

Study of Relaxations in Poly(methyl methacrylate)–Magneto Electrets by Thermally Stimulated Depolarization Current and Surface-Charge-Decay Mechanisms

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ABSTRACT: The effect of the forming temperature and the magnetic field was investigated for the charge retention and stability of poly(methyl methacrylate) (PMMA)–magneto electret (ME) samples with thermally stimulated discharge currents (TSDCs) and a surface-charge-decay mechanism. The measurements were performed on a pristine PMMA sample with a thickness of 20 μm . The comparative studies of charge decay with TSDC indicated a strong resemblance between the results of the two techniques of MEs of PMMA and were characterized by two

TSDC peaks, that is, an α peak at 110°C and a ρ peak at 160°C. The low-temperature peak (i.e., the α peak) was associated with dipolar relaxation, and the high-temperature peak (i.e., the ρ peak) was attributed to the self-motion of space charges in PMMA. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 29–34, 2011

Key words: activation energy; charge transfer; functionalization of polymers; glass transition; kinetics (polym.)

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is an amorphous thermoplastic frequently used in automotive, electrical, electronic, mechanical, radiation resistance, and medical applications. After the corona is charged, it can be used as a skin-permeation enhancer. The stability of dipole orientation and space charge storage of PMMA is directly related to the effect of drug–skin permeation. Hence, studies to establish the ability of space charge storage of magneto electrets (MEs) of PMMA for a electret–drug transdermal delivery system are of great importance. PMMA is also widely used as a dielectric in capacitors.^{1–5} The material possesses a high thermal stability compared to other polymeric materials. The thermal stability can further be improved by the magnetic processing of PMMA.

PMMA is composed of the strongly polar group $-\text{COOCH}_3$, which is present in the side chains. In other polymers, the backbone of the polymer contributes specific properties to the polymer. The molecular motion in polymers is subject to primary (intrachain) and secondary forces (i.e., ionic bonding, hydrogen bonding, dipolar interaction, and van der Waals interaction). The secondary forces are more

temperature-dependent for their low dissociation energy. Molecular motion affects the dielectric behavior, charge storage, and charge-transport properties of polymers. For these aspects, the knowledge of these properties is important for characterizing the electrical properties [i.e., trap density, charge density, electrical conduction, trap depth, relaxation time (τ_0), etc.] of the polymers.^{6–8}

The study of the surface-charge measurement of MEs is significant. In this study, the effect of different forming temperatures (T_f 's) and magnetic fields were used to examine the behavior of the initial charge density and the charge-decay characteristic of MEs. In this study, we investigated the influence of the magnetic field and the thermal effects on the charge storage, stability, and transport of detrapped charges formed in MEs of PMMA. Studies of the isothermal surface potential decay and thermally stimulated discharge (TSD) spectrum were performed.

MEs: STUDIES SO FAR

Various materials, such as plastics and organic and inorganic substances, are known for their persistent charge-holding abilities.^{9–11} These materials are well-known sources for the formation of MEs. In highly resistive materials, such as PMMA, polyethylene, and polyimide, space charges are mostly accumulated between the conductors and dielectric interfaces (rather than in the bulk of the insulation). MEs usually holds charges on the order of $10^{-10}\text{C}/\text{cm}^2$

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and are made up of an intrinsic isocharges and idiocharges. The isocharges do not vary much with the forming magnetic field (H_f), but the idiocharges do, and they depend mainly on the material type and T_f .^{12–14} During preparation, a permanent change in the refractive index ($\pm 3\%$) was also observed along the field directions. For lower H_f and T_f values, the increase in the refractive index was also reported.¹⁵ Some optically anisotropic ME materials have been noticed to change the plane of polarization.¹⁶

EXPERIMENTAL

ME preparation

The raw sample of PMMA was repeatedly washed with benzene to remove any frictional charges. The sample was covered on both sides with 99.9% pure aluminum foil. In a typical experiment, a pristine sample of PMMA in the form of a disc (diameter = 1.23 cm, thickness = 20 mm) was placed in a cavity made of brass and insulated by mica. The samples were placed in an ME chamber. The container was kept in a vertical direction between the electromagnets. A K-type thermocouple was used for temperature calibration. For the uniform distribution of heat, nonmagnetic heating elements were embedded in the outer plates of the container.

Thermal protocol

The thermal protocol is shown in Figure 1. At the desired temperature, the desired magnetic field was applied for about 1 h. The heating current was switched off after 1 h, and the sample was allowed to cool on its own to room temperature (at the same magnetic field). The thermal protocol was as follows:

Step 1 (A–B in Fig. 1): The environmental chamber temperature was increased from room temperature to the desired temperature.

Step 2 (B–C in Fig. 1): The temperature was held constant for about 1 h. However, during this (B–C) stage, the desired magnetic field was applied for the required duration.

Step 3 (C–D in Fig. 1): The temperature was then lowered to room temperature.

The same thermal protocol has been adopted in several polymer studies.^{17–19}

Measurement technique

Thermally stimulated discharge current (TSDC) is one of the important techniques used for investigating the electrical properties and charge-storage mechanism in dielectrics. During TSDC measurements, the magnitude of the temperature-dependent current is affected by the disorientation of the dipoles²⁰ and is deter-

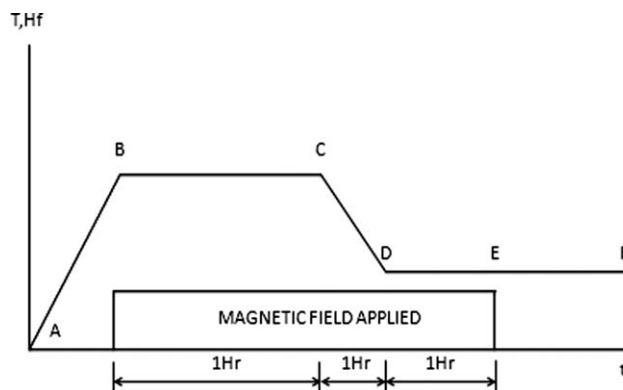


Figure 1 Thermal protocol used for the preparation of the MEs.

mined by the charge liberated from the traps.²¹ The magnetic field was supplied by an electromagnet (type HEM150, numbers 9 and 35, capacity = 1.7 T at 220 V). This was supplied by Polytronic Corp. (Mumbai, India). For the measurements, a Keithley-6517B (Keithley Instruments, Inc., Cleveland, Ohio) instrument was used.

The series of MEs were prepared under various T_f 's both below and above the glass-transition temperature (T_g) of PMMA (120°C). The different temperatures chosen were 60 and 90°C below the softening temperature and 120, 150, and 170°C above the softening temperature. At each of these T_f 's, 16 MEs were prepared with magnetic fields of 600, 1500, 3000, 3400, 4700, 5600, 6600, 7500, 8400, 9400, 10,300, 11,600, 12,500, 13,200, 14,400, and 15,000 G, which were obtained by passing currents of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, and 3.2 A, respectively, through the electromagnet coils. One blank sample was also prepared at each T_f (without magnetic field) to check the effect of other spurious charges due to friction or thermodielectric effects. The measurements were performed under similar atmospheric conditions (relative humidity = 40–50%), time (within 1 min), and thermal conditions (room temperature, $25 \pm 2^\circ\text{C}$).

RESULTS AND DISCUSSION

Surface-charge density

Figures 2 and 3 show the initial surface-charge density (σ_0 ; in C/cm^2) on both surfaces of the MEs for various T_f 's and magnetic fields (0.6–15.0 kG). The results could be separated into two portions: (1) those at less than T_g ($<120^\circ\text{C}$) and (2) those at T_g ($=120^\circ\text{C}$) and above T_g ($>120^\circ\text{C}$). Below T_g , the curves for the surface-charge densities on the north (N) and south (S) surfaces were positive and pointed toward the same nature of charge carriers on both surfaces.

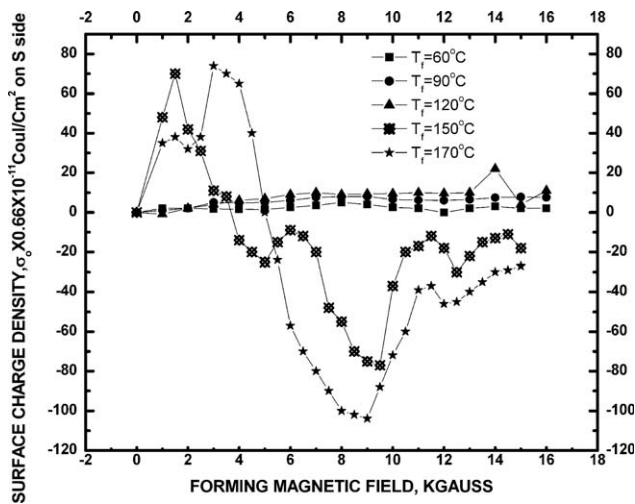


Figure 2 Effect of H_f on σ_0 on the N surface of the MEs.

Although the magnitude of σ_0 on the N and S surfaces was slightly different, the broad nature of the charge distribution was found to be similar in both cases. At a T_f of 120°C, a small amount of polarization was noticeable for two samples only. At this point, the nature of the charge was found to be completely different for the N surface and the S surface. On the other hand, for the samples prepared above T_{gr} , the magnetic field played crucial role, and the polarization depended on the magnetic field strength (H_p). Below a certain value of magnetic field (termed as the *transition field*), the surface charge on the N surface was negative, whereas that on the S surface was positive. On the other hand, the opposite trend was observed for higher H_p 's. Also, the value for this transition field increased with increasing T_f . From Figure 3, we anticipated that there was a linear relationship between T_f and H_p for the surface-charge density in the electrets. For the sam-

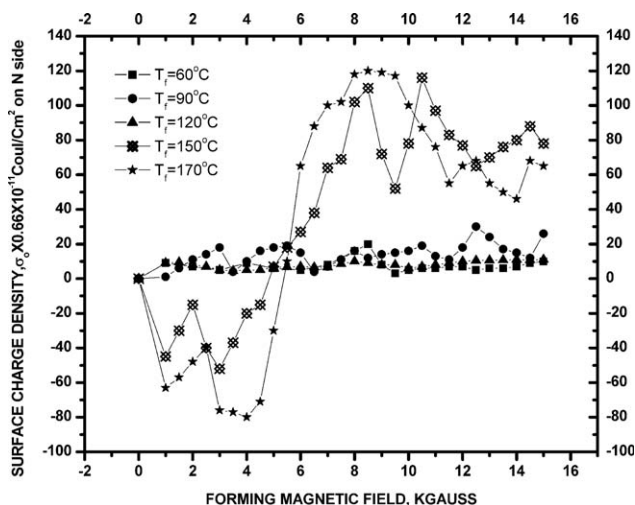


Figure 3 Effect of H_f on σ_0 on the S surface of the MEs.

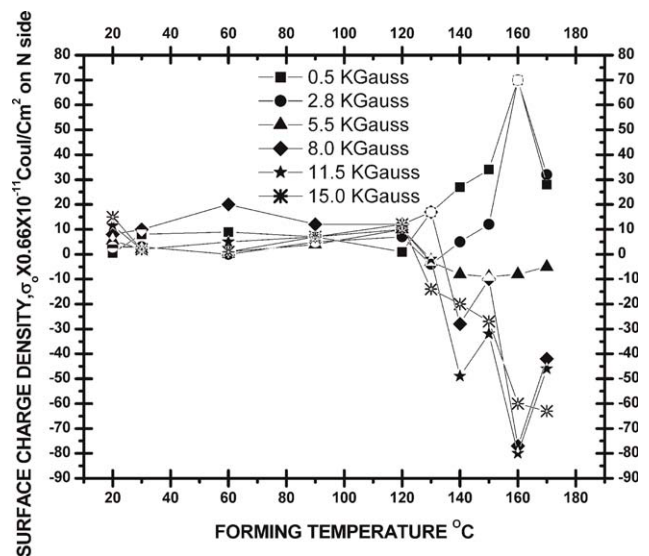


Figure 4 Effect of T_f on σ_0 on the N surface of the MEs at different H_p values.

ples prepared above the softening temperature, a mirror-type relationship existed between the charge distribution on the N and S surfaces. The maximum and minimum σ_0 values for the N surface were accompanied by a similar trend of a maximum and minimum on the S surface.

From the previous studies, we observed that the surface-charge density on the N-pole-facing electret surface was slightly greater than that on the S-pole-facing surface. For the MEs prepared above T_{gr} , polarization was noticed (for various H_f values). To better understand the surface-charge density of the MEs, the results were divided into two groups, namely, group X ($H_f = 0.6$ – 5.6 kG) and group Y (with higher H_p 's of 6.6 – 15.0 kG). The results are shown in Figures 4 and 5. In group X, at higher T_f 's, the surface charge on the N surface was negative, and that on the S surface was positive. Also, the two curves for the surface-charge density for the N and S surfaces crossed each other. This crossing point of the two curves was found to shift to the higher temperature region with increasing H_f . Between these regions, the N surface had a positive charge, and the S surface possessed a negative charge. Further, for group X, at higher T_f regions, the N surface showed a negative charge, and the S surface showed a positive charge. In group Y, the opposite trend was observed. At higher T_f 's, the N surface showed a positive charge, and the S surface had a negative charge. In this group, no such charge reversal on the N and S surfaces was noticeable. The surface charge remained positive on the N surface and negative on the S surface. In both the groups, an increase in the magnitude of the surface-charge density was observed with increasing T_f .

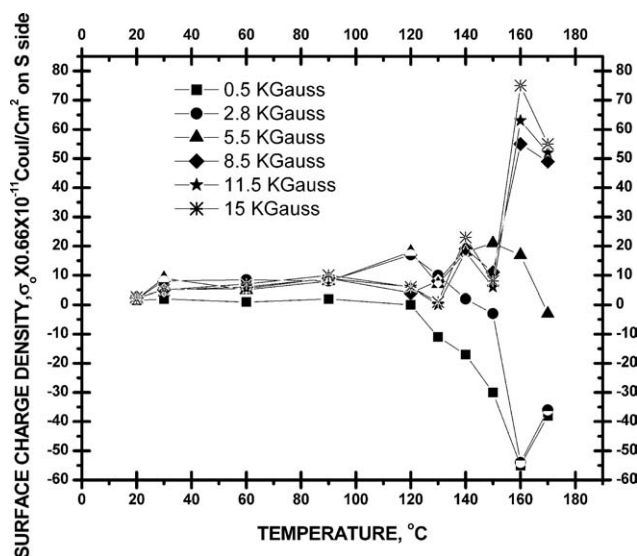


Figure 5 Effect of T_f on σ_0 on the S surface of the MEs at different H_p values.

TSDC

Figure 6 shows the TSDC current spectrum for the PMMA samples at polarizing fields (H_p 's) of 9650 G and at different poling temperatures (TPs; from 90 to 160°C). In all cases, two current maximums were obtained. These peaks were a current peak at 110–120°C (known as the α peak) and a current peak at 155–160°C (known as the ρ peak). A steady fall in the current was observed in the high-temperature regions (beyond 160°C). Maximum value of TSD current (I_{\max}) showed an increasing trend from 0.55 to 0.65 pA in the temperature zone of 90 to 120°C. This increase was not phenomenal, and I_{\max} attained a maximum value of 0.9 pA (for a 140°C TP).

These observations were in conformity with the nonisothermal charging mechanism of a polymer, where the polarizing current is supposed to consist of two components behaving differently as a function of temperature. The components are (1) the orientation of dipoles as a transient process, which results in the formation of the α peak, and (2) the conduction current derived due to decay processes related to conduction, and the motion of excess charges by space charge is limited by drift and diffusion for the ρ peak. In PMMA, the presence of carbonyl groups ($>C=O$) constitute the bulk of permanent dipoles. In the presence of a polarizing magnetic field, as the heating of the sample started, τ_0 of the dipoles decreased, and they were progressively oriented. This orientation became stronger and more rapid with increasing polarizing field. Consequently, the current maximum appeared with greater magnitude. The linear relationship between H_p and the peak magnitude showed the occurrence of a uniform induced bulk polarization and, hence, confirmed the dipole origin of the α peak.

On the basis of the location of the α peak, the dipole nature of the $>C=O$ groups could not be attributed as the cause of this current maximum. It was shown earlier that the dipolar relaxation due to the $>C=O$ group TSDC maximum occurred around 120°C. The dipolar nature of the peak depends on the sample thickness and the kind of electrode material used.^{22,23} Turnhout⁷ showed that usually thin samples release more charge than very thick ones and the peak intensity is at a maximum when $r_0/s = 0.5$ (where r_0 is the thickness of the charged layer and s is the thickness of the sample), the distinction between the actual polarization current and the conduction current can be made by the adoption of different heating rates during the TSDC process. This is thought to affect the characteristic of the former components; the faster heating rate shifts the TSDC maximum toward a higher temperature and enhanced magnitude.

In addition to dipoles, the immobilized space charges (residing near the electrodes) in electrets cannot be neglected. During heating, they are expected to mobilize and neutralize, either at the electrodes or in the sample, by recombination with charges of opposite sign. The forces driving the charges are their drift in the local magnetic field and diffusion, which tends to remove concentration gradients. In general, field-controlled self-drift prevails. At high temperatures, the self-motion space charge becomes accompanied by a second neutralization mechanism, namely, recombination with thermally generated carriers. These carriers are generated uniformly in the entire specimen by the dissociation of neutral entities. They are responsible for the conductivity of the material. The conductivity can be either electronic or ionic; in polymers, impurity ions contribute most to the ohmic conduction, as they show an appreciable conduction above T_g .²⁴

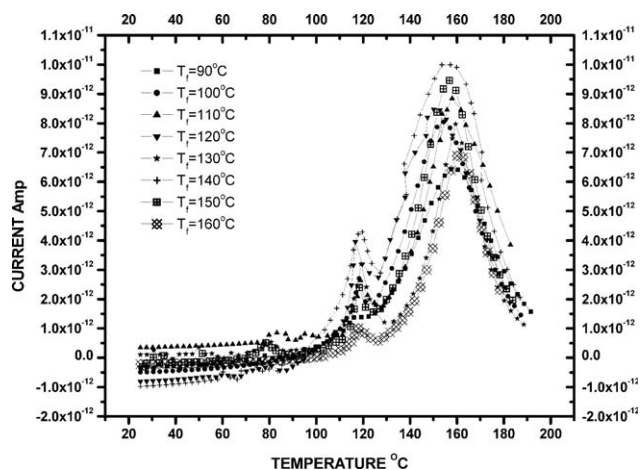


Figure 6 TSDC thermogram of the PMMA samples polarized at $H_p = 9650$ G with different TPs (90, 100, 110, 120, 130, 140, 150, and 160°C).

Activation energies and distribution function

There are numerous methods for calculating the activation energies from the TSDC spectra; one can take into consideration the initial rise of the thermocurrent, the half-width temperature of the peaks, or the least squares fit. In this study, we used the method proposed Bucci et al.,²⁵ which led us to the following equations:

$$A = -k \frac{d \ln \alpha(T)}{d\left(\frac{1}{T}\right)} \quad (1)$$

where, A = Activation Energy, k = Boltzmann constant, α = alpha peak, T = Temperature in Kelvin.

$$\alpha(T) = J/Ps(T) \quad (2)$$

$$Ps(T) = -s \int_{T_u}^T j dT$$

where, J = Current, P = Degree of Polarization, s = Distribution in natural frequencies and T_u is the ultimate temperature when J reaches zero. All of these methods hold only for nondistributed polarizations. For s distribution in natural frequencies in the case of the initial rise of the thermocurrent in TSD, eq. (3) exists:

$$k \frac{k \ln J}{d\left(\frac{1}{T}\right)} = -cA \quad (3)$$

where c is a constant. The same holds for the Bucci, Fieshi & Guidi (BFG) equation. Taking into consideration some particular distribution functions, one can prove that $c = 1$ for the Wagner and Gevers distribution and $c = m$ for the Fouss-Kirkwood and Cole-Cole distribution functions, where m is a parameter of these distributions.

To calculate the distribution functions from the TSD data, we used the Staverman and Schwarzl approximation of the inverse Laplace transform of eq. (2), taking into consideration only the second-order approximation. We introduced the logarithmic distribution function, normalized to the maximum value:

$$L\left(\frac{\tau_r}{\tau_o}\right) = f \ln(\tau_r/\tau_o) \quad (4)$$

where, $\tau_r = 1/\alpha_r$; τ_o is the most probable value of τ_r and $u = \ln(\tau_r/\tau_o)$ and m ; α , β are parameters functions:

$$L_1\left(\frac{\tau_r}{\tau_o}\right) = \left[\frac{T^2 J(T)}{T_m^2 J_m}\right] e^x = 1 \quad (5)$$

$$\frac{L_2}{L_1} = \frac{L_1}{L_m} = \left\{ \frac{T^2 d\left[\frac{j(T)}{J_m}\right]}{s T_m^2 dT} \right\} e^x = 0.5 \quad (6)$$

where, L_1 is logarithmic distribution function normalized at $e^x = 1$; L_2 is Logarithmic distribution function

normalized at $e^x = 0.5$; L_m = Logarithmic distribution function, normalized to the maximum value.

$$\frac{\tau_r}{\tau_o} = \frac{e^x T^2 \alpha(T)}{T_{\max}^2 \alpha(T_{\max})}$$

where T_m and J_m are the temperature and current density values for the maximum TSDC peak, respectively, and T_{\max} is the maximum Debye relaxation for τ_o . For our calculations, we assumed that T_m was equal to T_{\max} . To compare the results obtained with those found in dielectric and mechanical loss measurements, we took two of the semiempirical distribution functions derived for the interpretation of dynamic measurements. These were the symmetrical Fouss-Kirkwood distribution, given in eq. (7):

$$f(u) = \frac{m \cos\left(\frac{m\pi}{2}\right) \times \cosh(mu)}{\cos^2\left(\frac{m\pi}{2}\right) + \sinh^2(mu)} \quad (7)$$

and the two-parameter asymmetrical Havriliak-Negami function, given in eq. (8):

$$f(u) = \frac{1}{\pi} \sin(\beta\theta) \times \{1 + \exp[-2u(1 - \alpha)]\} + 2 \exp\{-u(1 - \alpha)\} \cos \pi(1 - \alpha) - \beta/2 \quad (8)$$

where

$$\theta = \tan^{-1} \left\{ \frac{\sin \pi(1 - \alpha)}{\exp[(1 - \alpha)u] + \cos \pi(1 - \alpha)} \right\}$$

For both distributions $u = \ln(\tau_r/\tau_o)$ and m , α , and β are parameters of these functions, θ is the asymmetrical Havriliak-Negami function. In our case, on the basis of these calculations (all of the numerical calculations of these equations were performed on MATLAB software, Massachusetts), activation energies of 1.20–1.45 eV were obtained for the peaks at 160°C.

CONCLUSIONS

MEs of PMMA were prepared successfully for various applicable domains. The surface-charge density and initial charge density did not show any regular variation with H_p . A similar observation was obtained for TSDC of the PMMA-MEs. On the other hand, L_{\max} showed regular variation with T_f . Also, we observed that the peak positions did not shift for the α and ρ peaks. This indicated that at the high poling magnetic field (9650 G), all of the subpolarizations were activated, and the trapping of charge carriers did not take place at different energy levels. Also, an increase in the stability of the MEs was observed with increasing poling magnetic field and was not dependent much on the TP or on the initial charge density. Various mathematical functions were applied to

calculate the activation energies. The value was found to be between 1.20 and 1.45 eV for the 160°C peak.

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