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Influence of Environmental Aging on the Dielectric and Conductivity Behavior of Polyimide

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Abstract— Polyimide (PI) is extensively used in aerospace applications owing to its exceptional properties. However, exposure to harsh environmental conditions, including heat and humidity, can significantly affect its performance. Understanding the effects of aging on PI is important for ensuring its long-term reliability in aerospace systems. This research presents the impact of thermal oxidative aging and humidity on the dielectric performance of polyimide (PI). Aging was conducted at 250°C for 170 hours under controlled humidity conditions, facilitating thermal oxidative degradation and moisture absorption in polyimide. The results of Scanning Electron Microscopy (SEM) analysis revealed surface degradation in aged PI, characterized by micro-voids and cracks that facilitated moisture ingress into the bulk material. The aging process led to the formation of polar molecules, including moisture-induced hydroxyl groups, which enhanced the polarization ability and AC conductivity of PI. To analyze these conductivity changes, Jonscher's Power Law and the Almond-West formalism were employed. The fitting of AC conductivity data using these models provided insights into the frequency-dependent charge transport behavior in fresh and aged PI. The extracted parameters, including DC conductivity, crossover frequency, and relaxation time, demonstrated that aging resulted in increased charge transport and a shift in the frequency response. While the bulk resistivity decreased, the carrier density and mobility were notably enhanced, leading to an increase in leakage current density. At high electric fields (100 MV/m), the leakage charge density increased by 8.4% due to the aging process. These findings highlight the impact of both thermal oxidative and humidity-induced aging on the dielectric and microscopic properties of PI, which is essential for assessing its reliability in aerospace applications under harsh environmental conditions.

Keywords—Polyimide, SEM, Polarization Charge Density, AC Conductivity, Leakage Current

I. INTRODUCTION

The electrification of aviation demands high-performance engineering materials for aircraft wiring and cables, requiring lightweight, thermally stable, and highly durable polymers to enhance efficiency, safety, and reliability in high-voltage electrical systems. The insulating materials used in aeronautics are referred to advance engineering materials which are governed by current standards and requirements. Various polymer materials fulfill these requirements due to their flexibility, cost-effective manufacturing, and superior dielectric properties. Aircraft wiring and cabling insulation primarily utilize Polytetrafluoroethylene (PTFE), Ethylene tetrafluoroethylene (ETFE), Fluorinated Ethylene Propylene (FEP), Polyether ether ketone (PEEK), Perfluoroalkoxy (PFA), and Polyimide (PI) [1,2].

PI is widely used in the aerospace industry e.g. used as insulation material for aircraft wiring and flexible printed circuits due to their excellent electrical properties. However, long term exposure to harsh environmental conditions, including high temperature and humidity, can significantly affect its performance. Aging, itself is a nonlinear and complex phenomenon, which is strongly dependent on applied stress factor, aging time duration and material under stress itself. During operation, aircraft wiring and cabling systems endure extreme conditions, which includes variation of temperatures from -85°C to 300°C, pressures from 1 atm to 0.2 atm, high humidity variations, and continuous vibrations. Among these environmental factors, thermal stress and humidity are the predominant factors, leading to material deterioration and potential failure of the electrical insulation system [3,4].

Extensive studies have been conducted on the dielectric behavior of PI [5–7]. However, studies on the impact of thermal aging on its dielectric performance remain limited and often inconsistent. Additionally, PI susceptibility to moisture absorption (up to 3 wt.%) significantly affects its insulating properties, leading to increased permittivity, reduced resistivity, and mechanical degradation, including cracking, delamination, and adhesion loss [8–11]. Despite this, investigations on the combined effects of thermal oxidative aging and humidity on the dielectric performance in aerospace environments are scarce. Given the extreme operating conditions, understanding PI dielectric response to thermal exposure and humidity is critical for aerospace applications. This research presents the influence of thermal oxidative aging and humidity on the dielectric and conductivity behavior of PI. The change in surface and bulk microscopic morphology of PI due to aging along with polarizability, AC conductivity, volume resistivity and leakage current density is presented.

II. EXPERIMENTAL SETUP

A. Materials

Polyimide (PI) were obtained in form of films (0.1mm thick, 50mm wide) from Shenzhen Jinyuanbao Plastics Materials Co., Ltd. The chemical arrangement of PI is highlighted in Figure 1.

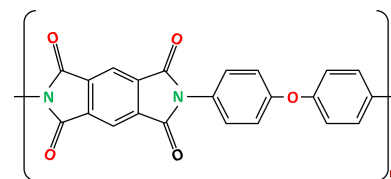


Fig. 1. Chemical composition of PI

B. Aging Profile

PI films (0.1 mm thick) were cut into 50×200 mm samples and mounted on wire mesh shelves inside an oven, maintaining a 5 cm gap from the walls to ensure uniform airflow. The samples underwent thermal oxidative aging at 250°C , following the profile in Figure 2. After lapse of 20 h of thermal exposure, the temperature of oven was decreased to 90°C , and samples were subjected to a 3 h humidity shower at 90% RH. The temperature was then restored to 250°C , continuing the aging process as outlined in Figure 2. After 170h of aging process, samples are taken out and cooled at ambient atmospheric conditions and subjected to degradation study.

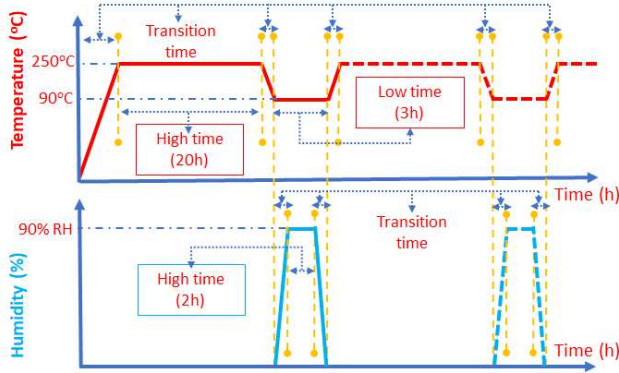


Fig. 2. Profile for thermal oxidative aging with humidity

C. Characterization Techniques

SEM analysis was conducted using a Hitachi SU8600 (Japan) to examine the microstructural morphology of the surface and bulk of PI samples. AC conductivity and volume resistivity of PI samples were measured at room temperature using a Novocontrol Concept 80 broadband dielectric analyzer over a frequency range of 10^{-1} Hz to 10^6 Hz. Polarization charge density and leakage current density were measured using a PolyK ferroelectric tester system (USA) at 25°C and an applied field of 0–100 MV/m, respectively.

III. RESULTS AND DISCUSSION

A. Scanning Electron Microscopy (SEM)

Microscopic morphology of surface and bulk for fresh and aged samples is shown in Figure 3. The SEM surface morphology reveals a smooth, defect-free surface in fresh PI sample, whereas aged PI exhibits microvoids, pits, and a granular morphology. Aging-induced thermal stress leads to micron-sized cracks, which can propagate, facilitating moisture ingress and compromising structural and dielectric integrity. Surface morphology of aged sample is revealing severe surface degradation, including surface roughening, microcracks, and peeling, indicative of oxidation-induced embrittlement. Additionally, region highlighted with circle shown in bulk of aged sample suggests oxidation by-products, impurities, or moisture-induced residues. These findings confirm aging-driven degradation, characterized by chain scission and oxidation-induced embrittlement.

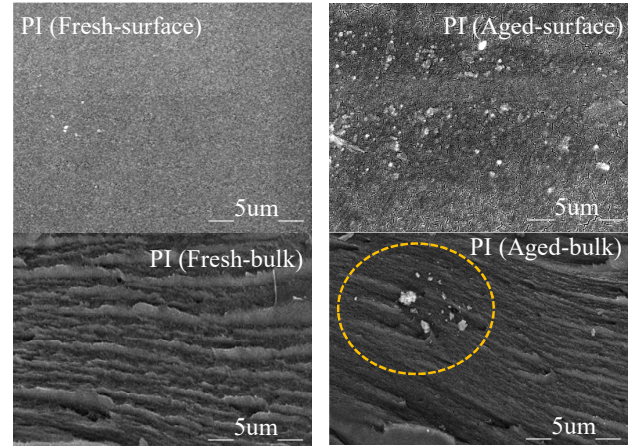


Fig. 3. Surface and bulk morphology of PI samples

B. Polarization Charge Density

The polarization charge density of PI samples, as shown in Figure 4, reveals an increase in polarization of PI due to aging. At a given frequency (e.g., 50 Hz), the relative permittivity depends on the degree of polarization, which is influenced by several factors such as free volume proportion and polar group content. Aging of PI induces the formation of low-mass polar molecules and free radicals, including aromatic nitriles, aniline, toluidine. PI is also susceptible to water absorption. Moisture ingress in PI as indicated in SEM discussion may result in formation of polar hydroxyl groups which further increases polarization in PI. These polar species consequently enhance polarization charge density of PI under an electric field. [12].

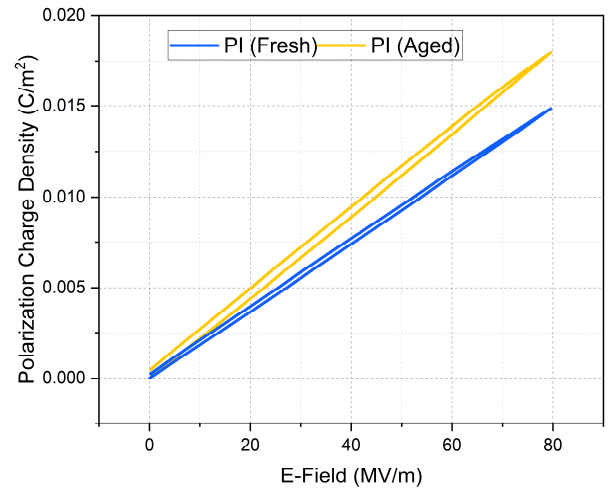


Fig. 4. Variation of polarization charge density of PI samples

C. AC Conductivity, Volume Resistivity & Leakage Current

The conductivity usually follows Jonscher's power law which can be expressed as following [13]:

$$\sigma(\omega) = \sigma_{DC} + A\omega^n \quad 1$$

Where σ_{DC} denotes the frequency independent dc conductivity of the sample, and $A\omega^n$ corresponds to the purely dispersive component of the AC conductivity, which follows a power-law dependency on the frequency ω with an exponent n ($0 \leq n \leq 1$). The exponent n characterizes the degree of interaction between mobile ions and the surrounding lattice in a material, while constant A is associated with the degree of polarizability. The recorded data of conductivity of the PI samples are fitted with equation (1) and shown in Figure 5. The results of Joncher's power law fitting are listed in Table 1.

It is evident from the results that the conductivity at low frequency σ_{DC} is increased in PI as a result of aging. The aged PI shows higher DC conductivity in comparison with the fresh PI. The increase in conductivity is referred to the formation of polar molecules during aging, which contribute to the density of mobile charge carriers. The presence of these polar molecules enhances long-range charge transport, which is reflected in the higher σ_{DC} . At high frequencies, the conductivity is dependent on the frequency and determined by $A\omega^n$. As per Joncher's theory, the frequency-dependent behavior of conductivity can be attributed to the relaxation behavior of the ionic atmosphere caused by mobile charge carriers. The aged PI exhibits a higher value of A , indicating a stronger frequency-dependent contribution to the conductivity. This suggests that the polar molecules formed during aging not only enhance DC conductivity but also increase the localized charge carrier hopping or dipole relaxation mechanisms. The higher value of A in case of aged PI also highlights higher strength of polarizability and implies greater interaction between the electric field and the disordered structure, which aligns with the expected increase in AC conductivity for the aged PI sample.

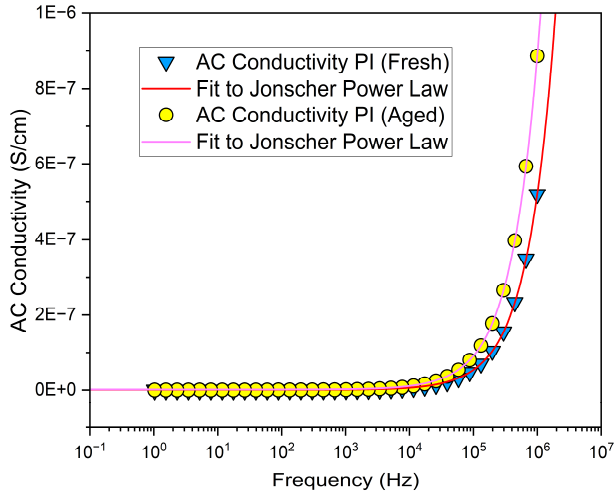


Fig. 5. AC conductivity variation with frequency fitted with Jonscher's Power Law

The minimal change in n (for both fresh and aged samples of PI) indicates that the aging process does not drastically alter the underlying conduction mechanism. Instead, it enhances the

overall conductivity by increasing charge carrier density and mobility. This is consistent with the introduction of polar molecules and increased charge carrier density in the aged material [14].

Table 1. AC conductivity parameters for fitted Jonscher's Power Law

AC Conductivity	Parameters	Value	R^2 (%)
PI (Fresh)	σ_{DC}	7.0229E-10	99.99
	A	5.47342E-13	
	n	0.99629	
PI (Aged)	σ_{DC}	1.512E-9	99.98
	A	9.39036E-13	
	n	0.99578	

The conductivity curves of PI samples are also fitted with Almond West Formalism in Figure 6 to further investigate into the conduction mechanism of PI samples. The frequency dependence of conductivity can be expressed by Almond West expression as following [15]:

$$\sigma(\omega) = \sigma_{DC} \left[1 + \left(\frac{\omega}{\omega_c} \right)^n \right] \quad 2$$

Where σ_{DC} denotes the DC conductivity of the samples, n is the exponent of power-law exponent which describes the electrical relaxation behavior of the material, usually with ($0.5 \leq n \leq 1$), [16] and ω_c refers to the hopping rate of the charge carriers, which defines the crossover frequency from low frequency (DC region) to the AC dispersive conductivity region for $\omega \geq \omega_c$.

Also, the conductivity (σ) can be written in terms of charge amount (q), charge carrier mobility (u) and charge density (n_c) as following:

$$\sigma = qn_c u \quad 3$$

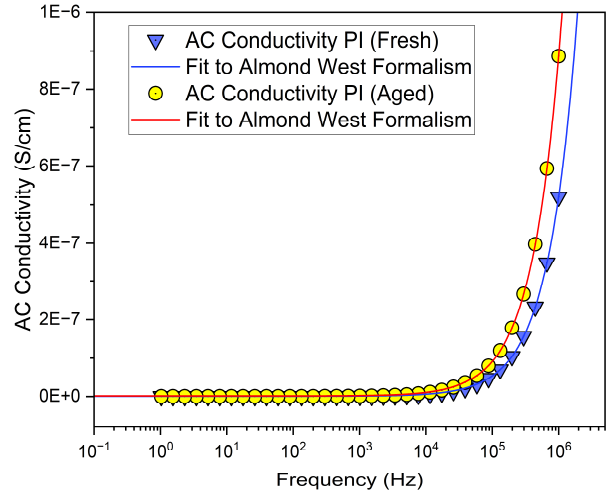


Fig. 6. AC conductivity variation with frequency fitted with Almond West Formalism

The results shown in Table 2 highlights that the DC conductivity increases notably in the aged PI sample compared

to the fresh one. This is consistent with the Jonscher's power law results in Table 1, which also showed higher σ_{DC} in aged PI. The increase in conductivity is due to the formation of polar molecules in the aged PI, which enhance the density (n_c) and mobility of charge carriers (u). The crossover frequency increases in the aged PI in comparison with the fresh sample. A higher value of ω_c suggests that the aged PI sample has faster charge carrier dynamics. Exposure to elevated temperatures can cause chain scission in PI, resulting in increased molecular mobility. This enhanced mobility typically leads to a shift of ω_c to higher frequencies, corresponding to shorter relaxation time (τ) as highlighted in Table 2 [17].

Table 1. AC conductivity parameters for fitted Almond West Formalism

AC Conductivity	Parameters	Value	R^2 (%)
PI (Fresh)	σ_{DC}	7.29215E-10	99.98
	ω_c	1370.09461	
	n	0.99647	
	τ	1.16163E-4	
PI (Aged)	σ_{DC}	1.45862E-9	99.97
	ω_c	1600.32683	
	n	0.99557	
	τ	9.94515E-5	

It is observed that the increase in polarization results in the decrease in bulk resistivity of material [18,19]. The increase in conductivity and decrease in resistivity in aged PI samples (highlighted in Figure 7) further confirm the presence of polar molecules and chain scission effects. Aged PI sample shows a decrease in resistivity prominent in the low frequency region, indicating increased charge carrier availability. This suggests that aging introduces more free charge carriers due to polar molecule formation and possible chain scission. Both fresh and aged PI reach a resistivity plateau, meaning that at high frequencies, the material response is dominated by the same AC conduction mechanisms. This aligns with your previous Almond-West and Jonscher power law results, where conductivity was found to increase in aged PI.

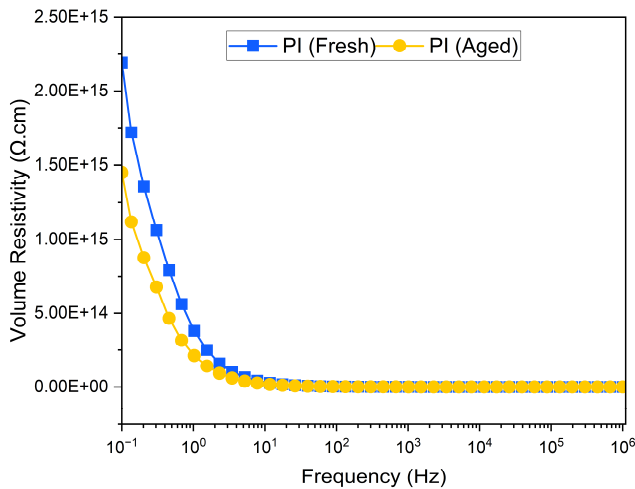


Fig. 7. Variation of volume resistivity with frequency in PI samples

The relationship of leakage current density (J) and conductivity (σ) under e-field (E) is given as following:

$$J = \sigma E \quad 4$$

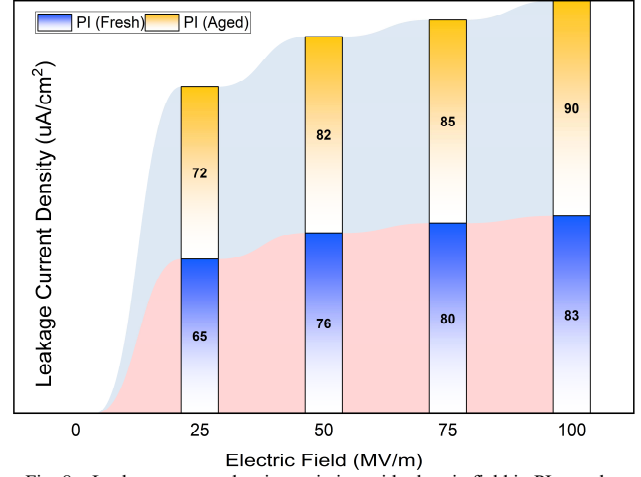


Fig. 8. Leakage current density variation with electric field in PI samples

Figure 8 illustrates the impact of aging on the leakage current density of PI samples, showing an increase in leakage current with the increase of applied electric field. At low e-field strength e.g. at 50 MV/m, the increase in the leakage current density of PI due to aging is 7.8%. This increase is more prominent at high field strength e.g. 8.4% at 100 MV/m. Aging-induced degradation leads to the formation of low-mass polar molecules, radicals, and pyrolysis byproducts, which act as charge carriers [14]. This results in an increased charge density (n_c), enhancing conductivity (σ) and subsequently leakage current density (J), as described by equations (3) and (4). Overall, thermal aging deteriorates the dielectric properties of PI, increasing both the conductivity and leakage current density.

IV. CONCLUSION

In this research, the influence of thermal oxidative aging and humidity on the dielectric behavior of PI was presented. The SEM results revealed surface degradation including micro-voids and cracks which facilitated moisture ingress in PI bulk. As a result of aging, the polarization ability of PI increased due to generation of polar molecules including the moisture induced polar hydroxyl groups. These polar species increased the AC conductivity and reduced the bulk resistivity of PI. The carrier density and mobility in PI is enhanced due to aging which enhanced the leakage current density. The leakage current density of PI increased 8.4% at higher electric fields (100 MV/m) due to aging process. Overall, the surface and bulk properties including the microscopic morphology and dielectric properties are deteriorated as a result of aging. The findings can open pathways for further investigations into the temperature dependent molecular dynamics, verifying the suitability of PI for harsh environmental conditions in aerospace applications.

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