

Charge dynamic characteristics in corona-charged polytetrafluoroethylene film electrets^{*}

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Abstract: In this work, the charge dynamics characteristics of injection, transport and decay in porous and non-porous polytetrafluoroethylene (PTFE) film electrets were investigated by means of corona charging, isothermal and thermal stimulating surface-potential decay measurements. The results showed that the initial surface potential, whether positively or negatively charging, is much higher in non-porous PTFE than in porous PTFE. For porous film the value of initial surface potentials increases with increase of film thickness. Higher charging temperature can remarkably improve charge stability. The charge dynamics are correlated to materials microstructure according to their scanning electron micrographs. For non-porous PTFE films, polarizability change of C-F bonds is the main origin of electret charges; but for porous PTFE film a large number of bulk and interface type traps are expected because of the greater area of interface and higher crystallinity.

Key words: Polymer electrets, Charge dynamics, Material microstructure

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INTRODUCTION

Polytetrafluoroethylene (PTFE) is one of the most important high insulating organic polymer electret material which have been applied in many fields such as sensors, generators and motors, dose-meters, and air filters at high temperature, biofunctional materials etc., especially since the excellent charge storage stability and high quasi-static and dynamic piezoelectric coefficients in porous PTFE film are reported (Xia *et al.*, 1999; Schwödiauer *et al.*, 2000; Kressmann *et al.*, 1996). Various models based on kinetic equations taking into consideration capture and release from traps, creation of carrier pairs, recombination, stochastic

hopping, etc. have been proposed for electrets phenomena (Hillenbrand and Sessler, 2000). However, many experimental studies showed that the electret phenomena in porous film were very different from those in non-porous film (Xia *et al.*, 1999). The popular theories cannot explain the difference of charge dynamics between porous and non-porous polymer electrets. For example, a very high surface potential can be deposited on the surface of the non-porous film during corona charging without a control grid, but such phenomenon cannot be observed in porous film. And for thicker film, higher surface potentials can be gained for porous film; but not remarkably for non-porous film. In addition, the high quasi-piezoelectric coefficients in porous PTFE had been measured only on samples without evaporated electrodes (Gerhard-Mulhaupt *et al.*, 2000).

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In this work non-porous and porous PTFE film with different thickness and porosity were charged by corona charging method, and their charge behavior of injection, transport and decay were investigated by measurements of isothermally and thermally stimulating surface-potential decay measurement, etc. Their scanning electron micrographs showed that their charge dynamics correlated to the film microstructure.

MATERIALS AND EXPERIMENT METHODS

Perfluoropolymer films

Porous PTFE film of 90 μm thickness (~70% porosity) and 150~170 μm thickness (~50% porosity) were obtained from the Shanghai Plastic Institute, China. Porous PTFE film of 63 μm thickness (91% porosity) was obtained from Goodfellow Cambridge Limited. Non-porous PTFE samples were commercially available for 50 μm thick Teflon PTFE films of Du Pont Co. All samples were cleared with iso-propranol before being charged and then cut into 3 cm \times 3 cm square.

Positive and negative corona charging at elevated temperatures

A 100 nm cylindrical aluminum electrode with diameter of 1.5 cm was evaporated on one side in vacuum. Positive or negative charging was achieved by point-to-plane corona discharging in air under normal conditions (ambient temperature of 30 $^{\circ}\text{C}$, 90 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$, atmospheric pressure of 101.3 kPa, and relative humidity of 45%). The aluminized side of the film was placed on a heated and electrically grounded metal plate. The air gap between the needle electrode and sample surface was 4 cm so that the plasma near the needle tip could not affect the sample directly and the charged sample area was several centimeters in diameter. Unless specially pointed out, the charging condition was as follows: needle electrode voltage was ± 12 kV, charging time was 5 minutes. After charging, the samples were stored in small boxes to minimize charge decay by ions in the surroundings.

Measurements of isothermally and thermally stimulating surface potentials decay

The effective surface potentials were determined by means of non-contacting field-compensating electrostatic voltmeters (Model 344, TREK, USA). After being charged at elevated temperature, samples were usually immediately moved from charging chamber into a grounded metal plate for measuring surface potentials, so that the potential decay due to higher temperature was avoided. For the measurement of thermally stimulating surface potential decay, heating rate was 6 $^{\circ}\text{C}/\text{min}$ from RT to 260 $^{\circ}\text{C}$ and the surface potential value was recorded at intervals of 10 $^{\circ}\text{C}$.

EXPERIMENTAL RESULTS AND DISCUSSION

Corona charging behavior

When electrets are formed by corona charging, various kinds of ions derived from the corona discharge in the air are injected from electrode to materials. Some of the ions recombine on the surface of the materials, giving rise to chemical changes in it, while the remaining ions penetrate into the bulk of the materials, where their charge becomes trapped, first by deep traps, then by shallow traps, following which may be released by corona-generated excited molecules and transferred into the bulk of the material in the internal electric field related to the injected charge (Hilczler and Malecki, 1986). The trapped charge density is monitored by means of surface potentials measurement. Fig.1 displays the results of initial surface potentials as a function of charging temperature for different thick porous and non-porous films. The results showed that the initial surface potentials of non-porous film were much higher than those of porous film, the difference being about 1500 V. And the initial surface potentials for porous film increased with increase of film thickness. The observed small decrease of surface potentials with increase of the charging temperature was attributable to the increase of conductivity, and the decreased magnitude was almost the same

for films of different thickness.

It is generally known that initial surface potentials mainly originate from surplus charges deposited on film surface. For the porous film, corona charges can penetrate it through the void to reach the rear of the electrode during charging and decay. A large number of surplus charges cannot be deposited, so very high surface potentials are not accumulated. In non-porous film, surplus charges cannot decay through the rear of the electrode due to the very small volume conductivity and absence of free path. They decay mainly through recombination. Therefore, very high surface charge density can be developed. Besides, for porous film, the thicker the film, the more charges can be stored, therefore the surface potentials are higher.

Fig.1 also shows that the effect of corona polarity on initial potentials is not remarkable whether for porous or for non-porous PTFE samples. This

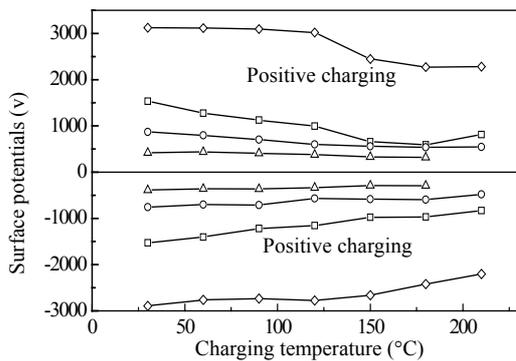


Fig.1 Initial surface potentials as a function of charging temperature for different PTFE film —◇— 50 μm non-porous film; —□— 160 μm; —○— 90 μm; —△— 63 μm porous film

indicates that the initial surface potentials were mainly derived from surplus deposited charges.

Thermally stimulating surface potential decay

In order to reveal the thermal stability of the charge in electret films, a measurement of the surface potential decay due to thermal stimulation was carried out. Samples were charged at 30 °C, 90 °C and 150 °C, respectively, and then were stored for 5 days in a small closed box so that some surplus deposit charges can be eliminated. The experiment was performed in a closed chamber where the sample was put on a grounded metal plate. The results are plotted in Fig.2 for 50 μm thick non-porous and Figs.3 and 4 respectively for 63 μm and 90 μm thick porous PTFE film. The results indicated that initial decay temperature, at which surface potentials start to decay, increases with increase of charging temperature, which means

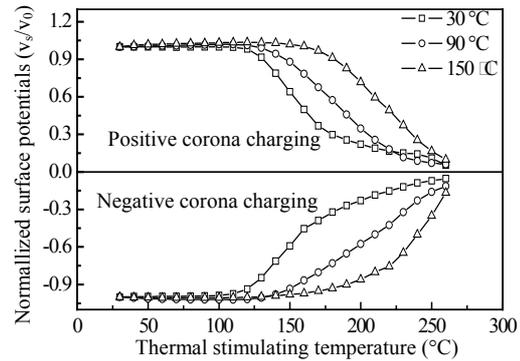


Fig.2 Thermally stimulate surface potential decay of 50 μm thick non-porous PTFE film charged at different temperature

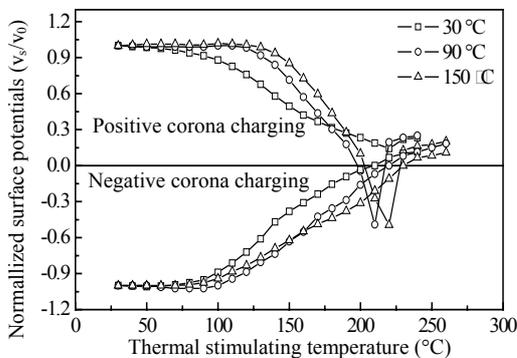


Fig.3 Thermally stimulate surface potential decay of 63 μm thick porous PTFE film charged at different temperature

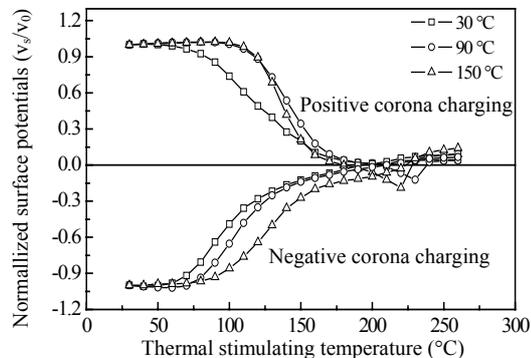


Fig.4 Thermally stimulate surface potential decay of 90 μm thick porous PTFE film charged at different temperature

increased charge stability. Positively and negatively charged films exhibit similar behavior. Fig.2 showed that the initial decay temperature of non-porous film increases regularly with increase of charging temperature. For the porous PTFE the regularity was not obvious, but the initial decay temperature of samples charged at 30 °C was the lowest.

It was very interesting that there was a strong reverse discharge peak between 210 °C and 230 °C for the porous PTFE films positively charged at 90 °C and 150 °C, but these phenomena were not observed in negative corona charging samples.

Correlation of charge dynamics and materials microstructure

PTFE film is usually composed of crystalline and noncrystalline phases. Its microstructure, as revealed by Bunn *et al.*(1958), consists of long but rather narrow bands containing fine parallel striations perpendicular to the band length. The striae are PTFE crystallites which were platelets separated from each other by noncrystalline regions. The ratio of crystalline to noncrystalline phase is mainly responsible for the structural difference between porous and non-porous films as shown as in Figs.5, 6 and 7, respectively for 50 μm thick non-porous, 63 μm and 90 μm thick porous PTFE films. In non-porous film, the noncrystalline phase is dominant and the striation structure of crystallites does not appear (Fig.5). In porous film there are large voids as well as fibrillate morphology materials between voids. That implies larger interface and higher crystallinity resulting from better

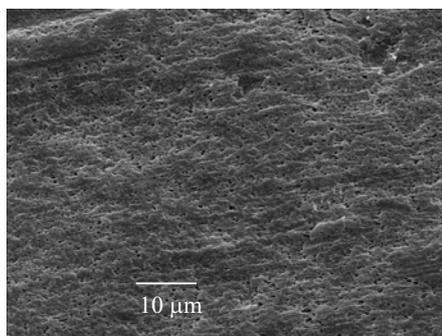


Fig.5 Scanning electron micrographs of 50 μm thick non-porous PTFE film

orientation of molecules. The difference of charge dynamics between porous and non-porous films is correlated to the degree of crystallization.

Basically, the charge storage in electrets could occur at three structural levels. The primary level is charge trapping at particular sites of the chain due to for example, strong electronegative bonds. The secondary level is charge trapping in free volume. The third level is charge trapping at crystallites and interfaces between different materials (Winstle, 1973). In PTFE materials the primary level trap originates from the change of polarizability of C-F bonds, and second and third type traps are correlated to the film microstructure. For non-porous film, charge carriers cannot be injected from surface to bulk due to the absence of a free path during corona charging. Corona charges will mainly reside on the surface of the charged side and only cause the polarizability change

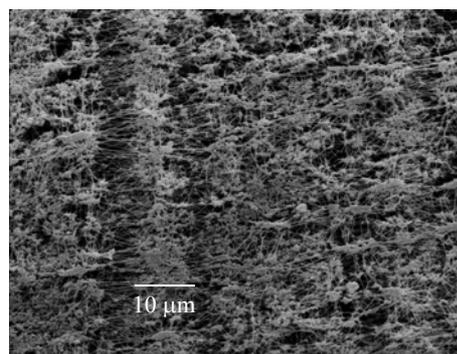


Fig.6 Scanning electron micrographs of bidirectionally stretched porous PTFE film of 63 μm thickness and porosity of 91%

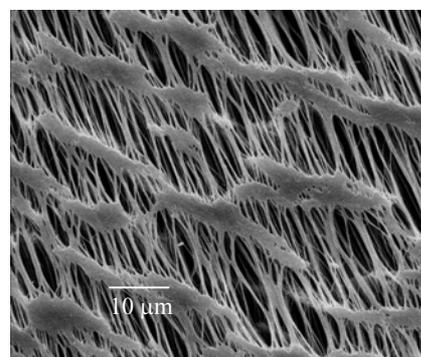


Fig.7 Scanning electron micrographs of unidirectionally stretched porous PTFE film of 90 μm thickness and porosity of 50%

of the C-F bond on the near-surface when the film is charged at room or lower temperature. Because the polarization of C-F bond shifts gradually from film surface to the bulk with the increase of charging temperature, the polarizability charges shift to the bulk and more or less uniformly distributed bulk charges of high density are developed (Sessler and Yang, 1996), which is also proved by means of piezoelectrically-generated pressure-step method (Gerhard-Mulhaupt *et al.*, 1998). As shown in Fig.2, charge stability displays a regular improvement with increase of charging temperature for non-porous films. For porous film, the corona charges can be injected to its volume through void and be trapped in particular sites or in free volume. Therefore, a large number of second and third type traps are expectable beside primary trap because of the greater area of interface and higher crystallinity. Although corona charging at elevated temperature is conducive to the change of polarizability of C-F bonds in the bulk, the effect of charging temperature on the stability of the second and third type trap charges is less, so that the improvement of charge stability with increase of charging temperature is not distinct as that in the primary type trap charges.

CONCLUSION

1. Whether positively or negatively charging, the initial surface potentials are much higher in non-porous film than in porous film, and decrease with increase of the charging temperature. The initial surface potentials for porous film increase with increase of film thickness.

2. The charge stability of non-porous film increases regularly with increase of charging temperature. For the porous PTFE, the regularity is not obvious, but the initial decay temperature of samples charged at 30 °C is the lowest.

3. The ratio of crystalline to noncrystalline phase is mainly responsible for the structural difference between porous and non-porous films. Therefore, the difference of their charge dynamics is correlated to the degree of crystallization.

4. For non-porous PTFE films, the polarizability of the C-F bonds increases and shifts to the bulk when charging temperature increases, which yields more or less uniformly distributed bulk charges, indicating that the polarizability change of the C-F bonds is the main origin of electret charges. For porous PTFE film, the corona charges can be injected to its bulk through the void and be trapped in particular sites or in free bulk, so a large number of second and third type trap charges are expected beside primary trap charges because of the greater area of interface and higher crystallinity.

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