

**CHAPTER V**  
**ELECTRORHEOLOGICAL PROPERTIES OF PDMS\_PEDOT/PSS/EG**  
**BLENDS**

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**Abstract**

Electrorheological properties of PDMS\_PEDOT/PSS/EG blends were investigated for electroactive actuator applications. Experiments were carried under the oscillatory shear mode and with applied electric field strength varying from 0 to 2 kV/mm. The storage modulus,  $G'$ , of PDMS\_PEDOT/PSS/EG depended on the electric field strength; the storage modulus ( $G'$ ) increased with increasing electric field strength. PEDOT/PSS particles were synthesized via the chemical oxidative polymerization and mixed with EG to improve the electrical conductivity. For the electrorheological properties of PDMS\_PEDOT/PSS/EG blends, with the PEDOT/PSS/EG particle concentrations of 5, 10, 15, and 20 vol%, the storage modulus  $G'$  of polymer blends, were generally higher than those of pure PDMS. The storage modulus responses increased with electric field linearly within the range of 0.002-1 kV/mm. This can be attributed to the PDMS and PEDOT/PSS/EG particles which became polarized, and induced dipole moments were generated, leading to intermolecular interactions along the direction of electric field. The storage modulus sensitivity,  $\frac{\Delta G'}{G'_0}$ , attained maximum  $G'$  sensitivity values of 8.7%, 9.0%, and 15.2%, at particle concentrations of 5, 10, and 15 vol% at the electric field strength of 2 kV/mm, respectively.

**Keywords:** Electrorheological properties, PEDOT/PSS, PDMS, Dynamic moduli, Second doping, EG

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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  $-100^{\circ}\text{C}$  to over  $200^{\circ}\text{C}$  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 polyaniline-polyisoprene composite for biosensor application [5], a polyaniline-EPDM composite [6], and  $\text{TiO}_2$  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(styrene 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].

PEDOT/PSS has emerged as a promising conductive polymer for various applications. 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]. However, PEDOT/PSS also suffers from low conductivity: commercially available PEDOT/PSS [10] has a conductivity of less than 1 S/cm, which is lower than that of some other conducting polymers by one or two orders of magnitude. Recently, it has been observed that the conductivity of PEDOT/PSS films can be enhanced by more than an order of magnitude by the addition of polyalcohols (alcohols with more than two OH groups on each molecule) or high-dielectric solvents, such as dimethyl sulfoxide (DMSO), to a PEDOT/PSS solution [11, 12, 13]. The mechanism for this observed conductivity enhancement has been debated.

In our work, we are interested in increasing the electrical conductivity of PEDOT/PSS by a secondary doping with ethylene glycol (EG). The synthesized PEDOT/PSS/EG was developed as a substitute for artificial muscles. We focus particularly on the effects of PEDOT/PSS/EG particle concentration within PDMS gel under various electric field strengths on the storage modulus ( $G'$ ).

### **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 the Maxwell-Wagner Polarization [14]. All ER particles possess some level of conductivity. Davis [15, 16] 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 [14] 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 ( $\epsilon_k^*$ ) of the dispersed and continuous phases can be written as:

$$\epsilon_k^* = \epsilon_k - j(\sigma_k / \epsilon_0 \omega_e) \quad (1)$$

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 [14],  $\nabla^2 \psi^* = 0$ , subject to the boundary conditions at the interface:

$$\psi^{*i} = \psi^{*0} \quad (2)$$

$$\epsilon_p^* \nabla \psi^{*i} \cdot \mathbf{n} = \epsilon_m^* \nabla \psi^{*0} \cdot \mathbf{n} \quad (3)$$

The solution for the complex potential is shown below:

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

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

where  $\beta^* = \frac{(\epsilon_p^* - \epsilon_m^*)}{\epsilon_p^* + 2\epsilon_m^*}$ .

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

$$F_{ij}(R_{ij}, \theta_{ij}) = \frac{3}{16} \pi \epsilon_0 \epsilon_m \sigma^2 \beta_{eff}^2(\omega_e) E_{rms}^2 \left( \frac{\sigma}{R_{ij}} \right)^4 \left\{ (3 \cos^2 \theta_{ij} - 1) e_r + (\sin 2\theta_{ij}) e_\theta \right\} \quad (6)$$

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

$$\beta_{eff}^2 = \beta_d^2 \frac{\left[ (\omega_e t_{mw})^2 + \beta_c / \beta_d \right]^2 + (\omega_e t_{mw})^2 \left[ 1 - \beta_c / \beta_d \right]^2}{\left[ 1 + (\omega_e t_{mw})^2 \right]^2} \quad (7)$$

where  $\beta_d = \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}$ ,  $\beta_c = \frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m}$ , and  $t_{mw} = \epsilon_0 \frac{\epsilon_p + 2\epsilon_m}{\sigma_p + 2\sigma_m}$ .

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  $\beta_{eff}$ , 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 [14]:

$$\lim_{\omega_e t_{mw} \rightarrow \infty} \beta_{eff}^2(\omega_e) = \beta_d^2 \quad (8)$$

While in the DC limit:

$$\lim_{\omega_e t_{mw} \rightarrow 0} \beta_{eff}^2(\omega_e) = \beta_c^2 \quad (9)$$

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

When the particle conductivity is much larger than the matrix conductivity ( $\sigma_p \gg \sigma_m$ ), the field strength in the region between two closely spaced particles will be much larger than the nominal field strength. Under large electric fields, the matrix conductivity increases with field strength. Foule *et al.* [17] have investigated the role of non-linear conduction in ER, and developed approximate expressions for the electrostatic interaction between conducting particles when non-linear conduction controls the behavior.

Consider a pair of conducting spheres with conductivity  $\sigma_p \gg \sigma_m$ , aligned with the electric field (Figure 1). In the absence of nonlinear effects, each sphere surface would be at constant potential. However, in the region near the point of contact between the spheres, the field in the matrix essentially saturates due to the

enhanced conductivity. With the force per unit area given by  $\varepsilon_0 \varepsilon_m E_{loc}^2 / 2$ , the electrostatic interaction between the spheres is approximately:

$$F = 4\pi a^2 \varepsilon_0 \varepsilon_m E_0^2 (a/\delta)^2 \quad (10)$$

where  $\delta$  is the radius of the inner region, which determined by requiring that the conductance through the sphere equals the conductance through the outer matrix region in order to minimize energy dissipation

For small applied electric fields, in which case the matrix conductivity in the outer region remains constant,  $\delta$  is given by:

$$(a/\delta) \ln(a/\delta) = \Gamma/\pi \quad (11)$$

independent of field strength, where  $\Gamma = \sigma_p / \sigma_m \gg 1$ . Thus the force of attraction is:

$$F \approx 4\pi a^2 \sigma_0 \sigma_m K_\Gamma^2 \Gamma^2 E_0^2 \quad (12)$$

where  $K_\Gamma = [\pi \ln(a/\delta)]^{-1}$ , independent of  $E_0$ . The force is still proportional to  $E_0^2$  when non-linear conduction is limited to the inner region [14].

For large applied electric fields, [17] the fluid conductivity in the outer region will be enhanced. Onsager's theory of the field-enhanced solute dissociation is used to arrive at an approximate expression for the field-dependent fluid conductivity:

$$\sigma_m(E) = \sigma_m(O) \left\{ (1-A') + A' \exp \left[ \left( \frac{E}{E'} \right)^{1/2} \right] \right\} \quad (13)$$

where  $A' = 0.1$  and  $E' = 0.335$  kV/mm for non-polar liquids with  $\varepsilon_m = 2.2$ .  $\delta$  is again determined by balancing the conductance in the solid with that in the outer region, and the force of attraction becomes:

$$F \approx 2\pi a^2 \varepsilon_0 \varepsilon_m E' E_0 \left\{ \ln \left[ \left( \frac{10\Gamma}{\pi} \right) \left( \frac{2E_0}{E'} \right)^{1/2} \right] \right\}^2 \quad (14)$$

The force is now linear in  $E_0$  to a first approximation, and display a very weak dependence on  $\Gamma$ . A similar formula can be obtained by a simpler model:

$$F \approx 2\pi a^2 \varepsilon_0 \varepsilon_m E' E_m \quad (15)$$

where  $E_m \approx 30-40$  kV/mm is the maximum local field strength.

Experimental measurements of the force between two half spheres agreed well with these predictions, with the force varying as  $E_0^2$  at low fields, and as  $E_0^1$  at large fields, over a wide range in  $\Gamma$  (3-1500).

A similar analysis for perfectly insulating spheres with a surface conductivity leads to similar results. This study suggests that leakage current and heating are unescapable consequences of ER activity for DC or low frequency AC fields, and that the two spheres interaction is not very sensitive to the conduction mechanism [14, 17].

## **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,  $\text{Na}_2\text{S}_2\text{O}_8$  (AR grade, Aldrich), was used as the oxidant. Distill water and ethylene glycol, EG (AR grade, Aldrich) were used as solvents. 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 (10.65 g, 75 mmol), 439 g of 5.99 wt% PSS solution and  $\text{Na}_2\text{S}_2\text{O}_8$  (21.4 g, 104 mmol) in water (2062 ml). After initial stirring at room temperature for 10 minutes,  $\text{Fe}_2(\text{SO}_4)_3$  (187 mg) 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.

### Secondary Doping of PEDOT/PSS with Ethylene Glycol (EG)

The synthesized PEDOT/PSS solution and ethylene glycol (EG) were mixed at the volume ratios of 5:1, 5:2, 5:3, 5:4 and 5:5 (PEDOT/PSS:EG). The mixed solution of PEDOT/PSS and EG was filtered and stirred continuously for 24 hrs at room temperature. After this period, the PEDOT/PSS/EG particles were prepared by

casting the solution on glass substrates. The samples were dried in an oven at 100°C for 24 hrs.

#### Characterization Method

Fourier-transform infrared spectrometer (FT-IR), PEDOT/PSS and PEDOT/PSS/EG were 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  $\pm 4 \text{ cm}^{-1}$ , covering a wavenumber range of 4000-400  $\text{cm}^{-1}$  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 and PEDOT/PSS/EG were 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<sub>2</sub> atmosphere [18].

Scanning electron micrographs were taken with a JEOL, model JSM-5200 scanning electron microscope to determine the morphology of PEDOT/PSS and PEDOT/PSS/EG in powder forms and the polymer blends PDMS\_PEDOT/PSS and PDMS\_PEDOT/PSS/EG at various particle concentrations. We used an acceleration voltage of 15 kV with magnifications of 100, 500, and 1,000 times.

The electrical conductivity of PEDOT/PSS and PEDOT/PSS/EG were measured by a custom-built two-point probe coupled with an electrometer (Keithley, Model 6517A). The specific conductivity  $\sigma$  (S/cm) value of the pellets was obtained by measuring the bulk pellet resistance  $R$  ( $\Omega$ ). The relation  $\sigma = (1/Rt)(1/K) = (I/Vt)(1/K)$  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 PDMS\_PEDOT/PSS and PDMS\_PEDOT/PSS/EG Blends

The PEDOT/PSS and PEDOT/PSS/EG powder were sieved with a mesh particle size of 38  $\mu\text{m}$  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 PEDOT/PSS particles 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 blended 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. The PDMS\_PEDOT/PSS/EG blends were prepared using the same procedure for preparing PDMS\_PEDOT/PSS.

#### 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/EG blends (blends ratio 5, 10, 15 and 20 %vol) (PDMS\_5%PEDOT/PSS/EG, PDMS\_10%PEDOT/PSS/EG, PDMS\_15%PEDOT/PSS/EG and PDMS\_20%PEDOT/PSS/EG) the strain used was 3.0%. Then frequency sweep tests were carried out to measure  $G'$  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\_PEDOT/PSS/EG 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 and PEDOT/PSS/EG

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  $\text{cm}^{-1}$  can be assigned to the thiophene ring [3]. The peak at 875  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  is a characteristic absorption peak of polystyrene [19], and its derivative functionalized with the sulfonate groups ( $\text{SO}_3^-$ ) is identified by the presence of the peaks at 1203 and 1102  $\text{cm}^{-1}$  [3]. From the FT-IR spectrum, we have shown evidences that the synthesized polymer was a combination of PEDOT and PSS [3, 19]. After second doped with EG, PEDOT/PSS/EG, the characteristic peaks of the polyalcohol EG appeared on FT-IR spectra. There appears a broad peak of hydroxy functional group occurring from 3600 to 3000  $\text{cm}^{-1}$ .

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 degradations of PSS and PEDOT chains. After secondary doping with EG; PEDOT/PSS/EG, we observed five transitions in PEDOT/PSS/EG, 30-140°C, 180-360°C, 360-450°C, 450-600°C and 600-900°C; they can be referred to as the losses of water, the losses of the residue solvent EG, the side chain degradation, the polymer backbone degradation of PSS and PEDOT chains. From the TGA results, we verified the existence of the residual EG in the PEDOT/PSS particles.

From XRD patterns of PEDOT/PSS and PEDOT/PSS/EG, there is no characteristic peak that can be observed. We observed that all samples are amorphous with short-range structural orders. This conformational change of the

PEDOT chains in the film may make the backbones pack better, but it does not significantly increase the degree of crystallization of the PEDOT/PSS/EG which can be detected by X-ray diffraction [9]. This is different from the secondary doping of polyaniline [20]. The solvent can affect the conformation of polyaniline chains in solution, so that highly crystalline polyaniline film can be formed when an appropriate solvent is selected.

The mean particle diameter of PEDOT/PSS and PEDOT/PSS/EG was determined to be approximately 30 $\mu\text{m}$  (SD = 4) and 31 $\mu\text{m}$  (SD = 4), respectively. The particle microstructure was observed using scanning electron microscopy (SEM). These irregular shape particles appear to be moderately dispersed in PDMS matrix (Figure 3).

The specific conductivity of PEDOT/PSS was measured by a custom-built two point probe (Keithley, Model 6517A). From Table 1, the specific conductivity of PDMS was  $1.9 \times 10^{-8}$  S/cm with a standard deviation of  $2.8 \times 10^{-9}$  S/cm and the specific conductivity of PEDOT/PSS was 27.5 S/cm with a standard deviation of 0.6 S/cm. The specific conductivity of the secondary doping PEDOT/PSS/EG at volume ratios (PEDOT/PSS:EG) 5:1, 5:2, 5:3, 5:4, and 5:5 were 563.5 (SD = 7.6), 586.5 (SD = 7.7), 556.1 (SD = 14.2), 621.6 (SD = 31.8) and 585.2 (SD = 6.4) S/cm, respectively. We observe the increase in the conductivity of PEDOT/PSS after treated with EG more than an order of magnitude. The conductivity enhancement is presumably due to the increase of the charge-carrier mobility resulting from the conformational change of the PEDOT chain [9]. The interaction between the additive and the PEDOT chains may be the driving force for the conformational change. One common point for EG is that it has two polar groups in a molecule, and they can form hydrogen bond to sulfonate or sulfonic acid groups of PEDOT/PSS. One polar group of the additive may form a hydrogen bonds to the sulfonate or sulfonic acid group of PEDOT/PSS, while another polar group may be very close to the PEDOT chain which leads to an interaction between the dipole of this polar group and the dipole moment or the positive charge on the PEDOT chains [9]. This dipole-dipole or dipole-charge interaction may be the driving force for the conformational change of the PEDOT chains. Two kinds of resonant structures, the benzoid and quinoid structures, have been proposed for PEDOT (Figure 2) [21, 22]. There are two

conjugated  $\pi$ -electrons on the  $C_{\alpha}$ - $C_{\beta}$  bond in the benzoid structure, and no conjugated  $\pi$ -electrons on the  $C_{\alpha}$ - $C_{\beta}$  bond in the quinoid structure. This suggests a transformation of the resonant structure of the PEDOT chain after the conductivity enhancement of the PEDOT/PSS by second doping [9, 10].

The benzoid structure may transform into the quinoid structure after the treatment, so that the quinoid structure becomes dominant in the high-conductivity PEDOT/PSS/EG particles. The transformation of the chemical structure of PEDOT chains is presumably due to the conformational change of the PEDOT chains in the PEDOT/PSS/EG. Coil and linear or expanded-coil conformations have been proposed in PEDOT [20]. The favored structure is the quinoid structure because of the high charge-carrier mobility. Therefore, resonant structure transformation after the treatment indicates the conformational transformation of PEDOT chains from the coil into linear conformation [9, 20, 21, 22].

#### Electrorheological Properties of PDMS\_PEDOT/PSS/EG

##### *Effect of PEDOT/PSS/EG Composition in the Absence of Electric Field*

The effect of PEDOT/PSS/EG particle concentration on the electrorheological properties of polymer blends (PDMS\_PEDOT/PSS/EG) was investigated next. PDMS with crosslinking ratio of 15 vol% was chosen and blended with PEDOT/PSS/EG particles; PEDOT/PSS: EG = 5:1; to form PDMS\_PEDOT/PSS/EG at volume ratio. Figure 4 shows the comparisons of the storage modulus ( $G'$ ) vs. frequency, between polymer blends of various concentrations, at electric field strengths of 0 and 2 kV/mm. PEDOT/PSS/EG particle concentrations studied were 5, 10, 15, and 20 vol% (PDMS\_5%PEDOT/PSS/EG, PDMS\_10%PEDOT/PSS/EG, PDMS\_15%PEDOT/PSS/EG and PDMS\_20%PEDOT/PSS/EG).  $G'$  increase with PEDOT/PSS/EG particle concentrations and electric field strength. The data suggests that PEDOT/PSS/EG 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  $G'(\omega)$ .

Concentration effect has been reported by others researchers. Shiga (1997) [23] 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/EG Composition under Electric Field*

The effect of electric field strength on the rheological properties of PDMS\_PEDOT/PSS/EG blends at various PEDOT/PSS/EG particle concentrations was investigated in the range between 0-2 kV/mm. Figure 4 shows the comparison of the storage modulus ( $G'$ ) between the blends of various concentrations at electric field strengths of 0 and 2 kV/mm. The storage modulus ( $G'$ ) of each polymer blends system generally increase with increasing electric field strength.

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, 24]. 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]:

$$p = \epsilon_0 \epsilon_r E^2 \quad (16)$$

where  $\epsilon_0$  and  $\epsilon_r$  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, 24, 25]. 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  $G'(\omega)$ . Yang *et al.* (2003) [25] 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.

Figure 5 the storage modulus response ( $\Delta G'$ ) of PDMS\_PEDOT/PSS/EG blends at various particle concentrations ( $\Phi = 0, 5, 10$  and  $15\text{vol}\%$ .) vs. electric field strength at frequency  $1 \text{ rad/s}$ , strain  $3.0\%$  and at  $27^\circ\text{C}$ . The increase in  $\Delta G'$  with electric field is linear within the range of  $0.002$  to  $1 \text{ kV/mm}$ . The storage modulus response values,  $\Delta G'(\omega)$ , of these systems at electric field strength of  $2 \text{ kV/mm}$  are  $2963, 3674, 4228$  and  $8896 \text{ Pa}$  for PDMS\_0%PEDOT/PSS/EG, PDMS\_5%PEDOT/PSS/EG, PDMS\_10%PEDOT/PSS/EG and PDMS\_15%PEDOT/PSS/EG, respectively. The corresponding storage modulus sensitivity values, defined as  $\frac{\Delta G'(\omega)}{G'_0(\omega)}$ , of these polymer blends systems (PDMS\_5%PEDOT/PSS/EG, PDMS\_10%PEDOT/PSS/EG and PDMS\_15% PEDOT/PSS/EG) at electric field strength of  $2 \text{ kV/mm}$  are  $8.7\%, 9.0\%$  and  $15.2\%$ , respectively.

Our results suggest that in the absence of the electric field, the PEDOT/PSS/EG particles were randomly dispersed within the PDMS matrix and there was no particle-particle interaction. As the electrical field was applied, both PDMS and PEDOT/PSS/EG particles became polarized and induced dipole moments were generated, leading to intermolecular interactions. These intermolecular interactions resulted in the loss of chain free movements and in higher chain rigidity, as indicated by a higher  $G'(\omega)$ . Thus, the electric field can effectively enhance the elastic modulus of our conductive polymer-PDMS blends, consistent with the results of other polymer blends [23, 24, 25].

Lui *et al.* (2001) [26] 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) [23] reported that, for the PMACo particles in silicone gel, the increase in the elastic modulus induced by an electric field was  $4 \text{ kPa}$  with the particle volume fraction of  $0.3$ , and the applied electric field of  $2 \text{ kV/mm}$ .

Figure 6 shows the comparison of the storage modulus ( $G'$ ) of PDMS\_PEDOT/PSS/EG blends at various electric field strengths (0, 1 and 2 kV/mm) vs. particle concentrations ( $\Phi = 0, 5, 10,$  and  $15$  vol%.) at frequency 1 rad/s, strain 3.0% and  $27^\circ\text{C}$ . As the particle volume fraction increases, the storage modulus appears to increase linearly with particle volume fraction. The storage modulus values,  $G'(\omega)$  at electric field strength of 0 kV/mm, are 10167, 37835, 44130 and 54734 Pa for PDMS\_0%PEDOT/PSS/EG, PDMS\_5%PEDOT/PSS/EG, PDMS\_10%PEDOT/PSS /EG and PDMS\_15%PEDOT/PSS/EG, respectively. At electric field strength of 1 kV/mm, the storage modulus values,  $G'(\omega)$  are 12294, 39790, 46676 and 59308 Pa for PDMS\_0%PEDOT/PSS/EG, PDMS\_5%PEDOT/PSS/EG, PDMS\_10%PEDOT/PSS/EG and PDMS\_15% PEDOT/PSS/EG, respectively. At the higher electric field strength (2 kV/mm), the storage modulus ( $G'$ ) values were 13104, 41123, 48058 and 63039 Pa for PDMS\_0%PEDOT/PSS/EG, PDMS\_5%PEDOT/PSS/EG, PDMS\_10%PEDOT/PSS /EG and PDMS\_15% PEDOT/PSS/EG, respectively. The storage modulus ( $G'$ ) appears to depend linearly with the particle volume fraction. The storage modulus sensitivity value, defined as  $\frac{\Delta G'(\omega)}{G'_0(\omega)}$ , of PDMS\_15%PEDOT/PSS/EG blends, attains a maximum  $G'$  sensitivity value of 15.2% at electric field strength of 2 kV/mm.

Our results suggest that at very low concentrations of the secondary doping PEDOT/PSS/EG (PDMS\_5%PEDOT/PSS/EG); the response of the polymer blends to the electric field was improved by adding EG. The added EG does not only enhance the electrical conductivity but it also improves the electroactive properties; the high sensitivity response of PDMS\_PEDOT/PSS/EG to the stimulate electric field. These results can be described by the conformational change of the PEDOT chains. Two kinds of resonant structures, the benzoid and quinoid structures, have been proposed for PEDOT [20]. After the conductivity enhancement of the PEDOT/PSS by second doping, a transformation of the resonant structure of the PEDOT chain occurs. The benzoid structure may transform into the quinoid structure after the treatment, so that the quinoid structure becomes dominant in the

high-conductivity PEDOT/PSS/EG particles. Coil and linear or expanded-coil conformations have been proposed in PEDOT. The favored structure is the quinoid structure because of the high charge-carrier mobility. Therefore, resonant structure transformation after the treatment indicates the conformational transformation of PEDOT chains from the coil into linear or expanded-coil conformations [10, 11]. Because of the transformation of the PEDOT chains to the linear conformation, the PEDOT/PSS/EG particles are easy to be stimulated by the applied electric field. We can conclude that the number of particles is too small and the distances between particles are too large in PDMS\_5%PEDOT/PSS/EG blend, the conformational change after treated with EG causes PEDOT/PSS fast stimulated by electric field.

From Figure 6, at higher concentrations (PDMS\_10% PEDOT/PSS/EG and PDMS\_15%PEDOT/PSS/EG) and when the distances between particles became smaller, we encountered stronger interparticle interactions [23, 26]. However, the low electric field strength ( $<0.2$  kV/mm) might be not strong enough or insufficient to induce optimum polarization in all particles at high particle concentrations due to the steric hindrance effect [26]. At the higher electric field strength ( $>0.2$  kV/mm), it is sufficient to induce polarization in particles at high particle concentrations. The storage modulus response shows a nonlinear dependent on the particle volume fraction. Liu *et al.* (2001) [26] 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. Moreover, PDMS\_15%PEDOT/PSS/EG is the optimum concentration of the PEDOT/PSS/EG particles and PDMS gel, as show in Figure 7; this concentration presents the highest value of the storage modulus response ( $\Delta G'$ ) at high applied electric field ( $>0.1$  kV/mm).

Figure 7(a) and Figure 7(b) show the comparison of the storage modulus response ( $\Delta G'$ ) of ; (a) PDMS\_5%PEDOT/PSS and PDMS\_5%PEDOT/PSS/EG , (b) PDMS\_15%PEDOT/PSS and PDMS\_15%PEDOT/PSS/EG blends vs electric field strength at frequency 1 rad/s, strain 3.0% and at 27°C. We observe the increase in the storage modulus response ( $\Delta G'$ ) after treated the PEDOT/PSS with EG; ( $\Delta G'$ ) of PDMS\_5%PEDOT/PSS and PDMS\_5%PEDOT/PSS/EG are 3121 and 3638 Pa and



PDMS\_15%PEDOT/PSS and PDMS\_15%PEDOT/PSS/EG are 6061 and 8896 Pa at electric field strength of 2 kV/mm. The added EG affects the electrorheological properties of PEDOT/PSS blends because the conformational change of the PEDOT chains from the coil structure to the expanded coil structure [9, 10].

#### Time Dependence of the Electrorheological Response

Finally, we investigate the temporal characteristics of the crosslinked PDMS and PDMS\_PEDOT/PSS/EG blends at particle concentration of 5 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 8(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 [18].

Figure 8(b) shows the change in  $G'$  of PDMS\_5%PEDOT/PSS/EG 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. The PDMS\_5%PEDOT/PSS/EG blend is a nearly reversible system at both of electric field strengths. The results suggest that there are some irreversible interactions between PDMS molecules and PEDOT/PSS/EG particles, perhaps due to the interaction between the residue polarized molecules [18].

#### **Conclusions**

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

PEDOT/PSS particles were synthesized via the chemical oxidative polymerization and mixed with EG to improve the electrical conductivity. The PEDOT/PSS/EG particles were used for investigating the electrorheological properties by blending with PDMS; PDMS\_PEDOT/PSS/EG. For the electrorheological properties of PDMS\_PEDOT/PSS/EG blends, with the PEDOT/PSS/EG particle concentrations of 5, 10, 15, and 20 vol%, the dynamic moduli,  $G'$  of each polymer blends, are generally higher than those of pure PDMS due to PEDOT/PSS/EG 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 0.02-1 kV/mm. This can be attributed to the PDMS and PEDOT/PSS/EG particles become polarized and induced dipole moments are generated, leading to intermolecular interactions along the direction of electric field. The storage modulus sensitivity,  $\frac{\Delta G'}{G'_0}$ , attains a maximum  $G'$  sensitivity values of 8.7%, 9.0%, and 15.2%, at particle concentrations of 5, 10, and 15 vol% at the electric field strength of 2 kV/mm, respectively. When comparing the storage modulus response ( $\Delta G'$ ), we observe the increase in the storage modulus response ( $\Delta G'$ ) after treating the PEDOT/PSS with EG; ( $\Delta G'$ ) of PDMS\_5%PEDOT/PSS and PDMS\_5%PEDOT/PSS/EG are 3121 and 3638 Pa and PDMS\_15%PEDOT/PSS and PDMS\_15%PEDOT/PSS/EG are 6061 and 8896 Pa at electric field 2 kV/mm. The added EG affects the electrorheological properties of PEDOT/PSS blends because the conformational change of the PEDOT chains from the coil structure to the expanded coil structure.

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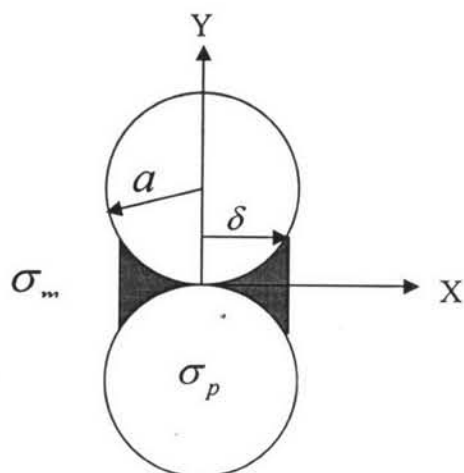
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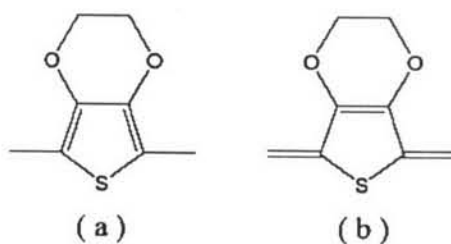
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**Table 1** Determination the specific conductivity (S/cm) and particle size ( $\mu\text{m}$ ) of PEDOT/PSS and second doped PEDOT/PSS with EG

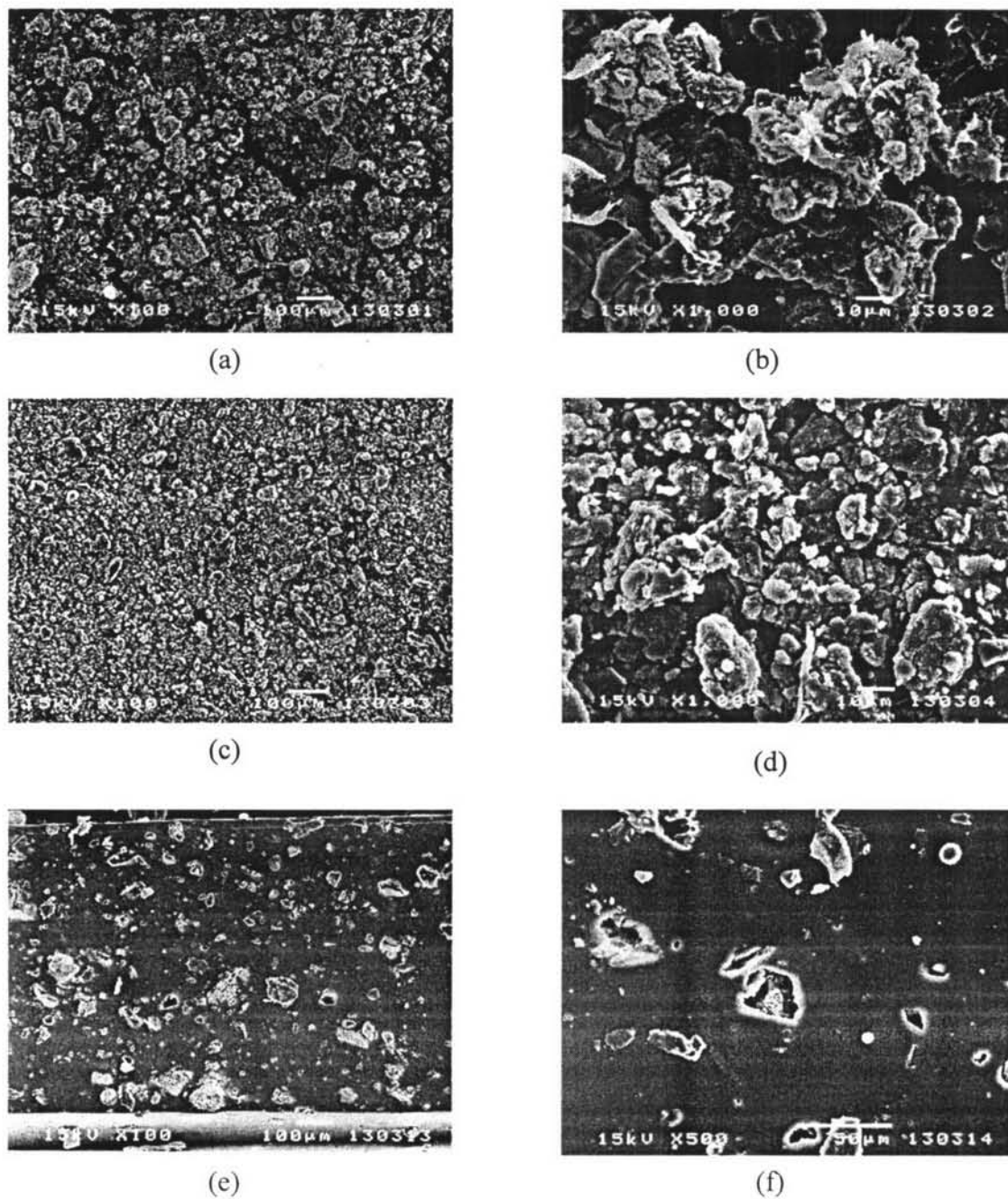
Code	Particle size ( $\mu\text{m}$ )		Specific conductivity (S/cm)			
	average	SD	1	2	average	SD
PDMS	-	-	$1.7 \times 10^{-8}$	$2.1 \times 10^{-8}$	$1.9 \times 10^{-8}$	$2.8 \times 10^{-9}$
PEDOT/PSS	30	4	27.9	27.1	27.5	0.6
PEDOT/PSS:EG=5:1	31	4	576.0	558.3	563.5	7.6
PEDOT/PSS:EG=5:2	32	5	591.9	581.0	586.5	7.7
PEDOT/PSS:EG=5:3	31	4	566.1	546.0	556.1	14.2
PEDOT/PSS:EG=5:4	32	3	599.1	644.1	621.6	31.8
PEDOT/PSS:EG=5:5	33	4	589.7	580.6	585.2	6.4



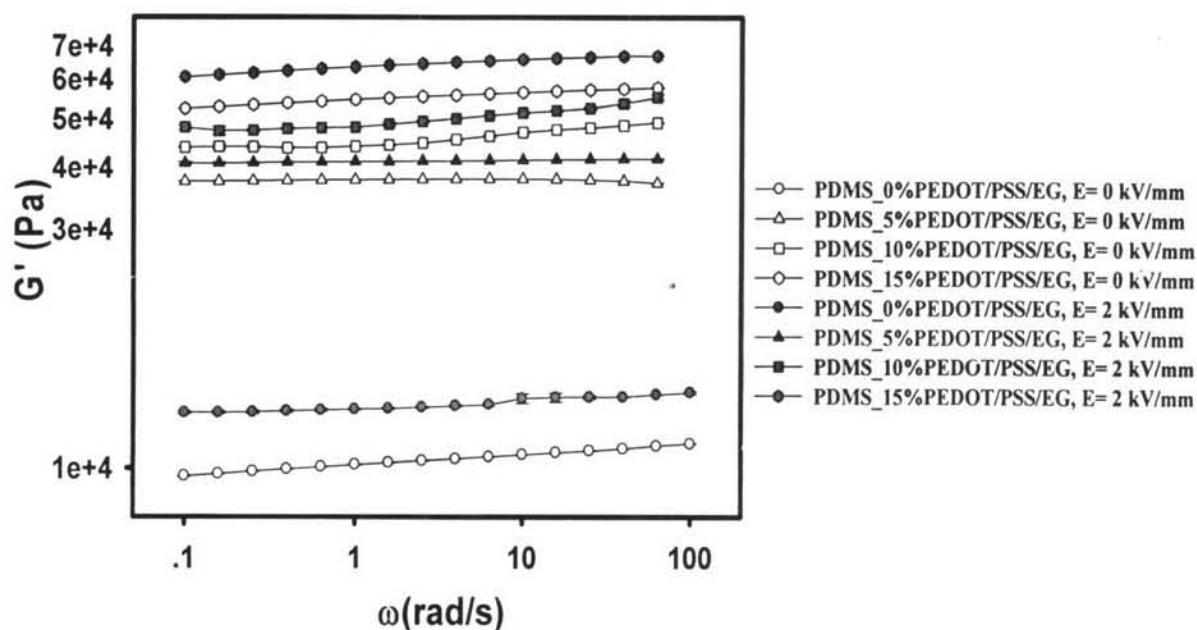
**Figure 1** Two spheres, each of radius  $a$ , aligned with the applied electric field. The potential difference between the spheres centers is  $U$ ;  $U = 2aE_0$ .  $\delta$  specifies the radius of the inner region where the electric field in the continuous phase saturates.



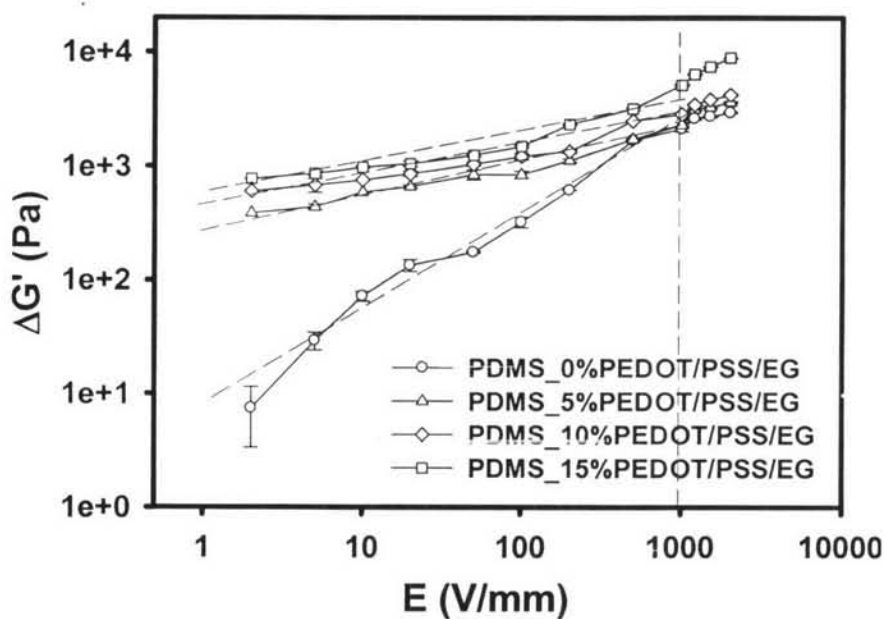
**Figure 2** (a) the benzoid structure; and (b) the quinoid structure of a unit of PEDOT.



**Figure 3** The morphology of PEDOT/PSS and PEDOT/PSS/EG powder at magnifications of: (a) 100; and (b) 1000 and the morphology of PDMS\_10%PEDOT/PSS blends at magnifications of: (e) 100; and (f) 500.

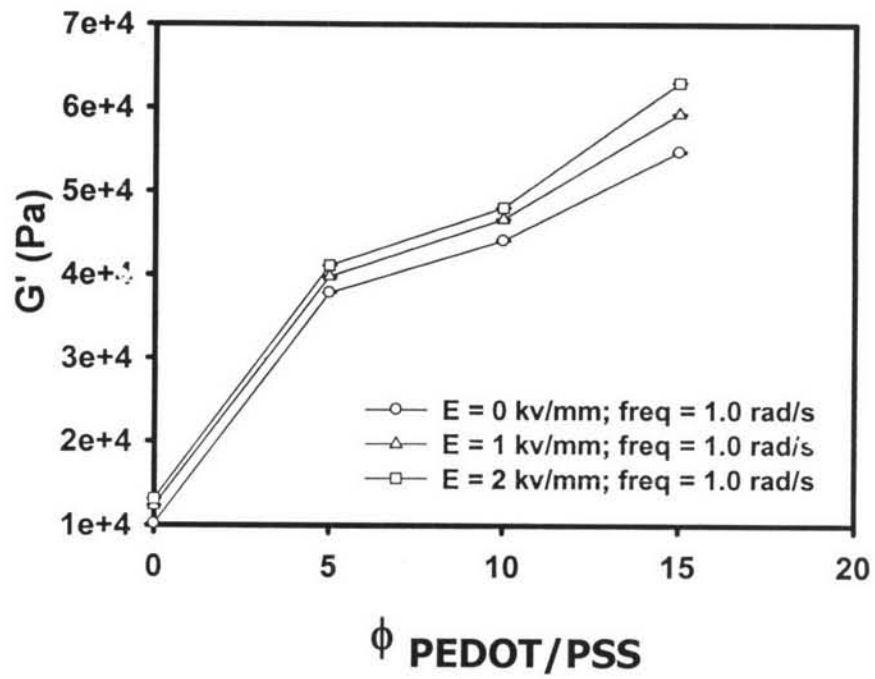


**Figure 4** Comparison of the storage modulus of PDMS\_PEDOT/PSS/EG blends at various particle concentrations ( $\Phi = 5, 10$  and  $15$  vol.%) vs. frequency, strain 3.0%,  $27^\circ\text{C}$  at electric field strengths of 0 and 2 kV/mm.

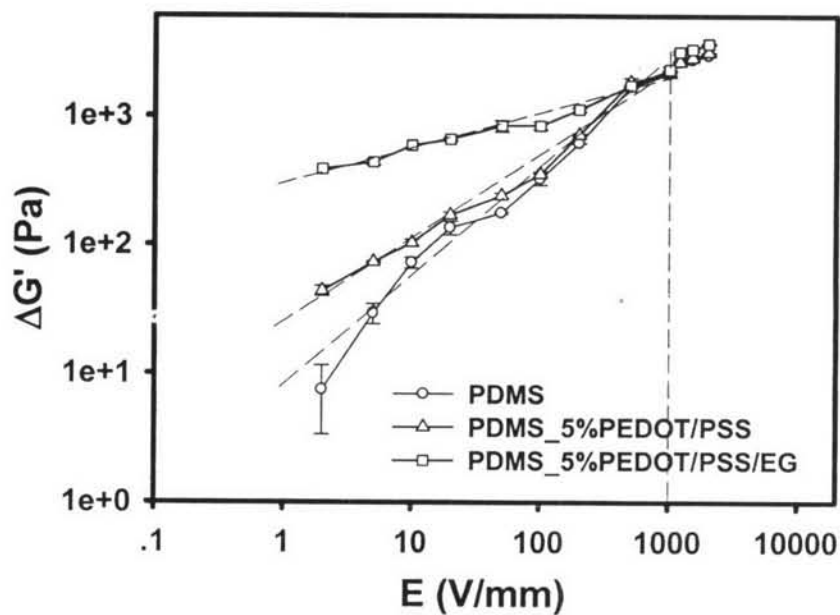


**Figure 5** The storage modulus response ( $\Delta G'$ ) of PDMS\_PEDOT/PSS/EG blends at various particle concentrations ( $\Phi = 0, 5, 10$  and  $15$  vol.%) vs. electric field strength at frequency 1 rad/s, strain 3.0% and at  $27^\circ\text{C}$ .

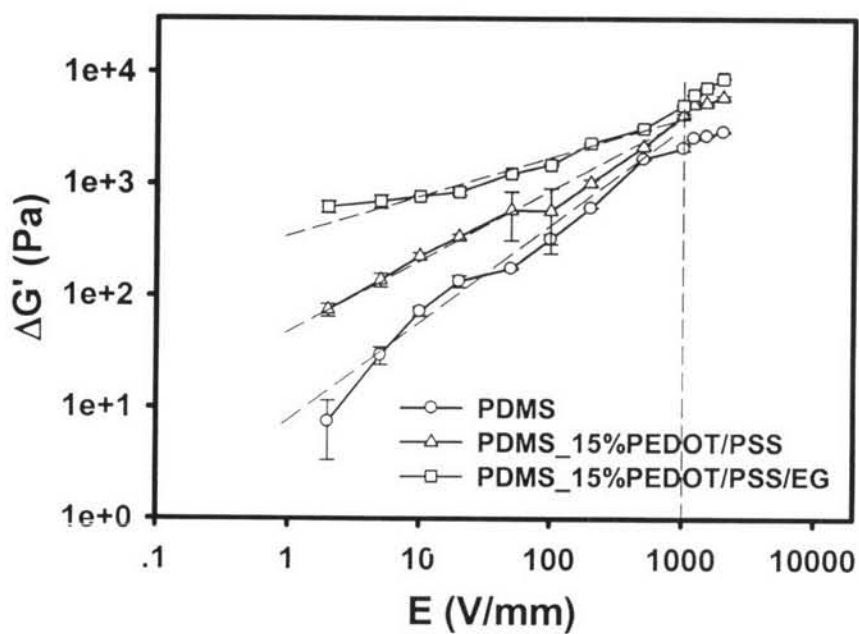




**Figure 6** Comparison of the storage modulus ( $G'$ ) of PDMS\_PEDOT/PSS/EG blends at various electric field strength (0, 1 and 2kV/mm) vs. particle concentrations ( $\Phi = 0, 5, 10,$  and 15 vol%.) at frequency 1 rad/s, strain 3.0% and 27°C.

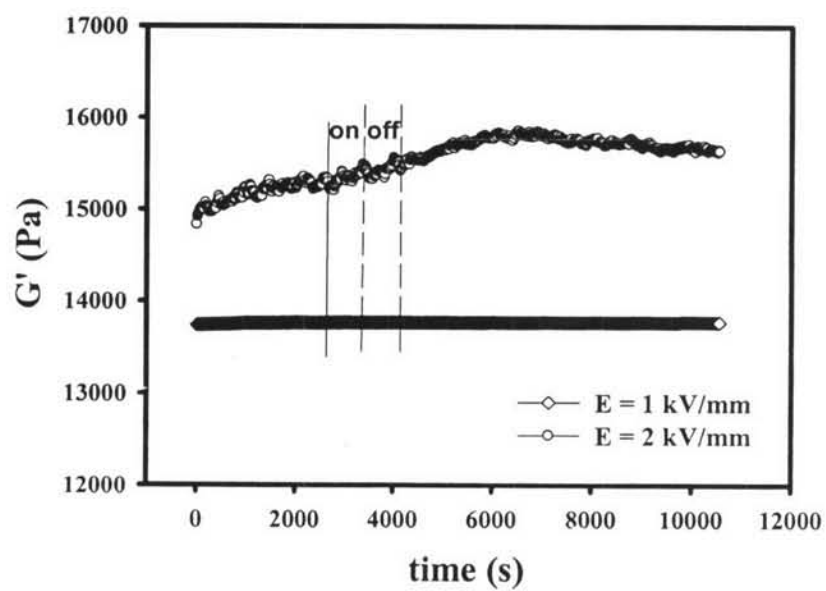


(a)

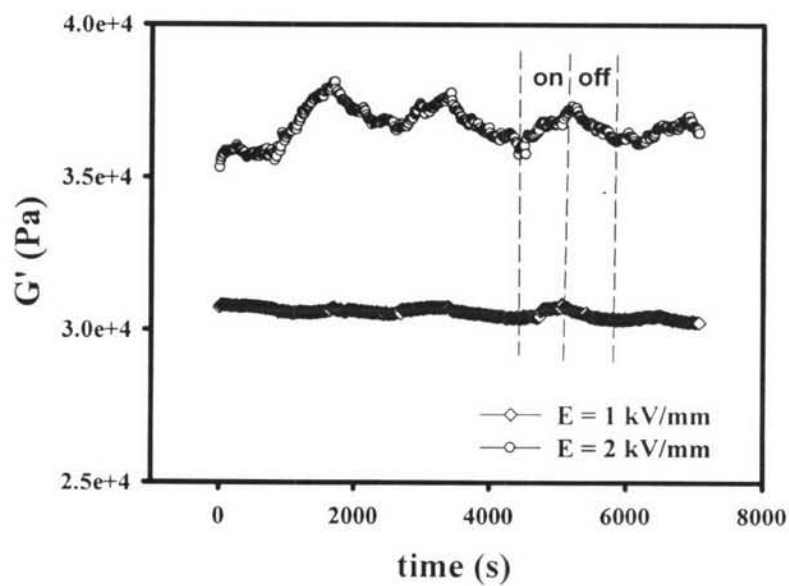


(b)

**Figure 7** Comparison of the storage modulus response ( $\Delta G'$ ) of: (a) PDMS\_5%PEDOT/PSS and PDMS\_5%PEDOT/PSS/EG; (b) PDMS\_15%PEDOT/PSS and PDMS\_15%PEDOT/PSS/EG blends vs electric field strength at frequency 1 rad/s, strain 3.0% and at 27°C.



(a)



(b)

**Figure 8** 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; and (b) PDMS\_5%PEDOT/PSS/EG blends.