Instability of High-Energy-Density Insulating Polymers

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Summary We discovered various modes of instabilities in polymers under voltages for the first time. For example, we observed that under a voltage the flat surface of a substrate-bonded polymer can locally fold against itself to form a pattern of creases. As the voltage further rises, the creases increase in size and decrease in density, and strikingly evolve into holes in the polymer. We explain the experimental observation with theoretical and numerical models. The theoretically predicted critical voltages for the instability match well with experimental results without using any fitting parameter. We further show that by solely preventing the instability, we increase energy density of various insulating polymers over 10 times.

Introduction

Electricity is a dominant way for transmitting energy in modern society. As electricity is usually transmitted at high voltages to reduce energy lost, insulating polymers for power cables need to sustain the high voltages. In addition, polymers with high permittivity and breakdown voltage have been widely used as organic capacitors for energy storage. It has been hypothesized that electromechanical instabilities are one major cause for electrical breakdowns in high-energy-density dielectric polymers [1-5]. However, the initiation and propagation of the instabilities have not been directly observed, because the electrical breakdown generally coincides with the instabilities. In this paper, we present a combined experimental and theoretical study of electromechanical instabilities in a substrate-bonded elastic polymer directly under an ultrahigh electric field. We will show that the polymer film can evolve into a pattern of creases and/or craters which can cause the electrical the breakdown of the polymer

Experimental results

The experimental setup is described briefly here. For details, please refer to Ref[6-8]. A layer of a solid polymer is bonded on an insulating substrate. The insulating substrate is taken to be much more rigid than the polymer, so that it does not deform with the polymer to avoid electrical breakdown. The bottom surface of the substrate is coated with a metal layer (e.g. gold), and the top surface of the polymer is covered with a compliant electrode (e.g. NaCl solution), which deforms conformally with the polymer surface and enables the observation of the instability. A DC voltage is applied between the two electrodes.

Figure 1 illustrates the evolution of instability structures in a polymer film subject to a ramping voltage with a rate of 10V/s. The surface of the polymer film initially maintains a flat and smooth state without appreciable deformation [Fig 1(a)]. When the voltage reaches a critical value, some regions of the polymer surface suddenly folds upon itself to form a pattern of creases as shown in Figs 1(b) and 1(h). As the voltage increases, the pattern of creases coarsens by increasing their sizes (i.e. length and width) and decreasing their density (i.e. number of creases per area) as shown on Fig 1(c). As the voltage further rises, the center regions of some creases strikingly open, and a pattern of coexistent creases and craters form in the film [Fig 1(d)]. The thickness of the film within the crater is less than the surrounding regions as illustrated in Fig 1(i). All creases eventually deform into craters with further increase of the voltage [Fig 1(e)]. The diameters of the craters increase, as the applied voltage further rises [Fig 1(f)]. The polymer film may also be fractured at the craters due to large deformation.

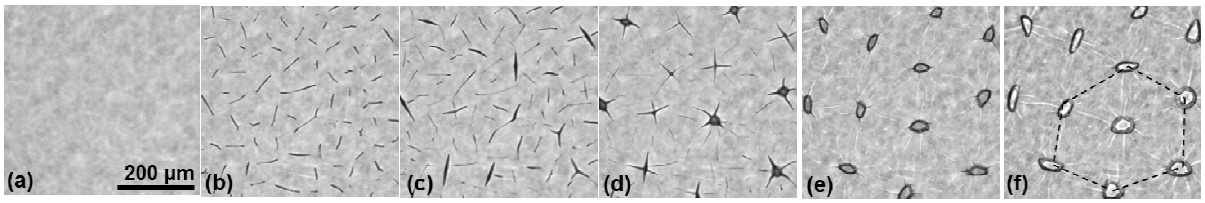

Figure 1. Instability evolution in a polymer film under a ramping voltage: flat state at 7kV(a), creased state at 8.8 kV (b), crease coarsening at 9.7 kV (c), coexistent states of creases and craters at 10.5 kV (d), crater state at 13.3 kV (e), and craters with larger diameters at 15.6 kV (f).

Theoretical Calculation

Now we calculate the critical electric field for the electro-creasing instability by comparing the potential energies in a region of the film in the flat and creased states [9, 10]. Because the polymer substrate does not affect the critical field, we neglect the substrate in the calculation. The potential energy in a unit thickness of the region can be expressed as

$$\Pi = \int_A W(\mathbf{F}) dA + \int_A \frac{1}{2}\varepsilon|\mathbf{E}|^2 dA - \int_S \Phi\omega dS \tag{1}$$

where $\mathbf{F}$ is the deformation gradient, $W(\mathbf{F})$ is the elastic energy density, ω is the surface charge density, and A and S are the area and contour of the region. The first term of Eq. (1) gives the elastic energy, and the second and third terms give the electrostatic potential energy of the region. Considering the scaling analysis, we neglect the surface energy of the film.

When the film is in a flat state, the elastic energy is zero and the electric field is uniform. The potential energy per unit thickness can be calculated as $\Pi_{flat} = -A\varepsilon E^2/2$, where E is the applied electric field. Next, we prescribe a downward displacement L to a line on the top surface of the region to form a crease as demonstrated in Fig 2(a). At the creased state, the deformation and electric field are non-uniform in the region. We analyze the coupled deformation and electric field using finite-element software, ABAQUS 6.10.1 with a user subroutine UMAT. The potential energy of the creased state Π_{crease} is then calculated using Eq. (1). The region is taken to deform under plain-strain conditions, and obey the neo-Hookean model with the elastic energy density $W = \mu(F_{iK}F_{iK} - 3)/2$. Due to symmetry, only right half of the region is calculated. The size of the calculation region is taken to be much larger (100 times) than the size of the crease, so that L is the only length scale relevant in comparing the potential energies in the flat and creased states [9]. The dimensional consideration determines that the potential energy difference has a form [9]

$$\Delta\Pi = \Pi_{crease} - \Pi_{flat} = \mu L^2 f\left(E\sqrt{\varepsilon/\mu}\right) \tag{2}$$

where $f\left(E\sqrt{\varepsilon/\mu}\right)$ is a dimensionless function. The potential energy difference is plotted as a function of the applied electric field in Fig 2(b). In absence of the applied field, the potential energy difference is positive, because $\Pi_{flat} = 0$ and the elastic energy of the crease gives a positive Π_{crease}. Thus the flat state is energetically preferable. As the applied electric field increases, the potential energy difference decreases, for the creased state has a lower electrostatic potential energy than the flat state. Once the electric field reaches a critical value E_c, the creased state has the same potential energy as the flat state (i.e. $\Delta\Pi = 0$) and the creasing instability sets in. As shown in Fig 2(b), the theoretical calculation gives $E_c \approx 1.03\sqrt{\mu/\varepsilon}$. The experimentally measured critical field for the electro-creasing instability is about $0.85\sqrt{\mu/\varepsilon}$. The theoretically predicted critical field is roughly consistent with the experimental data. The difference between the theoretical and experimental results may be due to the surface roughness of the polymer films, and/or the deviation of the films' dielectric and elastic behaviors from the assumed ones.

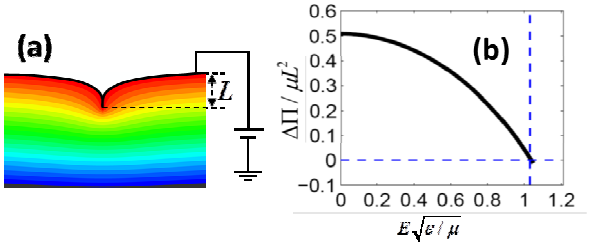

Figure 2. The equipotential contours in a film at the creased state (a), and the potential energy difference between the creased and flat states as a function of the applied electric field (b).

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