Transactions of the Materials Research Society of Japan 29[4] 1159-1162 (2004)

Measurement of Space Charge in Insulating Polymer by Pulsed Electroacoustic Method

Yutaka Kamei and Shigetaka Fujita
Department of Electrical and Electronic Engineering, Hachinohe Institute of Technology,
88-1, Myo Ohbiraki, Hachinohe 031-8501 Japan
Fax : 81-178-25-1430, e-mail : d99201@stud.hi-tech.ac.jp

The space charge density and distributions in an insulating polymer film (125 μm thick) were measured in room temperature air using the pulsed electro-acoustic (PEA) method. With specimens being set between the upper and lower electrodes, a pulse voltage was impressed between the electrodes to oscillate the space charges in the specimens so as to stir an acoustic wave. This acoustic wave was converted to an electrical signal through a piezoelectric element installed in close contact with the lower electrode. The electrical signal was amplified and observed by oscilloscope, then subjected to signal analyses on a computer to measure the space charge density and distributions in the specimens. A higher negative DC bias voltage was found to yield a higher space charge density even with the applied voltage being reset to 0 V. Specimens immersed in distilled water at about 20°C (having a resistivity of 3.3 MΩ · cm) recorded a higher space charge density immediately upon applied voltage input as they absorbed more moisture.

Keywords : polyimide, space charge, conduction current, thermal properties

1. INTRODUCTION

Polyimide films are the preferred group of heat-resistant polymers because they do not exhibit a softening point at temperatures up to 500°C, offering superior mechanical properties over temperatures from liquid helium temperature to 500°C (1). Moreover, polyimide films promise electrical insulation applications in harsh environments as they are rich in chemical resistance, including resistance to radiation, such as β-rays and γ-rays. However, because polyimides contain an imide bond in their molecular structure, they demonstrate a high coefficient of moisture absorption, which can result in degraded electrical insulation performance, posing practical problems. Problems related to dielectric, electrical conductance, and dielectric breakdown properties of polyimides have been reported (2)-(7), but there are few reports on the behavior of space charges that could adversely affect electrical insulation performance and the effects of moisture absorption on space charge formation (8)-(10).

This study measured the amount of moisture absorption, infrared absorption spectra and thermal characteristics of polyimide films immersed in deionized water to review the effects of moisture absorption. Further, specimens immersed likewise were impressed with a bias voltage to review changes in their space charge density and distributions over time to explore the effects of moisture absorption on space charge formation.

2. SPECIMENS AND EXPERIMENTATION METHOD

2.1 Specimens

Polyimide films (Kapton H, nominal: resistivity 10^{18} Ω · cm) manufactured by Du Pont-Toray Co., Ltd. were used as specimens. Figure 1 shows the molecular structure of the polyimide. Figure 2 shows the imide group. Specimens of two thicknesses were used, 125 μm for moisture absorption, thermal characteristic and space charge measurement purposes, and 50 μm for infrared absorption spectrum measurement. The specimens were also organized into three sizes: 4.5 mm for thermal characteristic measurement, 50 mm × 50 mm for moisture absorption and space charge measurement, and 10 mm × 50 mm for infrared absorption spectrum measurement. The specimens were immersed in deionized water at about 20°C (having a resistivity of 3.3 MΩ · cm) for a predetermined period before they were subjected to various measurement processes.

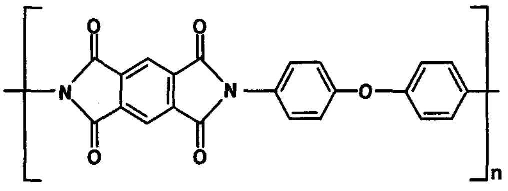


Fig.1 Molecular structure of polyimide.

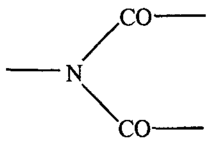


Fig.2 Imide group.

2.2 Experimentation method

Moisture absorption measurement was carried out using an electronic force balance in room temperature air. Infrared absorption spectrum measurement was carried out over the measuring frequency range of 400 cm^{-1} to 4000 cm^{-1} in the total reflection absorption measurement process using a Fourier-transform infrared spectrophotometer (FTIR-8300 manufactured by Shimadzu Corporation). Thermal characteristic measurement was conducted by measuring calorific value changes in a nitrogen gas atmosphere at a heating rate of 10°C/min over a temperature range of 30°C to 500°C using a differential scanning calorimeter (DSC-60 manufactured by Shimadzu Corporation). The space charge density and distributions were measured in room temperature air using the PEA (pulsed-electro acoustic) method. Figure 3 schematically shows the measurement apparatus. The principles of space charge measurement are outlined below. With a polyimide film (PI) being set between the upper and lower electrodes, a pulse voltage of 50 V, 400 Hz was impressed between the electrodes to oscillate the space charges in the PI so as to stir an acoustic wave. This acoustic wave was converted to an electrical signal through a piezoelectric element installed in close contact with the lower electrode. The electrical signal was amplified and observed on an oscilloscope (HP-54820 A, sampling rate: 2 GSa/s), then subjected to signal analyses on a computer to measure the space charge density and distributions in the PI. More specifically, after immersed specimens had been impressed with a DC bias voltage of -2.5 kV from the upper electrode for 360 minutes, the DC bias voltage was immediately reset to 0 V to measure the resultant space charge density and distributions over time.

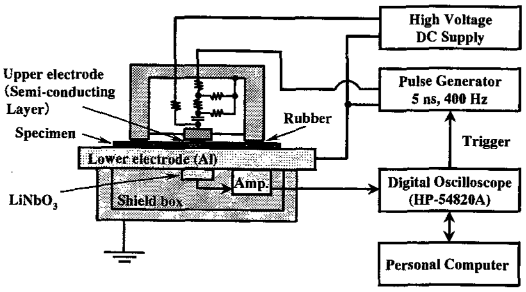


Fig.3 PEA measurement system.

3. RESULTS AND DISCUSSION

3.1 Amount of moisture absorption

Figure 4 shows the coefficient of moisture absorption of specimens immersed for 1 hour, 3 hours, 6 hours, 12 hours, 24 hours and 48 hours. The coefficient of moisture absorption in a specimen was measured by calculating the amount of moisture contained in the specimen from its weight difference from a non-immersed specimen [(weight of the immersed specimen - weight of the non-immersed specimen)/(weight of the non-immersed specimen) x 100]. The amount of moisture absorption increased over immersion time but peaked after 12 hours of immersion.

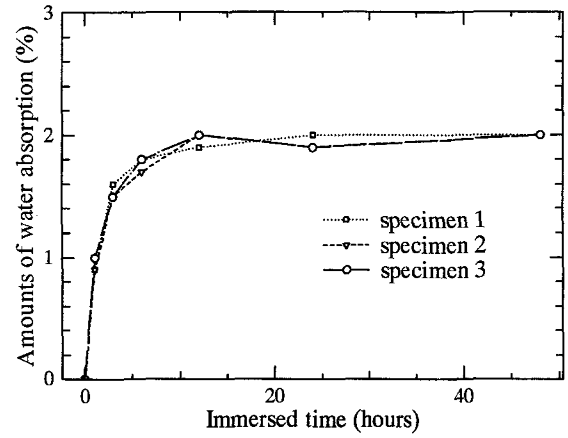


Fig.4 Amounts of water absorption

3.2 Infrared absorption spectra

Figure 5 plots the results of total reflection absorption measurement of specimens immersed in deionized water for 48 hours and non-immersed specimens over the measuring frequency range of 400 cm^{-1} to 4000 cm^{-1}. No difference was observed in infrared absorption spectrum between the non-immersed specimens and specimens immersed for 48 hours, with no change in their internal structure resulting from the moisture absorption. The deionized water present in the immersed specimens was presumably present in the free volumes between the molecules that make up the specimens in the form of water molecules, instead of bonding with these modules.

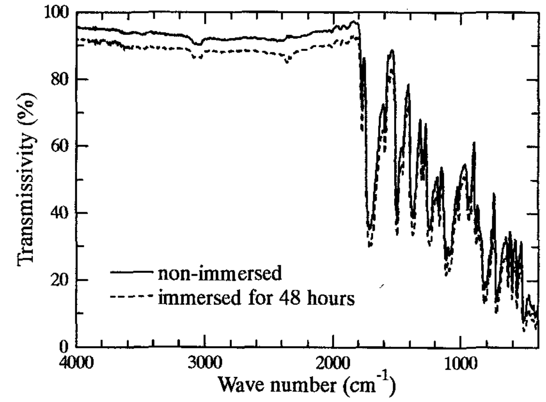


Fig.5 Infrared absorption spectra
for the non-immersed and immersed specimens.

3.3 Thermal characteristics

Figure 6 plots the differential scanning calorimetric results of specimens immersed for 3 hours, 6 hours, 12 hours, 24 hours, and 48 hours and non-immersed specimens. The non-immersed specimens began heat absorption at the commencement of measurement, demonstrating a heat absorption peak measuring 0.04 mW/mg at temperatures around 110°C but showed no significant changes from about 180°C in the vicinity of 400°C. Rising calorific values were confirmed at 400°C and after. The immersed specimens exhibited a heat absorption peak at around 110°C like their non-immersed counterpart. This peak escalated with increases in immersion time, rising to 0.09 mW/mg for the specimens immersed for 3 hours, to 0.1 mW/mg for those immersed for 6 hours, and to 0.11 mW/mg for those immersed for 24 hours and 48 hours. The non-immersed specimens also had minor peaks, suggesting absorption of moisture to some extent.

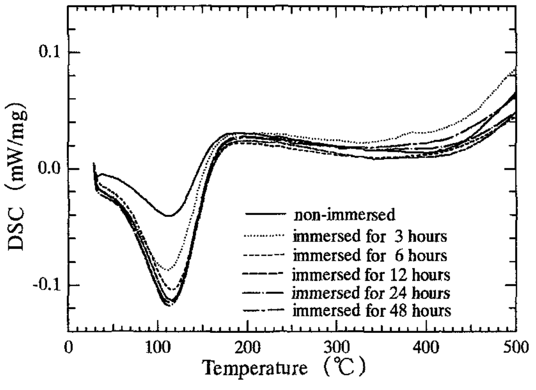
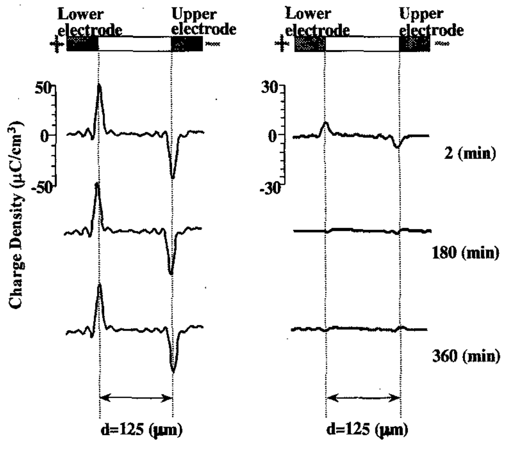


Fig.6 Characteristics of DSC.

3.4 Space charge characteristics

Figure 7 (a) shows the distributions of the space charge density in non-immersed specimens after they had been impressed with a negative bias voltage of -2.5 kV for 2 minutes, 180 minutes, and 360 minutes. Negative space charges developed on the upper electrode, with positive charges on the lower electrode. Figure 7 (b) shows the space charge densities observed in non-immersed specimens. After these specimens had been impressed with a negative bias voltage of -2.5 kV for 360 minutes, the bias voltage was immediately reset to 0 V to measure the space charge density 2 minutes, 180 minutes, and 360 minutes later. Two minutes later, minor negative space charges developed in the upper part of the specimens, with minor positive charges appearing on the lower electrode. These charges may account for portions of the charges developed on the electrodes through polarization during the voltage impression process. The minor charges on the upper and lower electrodes were found to decrease over time.

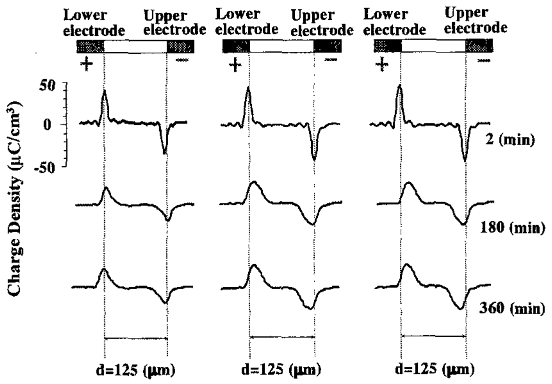


(a) During application of bias voltage.

(b) After bias voltage was returned to 0V.

Fig.7 Space charge density of non-immersed specimens.

Figure 8 (a), (b), and (c) show the space charge densities in specimens immersed for 1 hour, 24 hours, and 48 hours after they had been impressed with a bias voltage of -2.5 kV for 2 minutes, 180 minutes, and 360 minutes. Comparative studies of Figure 8 (a) to (c) indicate that peaks broadened over immersion time, promoting the charge injection into the specimens during the voltage impression process.



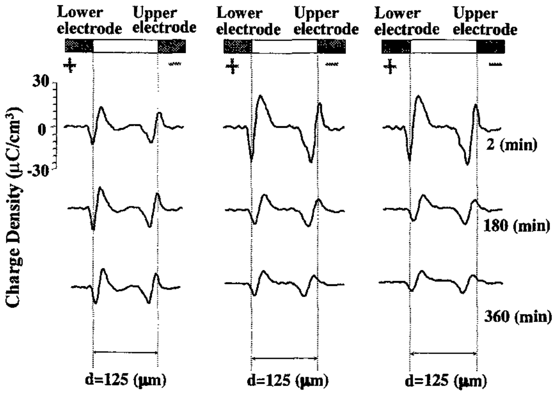
(a) immersed for 1 hour

(b) immersed for 24 hours

(c) immersed for 48 hours

Fig.8 Space charge density of immersed specimens during application of the negative bias voltage.

Figure 9 (a), (b), and (c) show the space charge densities observed in specimens immersed for 1 hour, 24 hours, and 48 hours. After these specimens had been impressed with a negative bias voltage of -2.5 kV for 360 minutes, the bias voltage was immediately reset to 0 V to measure the space charge density 2 minutes, 180 minutes, and 360 minutes later. Two minutes later as shown in Figure 9 (a), negative space charges developed in the upper part of the specimens, which in turn induced positive charges on the upper electrode. Further, positive space charges appearing in the lower part of the specimens induced negative charges on the lower electrode. Homo space charges were thus found to shape inside the specimens while they were impressed with the voltage. This may be the consequence of the barrier between the electrodes and polyimide film being lowered after its absorption of moisture having a lower dielectric constant (11). Moisture absorption may have presumably facilitated the injection of many homocharges. In the meantime, the space charges in the specimens may have transferred gradually as the space charge density declined. Comparative studies of Figure 9 (a) to (c) suggest that the space charge density 2 minutes later increased over immersion time, but 360 minutes later began to decrease, promoting the space charge transfer to the electrodes.



(a) immersed for 1 hour (b) immersed for 24 hours (c) immersed for 48 hours

Fig.9 Space charge density of immersed specimens after the applied voltage was reduced to 0 V.

4. CONCLUSIONS

The amount of moisture absorption, infrared absorption spectra, thermal characteristics and space charges of a polyimide film immersed in deionized water were measured. The polyimide film was found to absorb more moisture as it was immersed longer, but showed little change after 12 hours of immersion. Little difference was observed in infrared absorption spectrum between non-immersed specimens and specimens immersed for 48 hours, with no change in their internal structure resulting from the moisture absorption. As for thermal characteristics, evidence of a marked absorption was observed at temperatures around 110°C. Specimens immersed longer absorbed more moisture inside, with the heat absorption peak escalating. Further, specimens immersed longer recorded larger space charges immediately after bias voltage input but had a rapidly declining rate of space charge over time.

5. REFERENCES

[1] L. E. Amborski, *Ind. Chem.*, **2**, 189 ,1963

[2] M. Nagao, G. Sawa & M. Ieda, *Trans. Inst. Elec. Japan*,**97-A**, 279 ,1977

[3] E. Sacher, *IEEE Trans. Electr. Insul.*, **EI-13**,94 ,1978

[4] G. Sawa, K. Iida, S. Nakamura & M. Ieda, *IEEE Trans. Electr. Insul.*, **EI-15**, 112,1980

[5] S. Fujita, K. Shinyama & M. Baba, *Abs. DRP*, 136,1998

[6] E. Sacher, *IEEE Trans. Electr. Insul.*, **EI-14**, 85,1979

[7] J.Melcher et al., *IEEE Trans. Electr. Insul.*, **EI-24**, 31,1989

[8] Y. Kamei, S. Fujita & M. Baba, *Proc. ISE*, 67, 1999

[9] Y. Kamei, M. Baba & S. Fujita, *Institute of Electrical Engineers National Convention Lecture Collection [2]*, 579, 2000.

[10] Y. Kamei, S. Fujita, *Institute of Electrical Engineers National Convention Lecture Collection [2]*, 241, 2001.

[11] Institute of Electrical Engineers, *Phenomenology of Dielectrics*, 232, 1973.

(Received October 11, 2003; Accepted March 10, 2004)