



CHAPTER V

DIELECTROPHORESIS FORCE AND DEFLECTION OF ELECTROACTIVE POLY(P-PHENYLENE VINYLENE)/POLYDIMETHYLSILOXANE

5.1 Abstract

The effects of PPV volume fraction and electric field strength on the electromechanical properties and the deflection of PPV/PDMS blend gels were investigated experimentally. The electromechanical properties of the PPV/PDMS blends were measured under oscillatory shear mode at a temperature of 27 °C. On application of an electric field, the storage modulus response, $\Delta G'$, increases between 7-50%, depending on PPV volume fraction, as the electric field strength is varied between 0 and 2 kV/mm. The stress generated is caused by the induced polarized PPV particles leading to interparticle interactions. With an external electric field applied, the PPV/PDMS films, suspended in silicone oil between copper electrodes, respond with significant and rapid deflections toward the anode, indicating the attractive interaction between the anode and the polarized PPV particles embedded in PDMS network. As the electric field is removed, the PPV/PDMS films nearly recover their original positions and shapes due to the gravitational force, elasticity, and the reversibility of the polarized PPV particles. Thus, our PPV/PDMS system is a reversible bending system, consistent with the G' temporal response results. From the deformation data, the dielectrophoresis force, F_D , and the degree of deflection vary linearly with electric field.

5.2 Abbreviation

E_0	applied electric field strength
G'	storage modulus (Pa/s)
G''	loss modulus (Pa/s)
t_{ind}	induction time

t_{rec}	recovery time
ϕ	volume fraction
α	scaling exponent
γ	scaling exponent
σ	electrical conductivity
R	resistant
t	disk thickness
K	geometric correction fractor
β	relative polarizability
K_f	dielectric permittivity of medium
η^*	complex oscillatory steady shear viscosity
ω	frequency
F_D	dielectrophoresis force
F_d	elastic deflection force
N_c	mole of crosslinker
N_m	mole of monomer
v_1	the molar volume of solvent ($M_w/\text{density}$)
w_0	the original polymer weight
w_s	the swollen polymer weight
χ	the polymer-solvent interaction parameter
R	the universal gas constant, 8.29 N _m /mol.K,
δ	the solubility parameter
ν	number density of strands

5.3 Introduction

Actuator devices are utilized in many applications: space vehicles, robots, and artificial muscles. Specific requirements are reduced size, low mass, high power consumption, and low cost (Meijer *et al.*, 2000).

Conjugated conductive polymers have been extensively studied as they provide a unique class of material. Poly (p-phenylene vinylene), PPV, is one

conductive polymer that has been explored because of its non-linear optical properties, electroluminescence, and high electrical conductivity upon doping (Damlin *et al.*, 2002). The applications of PPV include non-linear semiconductors, light-emitting electrochemical cells, batteries, and sensors. PPV is a type of poly(arylene vinylene), PAV; PPV has a longer conjugation length than other PAVs (Ohnishi *et al.*, 1991). In order to find a material suitable for actuator applications, one has to overcome certain limitations such as poor stability, poor processability, and a low degree of mechanical response. One possible approach to improve these properties is to prepare a tailored blend of a conducting polymer embedded in a flexible elastomer. There has been much recent interest in using elastomers as actuator material (Kornbluh *et al.*, 2002): thermoplastic elastomers (Spontak *et al.*, 2000), silicone elastomers (Feher *et al.*, 2001 and Wissler *et al.*, 2005), and polyurethane (Jung *et al.*, 2007 and Varga *et al.*, 2005). Elastomers have many advantages: they are lightweight, have a high degree of mechanical response, and a fast response time.

Recently, the insertion of a conductive polymer into an elastomer forming a blend has been of keen interest. Conductive polymers can offer a variety of benefits to the host elastomer: variable conductivity, better thermal stability, and mechanical properties (Gorur, 2003). Poly(dimethylsiloxane)/polypyrrole blends, polyanilene-EPDM blends (Gorur, 2003), and TiO₂ embedded in PDMS gels were prepared for actuator applications and they showed moderate response under the action of an electric field (Zrinyi *et al.*, 2000). In our study, polydimethylsiloxane (PDMS) was selected as the elastomer matrix because of its unique properties, including high flexibility, solubility, and high temperature resistance (Cakmak *et al.*, 2004). These characteristics are desirable properties required to induce large actuation strain when subjected to an electric field (Gorur, 2003 and Zrinyi *et al.*, 2000). PPV was chosen as the conductive polymer to be embedded into the PDMS matrix.

In our work, we are interested in studying fabricated poly(p-phenylene vinylene)/polydimethylsiloxane elastomer blends as electroactive materials for actuator applications. The electromechanical properties and the deflections of soft and flexible PPV/PDMS blend gels are investigated in terms of PPV volume fraction and electric field strength.

5.4 Experimental Details

5.4.1 Materials

α,α' -dichloro-p-xylene and tetrahydrothiophene, THT (AR grade, Aldrich), were used to synthesize poly(p-xylylene-bis-tetrahydrothiophenium chloride). Acetone and methanol were used as received. Hydroxyl terminated polydimethylsiloxane, HO-PDMS (AR grade, Aldrich), with a density of 1.96 g/cm^3 and a kinematics viscosity of 18,000–20,000 cSt, was used as the matrix. Tetraethyl orthosilicated, TEOS (AR grade, Aldrich), and dibutyltin dilaurate (AR grade, Aldrich) were used as the initiator and the catalyst, respectively.

5.4.2 Synthesis of Poly(p-phenylene vinylene)

PPV was synthesized via a polyelectrolyte precursor according to the method of Burn *et al.*, 1992. To a suspension of 10 g of α,α' -dichloro-p-xylene in 150 mL of methanol, we added 15 mL of tetrahydrothiophene, THT. The resulting mixture was heated in a $50 \text{ }^\circ\text{C}$ oil bath overnight, and 250 mL of acetone was poured in to precipitate the salt p-phenylene dimethylene bis tetramethylene sulfonium chloride. The mixture was stirred in an icebath for 0.5 hr before filtration. The white solid salt obtained was washed with acetone and dried under vacuum at room temperature until two sequential weighings were the same. The yield was 85% (Burn *et al.*, 1992). Then 1.0 g of the washed and dried salt was dissolved in 7.5 cm^3 of methanol and then cooled to $0 \text{ }^\circ\text{C}$, and was added to 6.3 cm^3 of aqueous sodium hydroxide (0.4M). The reaction mixture was stirred for a duration of 120 min at $0 \text{ }^\circ\text{C}$, and was slightly acidified with 1 cm^3 of hydrochloric acid (0.4 M). The solution of 14.8 cm^3 was then dialyzed against a water-ethanol mixture (1:1, $3 \times 1000 \text{ cm}^3$) for over three days, after which the solvent was completely removed. The residue was redissolved in methanol. After cooling, the aqueous solution of poly [(p-phenylene) bis(tetrahydrothiophenechloride)] was poured onto a glass dish and allowed to evaporate at room temperature in a free air steam. After 24 hours, the yellowish-green precursor films were heated at $200 \text{ }^\circ\text{C}$ for 16 hr in vacuum to yield PPV

powder. The obtained PPV powder was ground by a jar mill for 2 days.

5.4.3 Preparation of PPV/PDMS Blends

PPV/PDMS blend specimens were prepared by the mechanical blending of synthesized PPV particles with HO-PDMS and TEOS at the crosslinking agent and monomer ratio (N_c/N_m) of 0.01, using dibutyltin dilaurate as the catalyst. The mixture was poured into a mold (diameter = 25 mm and height = 1 mm) and allowed to cure under a pressure of 0.6 atm, 27 °C for 4 hr.

5.4.4 Characterization Method

Fourier-transform infrared (FT-IR) spectra were obtained using a FT-IR spectrometer (Bruker, Equinox 55/ FRA 1065X). Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PPV powder thoroughly mixed and ground with dried KBr at a PPV:KBr ratio of 1:20 and was compressed into a disc. Scanning electron micrographs were taken with a JEOL, JSM-5200-2AE, using an acceleration voltage of 20 kV and a magnification of 350. A thermogravimetric analyzer (Dupont, TGA 2950) with a heating rate of 10 °C/min under N₂ atmosphere was used to determine the thermal behavior of PPV. A particle sizer (Malvern, Master-sizer X) was used to obtain the PPV particle size distribution and the mean sizes.

To determine the electrical conductivity, PPV disks (25 mm diameter and ~0.2 mm thickness) were prepared from compression with a hydraulic press. Electrical conductivity was measured using a custom-built two-point probe. The specific conductivity, σ (S/cm), was obtained by measuring the resistance, R, and using the following relation: $\sigma = (1/Rt)(1/K)$, where t is the film thickness and K is the geometric correction factor. A geometric correlation factor was obtained by using standard silicon wafer sheets with known specific resistivity values. The measurements were performed in the linear Ohmic regime. The measurements were carried out at 27 °C and repeated at least two times.

5.4.5 Electromechanical Properties Measurements

The electromechanical properties of the PPV/PDMS gels under oscillatory shear were measured at a fixed temperature of 27 °C by using a parallel plate fixture (Rheometric Scientific Inc., ARES). The sample diameter was 25 mm with a nominal thickness of 1 mm. Dynamic moduli, G' and G'' , were measured as functions of frequency and electric field strength. Linear viscoelastic regimes were determined in an absent of electric field and under applying electric field by strain sweep tests to determine the appropriate strains used in measuring G' and G'' . A frequency sweep test was then carried out to measure G' and G'' as functions of frequency (0.1-100 rad/s) at fixed strains of 1%. Pre-oscillatory shears at a frequency of 1 rad/s and fixed strains of 1% were applied to the PPV/PDMS gels under electric field (~ 10 min) to attain equilibrium polarizations before the measurements were taken.

5.4.6 Deflection Measurement

To study the elastic response of the PPV/PDMS gels to an electric field, films of the PPV/PDMS gels were vertically suspended in silicon oil between a pair of parallel copper electrode plates (40 mm long, 30 mm wide, and 1 mm thick). A rigid plastic clip was used to fix the top position of the gel, as shown in Figure 5.5 (a). A high DC voltage (UC5-30P HV Power Supply, Gamma High Voltage Research Inc.) was applied in a non-contact mode through the electrodes, which were 10 mm apart. The electric deflection 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).

5.5 Results and Discussion

5.5.1 PPV Characterization

The FT-IR spectra of the synthesized PPV indicate distinct adsorption peaks at 3022, 550, 830 and 1511 cm^{-1} . They represent the trans vinylene C-H stretching mode, the phenylene out of plane ring bending, the p-phenylene ring C-H out of plane bending, and the C-C ring stretching, respectively (Burn et al., 1992).

The TGA thermogram of the synthesized PPV shows only one degradation step at 554 °C, corresponding to the degradation reaction of the PPV main chain only (Cirpan *et al.*, 2003).

The PPV particle diameter is 46 μm with a standard deviation of ~ 4 μm . The particle microstructure was observed by a scanning electron microscope (SEM). Figure 5.1 shows the PPV particles (PPV) and PPV particles in the polymer blends (PPV/PDMS-10); they are quite irregular in shape. However, these irregular shaped particles appear to be moderately dispersed in the PDMS matrices. The specific conductivity value of the PPV particles is 7.89×10^{-8} S/cm.

5.5.2 Time Dependence of the Electromechanical Response

We first investigated the temporal characteristic of PPV/PDMS-10 blends at a particle volume fraction of 10 vol%, with an applied electric field switched on and off periodically, at $E = 1$ and 2 kV/mm. The temporal characteristic of PPV/PDMS-10 was measured in the linear viscoelastic regime at a strain of 1%, and a frequency of 1 rad/s. As can be seen in Figure 5.2, the storage modulus, G' of the PPV/PDMS blend immediately increases and rapidly reaches a steady state value when $E = 1$ kV/mm is switched on. When the electric field is switched off, G' decreases and nearly recovers its original value, indicating that it is a nearly reversible system. As the electric field is applied, G' is induced as a result of the dipole-dipole interactions between the PPV particles within the PDMS matrix (Lui *et al.*, 2001). As the electric field is removed, the dipole-dipole interactions vanish and the storage modulus decreases to the original value.

At an electric field strength of 2 kV/mm, the response of G' can be divided into two regimes: the initial regime — in which G' rapidly increases from $G' = 32,400$ Pa to 50,700 Pa on the first cycle and G' decreases from 52,700 Pa to 44,000 Pa ($\sim 17\%$ recovery) after the electric field is switched off — and the steady state regime — which subsequently shows a reversible cyclic response. On the first cycle, at an applied electric field of 2 kV/mm, G' does not recover its original value, indicating that some of the induced dipoles remain as residues within the PPV particles, leading to irreversible interparticle interactions between the PPV particles

after the electric field strength of 2 kV/mm is switched off.

The time required for G' to reach the steady-state value upon applying the field is called the induction time, τ_{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, τ_{rec} . For the PPV/PMDS-10 system, τ_{ind} decreases but τ_{rec} increases with increasing electric field strength. The τ_{ind} are 283 and 78 sec and the τ_{rec} are 131 and 163 sec at electric field strengths equal to 1 and 2 kV/mm, respectively. At high electric field strength, the PPV particles possess higher induced dipole moments and consequently higher residue dipole moments when the field is turned off. These residues are gradually decreasing in strength and thus a longer time (τ_{rec}) is required for the stronger interaction to fully subside. Since the induction times of all samples required to reach steady state are less than 600 sec, the pre-oscillatory shearing time required and used in the oscillatory shear mode experiments was thus set at 600 sec (~10 min) to ensure equilibrium polarization.

5.5.3 Electromechanical Properties of Poly(p-phenylene vinylene) / Polydimethylsiloxane, PPV/PDMS Blends

The effect of poly(p-phenylene vinylene) volume fraction on the electromechanical properties of polymer blends (PPV/PDMS blend) was investigated. The PPV volume fractions studied were 3, 5, 7, 10, 15, and 20 vol% for PPV/PDMS-3, PPV/PDMS-5, PPV/PDMS-7, PPV/PDMS-10, PPV/PDMS-15 and PPV/PDMS-20 respectively. Figure 5.3 (a) shows the dependence of the storage modulus, G' ($\omega = 1$ rad/s), of PPV/PDMS on the PPV volume fraction, ϕ , without an electric field applied and at strain equal to 1%. In the absence of an electric field, $E = 0$ V/mm, G' linearly increases with PPV volume fraction, consistent with the Einstein-Smallwood theory (Varga *et al.*, 2005):

$$G = G_e(1+k_e\phi_m), \quad (5.1)$$

where G_e denotes the modulus of the elastomer without any solid particles, k_e is the Einstein- Smallwood parameter, and ϕ_m is the volume fraction of the filler particles (Zrinyi *et al.*, 2000). G' increases with the PPV volume fraction because the PPV particles in the polymer blends act as fillers within the matrix; they can store or

absorb the stresses within the matrix (Krause *et al.*, 2001).

The effect of electric field strength on the electromechanical properties of the PPV/PDMS blend at various PPV volume fractions was investigated in the range between 0-2 kV/mm. The storage modulus (G') of each polymer blend system generally increases with increasing electric field strength, as also shown in Figure 5.3 (a). As an electric field is applied, both PDMS segments and PPV particles become polarized and induced dipole moments are generated, leading to intermolecular electrostatic interactions. These intermolecular interactions result in higher rigidity of the blends as indicated by the higher G' (Pa) obtained, which can be physically interpreted to be due to the decrease in the number of freely moving chains (Lui *et al.*, 2001 and Krause *et al.*, 2001), or an the increase in the number of effective strands per unit volume.

In Figure 5.3 (a), we also show the storage modulus response $\Delta G'_{2kV/mm}$, $\Delta G' = G'_E - G'_0$, where G'_E is the G' value of the system under electric field, and G'_0 is the G' value of the system without electric field (in secondary axis) vs PPV volume fraction. As the PPV volume fraction increases, the storage modulus response appears to increase linearly with PPV volume fraction and it reaches a maximum value at 10 vol%. At very low PPV volume fraction, the number of PPV particles is too small and the distances between PPV particles are too large to create a sufficiently strong particle interaction (Gorur *et al.*, 2003). At a higher PPV volume fraction, the distances between the PPV particles become smaller and the systems possess stronger interparticle interactions (Shiga *et al.*, 1997). Above 10 vol%, the interparticle force decreases due to the multidipole effect, in which dipole moments of particles interfere with each other (Krause *et al.*, 2001). Liu *et al.* (2001) reported a similar effect for the silicone/silica elastomer. They found that at a volume fraction above 55 vol%, the shear modulus decreased since the interparticle force diminished with the steric hindrance effect.

The electromechanical G' sensitivity is defined as $\Delta G'/G_0 = (G'_E - G'_0)/G'_0$. The storage modulus response values, $\Delta G'$ (Pa), of these systems at electric field strength of 2 kV/mm are 8900, 10650, 12700, 15040, 16750, 13960, and 3350 Pa for PDMS ($N_c/N_m = 0.01$), PPV/PDMS-3, PPV/PDMS-5, PPV-/PDMS-7,

PPV/PDMS-10, PPV/PDMS-15, and PPV/PDMS-20, respectively. The corresponding storage modulus sensitivity values of these polymer blend systems at electric field strength of 2 kV/mm are 41, 42, 45, 46, 50, 36, and 7%, respectively. The system PPV_0/PDMS_10 thus possesses the maximum sensitivity.

Figure 5.3 (b) shows the storage modulus response ($\Delta G'$) vs electric field of various polymer blends at a frequency of 1 rad/s, and at a strain of 1%. The dependence of $\Delta G'$ on electric field follows a scaling behavior: $\Delta G' = aE^\alpha$ within the electric field range of 0.2 to 1 kV/mm. At E higher than 1 kV/mm, the storage modulus seems to level off or become saturated. As the electric field between the adjacent particles becomes too large, the dielectric breakdown strength of the continuous phase is exceeded, limiting the electrostatic interparticle force (Krause *et al.*, 2001).

In Figure 5.3 (a) and (b), the storage modulus responses ($\Delta G'$) are plotted in log-log scale versus PPV volume fraction and electric field strength, in order to compare our data with the theory proposed by Shiga *et al.* (1997):

$$\Delta G = (9/4) C \epsilon_m \kappa^2 E^2, \quad (5.2)$$

where ΔG is the elastic modulus response, C is the volume fraction of particles, ϵ_m is relative dielectric constant of the matrix, and E is the applied electric field strength. κ is defined from the conductivity of the PDMS matrix and PPV particles in the presence of a dc electric field:

$$\kappa = (\sigma_2 - \sigma_1) / (\sigma_2 + 2\sigma_1), \quad (5.3)$$

where σ_1 and σ_2 are the conductivity values of the matrix and the particle, respectively. The scaling exponent β of $\Delta G' = b\phi^\beta$ on particle volume fraction is equal to 1.1, a value close to the theoretical value of 1 in Equation 5.2. On the other hand, the scaling exponent α of $\Delta G'$ on the electric field strength is found to vary between 1.00 and 1.95. This value differs from the theoretically predicted value of 2; this may originate from the nature of random particle distribution. As an electric field is applied, the induced dipoles attract each other when the PPV particles are aligned end-to-end, but repel each other when side by side (Shiga *et al.*, 1997). In the theory of Equation 2, the particles were assumed to be connected and aligned as strings.

5.5.4 Power Consumption

The power consumption of electroactive polymer actuators for active control is an important parameter for evaluating the performance of a smart structural system. The power consumption is simply the product of the current passed through the material systems and the applied voltage. Figure 5.4 shows the current vs electric field strength of PDMS and PPV/PDMS blends, at a frequency of 1 rad/s, strain equal to 1%, and a temperature of 27 °C. For both pure PDMS and PPV/PDMS blend systems the currents are $\sim 1-1.5 \mu\text{A}$ and independent of electric field strength at low electric field strength (below 1kV/mm); but they increase dramatically (above 1kV/mm). Overall, the current leakage in our material systems is quite low and in the order of μA . The sharp rise in the current at high electric field strengths is due mainly to a direct jump between the electrodes, and a smaller contribution from the jump between dilute conductive particles suspended in the matrices. Finally, we calculated the maximum power consumption of both systems, which turns out to be in the order of mW/mm.

5.5.5 Deflection under Electric Field

Finally, we investigated the effects of particle concentration and electric field strength on the deflection of soft and flexible PPV/PDMS blend films suspended in silicone oil between two copper electrodes. The amount of deflection of the PPV/PDMS films at the specific electric field strength can be described by the parameters d , l , and θ as shown in Figure 5.5 (a). Figure 5.5 (b) illustrates the effect of electric field strength on the deflection of the PPV/PDMS-10 film, 0.5 mm x 2 mm x 11 mm, suspended in the silicone oil (100 cSt). As an external electric field is applied, the PPV/ PDMS-10 film responds with a significant and rapid deflection towards the anode, with the degree of deflection depending on the electric field strength, indicating the attractive interaction between the anode and the polarized PPV particles embedded in the PDMS network. As the electric field is removed, the PPV/PDMS nearly completely recovers its original position and its straight shape, as a result of gravitational force, the matrix elasticity, and the reversibility of the depolarized PPV particles. Thus, the PPV/PDMS-10 appears to be a reversible

deflection system, consistent with the G' temporal response results.

The values of the observed deflection parameters — d , l and $\theta \approx \arctan(d/l)$ — of the PPV/PDMS films at various electric field strengths and particle concentrations are tabulated in Table 5.1. The displacement of the free bottom end of the gel (d) and the degree of deflection (θ) increase with electric field strength. As the electric field is applied, the freely suspended end of the PPV/PDMS films deflect towards the anode site because of the attractive interaction between the anode and the polarized PPV particles. As a higher electric field strength is applied, stronger dipole moments are expected to be generated, leading to a higher degree of deflection. In Figure 5.6 (a), the degree of deflection (θ) is plotted versus electric field strength in order to investigate the effect of PPV volume fraction. The θ of each PPV/PDMS system linearly increases with electric field strength. However, we may identify the electrical yield points of 170, 80, and 240 V/mm for PPV/PDMS-3, and PPV/PDMS-10 and PPV/PDMS-20, respectively. The electrical yield point is defined as the electric field strength required to initiate a deflection of a PPV/PDMS film. The degree of bending, θ , of PPV/PDMS-10 at specific electric field strength is higher than the θ of PPV/PDMS-3 since the PPV/PDMS-10 system has a higher amount of polarized particles, or a higher attractive interaction between the anode and the polarized PPV particles. In contrast to the PPV/PDMS-10 system, the PPV/PDMS-20 system shows a lower θ than the PPV/PDMS-3. This may result from the higher rigidity (G') of the PPV/PDMS-20.

Filipcsei *et al.* (2000) reported a similar effect for the weakly crosslinked PDMS gels containing finely distributed TiO_2 suspended in silicone oil (DC 200, Fluka) under the action of an external electric field. They discovered a driving mechanism to induce the deformation and movement of neutral polymer gels in a non-conducting medium. Since the particles cannot leave the gel matrix, all forces acting on the particles are directly transmitted to the polymer chains, resulting in either the locomotion or the deformation of the gel (Filipcsei *et al.*, 2000). With increasing field intensity, the deflection of the free end of the gel increased. At small field intensities (< 3 kV/cm), the relationship between the deflection and electric field strength was approximately linear.

We next investigated the dielectrophoresis force, F_D , produced by the electric field. The dielectrophoresis force refers to the force exerted on the induced dipole moments of uncharged PPV particles and PDMS molecules by an electric field. F_D can be calculated from the static force balances between the weight of the sample and the elastic deflection force, F_d . The resultant F_D can be written as:

$$F_D = mg \sin \theta + F_d \quad (5.4)$$

where F_d is the elastic deflection force required to produce a bending as can be derived from the theory of linear elasticity (Gere *et al.*, 1991),

$$v(y = 0, x = 0) = \frac{F_d l^3}{3EI}, \quad (5.5)$$

where v is the displacement of the free bottom end of the PPV/PDMS film, E is the Young's modulus which is equal to $2G(1+\nu)$, G is the shear modulus (taken to be $G'(\omega = 1 \text{ rad/s}) \approx 25,000, 34,400, \text{ and } 45,900 \text{ Pa}$ for PPV/PDMS-3, PPV/PDMS-10, and PPV/PDMS-20, respectively, ν is Poisson's ratio ($= 0.5$ for an incompressible

sample), I is the moment of inertia $\frac{1}{12} t^3 w$, t is the thickness of the PPV/PDMS film, w is the width of the PPV/PDMS film, and l is the length of the PPV/PDMS film (Gere *et al.*, 1991). Table 5.1 shows the calculated F_D values of the PPV/PDMS at various electric field strengths and crosslinking ratios. The F_D of each blend system increases linearly with electric field strength, as shown in Figure 5.6 (b). A higher electric field strength induces a larger dielectrophoresis force onto the PPV/PDMS sample, and thus a larger degree of deflection is produced. The F_D of PPV/PDMS-10 is higher than the F_D of PPV/PDMS-3 since the PPV/PDMS-10 system has a higher amount of polarized particles, thus there is a stronger attractive interaction between the anode and the polarized PPV particles. However, the PPV/PDMS-20 system shows a lower F_D than the PPV/PDMS-3. This result is similar to the displacement experiment of high particle concentration (Krause *et al.*, 2001); the underlying factors are the particle steric hindrance (Lui *et al.*, 2001) and the electrostatic moment beyond the dipole (Parthasarathy *et al.*, 1996), operative at high particle concentrations.

In the last column of Table 5.1, we tabulate the deflection force, F'_d ,

from the nonlinear elasticity theory (Timoshenko et al., 1970) in which the bending produces a curvature on the beam. Both deflection 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.* (2001) reported a dependence of applied voltage on the dielectrophoresis force of a TiO_2 -loaded crosslinked PDMS gels cylinder suspended in silicone oil. The TiO_2 content of the TiO_2 /PDMS gel was 3 %v/v. They predicted that the electrophoresis force was proportional to electric field square:

$$\rho_f = \frac{f_{DEP}}{r^2 \pi} = \frac{CVV}{r^2 \pi d} = \text{const} V^2, \quad (5.6)$$

where ρ_f is the force density (N/cm^2), f_{DEP} is the dielectrophoresis force (N), r is the radius of the cylindrical PDMS gel (cm), C is the capacitance (C/V), V is the applied voltage (kV), and d is the gap distance between the two parallel electrodes (cm). The prediction differs from our finding which may originate from the smaller size of the TiO_2 particles ($\sim 0.3 \mu\text{m}$) relative to our PPV size of ($\sim 46 \mu\text{m}$). The former should possess a more uniform size distribution. In addition, it is known that the magnitudes of the deflection and the dielectrophoresis force may presumably depend on the samples initial length and shape (Filipcsei *et al.*, 2000).

Next we observed the response time of each PPV/PDMS blend at various electric field strengths. The induction time (t_{ind}) is the time required for the PPV/PDMS films to reach steady-state deflection under applied electric field. The time required for PPV/PDMS films to relax towards its original shape and position when the electric field is turned off is called the recovery time, t_{rec} . For all of the PPV/PDMS films, the t_{ind} decreases and t_{rec} increases with electric field strength, as shown in Table 5.1. The τ_{ind} are 19.0, 15.7, 12.2, and 5.5 sec, and the τ_{rec} are 3.9, 4.8, 5.9, and 8.0 sec at an electric field strength of 150, 250, 350 and 450 V/mm, respectively, for PPV/PDMS-3. The increase in t_{rec} with electric field is in agreement with τ_{rec} : at high electric field strength, higher residue dipole moments are gradually decreasing in strength, and thus longer time (t_{rec}) is required for the stronger interaction to fully subside.

5.6 Conclusions

The electromechanical properties of the PPV/PDMS blends, with PPV particle volume fractions of 3, 5, 7, 10, 15, and 20 vol%, the storage modulus of each polymer blend is higher than the crosslinked PDMS due to the PPV particles within the matrix acting as fillers. They can absorb the stresses within the matrix. The dependence of $\Delta G'$ on electric field follows a scaling behavior: $\Delta G' = aE^\alpha$, $\alpha \approx 1.00 - 1.95$, within the electric field range of 0.2 to 1 kV/mm. This is the result of the polarized PPV particles leading to interparticle interaction. The storage modulus

sensitivity, $\frac{\Delta G'}{G'_0}$, attains a maximum G' % sensitivity values of 41, 42, 45, 46, 50, 36, and 7% at particle concentrations of 0, 3, 7, 10, 15, and 20 vol% at an electric field strength of 2 kV/mm, respectively. For the G' temporal characteristic of the PPV/PDMS-10 under electric field strengths of 1 kV/mm, data indicate that it is nearly a reversible system, consistent with the deflection experiment. The degree of deflection of the PPV/PDMS films and the dielectrophoretic forces, F_D , increase linearly with electric field strength. Thus, we clearly demonstrate that our blend systems (PPV/PDMS) may be used as a new type of low-power consumption linear electromechanical actuators.

5.7 References

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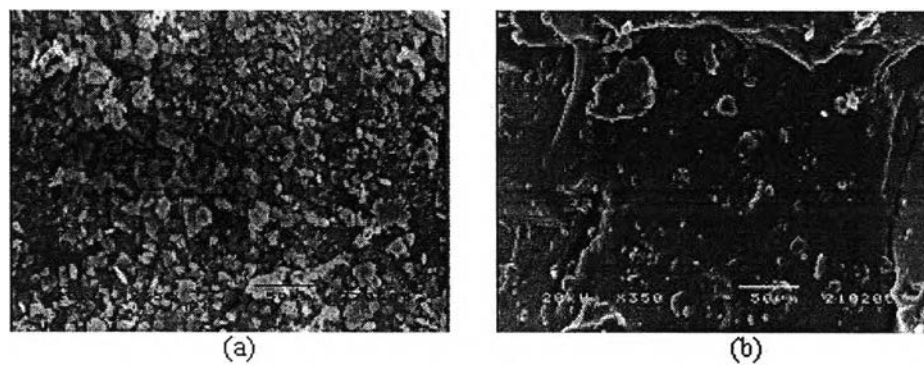
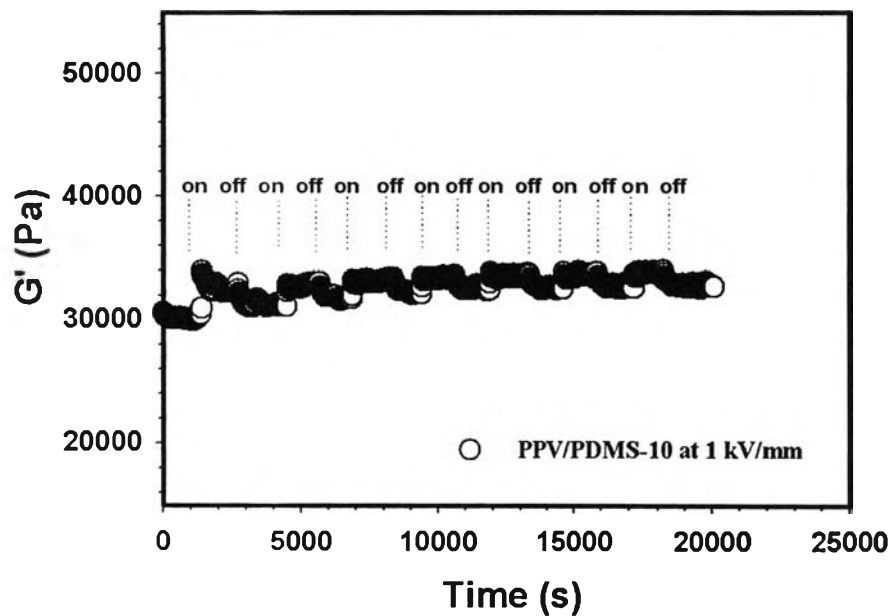
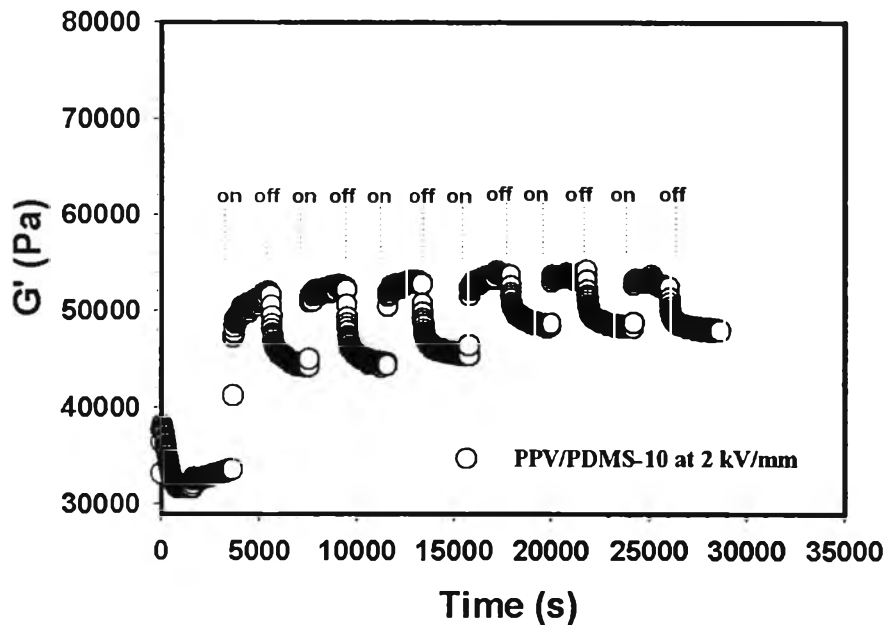


Figure 5.1 Morphology of a) poly (p-phenylene vinylene), PPV, and b) poly(p-phenylene vinylene)/polydimethylsiloxane blends, PPV/PDMS-10 at a magnification of 350.

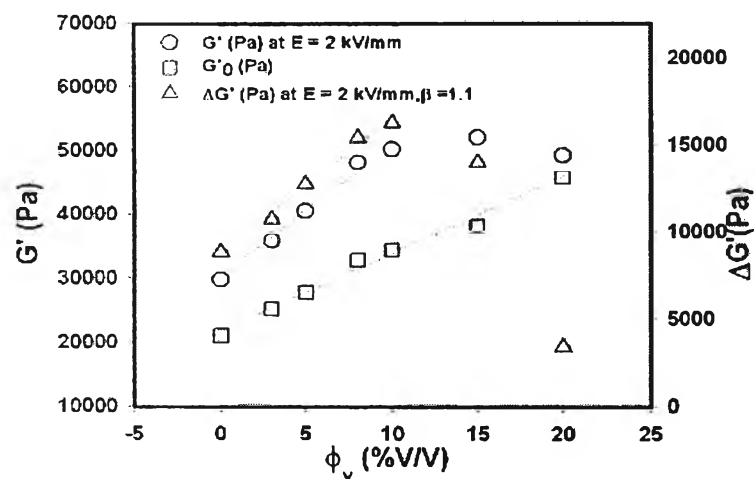


(a)

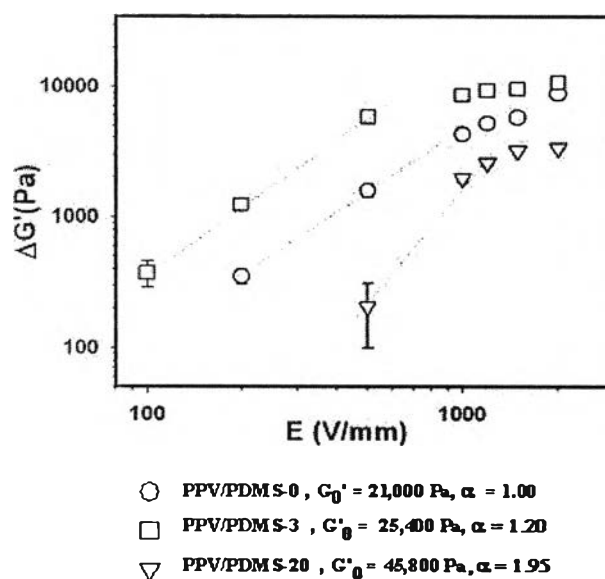


(b)

Figure 5.2 Temporal response of PPV/PDMS-10 with electric field strength of (a) 1000 and (b) 2000 V/mm, at 27 °C, frequency of 1 rad/s, and strain of 1%.



(a)



(b)

Figure 5.3 Effect of particle volume fraction of the PPV/PDMS blends on: (a) storage modulus response $\Delta G'$ ($\omega = 1$ rad/s) vs particle concentration at electric field strengths of 2 kV/mm, and the storage modulus at $E = 0$ (G'_0) and 2 kV/mm ($G'_{2\text{kV/mm}}$); (b) the storage modulus response $\Delta G'$ ($\omega = 1$ rad/s) vs electric field strength with strain = 1% and temperature = 27 °C.

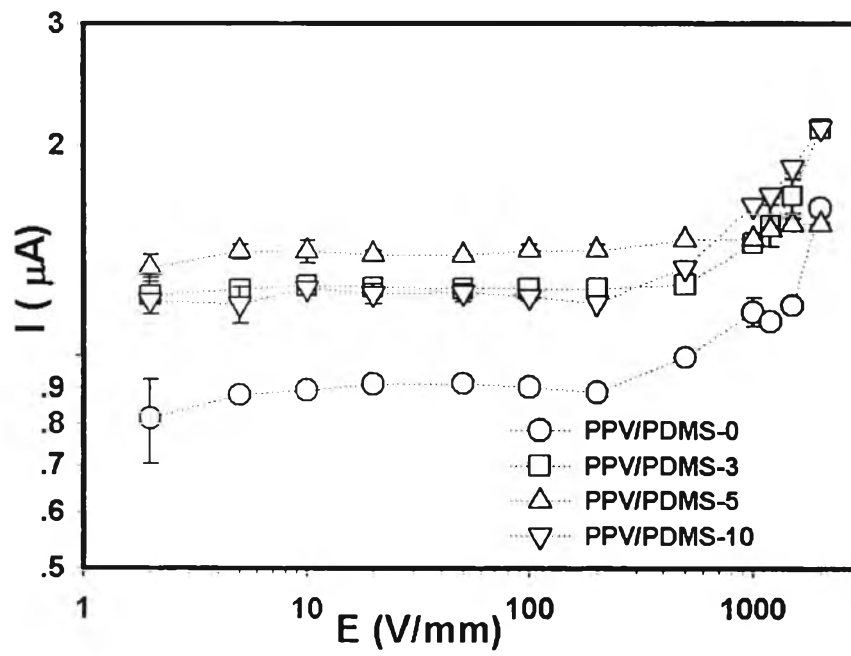


Figure 5.4 Current vs electric field strength of the PPV/PDMS blends.

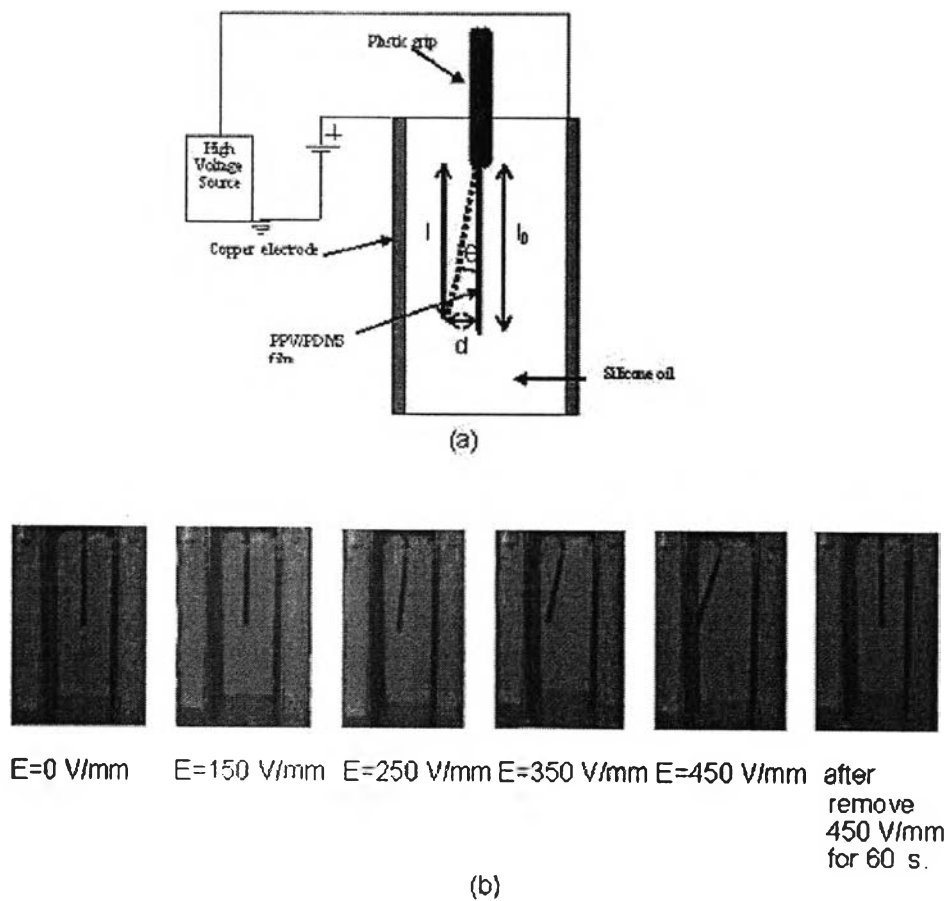
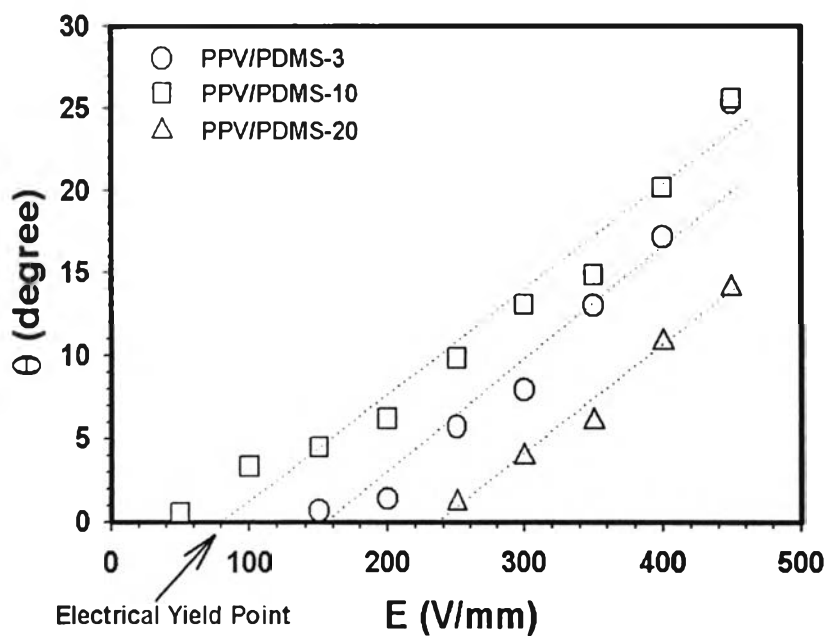
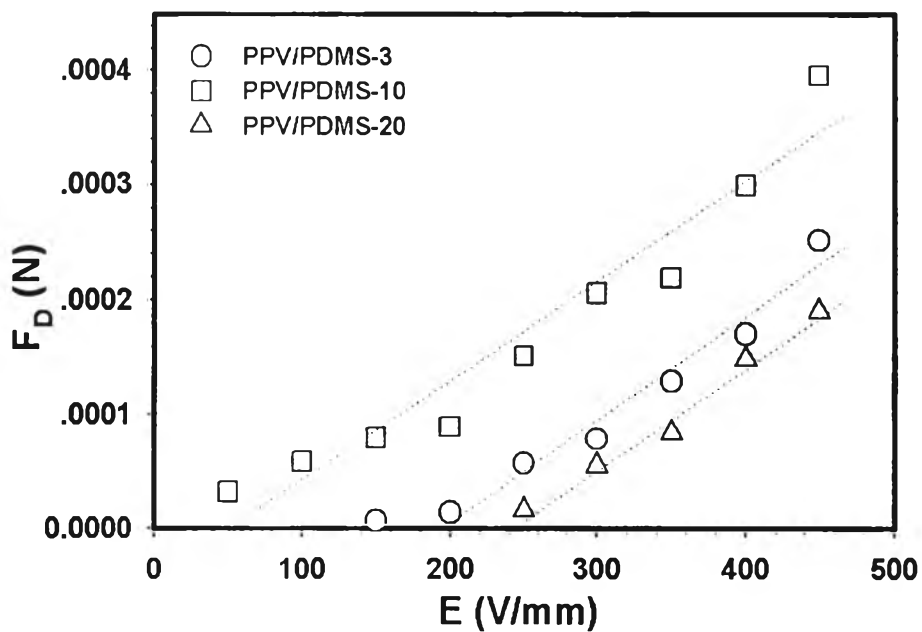


Figure 5.5 Schematic of the deflection experiment set up, (a) and deflections of PPV/PDMS-10 film, (b) as a function of electric field strength.



(a)



(b)

Figure 5.6 Degree of deflection, θ (degree), (a) and dielectrophoresis force, F_D (N), (b) vs electric field strengths of PPV/PDMS films.