 20 minutes. While volume resistivity \( \rho_v \) was estimated by applying a voltage potential across opposite sides of the tested sample and assessing the resultant current through the samples, the surface resistivity \( \rho_s \) was obtained by applying a voltage potential across the sample's surface and measuring the resultant current.

E. High-voltage testing – dielectric strength

High voltage (HV) testing was carried out to measure dielectric strength (dynamic method with a voltage increase rate of 0.5 kV/s). The material's behaviour under HV was observed during the AC voltage test at 50 Hz. A laboratory equipment containing a power supply unit (HighVolt, type LM30) with a control transformer, a control unit (HighVolt, type SM4) and a high voltage system (all except the electrode system were manufactured by HighVolt). The high voltage system contains a cascade of two cylindrical oil transformers connected via a power resistor and a pair of serially connected grounded capacitors to the electrode system. The electrode system consisted of an upper cylindrical electrode with a diameter of 10 mm and a lower cylindrical electrode with a diameter of 20 mm. The HV test was performed on samples (i) in air and (ii) immersed in high performance insulating oil Nytro Lyra X as a comparison method. Each sample was treated 3 times under the HV load.

III. RESULTS AND DISCUSSION

The simultaneous thermal analysis (STA) results are presented in Fig. 1. From the temperature dependence of the weight loss, it is evident that there was no weight loss of the self-healing HELIOS material during gradual heating up to about 200 °C. Once this temperature was exceeded, chain scission of polymer backbones into smaller units occurs in the temperature range from 200 to 400 °C. This gradual degradation process was followed by rapid thermal decomposition of the test material in the temperature range 400 to 475 °C, accompanied by a pronounced exothermic reaction, visible in the heat-flow signal, and a sudden drop in mass from the original 90 to 0 %.

Fig. 1. Results of simultaneous thermal analysis – dependencies of weight loss and heat flow on temperature.

The changes in dielectric constant and loss factor values in the temperature range from -30 °C to 60 °C and frequency range
from 1 Hz to 1 MHz are presented in Figs. 2-3. The BDS results showed one significant polarization transition as increased conductivity at elevated temperatures and low frequencies. At the highest measured temperature of 60 °C, the dielectric constant was at the level of 1.4E+03 and the loss factor with the measured value of 1E+04. A detailed overview of selected dielectric constant and loss factor values is given in Table I (for temperatures of 25 °C during the first cooling and 50 °C during the first heating).

![Fig. 2. Frequency-temperature dependencies of the real part of complex relative permittivity.](image)

![Fig. 3. Frequency-temperature dependencies of the imaginary part of the complex relative permittivity.](image)

Comparable values of volume and surface resistivities are summarized in Table II. The average value of tested five HELIOS samples is 1.07E+09 Ω·cm for volume resistivity and 1.94E+09 Ω for surface resistivity. Both measured values are considered relatively low for an insulating material. They could lead to the assumption that the material will suffer a faster dielectric breakdown in a high-intensity electric field.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Dielectric constant (-)</th>
<th>Loss factor (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C (1st cooling)</td>
<td>25 °C (1st heating)</td>
</tr>
<tr>
<td>1.1E+01</td>
<td>18.590</td>
<td>1.15E+02</td>
</tr>
<tr>
<td>5.8E+01</td>
<td>16.726</td>
<td>2.26E+01</td>
</tr>
<tr>
<td>1.1E+02</td>
<td>16.079</td>
<td>1.22E+01</td>
</tr>
<tr>
<td>1.2E+03</td>
<td>14.409</td>
<td>2.01E+00</td>
</tr>
<tr>
<td>9.0E+03</td>
<td>13.225</td>
<td>1.35E+00</td>
</tr>
<tr>
<td>9.5E+04</td>
<td>10.895</td>
<td>1.95E+00</td>
</tr>
</tbody>
</table>

![Table I. Selected Values of Dielectric Constant and Loss Factor for Tested Self-Healing HELIOS Material](image)

Measured values of HV testing (measured breakdown voltages and calculated dielectric strength) are given in Table III for samples tested in oil and in air. For both samples measured in oil and air, the dielectric strengths are in the range of 12 – 14 kV/mm, with average breakdown voltages of 8-9 kV. According to the obtained result, it can be concluded that the HELIOS's structure could service the highest permissible voltage for equipment of 52 kV [7] as a device for high-voltage insulation, with a minimum thickness of 5 mm for the material layer.

<table>
<thead>
<tr>
<th>Description of the measured values</th>
<th>Resistivities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume $p_v$ (Ω·cm)</td>
</tr>
<tr>
<td>Average value</td>
<td>1.07E+09</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.39E+08</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>1.30E-01</td>
</tr>
</tbody>
</table>

![Table II. Summarized Values of Volume and Surface Resistivities for Self-Healing HELIOS Material](image)

<table>
<thead>
<tr>
<th>Tested samples 50 x 50 mm voltage increase 0.5 kV/sec.</th>
<th>Breakdown voltage</th>
<th>Dielectric strength (kV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HELIOS 2 HV in air</td>
<td>8.289</td>
<td>8.739</td>
</tr>
</tbody>
</table>

![Table III. Breakdown Voltage Values](image)

The effects of material degradation caused by decomposition are significant and are shown in Fig. 4. Darker structures and hollow with rounded edges showed an important effect of raising the temperature and melting the material around the electrodes. These effects are common in the electrothermal...
breakdown. Numerous minor cracks and large gaps between darker areas indicate shrinkage of the material under maximum load (visible blackening). The liquid phase of the material, which filled a small space around the conductive channel, was also detected in the area of decomposed material after the test was completed. Furthermore, it can be stated that the increase in voltage causes such an energy load on the material that leads to rapid ignition of the material in the contact area between the electrodes. Initially, there was development of discharge activity followed by significant heating of the material, and then burning occurred.

![Image](image1.jpg)

**Fig. 4.** Carbonized traces due to a breakdown of the HELIOS samples (left picture – overall hollow view, right picture – zoomed view of the hollow).

**A. Self-healing evaluation**

By observing the self-healing process of the HELIOS square samples, it was discovered that the process is intrinsic at room temperature. The restoration of the material came shortly after the material was cut-out, by creating traces of the bonding shown in Fig. 5.

![Image](image2.jpg)

**Fig. 5.** An observation of the self-healing process under the microscope.

**IV. CONCLUSION**

Simultaneous thermal analysis revealed that the material structure is stable up to 200 °C, and weight loss is less than 10% up to 350 °C. However, it is necessary to point out that the weight began to decrease at 200 °C. Broadband dielectric spectroscopy results are not in favour of the material’s potential usefulness in standard electrical insulation systems. Dielectric losses are relatively high at low frequencies, especially at temperatures of 50 °C and above, which can be still considered ordinary operating temperatures for electrical insulation materials. The high voltage tests of the self-healing material showed an exciting phenomenon in the formation of thin layers, which tend to heal after rapid failure. However, it should be mentioned that the healing process is not ideal, and the low-viscosity phase is present long after the breakdown. When higher levels of applied electrical voltage are reached, and discharge activity occurs, the material quickly ignites.

Based on the performed tests and analyses, the tested HELIOS material could be used as an electrical insulating material mainly in low-temperature applications without continuous mechanical stresses and at the minimal possible occurrence of unexpected failures due to subsequent temperature rise and discharge activities. In addition, it might be suitable to use as an insulation sealing material or filling material, e.g., in the bushing, where would be no problems with ignition or rupture of the material's structure. However, the HELIOS material does not appear to be suitable for directly forming cover insulation layers. The material should achieve increased thermal stability, reduced flammability, and possess higher material stiffness for the case of using the self-healing material in standard electrical insulation applications. Future work on improving the material properties for such applications will be needed.

**ACKNOWLEDGMENT**

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**REFERENCES**

[7] International standard IEC 60840, "Power cables with extruded insulation and their accessories for rated voltages above 30 kV (Um= 36 kV) up to 150 kV (Um= 170 kV) – Test methods and requirements", edition 3.0 2004.