Dielectric Characterization of High-Performance Spaceflight Materials

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Abstract. As commercial space travel increases, the need for reliable structural health monitoring to predict possible weaknesses or failures of structural materials also increases. Monitoring of these materials can be done through the use of dielectric spectroscopy by comparing permittivity or conductivity measurements performed on a sample in use to that of a pristine sample from 100 µHz to 3 GHz. Fluctuations in these measured values or of the relaxation frequencies, if present, can indicate chemical or physical changes occurring within the material and the possible need for maintenance/replacement. In this work, we establish indicative trends that occur due to changes in dielectric spectra during accelerated aging of various high-performance polymeric materials: ethylene vinyl alcohol (EVOH), Poly (ether ether ketone) (PEEK), polyphenylene sulfide (PPS), and ultra-high molecular weight polyethylene (UHMWPE). Uses for these materials range from electrical insulation and protective coatings to windows and spacecraft parts that may be subject to environmental damage over long-term operation. Samples were prepared by thermal exposure and, separately, by ultraviolet/water-spray cyclic aging. The aged samples showed statistically-significant trends of either increasing or decreasing real or imaginary permittivity values, relaxation frequencies, conduction or the appearance of new relaxation modes. These results suggest that dielectric testing offers the possibility of nondestructive evaluation of the extent of age-related degradation in these materials.

INTRODUCTION

Spaceflight materials are subjected to a wide range of conditions both while in-service and not in-service which can decrease the material’s ability to perform its intended function. Many of the materials used for the launch of a spacecraft can be affected by the uptake of water from the air when subjected to high humidity in the environment, the sun’s radiation, by accidental damage during maintenance or while in-service, causing the material to wear out before its intended life span or fail prematurely. These issues can cause high maintenance costs and, in the extreme cases, loss of life and property from the failed detection of flaws within the material. Since many of the current launch sites for space bound companies within the United States are located in warm, high humidity environments, the detection and prevention of a material’s weakening is of high importance.

Dielectric spectroscopy is expanding in popularity as a technique used to measure a material’s properties nondestructively but there are still gaps in knowledge on how a material will respond, from a dielectric standpoint, after being degraded. The analysis of these materials is useful for the understanding of their complex permittivities and their response to the changes of their surroundings. Using this understanding combined with the use of capacitive sensors to obtain the measurements, the materials can be monitored for unwanted changes that occur over time. Due to their important roles as high thermal, chemical, or radiation resistant materials, ethylene vinyl alcohol (EVOH), poly (ether ether ketone) (PEEK), polyphenylene sulfide (PPS) and ultra-high molecular weight polyethylene (UHMWPE) were chosen for study.
EXPERIMENTAL PROCEDURE

Sample Materials

Sheets of ethylene vinyl alcohol (EVOH) with a nominal thickness of 0.050 mm was purchased from Kuraray (film grade EF-E50). Sheets of poly (ether ether ketone) (PEEK), polyphenylene sulfide (PPS) and ultra-high molecular weight polyethylene (UHMWPE) with nominal thicknesses of 0.127 mm, were purchased from CS Hyde (part numbers: 37-5F-24x24, 40-5F-24, and 19-5F-24, respectively). The samples were stored in the laboratory in the rolls they were packaged in. The laboratory conditions average about 35% RH and 24°C. For each material, circular disks with diameters of 7 and/or 20 mm were punched from as-received and aged sheets a few hours before the initial dielectric spectroscopy measurements were performed. Ten thickness measurements were made across each sample using a Mitutoyo high-accuracy micrometer (+/- 0.0001 mm) and the average thickness was determined.

Dielectric Spectroscopy

Low- and high-frequency dielectric measurements were performed on the materials using a Novocontrol broadband dielectric spectrometer. The Novocontrol system Alpha AN Analyzer was used for low frequency measurements in the range 10 mHz to 10 MHz. For each measurement, the average sample thickness, a one-picofarad cell-stray, and the diameter of the sample (20 mm) were entered into Novocontrol’s WinDeta data acquisition and control software package, which computes the complex permittivity by removing the capacitive edge effects and dividing out the geometric capacitance associated with the test cell.

An Agilent 4991 Radio Frequency (RF) Impedance Analyzer was used for high-frequency measurements in the range 1 MHz to 3 GHz. Seven-millimeter-diameter disks of each material were used with the BDS 2100 7 mm RF sample cell. The same sample inputs as described in the previous paragraph were used here, with the exception of a zero picofarad cell-stray. Further, edge effect compensation was not necessary for these high-frequency measurements, being accounted for during the calibration process.

The calibration of the low frequency system was checked before and after each measurement by testing a known reference sample of Teflon. The low frequency system was recalibrated only if drift was noticed or after being powered down for a holiday. The high frequency system was calibrated before each test in addition to checks with a Teflon reference sample before and after testing.

Measured data was exported into WinFit for data visualization and curve-fitting analysis. The WinFit software relies on fitting a sum of a conductivity term and the Havriliak-Negami function to relaxations present in the measured data. Fitted characteristic parameters were compared in order to examine any spectral changes that occurred after accelerated aging of the sample materials. The WinFit model can be represented as the sum of a power law conductivity term and a number of Havriliak-Negami functions as shown in Eq. 1 [2].

\[ \varepsilon^*_{\text{HN}} = \varepsilon_\infty - \left( \frac{\sigma}{\varepsilon_\infty \omega \tau} \right) + \sum_{i=1}^{n} \Delta \varepsilon_i / \left(1 + (i \omega \tau_i)^{\beta\gamma} \right)^{\sigma/\beta} \tag{1} \]

In Eq. 1, \( \sigma \) is the conductivity, \( \varepsilon_\infty \) is the permittivity of free space, \( \omega \) is the angular frequency, \( \tau \) is the characteristic relaxation time, \( \alpha \) and \( \beta \) are the characteristic relaxation shape parameters (\( \alpha > 0 \) and \( \beta \leq 1 \)), but \( \beta \) can be greater than 1 if \( \alpha \beta \leq 1 \), and the power \( S \) is due to conductivity and electrode polarization effects (\( S \leq 1 \)) [2].

Multiple Havriliak-Negami functions can be applied to a spectrum (here summed over the index \( k \)) to characterize multiple relaxation processes. The relaxation processes observed in the materials discussed within this paper include beta, gamma and Maxwell-Wagner-Sillars (MWS) relaxations. Beta and gamma relaxations are sub-glass transition temperature relaxations that are typically characterized by chain movement and localized defect movement, respectively. A MWS relaxation is an interfacial relaxation present in heterogeneous materials when subjected to an electric field [4, 6].

Weathering Experiments

The materials were tested using the Q-SUN Xe-3 Xenon Test Chamber following ASTM G155, “Standard Practice for Operating the Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials” [17]. This standard tries to recreate the property changes associated with weathering effects that occur when non-metallic materials are exposed to sunlight, moisture, and heat. Exposure conditions are listed in Table 1.
TABLE 1. Weathering exposure conditions as suggested in Cycle 1 of Table X3.1 in [17].

<table>
<thead>
<tr>
<th>Filter Used</th>
<th>Daylight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiance:</td>
<td>0.35 W/(m²·nm)</td>
</tr>
<tr>
<td>Wavelength:</td>
<td>340 nm</td>
</tr>
<tr>
<td>Exposure Cycle:</td>
<td>102 minutes of light at 63 ± 2.5 °C black panel temperature</td>
</tr>
<tr>
<td></td>
<td>18 minutes of light and water spray (air temperature not controlled)</td>
</tr>
</tbody>
</table>

A sample of each material, measuring 22-cm-long by 5-cm-wide (8-11/16” by 2”), was placed in sample holders such that both sample surfaces were exposed, and was held in place by a circular ring. The samples, in their holders, were placed into the test chamber for six weeks of exposure. A 2.54-cm-long by 5-cm-wide (1” by 2”) portion was cut from each sample at one-week intervals and dielectric spectroscopy performed in order to monitor the degradation process. A normal week’s worth of cycles would end after the light and water spray portion of the cycle but due to the excess moisture altering the material’s dielectric response, samples were removed before the final light and water exposure. Before beginning a new week of exposure, the sample holders were repositioned within the chamber in order to minimize the effect of any local variations in irradiance or moisture levels in the test chamber.

Thermal Degradation Experiments

Using a Lab-Line Imperial V, Model 3488M oven, each material was aged following a modified version of ASTM D3045, “Standard Practice for Heat Aging of Plastics Without Load,” [18]. Three exposure times were chosen; one hour, one day and one week, at a temperature close to the material’s melting points (100 °C for EVOH and UHMWPE, 200 °C for PPS and 300 °C for PEEK) to monitor if changes in permittivity were observed as quickly as physical changes were observed (typically physical changes were seen after one hour of aging).

RESULTS

Ethylene Vinyl Alcohol

Weathering Experiments

After six weeks of weathering, no significant trends were observed within the dielectric spectral changes, for EVOH. Large variations of around +/−40 % occurred in the real permittivity but these changes did not develop into any distinct trends. A single β-relaxation was observed at around 200 kHz but it too varied inconsistently from week to week. One possible explanation for these observations is that some samples were removed earlier in the UV exposure cycle than others, possibly resulting in inconsistent moisture levels in the samples.

Thermal Degradation Experiments

After thermal degradation, EVOH exhibited an increase in both ε’ and ε’’ after thermal exposure at 100 °C (marked by red arrows in Fig. 1 (a) and (b), respectively). At 1 kHz ε’ increased from approximately 4.9 to 5.9 after one week of exposure. An increase in ε’’ values follows the same trend as for ε’.

A shift in the relaxation frequency from about 150 kHz, for the pristine sample, to about 30 kHz after one week of thermal aging was observed (marked by the right hand arrow in Fig. 1(b)). This is likely due to possible cross-linking and chain entanglement caused by the simultaneous thermal and ultraviolet radiation exposure.

Nonlinear curve fitting to measured ε’’ according to Eq. 1 revealed a general increase in Δε was observed for both relaxations. In addition to this increase, the conductivity, MWS relaxation frequency and ε∞ were found to increase with increased thermal aging (as shown by the fit parameters in Table 2). The exponential, α and β parameters showed no significant changes.
FIGURE 1. Thermally aged EVOH dielectric measurements plotted as $\varepsilon'$ versus log (frequency) (a) and log ($\varepsilon''$) versus log (frequency) (b). The red arrows indicate trends present within the data.

TABLE 2. Low frequency fit parameters for the thermally aged EVOH samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ (x10^{-13} S/m)</th>
<th>$S$</th>
<th>$\Delta\varepsilon$</th>
<th>$\varepsilon_{\infty}$</th>
<th>$\Delta\varepsilon_{\text{MWS}}$</th>
<th>$\varepsilon_{\infty}$</th>
<th>$\tau_1$ (s)</th>
<th>$\tau_{\text{MWS}}$ (s)</th>
<th>$\alpha_2$</th>
<th>$\beta_2$</th>
<th>$\theta_{\text{MWS}}$</th>
<th>$\beta_{\text{MWS}}$</th>
<th>$\varepsilon_{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low 2</td>
<td>0.60</td>
<td>0.63</td>
<td>2.05</td>
<td>0.38</td>
<td>7.67x10^{-7}</td>
<td>0.41</td>
<td>8.02x10^{-5}</td>
<td>0.28</td>
<td>1.00</td>
<td>0.98</td>
<td>2.34</td>
<td>2.34</td>
<td>2.23</td>
</tr>
<tr>
<td>Low 3</td>
<td>0.87</td>
<td>0.64</td>
<td>2.44</td>
<td>0.42</td>
<td>9.12x10^{-7}</td>
<td>0.40</td>
<td>1.73x10^{-4}</td>
<td>0.28</td>
<td>1.00</td>
<td>1.00</td>
<td>2.34</td>
<td>2.34</td>
<td>2.34</td>
</tr>
<tr>
<td>1 Hour</td>
<td>1.00</td>
<td>0.63</td>
<td>2.49</td>
<td>1.01</td>
<td>7.12x10^{-7}</td>
<td>0.42</td>
<td>3.38x10^{-5}</td>
<td>0.27</td>
<td>1.00</td>
<td>1.00</td>
<td>2.68</td>
<td>2.68</td>
<td>2.68</td>
</tr>
<tr>
<td>24 Hours</td>
<td>1.99</td>
<td>0.66</td>
<td>2.60</td>
<td>1.72</td>
<td>8.25x10^{-7}</td>
<td>0.43</td>
<td>7.89x10^{-6}</td>
<td>0.24</td>
<td>1.00</td>
<td>1.00</td>
<td>2.76</td>
<td>2.76</td>
<td>2.76</td>
</tr>
<tr>
<td>1 Week</td>
<td>1.03</td>
<td>0.64</td>
<td>2.06</td>
<td>1.72</td>
<td>6.66x10^{-7}</td>
<td>0.44</td>
<td>7.05x10^{-6}</td>
<td>0.26</td>
<td>1.00</td>
<td>1.00</td>
<td>2.66</td>
<td>2.66</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Poly (Ether Ether Ketone)

Weathering Experiments

In the case of PEEK, with increasing weathering exposure time, in general, both $\varepsilon'$ and $\varepsilon''$ increased (indicated by red arrows in Fig. 2). A large increase in conductivity, comparatively, was seen after week six, Fig. 2(b), which might be due to moisture. Also, the $\beta$-relaxation frequency decreased with time, from about 300 kHz to 100 kHz over the six-week period of weathering.

During the exposure period, no clear trends were observed within the fit parameters (Table 3) except for a general increase in $\Delta\varepsilon$ of the MWS relaxation and observed increase in $\varepsilon_{\infty}$ each week. The large amount of conductivity present in the Week 1 sample is likely due to excess water still present from the weathering cycle.

Thermal Degradation Experiments

In general, as the thermal aging progressed at 300 °C, $\varepsilon'$ increased (shown in Fig. 3(a)) and at 1 kHz all the aged samples had $\varepsilon'$ values greater than that of the pristine sample. The $\varepsilon''$ values, Fig. 3(b), suggest a decrease in the relaxation frequency from about 250 kHz to 200 kHz after one week, indicated by a red arrow and the fit parameters in Table 4, and an increase in $\varepsilon_{\infty}$. This slight decrease in relaxation frequency is likely attributed to some degree of chain entanglement restricting movement of the aromatic rings.
FIGURE 2. Weathered PEEK dielectric measurements plotted as $\varepsilon'$ versus log (frequency) (a) and log ($\varepsilon''$) versus log (frequency) (b). The red arrows indicate trends present within the data.

TABLE 3. Low frequency fit parameters for the weathered PEEK samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ ($x10^{-20}$ S/m)</th>
<th>$S$</th>
<th>$\Delta\varepsilon$ ($x10^{-2}$)</th>
<th>$\Delta\varepsilon_{MWS}$ ($x10^{-2}$)</th>
<th>$\tau_0$ (s)</th>
<th>$\tau_{MWS}$ (s)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\alpha_{MWS}$</th>
<th>$\beta_{MWS}$</th>
<th>$\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low 1</td>
<td>1.00</td>
<td>0.35</td>
<td>5.80</td>
<td>1.42</td>
<td>1.13$x10^{6}$</td>
<td>3.34$x10^{3}$</td>
<td>0.68</td>
<td>0.37</td>
<td>0.48</td>
<td>1.00</td>
<td>2.52</td>
</tr>
<tr>
<td>Week 1</td>
<td>3517</td>
<td>0.59</td>
<td>5.06</td>
<td>2.87</td>
<td>5.44$x10^{7}$</td>
<td>7.06$x10^{4}$</td>
<td>0.56</td>
<td>0.29</td>
<td>1.00</td>
<td>1.00</td>
<td>2.55</td>
</tr>
<tr>
<td>Week 2</td>
<td>1.00</td>
<td>0.33</td>
<td>4.59</td>
<td>1.66</td>
<td>6.56$x10^{7}$</td>
<td>1.30$x10^{1}$</td>
<td>0.58</td>
<td>0.40</td>
<td>1.00</td>
<td>0.05</td>
<td>2.56</td>
</tr>
<tr>
<td>Week 3</td>
<td>1.02</td>
<td>0.33</td>
<td>5.31</td>
<td>4.26</td>
<td>8.92$x10^{7}$</td>
<td>1.20$x10^{2}$</td>
<td>0.57</td>
<td>0.37</td>
<td>0.81</td>
<td>0.26</td>
<td>2.65</td>
</tr>
<tr>
<td>Week 4</td>
<td>1.00</td>
<td>0.34</td>
<td>5.39</td>
<td>4.40</td>
<td>1.08$x10^{6}$</td>
<td>2.66$x10^{2}$</td>
<td>0.56</td>
<td>0.35</td>
<td>0.80</td>
<td>0.29</td>
<td>2.76</td>
</tr>
<tr>
<td>Week 5</td>
<td>1.01</td>
<td>0.31</td>
<td>5.57</td>
<td>5.48</td>
<td>7.48$x10^{7}$</td>
<td>1.53$x10^{3}$</td>
<td>0.60</td>
<td>0.28</td>
<td>0.88</td>
<td>0.41</td>
<td>2.79</td>
</tr>
<tr>
<td>Week 6</td>
<td>370.5</td>
<td>0.38</td>
<td>5.80</td>
<td>10.20</td>
<td>7.12$x10^{7}$</td>
<td>1.10$x10^{2}$</td>
<td>0.59</td>
<td>0.24</td>
<td>0.87</td>
<td>1.00</td>
<td>2.75</td>
</tr>
</tbody>
</table>

FIGURE 3. Thermally aged PEEK dielectric measurements plotted as $\varepsilon'$ versus log (frequency) (a) and log ($\varepsilon''$) versus log (frequency) (b). The red arrows indicate trends present within the data.

TABLE 4. Low frequency fit parameters for the thermally aged PEEK samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ ($x10^{-20}$ S/m)</th>
<th>$S$</th>
<th>$\Delta\varepsilon$ ($x10^{-2}$)</th>
<th>$\Delta\varepsilon_{MWS}$ ($x10^{-2}$)</th>
<th>$\tau_0$ (s)</th>
<th>$\tau_{MWS}$ (s)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\alpha_{MWS}$</th>
<th>$\beta_{MWS}$</th>
<th>$\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low 2</td>
<td>1.00</td>
<td>0.38</td>
<td>4.52</td>
<td>1.79</td>
<td>7.06$x10^{4}$</td>
<td>3.65$x10^{4}$</td>
<td>0.58</td>
<td>0.43</td>
<td>0.82</td>
<td>1.00</td>
<td>2.37</td>
</tr>
<tr>
<td>Low 3</td>
<td>1.00</td>
<td>0.38</td>
<td>4.19</td>
<td>3.47</td>
<td>4.57$x10^{3}$</td>
<td>5.25$x10^{3}$</td>
<td>0.59</td>
<td>0.21</td>
<td>1.00</td>
<td>1.00</td>
<td>2.54</td>
</tr>
<tr>
<td>1 Hour</td>
<td>1.00</td>
<td>0.36</td>
<td>2.97</td>
<td>3.42</td>
<td>6.17$x10^{3}$</td>
<td>8.48$x10^{3}$</td>
<td>0.57</td>
<td>0.28</td>
<td>1.00</td>
<td>1.00</td>
<td>2.76</td>
</tr>
<tr>
<td>24 Hours</td>
<td>1.00</td>
<td>0.36</td>
<td>2.68</td>
<td>3.32</td>
<td>6.16$x10^{3}$</td>
<td>7.75$x10^{3}$</td>
<td>0.59</td>
<td>0.28</td>
<td>1.00</td>
<td>1.00</td>
<td>2.62</td>
</tr>
<tr>
<td>1 Week</td>
<td>1.00</td>
<td>0.36</td>
<td>3.43</td>
<td>3.88</td>
<td>5.73$x10^{3}$</td>
<td>1.02$x10^{4}$</td>
<td>0.57</td>
<td>0.25</td>
<td>1.00</td>
<td>1.00</td>
<td>2.88</td>
</tr>
</tbody>
</table>
Polyphenylene Sulfide

Weathering Experiments

With increasing exposure, \( \varepsilon' \), \( \varepsilon'' \) and the amount of conductivity for PPS increased with time (marked by red arrows in Fig. 4(a) and (b) respectively). The large increase in low frequency conductivity (shown in Table 5) masks the physical effects going on within this range but it appears that the \( \beta_{II} \)-relaxation shifted from \(1+ \text{ MHz} \) to roughly \(600 \text{ kHz} \) and a second relaxation appeared after three weeks at around \(300 \text{ Hz} \) and shifted to roughly \(2 \text{ Hz} \) after six weeks (marked by red arrows in Fig. 4(b)). These changes are likely due to the heavy thermal/radiation damage.

**FIGURE 4.** Weathered PPS dielectric measurements plotted as \( \varepsilon' \) versus log (frequency) (a) and log (\( \varepsilon'' \)) versus log (frequency) (b). The red arrows indicate trends present within the data.

**TABLE 5.** Low frequency fit parameters for the weathered PPS samples where “R” stands for retest.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \sigma ) (S/m)</th>
<th>( S )</th>
<th>( \Delta \varepsilon_{\text{dd}} )</th>
<th>( \Delta \varepsilon_{\text{MWS}} )</th>
<th>( \tau_{\text{dd}} ) (s)</th>
<th>( \tau_{\text{MWS}} ) (s)</th>
<th>( \alpha_{\text{dd}} )</th>
<th>( \alpha_{\text{MWS}} )</th>
<th>( \beta_{\text{dd}} )</th>
<th>( \beta_{\text{MWS}} )</th>
<th>( \varepsilon_{\infty} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low 1</td>
<td>( 1.06 \times 10^{20} )</td>
<td>0.42</td>
<td>( 4.65 \times 10^{-1} )</td>
<td>( 1.00 \times 10^{6} )</td>
<td>( 1.93 \times 10^{-7} )</td>
<td>( 1.00 \times 10^{11} )</td>
<td>0.22</td>
<td>0.01</td>
<td>0.04</td>
<td>0.40</td>
<td>2.35</td>
</tr>
<tr>
<td>Week 1R</td>
<td>( 9.34 \times 10^{17} )</td>
<td>0.41</td>
<td>( 6.65 \times 10^{-2} )</td>
<td>( 5.78 \times 10^{2} )</td>
<td>( 1.12 \times 10^{-2} )</td>
<td>( 1.75 \times 10^{6} )</td>
<td>0.48</td>
<td>0.36</td>
<td>0.58</td>
<td>1.00</td>
<td>2.74</td>
</tr>
<tr>
<td>Week 2</td>
<td>( 3.21 \times 10^{-18} )</td>
<td>0.24</td>
<td>( 1.32 \times 10^{-1} )</td>
<td>( 9.93 \times 10^{2} )</td>
<td>( 8.83 \times 10^{-4} )</td>
<td>( 5.97 \times 10^{7} )</td>
<td>0.59</td>
<td>0.35</td>
<td>0.04</td>
<td>1.00</td>
<td>2.81</td>
</tr>
<tr>
<td>Week 3</td>
<td>( 1.09 \times 10^{-15} )</td>
<td>0.47</td>
<td>( 3.07 \times 10^{-1} )</td>
<td>( 2.09 \times 10^{2} )</td>
<td>( 3.60 \times 10^{-2} )</td>
<td>( 2.61 \times 10^{7} )</td>
<td>0.45</td>
<td>0.53</td>
<td>0.20</td>
<td>1.00</td>
<td>2.82</td>
</tr>
<tr>
<td>Week 4</td>
<td>( 3.43 \times 10^{-16} )</td>
<td>0.32</td>
<td>( 3.09 \times 10^{-1} )</td>
<td>( 4.13 \times 10^{2} )</td>
<td>( 6.75 \times 10^{-5} )</td>
<td>( 1.90 \times 10^{7} )</td>
<td>0.40</td>
<td>0.39</td>
<td>0.24</td>
<td>1.00</td>
<td>2.62</td>
</tr>
<tr>
<td>Week 5</td>
<td>( 2.72 \times 10^{-14} )</td>
<td>0.53</td>
<td>( 4.25 \times 10^{-1} )</td>
<td>( 1.52 )</td>
<td>( 9.76 \times 10^{4} )</td>
<td>( 3.29 \times 10^{4} )</td>
<td>0.95</td>
<td>0.25</td>
<td>0.36</td>
<td>1.00</td>
<td>2.67</td>
</tr>
<tr>
<td>Week 5R</td>
<td>( 3.19 \times 10^{-14} )</td>
<td>0.91</td>
<td>( 7.50 \times 10^{-1} )</td>
<td>( 3.42 )</td>
<td>( 1.24 \times 10^{3} )</td>
<td>( 3.61 \times 10^{1} )</td>
<td>0.55</td>
<td>0.13</td>
<td>1.00</td>
<td>0.78</td>
<td>2.54</td>
</tr>
<tr>
<td>Week 6</td>
<td>( 9.02 \times 10^{-15} )</td>
<td>0.34</td>
<td>( 1.13 )</td>
<td>( 7.83 \times 10^{1} )</td>
<td>( 8.37 \times 10^{4} )</td>
<td>( 7.45 \times 10^{3} )</td>
<td>0.57</td>
<td>1.00</td>
<td>0.47</td>
<td>0.04</td>
<td>2.39</td>
</tr>
<tr>
<td>Week 6R</td>
<td>( 3.25 \times 10^{-14} )</td>
<td>0.97</td>
<td>( 1.61 )</td>
<td>( 6.96 \times 10^{1} )</td>
<td>( 1.07 \times 10^{2} )</td>
<td>( 2.27 \times 10^{4} )</td>
<td>0.48</td>
<td>0.64</td>
<td>1.00</td>
<td>0.18</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Thermal Degradation Experiments

After one week of thermal exposure of PPS at 200 °C the \( \beta_{II} \)-relaxation shifted from \(1+ \text{ MHz} \) to roughly \(200 \text{ kHz} \) but no other significant results were observed. The spurious data above \(250 \text{ kHz} \), Fig. 5(b), are due inaccurate measurements caused by the low capacitance values. Real permittivity values obtained during the week of thermal aging were within one standard deviation of the mean value measured on pristine samples and can be considered as representing no significant change. During thermal aging, a slight decrease in \( \Delta \varepsilon \) of the \( \beta_{II} \)-relaxation (shown in Table 6) was observed.
FIGURE 5. Thermally aged PPS dielectric measurements plotted as $\varepsilon'$ versus log (frequency) (a) and log ($\varepsilon''$) versus log (frequency) (b). The red arrow indicates trends present within the data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ (x10$^{-20}$ S/m)</th>
<th>$S$</th>
<th>$\Delta\varepsilon_{\text{gr}}$</th>
<th>$\Delta\varepsilon_{\text{MWS}}$</th>
<th>$\tau_{\text{gr}}$ (s)</th>
<th>$\tau_{\text{MWS}}$ (s)</th>
<th>$\alpha_{\text{gr}}$</th>
<th>$\alpha_{\text{MWS}}$</th>
<th>$\beta_{\text{gr}}$</th>
<th>$\beta_{\text{MWS}}$</th>
<th>$\varepsilon_{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low 2</td>
<td>1.00</td>
<td>0.35</td>
<td>0.39</td>
<td>3.24x10$^{-7}$</td>
<td>1.00x10$^{-11}$</td>
<td>0.30</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>Low 3</td>
<td>1.00</td>
<td>0.31</td>
<td>0.20</td>
<td>5.51x10$^{-7}$</td>
<td>6.06x10$^{-7}$</td>
<td>0.33</td>
<td>0.12</td>
<td>0.05</td>
<td>0.01</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>1 Hour</td>
<td>1.00</td>
<td>0.46</td>
<td>0.17</td>
<td>4.61x10$^{-11}$</td>
<td>2.54x10$^{-5}$</td>
<td>0.59</td>
<td>0.03</td>
<td>0.01</td>
<td>0.17</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>24 Hours</td>
<td>1.00</td>
<td>0.41</td>
<td>0.11</td>
<td>3.81x10$^{-7}$</td>
<td>2.12x10$^{-9}$</td>
<td>0.66</td>
<td>0.03</td>
<td>0.01</td>
<td>0.17</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>1 Week</td>
<td>1.00</td>
<td>0.41</td>
<td>0.11</td>
<td>3.81x10$^{-5}$</td>
<td>3.87x10$^{-10}$</td>
<td>0.63</td>
<td>0.03</td>
<td>0.01</td>
<td>0.19</td>
<td>2.17</td>
<td></td>
</tr>
</tbody>
</table>

**Ultra-High Molecular Weight Polyethylene**

*Weathering Experiments*

Over six weeks of weathering, the $\varepsilon'$ values measured on UHMWPE fluctuated but no significant trend was observed, Fig. 6(a). The $\varepsilon''$ values did, however, increase each week, Fig. 6(b), although data measured after 4-6 weeks of exposure fell within one standard deviation of the mean $\varepsilon''$ value measured on pristine UHMWPE. This increase can be attributed to the appearance of a relaxation at around 3 Hz after the second week, which shifted to lower frequencies with increasing exposure time, and a possible relaxation at around 200 kHz. The relaxation around 3 Hz is a $\gamma$-relaxation, likely caused by the motion of chain fragments or defects [14].

The conductivity and $\Delta\varepsilon$ values were found to, in general, increase each week (Table 7). These increases can also be explained by the presence of water (in the form of hydroxyl ions). Also, during the initial two weeks $\varepsilon_{\infty}$ exhibited a slight increase but after this time, the values tended to decrease.

*Thermal Degradation Experiments*

After a week of thermal aging at 100 °C, $\varepsilon'$ and $\varepsilon''$ for UHMWPE were observed to increase with time (Fig. 7). The values did not increase significantly during the first 24 hours of aging but after one week more noticeable changes were observed. The real permittivity increased from about 2.14 to about 2.18 during this time. Also, a relaxation around 2.5 Hz appeared and is likely the $\gamma$-relaxation caused by the presence of hydroxyl ions.

During thermal aging, in general, all the fit parameters were found to decrease with aging time. The relaxation time for the $\gamma$-relaxation is the exception to this trend as the values fluctuated between tests. All the fit parameters are shown in Table 8.
FIGURE 6. Weathered UHMWPE dielectric measurements plotted as $\varepsilon'$ versus log (frequency) (a) and log ($\varepsilon'$) versus log (frequency) (b). The red arrows indicate trends present within the data.

TABLE 7. Low frequency fit parameters for the weathered UHMWPE samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ (S/m)</th>
<th>$S$</th>
<th>$\Delta \varepsilon_1$</th>
<th>$\Delta \varepsilon_2$</th>
<th>$\tau_a$ (s)</th>
<th>$\tau_c$ (s)</th>
<th>$\alpha_\varepsilon$</th>
<th>$\alpha_c$</th>
<th>$\beta_\varepsilon$</th>
<th>$\beta_c$</th>
<th>$\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>1.00x10^{-20}</td>
<td>1.00</td>
<td>1.71x10^{-4}</td>
<td>3.03x10^{-3}</td>
<td>4.39x10^{-2}</td>
<td>3.46x10^{-1}</td>
<td>1.00</td>
<td>0.26</td>
<td>1.00</td>
<td>0.14</td>
<td>2.08</td>
</tr>
<tr>
<td>Week 1</td>
<td>1.02x10^{-20}</td>
<td>0.37</td>
<td>6.13x10^{-3}</td>
<td>1.89x10^{-2}</td>
<td>2.05x10^{-2}</td>
<td>9.18x10^{-5}</td>
<td>0.60</td>
<td>0.40</td>
<td>0.99</td>
<td>0.55</td>
<td>2.17</td>
</tr>
<tr>
<td>Week 2</td>
<td>1.10x10^{-20}</td>
<td>0.36</td>
<td>4.27x10^{-3}</td>
<td>1.85x10^{-2}</td>
<td>6.75x10^{-11}</td>
<td>3.63x10^{-2}</td>
<td>0.15</td>
<td>0.54</td>
<td>0.94</td>
<td>1.00</td>
<td>2.26</td>
</tr>
<tr>
<td>Week 3</td>
<td>2.56x10^{-19}</td>
<td>0.42</td>
<td>1.30x10^{-3}</td>
<td>3.25x10^{-2}</td>
<td>1.00x10^{-11}</td>
<td>6.02x10^{-2}</td>
<td>0.15</td>
<td>0.51</td>
<td>0.88</td>
<td>1.00</td>
<td>2.15</td>
</tr>
<tr>
<td>Week 4</td>
<td>3.28x10^{-17}</td>
<td>0.55</td>
<td>2.05x10^{-3}</td>
<td>3.27x10^{-2}</td>
<td>1.00x10^{-11}</td>
<td>1.05x10^{-1}</td>
<td>0.17</td>
<td>0.69</td>
<td>0.94</td>
<td>0.49</td>
<td>1.85</td>
</tr>
<tr>
<td>Week 5</td>
<td>4.19x10^{-17}</td>
<td>0.54</td>
<td>2.47x10^{-3}</td>
<td>3.97x10^{-2}</td>
<td>1.00x10^{-11}</td>
<td>9.74x10^{-2}</td>
<td>0.18</td>
<td>0.66</td>
<td>1.00</td>
<td>0.49</td>
<td>1.84</td>
</tr>
<tr>
<td>Week 6</td>
<td>7.59x10^{-17}</td>
<td>0.49</td>
<td>5.26x10^{-3}</td>
<td>7.93x10^{-2}</td>
<td>1.00x10^{-11}</td>
<td>1.27x10^{-1}</td>
<td>0.21</td>
<td>0.49</td>
<td>0.82</td>
<td>0.66</td>
<td>1.69</td>
</tr>
<tr>
<td>Week 6 Ext</td>
<td>1.44x10^{-17}</td>
<td>1.00</td>
<td>2.10x10^{-2}</td>
<td>2.80x10^{-1}</td>
<td>8.90x10^{-6}</td>
<td>8.35</td>
<td>0.86</td>
<td>0.25</td>
<td>0.02</td>
<td>1.00</td>
<td>1.79</td>
</tr>
</tbody>
</table>

FIGURE 7. Thermally aged UHMWPE dielectric measurements plotted as $\varepsilon'$ versus log (frequency) (a) and log ($\varepsilon'$) versus log (frequency) (b). The red arrows indicate trends present within the data.

TABLE 8. Low frequency fit parameters for the thermally aged UHMWPE samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma$ (S/m)</th>
<th>$S$</th>
<th>$\Delta \varepsilon_1$</th>
<th>$\Delta \varepsilon_2$</th>
<th>$\tau_a$ (s)</th>
<th>$\tau_c$ (s)</th>
<th>$\alpha_\varepsilon$</th>
<th>$\alpha_c$</th>
<th>$\beta_\varepsilon$</th>
<th>$\beta_c$</th>
<th>$\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low 2</td>
<td>1.00x10^{-20}</td>
<td>0.45</td>
<td>2.69x10^{-4}</td>
<td>8.12x10^{-3}</td>
<td>1.79x10^{-2}</td>
<td>1.21x10^{-3}</td>
<td>0.93</td>
<td>0.60</td>
<td>1.00</td>
<td>0.20</td>
<td>2.03</td>
</tr>
<tr>
<td>Low 3</td>
<td>1.38x10^{-16}</td>
<td>1.00</td>
<td>5.91x10^{-4}</td>
<td>1.58x10^{-3}</td>
<td>2.17x10^{-2}</td>
<td>7.62x10^{-3}</td>
<td>0.77</td>
<td>0.90</td>
<td>0.76</td>
<td>0.17</td>
<td>2.07</td>
</tr>
<tr>
<td>1 Hour</td>
<td>5.24x10^{-17}</td>
<td>0.89</td>
<td>1.30x10^{-3}</td>
<td>1.03x10^{-2}</td>
<td>1.06x10^{-1}</td>
<td>8.53x10^{-6}</td>
<td>0.74</td>
<td>0.34</td>
<td>0.50</td>
<td>0.78</td>
<td>2.09</td>
</tr>
<tr>
<td>24 Hours</td>
<td>3.71x10^{-19}</td>
<td>0.60</td>
<td>4.65x10^{-3}</td>
<td>2.68x10^{-1}</td>
<td>5.26x10^{-2}</td>
<td>7.49x10^{-3}</td>
<td>0.63</td>
<td>0.13</td>
<td>1.00</td>
<td>0.01</td>
<td>1.94</td>
</tr>
<tr>
<td>1 Week</td>
<td>1.00x10^{-20}</td>
<td>0.56</td>
<td>6.76x10^{-3}</td>
<td>5.78x10^{-1}</td>
<td>8.65x10^{-2}</td>
<td>7.05x10^{-10}</td>
<td>0.48</td>
<td>0.26</td>
<td>1.00</td>
<td>0.01</td>
<td>1.84</td>
</tr>
</tbody>
</table>
DISCUSSION

Each of the materials examined exhibited a strong tendency to oxidize as a result of the accelerated weathering process. This oxidation had different effects on each material’s dielectric properties due to their differences in chemical species but similar results were obtained. The typical chemical species formed due to oxidation were hydroxyl and carbonyl groups (verified by FTIR analysis). These groups had the general effect of causing an increase in ε’ (with a larger degree of change being observed in weathered than in thermally aged samples) and of causing the characteristic relaxation frequencies to decrease.

EVOH has two characteristic relaxations that occur within the frequency range being examined here, a MWS relaxation and a β-relaxation. The β-relaxation has been suggested to likely be caused by the local relaxation of crystalline regions or the movement of hydroxyl groups which may interact with each other from one vinyl alcohol group to another, inhibiting chain motion [4]. Despite having heavy oxidation and the samples being physically destroyed due to weathering, no significant changes in the β-relaxation were observed. In the thermally aged samples, however, a decrease in the β-relaxation frequency was observed. This could be the result of increased cross-linking or chain entanglement due to the increased amount of hydroxyl group interactions with the vinyl alcohol groups. Similar results were obtained in terms of the MWS relaxation but in the opposite way. With increased thermal aging time, the relaxation became more prominent and shifted to higher frequencies. This effect likely indicates that there was an increase in interfaces as a result of the polymer being held near its melting point for the extended amount of time in air and that the charges along the interfaces had more mobility.

PEEK, similarly to EVOH, has two relaxations within the frequency range studied that influence its dielectric response, a β-relaxation and a MWS relaxation. The β-relaxation is characterized by the localized non-cooperative motions of the chain fragments, primarily the rotation of the aromatic rings [9]. These two relaxations were observed to have their characteristic relaxation frequency decrease with increased accelerated weathering and thermal aging [4, 6]. These decreases are likely the result of increased cross-linking and oxidation that inhibit the mobility of the aromatic rings. The values of the real permittivity were also found to increase with increased aging [8].

Within the frequency range examined here, PPS has two relaxations (MWS and βII-relaxations) that contribute significantly to the spectrum. Another, the βI-relaxation, appears only after several weeks of weathering. The βII-relaxation is associated with the resonance of the aromatic ring while the βI-relaxation is due to the movement of the stiff chains [10, 12]. After accelerated weathering and thermal aging, the relaxation frequency of the βII-relaxation was observed to decrease for both experiments. This is due to oxidation of the aromatic rings and the sulfur atoms and cross-linking/crystallization because the relatively simple structure was replaced with more bulky groups that became more tightly bound together, decreasing the mobility of the aromatic rings.

UHMWPE has two possible low frequency relaxations, a γ-relaxation and a β-relaxation, which has a small effect on the measurements of the pristine samples. As weathering and thermal exposure increased the two relaxations shifted to lower frequency. The β-relaxation also became a more prominent feature within the dielectric spectra. This relaxation is characterized by the movement of defects within the normal structure that can include chain fragment, free radicals and alterations in the chemical structure [14].

CONCLUSIONS

It was found that oxidation, as a result of the accelerated weathering and thermal aging experiments performed on the materials, was the main influence on the observed modifications to the dielectric spectra and associated relaxations of EVOH, PEEK, PPS and UHMWPE. Material changes produced statistically significant increases in permittivity values for weathered samples of PEEK and PPS and thermally-aged samples of EVOH, PEEK, and UHMWPE, whose general trends agree with the reviewed literature. Also, changes within the characteristic relaxation frequencies and fit parameters were observed for each material. These observed alterations in the fitted parameters of the HN model used in the analysis of each material serve as a reference for future capacitive measurements to determine if the materials have undergone degradation due to environmental exposure.

ACKNOWLEDGMENTS

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REFERENCES