CHAPTER IV

ELECTRORHEOLOGICAL PROPERTIES OF PDMS_PEDOT/PSS BLENDS

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Abstract

Electrorheological properties of pure PDMS and PDMS_PEDOT/PSS blends were investigated as electroactive actuator applications. Experiments were carried under the oscillatory shear mode and with applied electric filed strength varying from 0 to 2 kV/mm. The storage modulus, G', of the pure PDMS depended on the electric filed strength; the storage modulus (G') increased with increasing electric filed strength. With the PEDOT/PSS particle concentrations of 5, 10, 15, and 20 vol%, the storage modulus G' of the polymer blends, were generally higher than those of pure crosslinked PDMS. The storage modulus response increase linearly with electric filed strength and their storage modulus sensitivity, $\frac{\Delta G'}{G'_0}$, attained a maximum values of 8%, 9%, 10%, and 9%, at particle concentrations of 5, 10, 15, and 20 vol% at the electric field strength of 2 kV/mm, respectively.

Keywords: Electrorheological properties, PEDOT/PSS, PDMS, Dynamic moduli # Corresponding author, email: <u>anuvat.s@chula.ac.th</u>, Tel: 662 218 4131,

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Introduction

The exchange of electrical energy for mechanical energy has been of scientific and technological interests for many decades. Electromechanical energy conversion has been applied in many applications such as muscle/insect-like actuators, robotic, etc [1]. Electroactive polymers (EAPs) offer promising and novel characters such as lightweight, high energy density and high flexibility, and they are material candidates for muscle-like actuators. Dielectric elastomers are a type of electric-field-activated electroactive polymers that are capable of producing large strains, fast response, and high efficiency [2]. Poly(dimethylsiloxane) [PDMS] is a potential candidate material for actuator applications. It has excellent dielectric properties, flexibility; it is sturdy enough to manipulate, biocompatible, highly inert, optically transparent, high stability towards ultraviolet radiation, high resistance towards oxidation and chemical attack, and large operating temperature window from -100°C to over 200 °C and showing stable behavior even for harsh environments. Owing to the combination of these properties with its adaptable molecular composition and excellent process-ability, PDMS systems attract attention for a variety of actuation applications like robotics, android heads and MEMS [3].

Recently, incorporation of a conductive polymer into a dielectric elastomer forming a composite has been of interest. Conductive polymers can offer a variety of benefits to the host elastomer: variable conductivity, better thermal stability, and mechanical properties [4]. Examples are a polyanilene-polyisoprene composite for biosensor application [5], a polyanilene-EPDM composite [6], and TiO₂ embedded in PDMS gels for actuator application [7]. Among the numerous conducting polymers that have been developed and studied over the past years, poly(3,4-ethylenedioxy thiophene), also known as PEDOT, has developed into one of the most successful materials, from both fundamental and practical perspectives [8]. The materials resulting from combination with poly(stylene sulfonic acid), PEDOT/PSS, is being applied in several applications ranging from antistatic material in photographic film to electrode material in inorganic electroluminescent lamps. It has many advantages over other conducting polymers, such as a high transparency in the visible range, excellent thermal stability, and it can be processed in aqueous solution [9, 10].

In our work, we are interested in developing PDMS_PEDOT/PSS blends as a substitute for artificial muscles. The mechanical properties and electrical properties will be investigated in terms of PEDOT/PSS particle concentration, and electric field strength.

The Electrorheological Effect (ER effect)

Because we are using an electrorheological elastomer, a simplified description of the ER effect in solid-like matrices is introduced and summarized here. The nature of the ER effect in conductive polymer gels or elastomers will be explained using Maxwell-Wagner Polarization [11]. All ER particles posses some level of conductivity. Davis [12, 13] has pointed out that for DC and low-frequency AC electric fields, particle polarization and particle interactions will be controlled not by the particle and matrix electrical permittivities, but rather by the particle and matrix conductivities. In DC field, mobile charged accumulating at the interface screen the field within a particle, and particle polarization is completely determined by conductivities.

The Maxwell-Wagner model [11] is the simplest description of particle polarization accounting for both particle and matrix bulk conductivities, as well as their permittivities. In this theory, the permittivities and conductivities of the individual phase are assumed to be constants, independent of frequency. The complex dielectric constants (ε_k^*) of the dispersed and continuous phases can be written as:

$$\varepsilon_k^* = \varepsilon_k - j(\sigma_k / \varepsilon_0 \omega_e) \tag{1}$$

where $j = \sqrt{-1}$, and the asterisks represent complex quantities.

Consider again an isolated sphere in a uniform A.C. electric field. The complex potential will still satisfy Laplace's equation in the bulk phases [11], $\nabla^2 \psi^* = 0$, subject to the boundary conditions at the interface:

$$\psi^{*i} = \psi^{*0} \tag{2}$$

$$\varepsilon_p^* \nabla \psi^{*i} \Box n = \varepsilon_m^* \nabla \psi^{*0} \Box n \tag{3}$$

The solution for the complex potential is shown below:

$$\psi^{*i} = -E_0 r \frac{3\varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \cos \theta e^{j\omega_e t}$$
(4)

$$\psi^{*0} = -E_0 r \left[1 - \beta^* \left(\frac{a}{r} \right)^3 \right] \cos \theta e^{j \omega_e t}$$
(5)

where $\beta^{\star} = \frac{\left(\varepsilon_{p}^{\star} - \varepsilon_{m}^{\star}\right)}{\varepsilon_{p}^{\star} + 2\varepsilon_{m}^{\star}}.$

The time-average force $(F_{ij}(R_{ij}, \theta_{ij}))$ on a sphere at the origin due to a second sphere at (R, θ) may be determined easily in the point-dipole limit,

$$F_{ij}\left(R_{ij},\theta_{ij}\right) = \frac{3}{16}\pi\varepsilon_{0}\varepsilon_{m}\sigma^{2}\beta_{eff}^{2}\left(\omega_{e}\right)E_{rms}^{2}\left(\frac{\sigma}{R_{ij}}\right)^{4}\left\{\left(3\cos^{2}\theta_{ij}-1\right)e_{r}+\left(\sin 2\theta_{ij}\right)e_{\theta}\right\}(6)$$

where $E_{rms} = E_0 / \sqrt{2}$, and the "effective relative polarization (β_{eff}^2)" is now:

$$\beta_{eff}^{2} = \beta_{d}^{2} \frac{\left[\left(\omega_{e}t_{mw}\right)^{2} + \frac{\beta_{c}}{\beta_{d}}\right]^{2} + \left(\omega_{e}t_{mw}\right)^{2} \left[1 - \frac{\beta_{c}}{\beta_{d}}\right]^{2}}{\left[1 + \left(\omega_{e}t_{mw}\right)^{2}\right]^{2}}$$
(7)

Where $\beta_d = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}$, $\beta_c = \frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m}$, and $t_{mw} = \varepsilon_0 \frac{\varepsilon_p + 2\varepsilon_m}{\sigma_p + 2\sigma_m}$.

The force is essentially equivalent to the ideal case except that the effective polarizability is now a function of field frequency, as well as the permittivities and the conductivities of both phases, The value of β_{eff} , and thus the pair force, depends on the frequency relative to the polarization time constant t_{mw} . In the limit of high frequencies, permittivities dominate the response [11]:

$$\lim_{\omega_{e^{l}mw} \to \infty} \beta_{eff}^{2} \left(\omega_{e} \right) = \beta_{d}^{2}$$
(8)

32

While in the DC limit:

$$\lim_{\omega_{e^{t}mw} \to 0} \beta_{eff}^{2} \left(\omega_{e} \right) = \beta_{c}^{2}$$
(9)

Thus conductivities control particle polarization forces, regardless of the permittivities.

Experimental

Materials

3,4-ethylenedioxythiophene, EDOT (AR grade, Aldrich), was used as the monomer. Poly(styrene sulfonic acid), PSS was used as the polyelectrolyte solution. Sodium persulfate, $Na_2S_2O_8$ (AR grade, Aldrich), was used as the oxidant. Distill water was used as solvent. Poly(dimethyl sulfoxide), PDMS, (AR grade, Aldrich), was used as the polymer matrix. Tetraethyl orthosilicate (AR grade, Aldrich) was used as the crosslinking agent.

Synthesis of Poly(3,4-ethylenedioxythiophene)/Polystyrene sulfonic acid (PEDOT/PSS)

PEDOT/PSS was prepared by mixing 3,4-ethylenedioxythiophene, 5.99 wt% -PSS solution and $Na_2S_2O_8$ in water. After initial stirring at room temperature for 10 minutes, $Fe_2(SO_4)_3$ was added and the mixture was stirred vigorously for 24 hrs. After this period, the dark aqueous PEDOT/PSS mixture was purified by ion exchanging with Lewatit M600 and Lewatit S100, resulting in dark blue, aqueous PEDOT/PSS. A nice, transparent film of PEDOT/PSS was obtained by casting the aqueous PEDOT/PSS at 100°C for 24 hrs.

Characterization Method

Fourier-transform infrared spectrometer (FT-IR), PEDOT/PSS was identified for functional groups by an FT-IR spectrometer (Thermo Nicolet, Nexus 670) operated in the absorption mode with 32 scans and a resolution of ± 4 cm⁻¹, covering a wavenumber range of 4000-400 cm⁻¹ using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PEDOT/PSS was intimately mixed with dried KBr at a ratio of PEDOT: KBr = 1:20. Samples were grounded with a mortar, mixed with KBr, and molded into pellets under the pressure of 8 tons.

The thermal stability of PEDOT/PSS was investigated using a thermogravimetric analyzer (DuPont, model TGA 2950) in a temperature range from 30 to 900°C with a heating rate of 10°C/min and under O_2 atmosphere [15].

Scanning electron micrographs were taken with a JEOL, model JSM-5200 scanning electron microscope to determine the morphology of PEDOT/PSS in powder forms and PDMS_PEDOT/PSS blends at various particle concentrations. We used an acceleration voltage of 15 kV with magnifications of 100 and 1,000 times.

The electrical conductivity of PEDOT/PSS was measured by a custom-built twopoint probe coupled with an electrometer (Keithley, Model 6517A). The specific conductivity σ (S/cm) values of the pellets were obtained by measuring the bulk pellet resistance R (Ω). The relation $\sigma = (1/\text{Rt})(1/\text{K}) = (I/\text{Vt})(1/\text{K})$ was used to calculate specific conductivity, where t is the pellet thickness (cm), I is current change (A), V is apply voltage (voltage drop) (V) and K is the geometric correction factor which is equal to the ratio w/l, where w and l are the probe width and the length, respectively. The geometrical correction factor (K) was determined by calibrating the two-point probe with semi-conducting silicon sheets of known resistivity values. These two probes were connected to a voltmeter (Keithley, Model 6517A) for apply constant voltage source and recording a change in current. Electrical conductivity values of several samples were first measured at various applied voltage to identify their linear Ohmic regimes.

Preparation of the PDMS_PEDOT/PSS Blends

The PEDOT/PSS powder was sieved with a mesh particle size of 38 μ m and dried at room temperature for 24 hours prior to their uses. The blends were prepared by mechanical blending of synthesized PEDOT/PSS particles with PDMS at various particle concentrations (5, 10, 15 and 20 vol%). PDMS fluid and a specific amount of particle were added to the mixture, which was then mechanically blended for about 5 min to disperse the particles. We used the crosslinking ratio of 15% weight. The

specific amount of crosslinking agent and catalyst were then added and the mixture was mechanically bended for 1 min to disperse the ingredients. The mixture was cast on the mold (diameter 25 mm) and bubbles were removed under a vacuum atmosphere at 25°C for 30 min

Electrorheological Properties Measurement

A melt rheometer (Rheometric Scientific, ARES) was used to measure rheological properties. It was fitted with a custom-built copper parallel plates fixture (diameter of 25 mm). A DC voltage was applied with a DC power supply (Instek, GFG 8216A), which can deliver electric field strength to 2 kV/mm. A digital multimeter was used to monitor voltage input. In these experiments, the oscillatory shear strain was applied and the dynamic moduli (G' and G") were measured as functions of frequency and electric field strength. Strain sweep tests were first carried out to determine the suitable strain to measure G' and G" in the linear viscoelastic regime. For PDMS PEDOT/PSS blends (blends 5, ratio 10, 15 and 20 vol%) (PDMS_5%PEDOT/PSS, PDMS 10%PEDOT/PSS, PDMS 15%PEDOT/PSS and PDMS_20%PEDOT/PSS) the strain used was 3.0%. Then frequency sweep tests were carried out to measure G' and G" of each sample as functions of frequency. The deformation frequency was varied from 0.1 to 100 rad/s. Prior to each measurement, each PDMS and PDMS_PEDOT/PSS blends samples were presheared at a low frequency (0.039811 rad/s), and the electric field was applied for 10 minutes to ensure the formation of equilibrium polarization before each measurement was taken. Each measurement was carried out at the temperature of 27°C and repeated at least two or three times.

Results and Discussion

Characterization of PEDOT/PSS

The FT-IR spectrum of the synthesized PEDOT/PSS was recorded to identify characteristic absorption peaks. The three absorption peaks at 1588, 1487 and 1395 cm⁻¹ can be assigned to the thiophene ring [3]. The peak at 875 cm⁻¹ corresponds to the symmetric vibration of C-O-C in the cyclic ether structure [3]. These results confirm the existence of PEDOT. Furthermore, the absorption peaks 3000-2800 cm⁻¹ is a characteristic absorption peak of polystyrene [16] and its derivative functionalized with the sulfonate groups (SO₃⁻) is identified by the presence of the peaks at 1203 and 1102 cm⁻¹ [3]. From the FT-IR spectrum, we present evidences that the synthesized polymer was a combination of PEDOT and PSS [3, 16].

The TGA thermogram of synthesized PEDOT/PSS shows four degradation steps at 30-110°C, 160-380°C, 380-560°C and 560-900°C corresponding to the losses of water, the side chain degradation, the polymer backbone degradation of PSS and PEDOT chains.

The mean particle diameter of PEDOT/PSS was determined to be approximately 30 μ m with a standard deviation of 4 μ m. The particle microstructure was observed using scanning electron microscopy (SEM). These irregular shape particles appear to be moderately dispersed in PDMS matrix (Figure 1).

The specific conductivity of PEDOT/PSS was measured by a custom-built two point probe (Keithley, Model 6517A). The specific conductivity of PEDOT/PSS was 27.5 S/cm with a standard deviation of 0.6 S/cm.

Electrorheological Properties of Pure PDMS

Effect of Electric Field Strength

The effect of electric field strength on the rheological properties of pure PDMS was investigated in the range of electric field strength between 0-2 kV/mm. Figure 2 shows the storage modulus $G'(\omega)$ vs. frequency of pure PDMS at various electric field

strengths. The storage modulus of pure PDMS generally increases monotonically with increasing electric field strength (0.2-2 kV/mm). Figure 3 shows the storage modulus responses ($\Delta G'$) and the storage modulus sensitivity ($\Delta G'/G_o'$) of pure PDMS as a function of electric field strength at frequency 1.0 rad/s and strain 3.0%. The storage modulus response and the storage modulus sensitivity $\frac{\Delta G'(\omega)}{G'_o(\omega)}$ appear to increase with

electric field as $\Delta G' \propto E^{\alpha}$, $\alpha = 0.88$ when E< 1 kV/mm [11]. The storage modulus response becomes saturated at higher electric field strength (> 1 kV/mm). The highest storage modulus responses value is 2964 Pa at electric field strength of 2 kV/mm. The corresponding storage modulus sensitivity value of the pure PDMS at electric field strength of 2 kV/mm is 29.2%.

As an electric field is applied, electrical dipole moments are generated and the electrostatic interaction between the polymer chains are induced leading to an intermolecular interaction acting like an electrical network. In addition, a voltage differential between the electrodes is known to create electromagnetic forces that act to pull the electrodes together [2, 17]. This attraction causes a compressive force to develop throughout the area of the electrodes and compresses the dielectric elastomer in the direction parallel to the electric field. The resulting effective (squeeze) pressure can be defined as [2]:

$$\mathbf{p} = \varepsilon_0 \varepsilon_r \mathbf{E}^2 \tag{10}$$

where ε_0 and ε_r are the permittivity of free space and the relative permittivity of polymer, respectively. E is the applied electric field. The response of the polymer is functionally similar to those of electrostrictive polymers, in which the response is directly proportional to the square of the applied electric field [1, 17, 18]. The intermolecular interaction and the electrostatic interaction result in the loss of chain free movements, the higher chain rigidity, and as a result the higher G'(ω). Yang *et al.* (2003) [18] reported a similar finding on the effect of increasing effective (squeeze) pressure; the radial and circumferential stresses changed from a tensile state to a compressive state at a critical effective pressure.

Electrorheological Properties of PDMS PEDOT/PSS

Effect of PEDOT/PSS Composition in the Absence of Electric Field

The effect of PEDOT/PSS particle concentration on the electrorheological properties of polymer blends (PDMS_PEDOT/PSS) was investigated next. PDMS with a crosslinking ratio of 15 vol% was chosen and blended with PEDOT/PSS particles to form PDMS_PEDOT/PSS blends. Figure 4 shows the comparisons of the storage modulus (G') of pure PDMS and PDMS_PEDOT/PSS blends at various particle concentrations vs. frequency, at strain 3.0%, and at electric field strengths of 0 and 2 kV/mm. PEDOT/PSS particle concentrations studied were 5, 10, 15, and 20 vol% (PDMS_5%PEDOT/PSS, PDMS_10%PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS). G' increases with PEDOT/PSS particle concentrations and electric field strength. The storage modulus G'(ω) of each polymer blends system are higher than those of the pure PDMS at any electric field strength. Close inspection of our data suggests that PEDOT/PSS particles in the polymer blends can act as fillers in the matrix; they can store or absorb the forces/stresses within the matrix [1]. A polymer blends system with a higher particle concentrations will generate a higher internal stress response than that of pure PDMS, and the higher storage modulus G'(ω).

Concentration effect has been reported by others researchers. Shiga (1997) [19] found that the shear modulus of silicone gel containing PMACo particles increased with increasing volume fraction of dispersed particles embedded in the gel. Krause *et al.* (2001) [1] reported that the compression modulus, in the absence of an electric field, increased by a factor of 2 when the PANI particle concentration was increased from 0 to 20 wt%. This was expected because the PANI particles should act as filler particles.

Effect of PEDOT/PSS Composition under Electric Field

The effect of electric field strength on the rheological properties of PDMS_PEDOT/PSS blends at various PEDOT/PSS particle concentrations was investigated in the range between 0-2 kV/mm. Figures 4 shows the comparisons of the

38

storage modulus (G') of pure PDMS and PDMS_PEDOT/PSS blends at various particle concentrations vs. frequency, at strain 3.0%, and at electric field strengths of 0 and 2 kV/mm. The storage modulus (G') of each polymer blend system generally increases with increasing electric field strength. Figure 5 shows the comparison of the storage modulus (G') of pure PDMS and PDMS_PEDOT/PSS blends at various electric field strengths (0, 1 and 2 kV/mm) vs. particle concentrations ($\Phi = 0, 5, 10, 15, \text{ and } 20\text{vol }\%$), at frequency 1.0 rad/s and strain 3.0%. The storage modulus increases linearly with particle volume frac*ion. The storage modulus values, G'(ω), are 12294, 36211, 45132, 61578 and 81097 Pa for PDMS, PDMS_5%PEDOT/PSS, PDMS_10%PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS, respectively, at electric field strength of 1 kV/mm. At the higher electric field strength (2 kV/mm), the storage modulus (G') values are 13130, 36903, 48487, 64710 and 85488 Pa for PDMS, PDMS_5%PEDOT/PSS, PDMS_15%PEDOT/PSS, PDMS_10%PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_15%PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_10% PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_10% PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_10% PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_10% PEDOT/PSS and PDMS_20%PEDOT/PSS, PDMS_10% PEDOT/PSS, PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS, respectively. Thus the storage modulus (G') varies linearly with the particle volume fraction up to 20 vol%, with or without electric field applied.

Our results suggest that at very low concentrations (PDMS_5%PEDOT/PSS); the number of particles is too small and the distances between particles are too large to create a significant particle interaction [20]. At higher concentrations (PDMS_15%PEDOT/PSS and PDMS_20%PEDOT/PSS) and when the distances between particles become smaller, we encounter stronger interparticle interactions [19, 20]. However, the electric field strength of 1 kV/mm is presumably not strong enough to induce effective polarization in all particles at high particle concentrations due to the steric hindrance effect [20]. At the higher electric field strength of 2 kV/mm, it is sufficient to induce strong polarization in particles at high particle concentrations, and consequently the higher in the storage modulus.

Liu et al. (2001) [20] reported a similar effect for silicone/silica elastomer. They found that the enhancement of shear modulus was negligible below 8.0vol%, but increased dramatically above this threshold concentration. At volume fraction above

55vol%, the shear modulus decreased because the interparticle force decreased with the steric hindrance effect.

Figure 6 shows the storage modulus response (ΔG^{2}) of pure PDMS and PDMS_PEDOT/PSS blends at various particle concentrations vs. electric field strength at frequency 1.0 rad/s, strain 3.0%, and at 27°C. The increase in the storage modulus response with electric field is linearly within the range of 0.002 to 1 kV/mm. According to the power law equation [11], the storage modulus response increases linearly with the electric field strength 0.002-1 kV/mm:

PDMS_0%PEDOT/PSS : $\Delta G' \propto E^{\alpha}$, $\alpha = 0.88$

PDMS_15%PEDOT/PSS : $\Delta G' \, \varpropto \, E^{\alpha}$, α = 0.70

PDMS_20%PEDOT/PSS : $\Delta G' \, \varpropto \, E^{\alpha}$, α = 0.10 ;when E< 1 kV/mm

For all particle concentrations investigated ($\Phi = 0$, 15 and 20 vol%) the increase in storage modulus response with the electric field is nonlinear within the range of 1-2 kV/mm. The storage modulus response becomes saturated at higher electric field strength (> 1 kV/mm).

Our results suggest that in the absence of the electric field, the PEDOT/PSS particles are randomly dispersed within the PDMS matrix and there is no particleparticle interaction. When electrical field is applied, both PDMS and PEDOT/PSS particles become polarized and induced dipole moments are generated, leading to intermolecular interactions. These intermolecular interactions result in the loss of chain free movements and in higher chain rigidity, as indicated by a higher G'(ω). Thus, the electric field can effectively enhance the elastic modulus of our conductive polymer-PDMS blends, consistent with the results of other polymer blends [17, 18, 20].

Lui et al. (2001) [20] reported that for the silicone/silica elastomers, for the random structure, the modulus exhibited a nearly quadratic dependence on field. For the aligned structure; the shear modulus increased quadratically with electric field at low values but saturated at high values. Shiga (1997) [19] reported that, for the PMACo particles in silicone gel, the increase in the elastic modulus induced by an electric field

was 4 kPa with the particle volume fraction of 0.3, and the applied electric field of 2 kV/mm.

Time Dependence of the Electrorheological Response

Finally, we investigate the temporal characteristics of the crosslinked PDMS and PDMS_PEDOT/PSS blends at particle concentration of 10 vol%, at various electric field strengths. The temporal characteristic of each sample was recorded in the linear viscoelastic regime at a strain of 3.0 %, and frequency of 1.0 rad/s.

Figure 7(a) shows the temporal response of pure PDMS at electric field strengths of 1 and 2 kV/mm, respectively. The pure PDMS is a nearly reversible system at both of electric field strengths. Our result here suggests that there are some irreversible interactions between PDMS molecules, perhaps due to the interaction between the residue polarized molecules [15].

Figure 7(b) shows the change in G' of PDMS_10%PEDOT/PSS system on electric field strengths of 1 and 2 kV/mm during a time sweep test, in which an electric field is turned on and off alternately. At the electric field of 1 kV/mm, G' immediately increases and rapidly reaches a steady-state value. Then, with the electric field off, G' decreases and nearly recovers its original value. Thus PDMS_10%PEDOT/PSS is a nearly reversible system at 1 kV/mm. At the electric field of 2 kV/mm, the response of G' can be divided into two regimes: the initial regime in which G' rapidly overshoots to a large value on the first cycle followed by a irreversible with electric field off; and the steady state regime in which G' subsequently exhibites a reversible cyclic response. The time required for G' to reach the steady-state value on applying the field is called the induction time, τ_{ind} . The τ_{ind} decreases with increasing electric field strength; they are 200 and 63 sec at electric field strengths equal to 1 and 2 kV/mm, respectively. 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} . It decreases with increasing electric field strength. The recovery times are 142 and 91 sec at electric field strengths equal to 1 and 2 kV/mm, respectively. The dependence of τ_{rec} on the electric field strength suggests

that the strains induced are quite large such that the relaxations can be essentially distinguished and observed.

Conclusions

In this study, electrorheological properties of pure PDMS and PDMS_ PEDOT/PSS blends were investigated by examining the effect of PEDOT/PSS particle concentration on the storage modulus, G', under the oscillatory shear mode at electric field strength various from 0 to 2 kV/mm. In pure PDMS systems, the storage modulus (G') increases with increasing electric field strength.

PEDOT/PSS particles were synthesized via the chemical oxidative polymerization and blended with PDMS gel. For the electrorheological properties of PDMS_PEDOT/PSS blends, with the PEDOT/PSS particle concentrations of 5, 10, 15, and 20vol%, the storage modulus, G' of each polymer blends, are generally higher than those of pure PDMS due to PEDOT/PSS particles within the matrix acting as fillers; they can store or absorb the forces/stresses within the matrix. The storage modulus responses increase with electric field linearly within the range of 0.002-1 kV/mm. This can be attributed to the fact that as PDMS and PEDOT/PSS particles become polarized and induced dipole moments are generated, leading to intermolecular interactions along the direction of electric field. The storage modulus sensitivity, $\frac{\Delta G'}{G'_0}$, attained a maximum G' sensitivity values of 8%, 4%, 10%, and 9%, at particle concentrations of 5, 10, 15, and 20vol% at the electric field strength of 2 kV/mm, respectively.

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References

- [1] Krause, S.; and Bohon, K.; Macromolecules. 2001, 34, 7179.
- [2] Kornbluh, R.; Perlrine, R.; Pei, Q.; Oh, S.; and Joseph, J.; Proc. of The first World Congress on Biomimetics. 2002.
- [3] Yinghong, X.; Xinyan, C.; Martin, D.C.; Journal of Electroanalytical Chemistry. 2004, 573, 43.
- [4] Küçükyavuz, S.; Sankir, M.; and Küçükyavuz, Z.; Synthetic Metals. 2002, 128, 247.
- [5] Shen, Z.; Xue, H.; and Li, Y.; Synthetic Metals. 2001, 124, 345.
- [6] Faez, R.; Schuster, R-H.; and De Paoli, M-A.; *European Polymer_Journal*. 2002, 38, 2459.
- [7] Zrínyi, M.; Fehér, J.; and Filipcsei, G.; Macromolecules. 2000, 33, 5751.
- [8] Kim, J.Y.; Jung, J.H.; Lee, D.E.; and Joo, J.; Synthetic Metals. 2002, 126, 311.
- [9] Ouyang, J.; Chu, C.; Chen, F.; Xu, Q.; and Yang, Y; Advanced Functional Materials. 2005, 15, 203.
- [10] Ouyang, J.; Xu, Q.; Chu, C.; Yang, Y.; Polymer. 2004, 45, 8443.
- [11] Parthasarathy, M.; Klingenberg, D.J.; *Materials Science and Engineering*. 1996, 17, 57.
- [12] Davis, L.C.; Appl. Phys. Lett, 1992, 60, 319.
- [13] Dukhin, S.S.; J. Surf. Coll. Sci., 1970, 3, 83.
- [14] Foule, J.N.; Atten, P.; and Felici, N.; J. Electrostat., 1994, 33, 103.
- [15] Chotpattananont, D.; Sirivat, A.; and Jamieson, A.M.; Colloid Polym Sci. 2004, 282, 357.
- [16] Christian, G.D.; and O'Reilly, J.E.; Instrumental Analysis 2nd Edition. Allyn and Bacon, Inc, USA. 1986.
- [17] Perline, R.E.; Kornbluh, R.D.; and Joseph, J.P.; Sensors and Actuators, Physical. 1998, A64, 77.
- [18] Yang, E.E.; Frecker, M.; Mockensturm, E.; Proc. of ASME International Mechanical Engineering, 2003.

[19] Shiga, T.; Advances in Polymer Science, Springer-Verlag Berlin Heidelberg, 1997, 134, 133.

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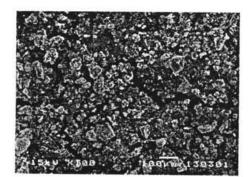
[20] Liu, B.; and Shaw, T.M.; Journal of Rheology. 2001, 45(3), 641.

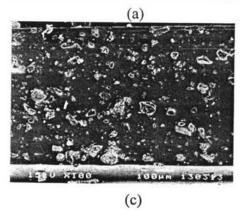
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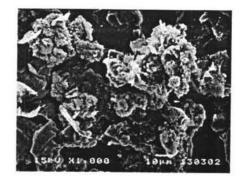
| Samples | Electric field (kV/mm) | Induction time (τ _{ind})(s) | Recovery time (τ_{rec}) (s) | $\Delta G'_{\text{ind}}$ | ∆G' _{rec} |
|-------------------|---------------------------|--|----------------------------------|--------------------------|--------------------|
| PDMS | 1 | 107 | 76 | 30 | 22 |
| | 2 | 114 | 75 | 232 | 98 |
| PDMS_10%PEDOT/PSS | 1 | 200 | 142 | 3760 | 3720 |
| | 2 | 63 | 91 | 4130 | 3947 |

 Table 1 Induction time and recovery time of pure PDMS systems and

 PDMS_10%PEDOT/PSS blends







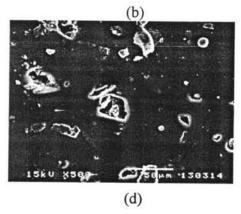


Figure 1 The morphology of PEDOT/PSS powder at magnifications of: (a) 100; and (b) 1000 and the morphology of PDMS_10%PEDOT/PSS blends at magnifications of: (a) 100; and (b) 500.

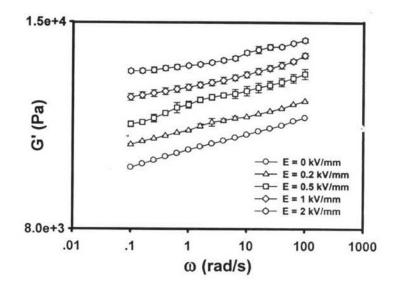


Figure 2 Storage modulus of pure PDMS at various electric field strengths vs. frequency, strain 3.0%, 27 °C, gap 0.820 mm.

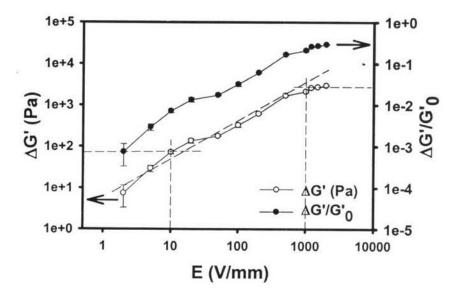


Figure 3 The storage modulus response ($\Delta G'$) and the storage modulus sensitivity ($\Delta G'/G_o'$) of pure PDMS vs. electric field strength at frequency 1.0 rad/s, strain 3.0%, 27°C, gap 0.820 mm when $G'_0 = 10167$ Pa.

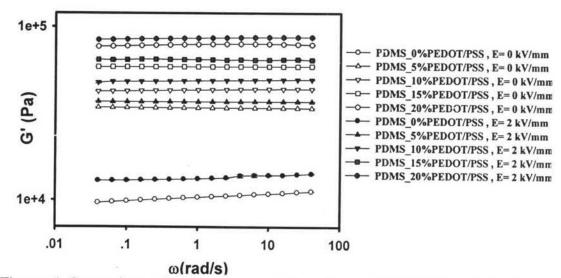


Figure 4 Comparison of the storage modulus of pure PDMS ($\Phi = 0$ %vol.) and PDMS_PEDOT/PSS blends at various particle concentrations ($\Phi = 5$, 10, 15, and 20 %vol.) vs. frequency, strain 3.0%, 27°C at electric field strengths of 0 and 2 kV/mm.

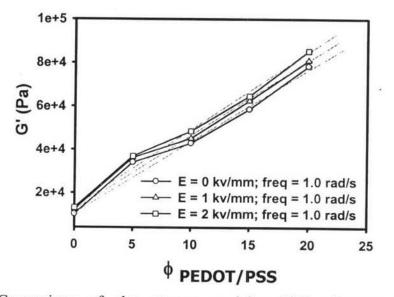


Figure 5 Comparison of the storage modulus (G') of pure PDMS and PDMS_PEDOT/PSS blends at various electric field strengths (0, 1 and 2 kV/mm) vs. particle concentrations ($\Phi = 0, 5, 10, 15$, and 20vol %), frequency 1.0 rad/s, strain 3.0% and at 27°C.

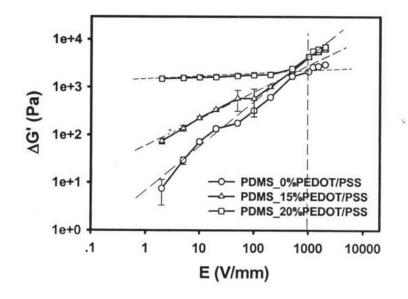
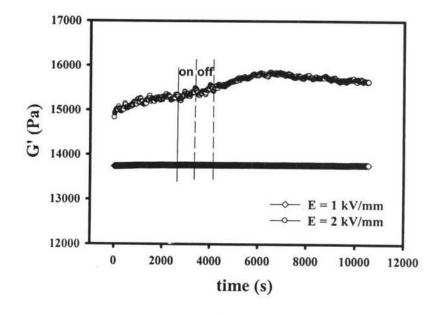
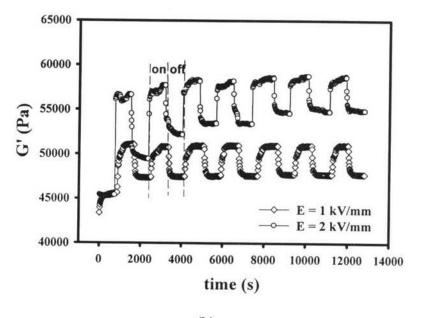


Figure 6 The storage modulus response ($\Delta G'$) of pure PDMS and PDMS_PEDOT/PSS blends at various particle concentrations vs. electric field strength at frequency 1.0 rad/s, strain 3.0% and at 27°C.



(a)



(b)

Figure 7 Temporal response of the storage modulus (G') at various electric field strengths (1 and 2 kV/mm) vs. time (s), frequency 1.0 rad/s, strain 3.0% and at 27°C of; (a) pure PDMS; (b) PDMS_10%PEDOT/PSS blends.