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Electromechanical Responses of a Crosslinked Polydimethylsiloxane

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Summary: A high molecular weight polydimethylsiloxane, PDMS, gel was prepared and investigated as an electroactive polymer actuator. Electromechanical properties of the PDMS gels were measured under an oscillatory shear mode at the temperature of 27 °C to determine the effects of crosslink ratio and electric field strength. The storage modulus, G', of PDMS gel increases linearly with crosslink density but nonlinearly with electric field. The increase in the storage modulus with crosslink density is due to the increase in the number of junction points and strands. With increasing electric field strength, the storage modulus increases as the electric field induces dipole moments generating the electrostatic forces within the matrices. The gel with the crosslink ratio of 0.01 possesses the highest G' sensitivity of 41% at 2 kV/mm. The temporal response of PDMS gels upon repeated applications of electric field strength of 2 kV/mm was investigated. For the crosslink PDMS ($N_c/N_m = 0.01$) system, at the electric field of 2 kV/mm, G' immediately increases and rapidly reaches a steady-state value. With electric field off, G' decreases and nearly recovers its original value. The crosslinked PDMS ($N_c/N_m = 0.01$) is nearly a reversible system. Finally, we investigated the bending response of the PDMS films, suspended in silicone oil between copper electrodes. From the deformation data, we estimated the dielectrophoresis force, F_D, to be a linear function of electric field strength.

Keywords: actuator; electroactive polymers; electrorheology; polydimethylsiloaxane

Introduction

Electroactive polymers (EAP) have emerged in the last decade as promising actuation materials in the field of muscle/insect-like actuators, robotics, and etc. The novel characters EAP are light-weight, high energy density, and high flexibility; all are suitable properties for an artificial muscle [1]. EAP can be divided into two major categories based on their activation mechanisms: electronic and ionic. Coulomb forces drive the electronic EAP, which includes the electrostrictive, the electrostatic, the piezoelectric, or the ferroelectric behaviors. This type of EAP materials can be made to withstand a large induced displacement while they are activated under DC voltage. In contrast to the electronic EAP, ionic EAPs are materials that involve mobility or diffusion of ions; they generally operate between two electrodes and in an electrolyte.[2]

Dielectric EAP is the one of electronic EAP in which an electric field can be applied to induce a large actuation strain while possessing low elastic stiffness and high dielectric constant. It has been reported that polydimethylsiloxane, PDMS, elastomer can easily bend under applied electric field.[3] In our work, we are interested in investigating the electromechanical properties of PDMS: the storage modulus response, the temporal

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response, the bending response, and its induced electrical force generated between two electrodes.

Experimental Part

Materials

High molecular weight hydroxyl terminated PDMS's (viscosity 18,000–20,000 cSt, Aldrich) were used as the polymer matrices. Tetraethyl orthosilicate (AR grade, Aldrich) and dibutyl thin dilaurate (AR grade, Aldrich) were used as the initiator and the catalyst, respectively. Silicone oil was purchased from Aldrich (viscosity 100 cSt, Aldrich).

Preparation of PDMS Gel and Electromechanical Property Measurement

Electromechanical properties of PDMS under an oscillatory shear at fixed temperature of 27 °C were measured in order to investigate the effects of crosslinking ratio and electric field strength. To study the effect of crosslinking ratio, PDMS at various crosslink ratios ($N_c/N_m = 0.001$, 0.003, 0.005, 0.01, 0.03 and 0.05: where N_c is moles of initiator and N_m is moles of PDMS), were prepared by mixing the high molecular weight hydroxyl terminated PDMS, tetraethyl orthosilicate, and dibutyl tin dilaurate at various initiator moles. The mixture was cast in a mold (diameter = 25 mm and height = 1 mm) and dried under vacuum at room temperature (27 °C) for 6 hrs. Electromechanical properties of PDMS under an oscillatory shear at fixed temperature of 27 °C were measured (Rheometric Scientific Inc., ARES). The dynamic moduli, G' and G'', were measured as functions of frequency and electric field strength. The linear viscoelastic regime was determined by the strain sweep test to determine the appropriate strain to be used to measure G' and G''. Frequency sweep test was then carried out measure G' and G'' as functions of frequency (0.1–100 rad/s) at fixed strains of 700% and 1% for pure PDMS fluid and for the crosslinked PDMS (crosslink ratios of 0.001, 0.003, 0.005, 0.01, 0.03 and 0.05), respectively. Pre-oscillatory shear at frequency of 1 rad/s, at fixed strains at 700% and 1% for pure PDMS fluid and for the crosslinked PDMS, under electric field (~10 min) was applied to the sample to ensure an equilibrium polarization before each measurement was taken.

Determination of M_c

The average molecular weight between crosslinks of the PDMS gels, M_c, was determined from the swelling in HPLC grade toluene at room temperature.[4] The version of the Flory-Rehner equation[4] was used for our PDMS systems:

$$M_c = \frac{\nu_1 \rho_2 \left(\nu_{2m}^{1/3} - \frac{\nu_{2m}}{2} \right)}{-\left[\ln(1-\nu_{2m}) + \nu_{2m} + \chi_1 \nu_{2m}^2 \right]} \tag{1}$$

where

$$\nu_{2m} = \frac{w_0}{\nu_{equil} \times \rho_2} \tag{2}$$

$$\nu_{equil} = \frac{w_0}{\rho_2} + \frac{w_s - w_0}{\rho_1} \tag{3}$$

$$\chi = 0.34 + \frac{\nu_1}{RT}(\delta_1 - \delta_2)^2 \tag{4}$$

and where ν_1 is the molar volume of solvent (M_w/density), ρ_2 is the polymer density, PDMS equal to 0.97 g/cm^3, ρ_1 is the solvent density or of toluene which is equal to 0.867 g/cm^3, w_o is the original polymer weight, w_s is the swollen polymer weight, χ is the polymer-solvent interaction parameter, R is the universal gas constant, 8.29 N_m/mol.K, T is the absolute temperature, 298 K, δ_1 is the solubility parameter of PDMS which is equal to 19.4 (MPa)$^{1/2}$, and δ_2 is the solubility parameter of toluene which is equal to 18.20 (MPa)$^{1/2}$.

Deflection Measurement

To study the elastic response of the PDMS gels to an electric field, films of the PDMS gels were vertically suspended into silicon oil between a pair of parallel copper electrode plates (40 mm long, 30 mm wide, and 1 mm thick). A rigid plastic thread was used to fix the top position of the gel (as shown in Figure 3). A high dc voltage was applied in a non-contact mode through the electrodes, which were 10 mm apart. The electric bending response of the gel was recorded by a video camera, and the deflection properties were analyzed by a digital image analyzer (Panasonic M3000, Japan). Both the voltage and the current were monitored as well. All the measurements were carried out at ambient temperature (27 °C).

Results and Discussion

Electrorheological Properties of Pure Polydimethylsiloxane

Effect of Crosslinking in the Absence of Electric Field

The effect of crosslinking on the rheological properties of pure polydimethylsiloxane (PDMS) was first investigated. The crosslinking ratios are 0.001, 0.003, 0.005, 0.01, 0.03 and 0.05 and the number density of strands, ν was determined from the relation $\nu = \rho N_{av}/M_c$. ν or the numbers of chemical strands per volume are equal to 3.7×10^{19}, 5.75×10^{19}, 1.00×10^{20}, 1.15×10^{20}, 1.27×10^{20}, and 1.40×10^{20} #strands /cm^3 for PDMS's with the crosslinking ratios of 0.001, 0.003, 0.005, 0.01, 0.03, and 0.05, respectively. The storage modulus of crosslink PDMS gels measured is independent of frequency, indicative of the gel nature. Thus, in the following, the storage modulus data will be presented only at frequency of 1 rad/s and at strain equal to 1%. Figure 1(a) shows the dependence of the storage modulus, G′, of PDMS on the number density of strands, ν, without electric field applied at a strain equal to 1%. In an absence of electric field, G′ initially increases almost linearly with the strand density, ν, up to 1.0×10^{20} strands/cm^3, consistent with the classical network theory:[5]

$$G \equiv \frac{nk_BT}{V} = \nu k_BT \tag{5}$$

where k_B is the Boltzmann's constant, T the absolute temperature (K), and ν is number of strands per unit volume (1/cm^3), $\rho N_{av}/M_c$. Above 1.15×10^{20} strands/cm^3, G′ evidently increases non-linearly with ν.

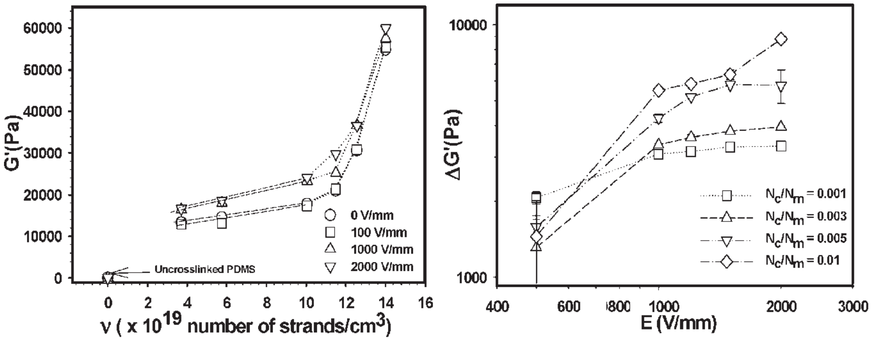
Effect of Crosslinking under Electric Field

The effect of electric field strength on the rheological properties of pure polydimethylsiloxane (PDMS), at various crosslinking ratios, was investigated in the range of electric field strength between 0–2 kV/mm. The storage modulus G′ (Pa) of each crosslinked PDMS system increases linearly with strand density, as shown in Figure 1(a). As a sufficiently high electric field strength is applied, dipole moments are generated leading to the electrostatic interaction between different strand segments in the matrix.[5,6] In addition, a voltage differential between the electrodes can generate electromagnetic forces that act to pull the electrode together.[5,7] This attraction causes a compressive force on the dielectric elastomeric in the direction of the electric field throughout the volume between the electrodes.[7] The resulting effective pressure can be written as:

$$P = \varepsilon_0 \varepsilon_r E^2 \tag{6}$$

where ε_0 and ε_r are the permittivity of free space and the relative permittivity of polymer, respectively.[7] Figure 2(b) shows the storage modulus responses ($\Delta G'$) vs. electric field of PDMS systems of various crosslinking ratios at frequency of 1 rad/s, and at strain equal to 1%. $\Delta G'$ increases with electric field up to $E = 1$ kV/mm, beyond that electric filed strength it levels off and becomes saturated at $E = 2$ kV/mm. $\Delta G'$, at a given E, is generally larger for a PDMS system with a higher crosslinking ratio. Theoretically, we expect $\Delta G'$ to show a quadratic dependence with E, corresponding to the model proposed by Perline *et al.*[5,6]

We next investigated the maximum G′ sensitivity the PDMS systems. The sensitivity is defined as $\Delta G'/G_o = (G'_E - G'_o)/G'_o$, where G'_E is the G′ value of system under electric field, and G'_o is the G′ value of system without electric field. The G′ sensitivity of the PDMS systems with the crosslinking ratios of 0.001, 0.003, 0.005,



(a) (b)

Figure 1.

Effect of crosslink density of PDMS: (a) storage modulus G′ ($\omega = 1$ rad/s) vs. number density of strand at electric field strengths of 0, 100, 1000 and 2000 V/mm; (b) storage modulus response $\Delta G'(\omega = 1$ rad/s) vs. electric field strength, strain = 1%, and temperature of 27 °C.

0.01, 0.03 and 0.05 at electric field strength of 2 kV/mm are 7%, 22%, 35%, 41%, 27% and 9%, respectively. Thus, the PDMS with the crosslinking ratio of 0.01 ($\nu = 1.15 \times 10^{20}$ number of strands /cm^3) possesses the highest G′ sensitivity. This result suggests that the system with the crosslinking ratio of 0.01 has moderate flexibility within the matrix in the absence of electric field such that its structure rigidity can be induced further by electric field. On the other hand, the lower crosslinked systems have a more fluid-like structure; free movement and relaxation of polymer chains are still allowed in the presence of electric field and they possess smaller responses. The higher crosslinked systems contain relatively smaller free volumes and have more rigid structures; they simply cannot respond further to or increase their rigidity further under the applied electric field.

Time Dependence of the Electromechanical Response

We next investigated the temporal characteristic of crosslinked PDMS ($N_c/N_m = 0.01$) under electric field strengths of 1 and 2 kV/mm. The temporal characteristic of each sample was measured in the linear viscoelastic regime at a strain of 1%, and at frequency of 1 rad/s. Figure 2 shows the change in G′ of crosslinked PDMS ($N_c/$

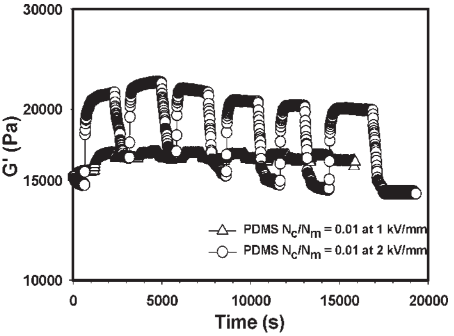


Figure 2.

Temporal response of PPV/PDMS90 with electric field strength of 1000 and 2000 V/mm and PDMS $N_c/N_m = 0.01$ with electric field strength of 2000 V/mm at 27 °C, frequency of 1 rad/s, and strain of 1%.

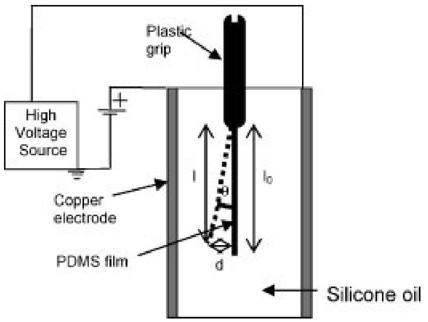


Figure 3.

The schematic diagram of the deflection experiment set up.

$N_m = 0.01$) on electric field strength of 1 and 2 kV/mm during a time sweep test, in which an electric field is turned on and off alternately. G′ immediately increases and rapidly reaches a steady-state value. When the electric field is off, G′ decreases and nearly recovers its original value. Thus, the crosslinked PDMS ($N_c/N_m = 0.01$) is nearly a reversible system. The time required for G′ to reach the steady-state value on applying the field is called the induction time, t_{ind} and the time required for G′ to decay towards its steady-state value when the electric field is turned off is called the recovery time, t_{rec}. t_{ind} are 290,280 and 273 s, and the t_{rec} are 150, 138 and 125 s for the PDMS systems with crosslinking ratios of 0.01, 0.03 and 0.05, respectively. The decrease of t_{ind} with the crosslink density suggests that at a higher strand density (ν more than 1.15×10^{20} chemical strands / cm^3, $N_c/N_m = 0.01$), the system possesses a more solid like behavior, thus it requires a shorter time to reach the equilibrium state and to relax back to its original state.

Deflection under Electric Field

Finally, we investigated the effect of crosslinking ratio and electric field strength on the deflection of soft and flexible crosslinked PDMS films. The amount of deflection of the PDMS films at a specific electric field strength can be described by parameters d, l and θ as shown in Figure 3. Figure 4 illustrates the effect of electric field strength on the bending of the PDMS film ($N_c/N_m = 0.01$), 1 mm × 3 mm × 18 mm, suspended in the silicone oil (100 cSt). When an external electric field is applied, the crosslinked PDMS film responds with a significant and rapid bending towards the anode with the amount of bending dependant on the electric field strength, indicating the attractive interaction between the anode and the polarized PDMS. Under electric field, the crosslinked bridges and the strands in the PDMS network inevitably change their molecular conformations due to the resultant dielectrophoresis force exerted by the electrodes, leading to a macroscopic shape change and/or motion.[8] As the electric field is removed, the crosslinked PDMS nearly recovers its original position and shape due to the gravitational force, its elasticity, and the reversible polarized PDMS. Thus, the crosslinked PDMS ($N_c/N_m = 0.01$) is also a reversible bending system, consistent with the G′ temporal response results.

The values of the observed bending parameters, d, l and $\theta \approx \arctan(d/l)$ of the crosslinked PDMS films at various electric field strength are tabulated in Table 1. The displacement of the free bottom end of the gel (d) and the degree of bending (θ) increase linearly with electric field strength. As the electric field is applied, the freely suspended end of the PDMS films bend towards the anode site because the attractive interaction between the anode and the dipole moments set up in the matrix. As a higher electric field strength is applied, stronger dipole moments are expected to be generated leading to a higher degree of bending obtained. In Figure 5(a), the degree of bending (θ) is plotted in linear

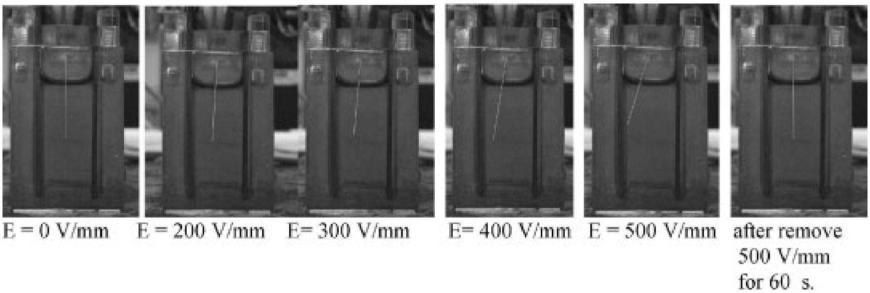


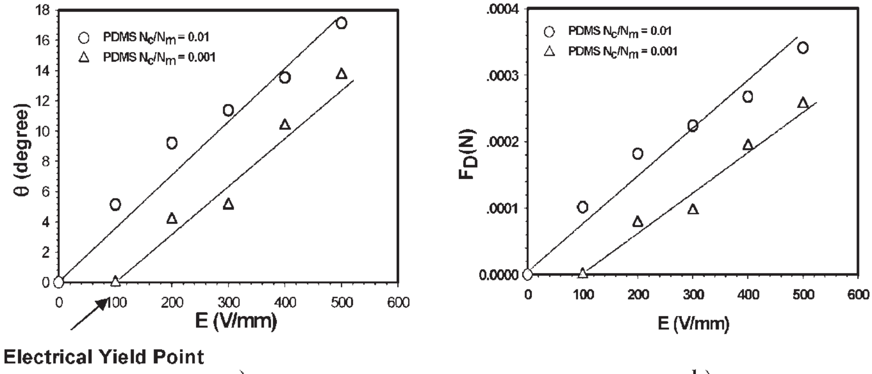
Figure 4.
Deflection of PDMS ($N_c/N_m = 0.01$) film as a function of electric field strength.

Table 1.
Effect of electric field strength on electrostiction behavior of PDMS films.

Sample[a)]	E (V/mm)	l (cm)	d (cm)	θ (degree)	t_{ind} (s)	t_{rec} (s)	mgsinθ ($\times10^{-4}$)	F_d ($\times10^{-5}$ N)	F'_d ($\times10^{-5}$ N)	F_D ($\times10^{-4}$N)
PDMS	0	1.78								
($N_c/N_m = 0.01$)	100	1.78	0.16	5.1	19	3.9	0.96	0.524	0.10	1.01
$m = 0.097$ g	200	1.75	0.28	9.2	16	4.8	1.72	0.98	0.87	1.82
$t = 0.00072$ m	300	1.75	0.35	11.4	14	5.5	2.12	1.21	1.07	2.24
$w = 0.003$ m	400	1.67	0.46	13.5	11	7.6	2.51	1.59	2.14	2.67
$l_o = 0.0178$ m	500	1.53	0.47	17.1	5	12.1	3.16	2.43	3.50	3.41
PDMS	0	1.80								
($N_c/N_m = 0.001$)	100	1.80								
$m = 0.107$ g	200	1.79	0.13	4.1	13	4.1	0.76	0.25	0.41	0.78
$t = 0.00069$ m	300	1.78	0.16	5.1	11	5.3	0.93	0.31	0.59	0.96
$w = 0.0031$ m	400	1.75	0.32	10.4	7	8	1.87	0.61	0.82	1.94
$l_o = 0.018$ m	500	1.68	0.41	13.7	3	12	2.48	0.79	1.40	2.56

[a)] m is the weight of PDMS sample; t is the thickness of PDMS film; w is the width of PDMS film; l_o is the initial length of PDMS film; $F_{d,}$ is calculated from small angle deflection approximation; $F'_{d,}$ is calculated from large deflection approximation (using $(l_o–l)/l_o$).

scale versus electric field strength in order to investigate the effect of crosslinking ratio. θ of both crosslinked PDMS systems linearly increases with electric field strength. However, we may identify the electrical yield point at electric field strength of 100 V/mm for the low crosslinking ratio, $N_c/N_m = 0.001$ system. The electrical yield point is defined as the necessary electric filed strength required to bend a crosslinked PDMS film. Because the lower crosslinked system has a lower number of strands in the PDMS network, it thus has a lower ability to generate the dielectrophoresis forces; thus it requires a higher field strength to changes its molecular conformation. Filipcsei *et al.* reported a similar effect for the weakly crosslinked PDMS gels containing finely distributed TiO_2 suspened in silicone oil (DC 200, Fluka) under action of external electric field.[9] They discovered a driving mechanism to induce deformation and movement of neutral polymer gels in non- conducting medium. Since the particles cannot leave the gel matrix, all force acting on the particles are directly transmitted to the polymer chains resulting in ethier the



a) b)

Figure 5.
a) Degree of bending, θ (degree) and b) dielectrophoresis force, F_D (N) vs. electric field strengths of the crosslinked PDMS films.

locomotion or the deformation of the gel [9]. With increasing field intensity, the deflection of the free end of the gel increases. At small field intensities (<3 kV/cm), the relationship between the deflection and electric field strength can be approximated to be linearly dependent. The elastic response of another elastomer, a polyurethane (PUE) under external field field, was studied by Ueda *et al.*[10] They reported the bending displacement of a PUE sheet under electric field applied through 2 electrodes at one end. The displacement was due to the dipole moments of the ester linkages within in the polymer chain induced by the electric field.[10]

We next investigate the dielectrophoresis force, F_D, produced by the electric field through the crosslinked bridges and the strands within the PDMS network, which is responsible for the change in the PDMS molecular conformation or the macroscopic shape change and/or motion.[8] F_D can be calculated from the static force static balances between the weight of the sample and the elastic deflection force, F_d. The resultant F_D can be written as:

$$F_D = mg\sin\theta + F_d \tag{7}$$

where F_d is the elastic deflection force required to produce a bending as can be derived from the theory of linear elasticity:[7]

$$v(y = 0,\ x = 0) = \frac{F_d l^3}{3EI} \tag{8}$$

where v is the displacement of the free bottom end of PDMS film, E is the Young's modulus which is equal to $2G(1+\nu)$, G is the shear modulus (taken to be $G'(\omega = 1$ rad/s$) \approx 12{,}000$ and 22,000 Pa for crosslinking ratios of 0.001 and 0.01, respectively), ν is the Poisson's ratio (=0.5 for incompressible sample), I is the moment of inertia $\frac{1}{12}t^3w$, t is the thickness of PDMS film, w is the width of PDMS film, and l is the length of PDMS film.[11] Table 1 shows the calculated F_D values of the crosslinked PDMSs at varoius electric field strengths and crosslinking ratios. For each crosslinked system, F_D increases linearly with electric field strength as shown in Figure 5(b). A higher electric field strength induces a larger dielectrophoresis force onto the PDMS sample thus a larger degree of bending is produced. In Table 1, the last column, we also calculated the defection force, F'_d, from the nonlinear elasticity theory[12] in which the bending produces a curvature on the beam. Both defection forces, F_d and F'_d, are quite comparable in magnitude. The linear deflection force F_d is believed to be more accurate since the bending observed occurs mostly at the clamped end and no sample curvature can be visibly identified.

Feher *et al.*[13] reported a dependence of applied voltage on the dielectrophoresis force of crosslinked PDMS gels containing TiO_2 suspened in silicone oil. They found that electrophoresis force was proportional to electric field square,

$$\rho_f = \frac{f_{DEP}}{r^2\pi} = \frac{CVV}{r^2\pi d} = constV^2 \tag{9}$$

where ρ_f is the force density (N/cm^2), f_{DEP} is the dielectrophoresis force (N), r is the radius of cylindrical PDMS gel (cm), C is capacitance (C/V), V is the applied voltage (kV) and d is the gap distance between the two pararell electrodes (cm). The result differs from our; this may originate from the filled polarizable particles, TiO_2, which can respond to an external electric field, leading to a larger electrophoresis force and the quadratic dependence. Our system with a crosslinking ratio of 0.01 shows a higher F_D than the system with a crosslinking ratio of 0.001. The former system has a larger number of strands and it is more susceptible to the dielectrophoresis force.[8]

Next we observed the response time of each crosslinked PDMS at various electric field strength. The induction time (t_{ind}) is the time required for PDMS films to reach the steady-state bending when applying the field. The time required for PDMS films decay toward its original point when the electric field is turned off is called the recovery time, t_{rec}. For each crosslinked PDMS film, t_{ind} decreases and t_{rec} increases with electric filed strength, as shown in

Table 1. The increase of t_{rec} with electric field indicates a longer relaxation time required to recover its original shape from a greater deformed state.

Conclusions

In the absence of electric field, the storage modulus of the PDMS systems increases linearly with crosslinking density due to the larger number of strands. For electric field strength between 0.5 to 2.0 kV/mm, storage modulus increases nonlinearly with electric field. For the G' temporal characteristic of the crosslinked PDMS ($N_c/N_m = 0.01$) under electric field strengths of 1 and 2 kV/mm, data indicate that it is nearly a reversible system consistent with the deflection experiment. The degree of bending of the PDMS films and the dielectrophoretic forces $F_{D,}$ increase linearly with electric field strength. Moreover, we observed the electrical yield point at electric filed strength of 100 V/mm for the lower crosslinked PDMS ($N_c/N_m = 0.001$).

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