

CHAPTER IV
ELECTRORHEOLOGICAL PROPERTIES OF
POLYTHIOPHENE/POLYISOPRENE ELASTOMER BLENDS

4.1 Abstract

Electrorheological properties of polyisoprene and polythiophene/polyisoprene blends were investigated as 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 dynamic moduli, G' and G'' , of the pure polyisoprene depended on the crosslinking ratio and electric field strength; the storage modulus (G') increased but the loss modulus (G'') decreased with increasing crosslinking ratio. However, the storage modulus (G') of the pure polyisoprene fluid exhibited no change with increasing electric field strength. For PI with the crosslinking ratios of 2, 3, 5 and 7 (PI_02, PI_03, PI_05 and PI_07), the storage modulus sensitivity, $\frac{\Delta G'}{G'_0}$, increased with electric field strength and attained maximum values of 10%, 60%, 25%, and 30%, respectively at the electric field strength of 2 kV/mm. For the blends of undoped polythiophene and polyisoprene (Pth_U/PI_03), with the undoped particle concentrations of 5%, 10%, 20% and 30 vol%, the dynamic moduli, G' and G'' of each blends, were generally higher than those of pure crosslinked polyisoprene (PI_03). Their storage modulus sensitivity, $\frac{\Delta G'}{G'_0}$, increased with electric field strength and attained a maximum value of 50%, 35%, 110% and 45%, respectively at the electric field strength of 2 kV/mm.

Keywords: Electrorheological properties, Polyisoprene, Polythiophene,
Dynamic moduli

4.2 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]. Polyisoprene or natural rubber is one type of dielectric materials which has many advantageous characters; inexpensive due to its natural source, flexible polymer, low swelling in water, high tensile strength, good resilience, high hot tensile, and well behaved hysteresis. These characteristics are desirable properties required to induce large actuation strain when subjecting the material to an electric field.

Recently, incorporation of a conductive polymer into a dielectric elastomer forming a composite 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 [3]. Examples are polyaniline-polyisoprene composite for biosensor application [4], polyaniline-EPDM composite [5], and TiO₂ embedded in PDMS gels for actuators application [6].

In our work, we are interested in developing polythiophene/polyisoprene elastomer blends as a substitute for artificial muscles. The mechanical properties, viscoelastic properties and electrical properties will be investigated in terms degree of polyisoprene crosslinking ratio, polythiophene 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 polymer gels or elastomers will be explained using the

one point dipole model. Polarization in the point dipole model occurs not at the surface of the particle but within it. If dipoles form in particles, an interaction between dipoles occurs and becomes stronger as the dipoles come close to each other. When the particles make contact with each other along the applied electric field, the interaction reaches a maximum. A balance between the electrostatic interaction and the elastic modulus of the solid matrix is important for the ER effect to transpire. If the elastic modulus of the solid matrix is larger than the sum of the interaction between particles, the ER effect may not be observed macroscopically. Therefore the matrix should be a soft material such as gels or elastomers to produce the ER effect [7].

We discuss theoretically the influence of microscopic interaction between polarized particles on the macroscopic mechanical properties of the polymer blends, in particular, the elastic modulus. Let us consider a hard sphere in a continuous matrix under an electric field. When the relative dielectric constant of particle (ϵ_p) is larger than that of matrix (ϵ_m), a point dipole in the particle is formed by application of an electric field. According to the classical theory, [7], the point dipole moment is given by:

$$\mu = 4\pi r^3 \epsilon_0 \epsilon_m \kappa E \quad (4.1)$$

$$\kappa = (\epsilon_p - \epsilon_m) / (\epsilon_p + 2\epsilon_m) \quad (4.2)$$

Equation (4.1) is an expression obtained formally for the volume polarizability of a particle, where r is the radius of the particle, ϵ_0 is the permittivity in vacuum ($= 8.854 \times 10^{-12}$ F/m), and E is the intensity of the applied field.

When two particles are aligned along the applied electric field and are in contact with each other, the dipole-dipole interaction (F) between two dipole particles is given by the following equation [7]:

$$F = (3/2)\pi r^2 \epsilon_0 \epsilon_m \kappa^2 E^2 \quad (4.3)$$

In a cubical gel, there are many straight migration paths of dispersed particles, which remain parallel to the direction of the applied field. The cube gel is deformed by a small shear strain in a direction perpendicular to the applied field. Assuming that electrostatic interactions between dispersed particles in a path are based only upon an interaction between two adjacent particles and that interaction

between paths of particles are negligible. Macroscopic mechanical properties such as storage and loss moduli can be estimated by multiplying the electrostatic force between adjacent particles at short range in the path, therefore an increase in elastic modulus due to an applied electric field ΔG is given as follows [7]:

$$\Delta G = (9/4)C\varepsilon_m\kappa^2E^2 \quad (4.4)$$

where ΔG is change in elastic modulus, C is the volume fraction of particles, ε_m is relative dielectric constant of matrix, and E is the intensity of the applied field. This states that ΔG is proportional to C , ε_m or E^2 . When these factors reach maximum values, ΔG is expected to become saturated.

4.3 Experimental

4.3.1 Materials

3-Thiopheneacetic acid, 3TAA (AR grade, Fluka), was used as the monomer. Anhydrous ferric chloride, FeCl_3 (AR grade, Riedel-delHean), was used as the oxidant. Chloroform, CHCl_3 (AR grade, Lab-Scan), methanol, CH_3OH (AR grade, Lab-Scan) was dried over CaH_2 for 24 hours under the nitrogen atmosphere and then distilled, were used as solvents. Diethyl ether was used as solvents. Polyisoprene, PI ($M_w = 40,000$, viscosity = 400 poise, Aldrich), was used as the polymer matrix. Dicumyl peroxide (AR grade, Fluka) was used as the crosslinking agent.

4.3.2 Instruments

The Fourier Transform Infrared Spectrometer (Thermo Nicolet, Nexus 670) with number of scans of 32, UV-Visible absorption spectrometer (Perkin Elmer, Lambda 10), Thermalgravimetric analyzer (DuPont, model TGA 2950) with the temperature scan from 30 to 800°C with a heating rate of 10°C/min under O_2 atmosphere were used to characterize the synthesized polythiophene and polythiophene/polyisoprene blends. Scanning electron microscope (JOEL, model JSM-5200-2AE) was used to determine the morphological structure of the synthesized polymers and polymer blends with the magnifications of 350 and 1,500

times at 20 kV. A custom-built two-point probe electrometer (Keithley, Model 6517A) was used to determine electrical conductivity of conductive polymer. A melt rheometer (Rheometric Scientific, ARES) was used to measure electrorheological properties. A DC power supply (Instek, GFG 8216A) can deliver electric field strength up to 2 kV/mm.

4.3.3 Synthesis of Poly(3-Thiopheneacetic acid) (P3TAA)

The reaction was by oxidative-coupling polymerization according to the method of Kim *et al.* [8]. 10.0 g of 3-thiopheneacetic acid was refluxed for 24 hours in 50 ml of dry methanol with 1 drop of concentrated H₂SO₄ in order to protect the oxidative decomposition of the carboxylic acid group of monomer during oxidative-coupling polymerization. The methanol was evaporated, and the residue was extracted with fresh diethyl ether. The extract was washed with deionized water, dried with anhydrous MgSO₄ and then filtered. The diethyl ether was evaporated from the filtrate by rotating evaporator.

Thiophene methylacetate (TMA) product was obtained after the diethyl ether was evaporated from the filtrate by rotating evaporator. In a 100 ml three-necked flask, a solution of 10 mmol of protected monomer in 20 ml of chloroform was added dropwise to a solution of 40 mmol of ferric chloride was dissolved in 30 ml of dry chloroform under nitrogen atmosphere. The molar ratio of the oxidant to monomer is 4:1 in all cases. The reaction was carefully maintained at 0°C ($\pm 0.5^\circ\text{C}$) for 24 hours. The reaction mixture was precipitated, by pouring into a large excess amount of methanol (1 L) to obtain polythiophene methylacetate (PTMA). The product was repeatedly washed with methanol and deionized water.

PTMA was hydrolyzed as follow; 0.5 g of PTMA was dissolved in 50 ml of 2.0 M NaOH solution and heated for 24 hours at 100°C. The mixture was filtered, neutralized and precipitated with a dilute HCl solution (~0.5 M) to obtain polymer product. The poly(3-thiophene acetic acid) (P3TAA) was washed several times with deionized water before vacuum drying at room temperature for 2 days.

4.3.4 Characterization Method

Fourier-transform infrared spectrometer (FT-IR), each poly(3-thiophene acetic acid) sample was identified for functional groups by 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 $4000\text{-}400 \text{ cm}^{-1}$ using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PTAA was intimately mixed with dried KBr at a ratio of P3TAA: KBr = 1:20. Samples were grounded with a mortar, mixed with KBr, and molded into pellets under the pressure of 8 tons.

UV-Vis spectra were recorded with a UV-Vis absorption spectrometer (Perkin-Elmer, Lambda 10). Measurements were taken in the absorbance mode in the wavelength range of 200-800 nm. Synthesized P3TAA was grinded into a fine powder, dissolved in DMSO at the concentration of $6.0 \times 10^{-5} \text{ M}$ and pipetted into the sample holder. Scan speed was 240 mm/min, and a slit width of 2.0 nm using a deuterium lamp as the light source.

The thermal stability of P3TAA was investigated using a thermogravimetric analyzer (DuPont, model TGA 2950) in a temperature range from 30 to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$ and O_2 atmosphere [9].

Scanning electron micrographs were taken with a JEOL, model JSM-5200 scanning electron microscope to determine the morphology of poly(3-thiophene acetic acid) in powder forms and polythiophene/polyisoprene blends at various particle concentrations. The scanning electron micrographs of polythiophene and polymer blends were obtained by using an acceleration voltage of 20 kV with magnifications of 350 and 1,500 times.

The particle sizes of poly(3-thiophene acetic acid) were determined by using a particle size analyzer (Malvern Instruments Ltd., Masterizer X Version 2.15).

The electrical conductivity of undoped poly(3-thiophene acetic acid) was studied by using a custom-built two-point 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 $\sigma = (1/Rt)(1/K) = (I/Vt)(1/K)$ 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.

The crosslink density can be measure by measurement of M_c is called equilibrium swelling. We determined M_c from knowing the swelling ability of certain solvents in a crosslinked network. The procedure of the crosslink density measurement is as follow: initially the samples were cut to $\approx 10 \times 10$ mm; then weight of each specimen was measured; we placed each specimen in a vial containing toluene for 3 day and the weight of the swollen sample was remeasured; three experiments using three different samples for each crosslinking ratio were carried out, and the results were averaged. The crosslink density was calculated from the following equations [10, 11, 12, 13];

$$M_c = \frac{v_1 \rho_2 \left(v_{2m}^{1/3} - \frac{v_{2m}}{2} \right)}{- \left[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 \right]} \quad (4.5)$$

$$v_{2m} = \frac{w_0}{v_{equil} \times \rho_2} \quad (4.6)$$

$$v_{equil} = \frac{w_0}{\rho_2} + \frac{w_s - w_0}{\rho_1} \quad (4.7)$$

$$\chi = 0.34 + \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \quad (4.8)$$

and
$$\text{Crosslinik density} = [2M_c]^{-1} \quad (4.9)$$

where v_1 is the molar volume of solvent ($M_w/\text{density}$), ρ_2 is polymer density, polyisoprene equal to 0.92 g/cm^3 , ρ_1 is solvent density, toluene equal to 0.867 g/cm^3 , w_0 is original polymer weight, w_s is swollen polymer weight, χ is

polymer-solvent interaction parameter, R is the universal gas constant, 8.29 N.m/mol.K, T is the absolute temperature, 298 K, δ_1 is the solubility parameter of polymer, polyisoprene equal to 17.02 (MPa)^{1/2}, and δ_2 is the solubility parameter of solvent, toluene equal to 18.20 (MPa)^{1/2}.

4.3.5 Preparation of Pure Polyisoprene

The electrorheological properties of pure polyisoprene were investigated in terms of electric field strength and crosslinking ratio. A specific amount of dicumyl peroxide was mixed with polyisoprene and cast onto a mold (diameter 25 mm). Various amounts of dicumyl peroxide were used to vary the degree of crosslinking (crosslinking ratios N_{DCP}/N_{PI} , 2, 3, 5 and 7). Existing bubbles were removed in a vacuum atmosphere at 25°C for 2 h. The fabrication of the crosslinked polyisoprenes was by compression molding at 175°C and 5 MPa for 7 min [14].

4.3.6 Preparation of the P3TAA/Polyisoprene Blends

The polythiophene powder was sieved with a mesh particle size of 38 μm and dried at room temperature for 24 hours prior to their uses. The blends were prepared by mechanical blending of undoped synthesized polythiophene particle at various particle concentrations (5, 10, 20, and 30 vol%) with polyisoprene. Polyisoprene fluid and a specific amount of crosslinking agent were added to the mixture, which was then mechanically blended for about 5 min to disperse the ingredients. The optimum degree of crosslinking, having the highest G' modulus sensitivity was used. (crosslinking ratio of about 3). The specific amount of particle was then added and the mixture was mechanically blended for 5 min to disperse the particles. The mixture was cast on the mold (diameter 25 mm) and bubbles were removed under a vacuum atmosphere at 25°C for 2 h. The fabrication of the P3TAA/crosslinked polyisoprenes blends (Pth_U/PI_03) was by compression molding at 175°C and 5 MPa for 7 min [14].

4.3.7 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. The appropriate strain was determined to be 220% for pure polyisoprene fluid (PI_00). For the crosslinked polyisoprene (PI_02, PI_03, PI_05 and PI_07) and undoped polythiophene/crosslinked polyisoprene blends (blends ratio 5, 10, 20, and 30 vol%) (Pth_U5/PI_03, Pth_U10/PI_03, Pth_U20/PI_03 and Pth_U30/PI_03) the strain used was 1%. 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 polyisoprene and polythiophene/polyisoprene blends samples were presheared at a low frequency (0.039811 rad/s), and then 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.

4.4 Results and Discussion

4.4.1 Characterization of Poly(3-thiophene acetic acid)

The FT-IR spectrum of the synthesized P3TAA was recorded to identify characteristic absorption peaks [8]. The characteristic peaks of P3TAA were found at 3200-3000 cm^{-1} , 3000-2800 cm^{-1} , 1700 cm^{-1} , 1300-1200 cm^{-1} and 830 cm^{-1} . These peaks can be assigned to the C-H bond stretching on the thiophene ring; the aliphatic C-H bond stretching; the carboxylic acid C=O stretching; the thiophene ring stretching; the carboxylic acid C-O stretching and the out-of-plane thiophene C-H stretching, respectively [8]. The most characteristic feature in this spectrum is the

extremely broad O-H absorption occurring in the region from 3400-2400 cm^{-1} ; it can be attributed to the strong hydrogen bonding of the dimmer. This absorption band often obscures the C-H stretching vibration peak occurring in the same region. It is obvious from the absorption peak at around 1700 cm^{-1} that the ester groups were not deteriorated during the oxidative polymerization.

The UV-visible absorption spectra of synthesized P3TAA solution in DMSO shows absorption peaks at 275 nm and 415 nm corresponding to the π - π^* transition of the bithiophene unit and the polymer backbone, respectively [8, 15,16].

The TGA thermogram of synthesized P3TAA shows two degradation steps at 200°C and 440°C corresponding to the side chain degradation and the backbone degradation, respectively [9]. The polythiophene/polyisoprene blends (Pth_U/PI_03) have a better thermal stability with increasing polythiophene particle concentration.

The mean particle diameter of P3TAA was determined to be approximately 20 μm with standard deviation of 3 μm . The particle microstructure was observed using scanning electron microscopy (SEM). Figure 4.1 shows the shapes of the undoped P3TAA and undoped P3TAA particles in polymer blends; they are quite irregular in shape. However, these irregular shape particles appear to be well dispersed in the polyisoprene matrix [9].

The specific conductivity of undoped P3TAA (Pth_U) was measured by a custom-built two point probe (Keithley, Model 6517A). The specific conductivity of Pth_U was 3.01×10^{-6} S/cm with standard deviation of 1.01×10^{-7} S/cm.

4.4.2 Electrorheological Properties of Pure Polyisoprene

4.4.2.1 *Effect of Crosslinking in the Absence of Electric Field*

The effect of crosslinking on the rheological properties of pure polyisoprene (PI) was first investigated. The crosslinking ratios were 2, 3, 5 and 7 (PI_02, PI_03, PI_05 and PI_07). The crosslink density increases with the increasing crosslinking ratios as shown in Table 4.1. For the PI_02 system, $N_{\text{DCP}}/N_{\text{PI}}$ and the crosslink density are 2.00 and 3.733×10^{-5} mol/cm³, respectively. For a

higher crosslinked system of PI_07, N_{DCP}/N_{PI} and the crosslink density are 7.02 and $15.175 \times 10^{-5} \text{ mol/cm}^3$, respectively. Figures 4.2(a) and 4.2(b) show the storage modulus (G') and loss modulus vs. frequency with electric field of 0 and 2 kV/mm at strain 1%. G' increased monotonically with increasing crosslinking ratios [1]. On the other hand, Figure 4.2(b) shows that the loss modulus (G'') decreased with increasing crosslinking ratio. These results clearly suggest that with increasing amount of crosslinking ratio or the crosslink density, free movements of polymer chains are prohibited resulting in lesser molecular friction, and the polyisoprene behavior changes from that of a fluid-like behavior (PI_03) to that of a solid-like behavior (PI_07) in which the storage modulus increased [7].

4.4.2.2 Effect of Crosslinking under Electric Field

The effect of electric field strength on the rheological properties of pure polyisoprene (PI), at various crosslinking ratios, was investigated in the range of electric field strength between 0-2 kV/mm. The storage modulus $G'(\omega)$ of each crosslinked polyisoprene system generally increased at high electric field strength (0.5-2 kV/mm). Figure 4.3 shows the storage modulus responses ($\Delta G'$) of various crosslinked polyisoprene systems as functions of electric field strengths at frequency 1 rad/s and strain 1%. The storage modulus responses appear to increase linearly with electric field. The storage modulus responses values at electric field strength of 2 kV/mm were 500, 4097, 5002, and 8894 Pa for PI_02, PI_03, PI_05, and PI_07, respectively. The corresponding storage modulus sensitivity value, defined as $\frac{\Delta G'(\omega)}{G'_0(\omega)}$, of the crosslinked polyisoprene systems (PI_02, PI_03, PI_05, and PI_07) at electric field strength of 2 kV/mm were 10%, 60%, 25%, and 30%, respectively.

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 creates 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]:

$$p = \epsilon_0 \epsilon_r E^2 \quad (4.10)$$

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 $G'(\omega)$. 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.

Figure 4.4 shows the storage modulus responses ($\Delta G'$) as functions of crosslink density of the crosslinked polyisoprene at electric field strength of 1 kV/mm and 2 kV/mm. The storage modulus responses increase with increasing crosslink density. The highest crosslink density system (PI_07, crosslink density = 15.175×10^{-5} mol/cm³) shows the highest storage modulus response of 4000 and 8894 Pa at electric field strengths of 1 and 2 kV/mm, respectively. However, the storage modulus sensitivity value defined as $\frac{\Delta G'(\omega)}{G'_0(\omega)}$, of the

crosslinked polyisoprene system; PI_03 system (crosslink density = 6.107×10^{-5} mol/cm³) has the highest G' sensitivity: 60% at electric field strength of 2 kV/mm.

This result suggests that the PI_03 system contains a balance between the solid-like and the fluid-like behaviors; it has enough flexibility within the matrix in the absence of electric field such that its structure rigidity can be further induced with electric field. On the other hand, the lower crosslinked system (PI_02) has a more fluid-like structure than other systems; free movement and relaxation of polymer chains are still allowed in the presence of electric field and consequently they are affected with lesser intermolecular interactions. The higher crosslinked systems (PI_05 and PI_07) contain relatively more solid-like structures and hence possess higher storage modulus values. The polymer segments and chains are quite

rigid and fixed in the absence of electric field; they simply cannot respond any further to intermolecular interaction under the applied electric field.

4.4.3 Electrorheological Properties of Polythiophene/Polyisoprene blends

4.4.3.1 *Effect of Polythiophene Composition in the Absence of Electric Field*

The effect of polythiophene particle concentration on the rheological properties of polymer blends (Pth_U/PI) was investigated next. The PI_03 system, with crosslinking density of $6.107 \times 10^{-5} \text{ mol/cm}^3$ was chosen and blended with poly(3-thiopheneacetic acid) particles; this system exhibits the maximum G' sensitivity amongst various systems studied. Figures 4.5(a) and 4.5(b) show comparisons of the storage modulus (G') and the loss modulus (G'') vs. frequency between polymer blends of various concentrations, at electric field strengths of 0 and 2 kV/mm. Polythiophene particle concentrations studied were 5, 10, 20, and 30 vol% (Pth_U5/PI_03, Pth_U10/PI_03, Pth_U20/PI_03 and Pth_U30/PI_03). Both G' and G'' increase with polythiophene particle concentrations and electric field strength. The storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ of each polymer blends system are higher than those of the PI_03 system at any electric field strength. Close inspection of our data suggests that polythiophene particles in the polymer blends acted 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 PI_03 system, and the higher storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$.

Concentration effect has been reported by others researchers. Shiga (1997) [7] 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.

4.4.3.2 Effect of Polythiophene Composition under Electric Field

The effect of electric field strength on the rheological properties of polythiophene/polyisoprene blends (Pth_U/PI) at various polythiophene particle concentrations was investigated in the range between 0-2 kV/mm. Figures 4.5(a) and 4.5(b) show the comparison of the storage modulus (G') and the loss modulus (G'') between the blends of various concentrations at electric field strengths of 0 and 2 kV/mm. The storage modulus (G') and the loss modulus (G'') of each polymer blends system generally increase with increasing electric field strength. Figure 4.6 shows the storage modulus responses ($\Delta G'$) vs. electric field of various polymer blends systems at frequency of 1 rad/s, and strain equal to 1%. The increase in $\Delta G'$ with electric field is nonlinearly within the range of 0.1 to 2 kV/mm. The storage modulus response values, $\Delta G'(\omega)$, of these systems at electric field strength of 2 kV/mm were 4097, 5446, 4026, 19161, and 33857 Pa for PI_03, Pth_U5/PI_03, Pth_U10/PI_03, Pth_U20/PI_03 and Pth_U30/PI_03, respectively. The corresponding storage modulus sensitivity values, defined as $\frac{\Delta G'(\omega)}{G'_0(\omega)}$, of these polymer blends systems (Pth_U5/PI_03, Pth_U10/PI_03, Pth_U20/PI_03 and Pth_U30/PI_03) at electric field strength of 2 kV/mm were 50%, 35%, 110%, and 45%, respectively.

Our results suggest that in the absence of the electric field, the polythiophene particles were randomly dispersed within the polyisoprene matrix and there was no particle-particle interaction. As the electrical field was applied, both polyisoprene and polythiophene 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-polyisoprene blends, consistent with the results of other polymer blends [17, 18, 19].

Lui *et al.* (2001) [19] 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) [7] 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.

Figure 4.7 shows the storage modulus responses ($\Delta G'$) of polythiophene/polyisoprene blends vs. particle volume fraction at electric field strengths of 1 and 2 kV/mm. As the particle volume fraction increased, the storage modulus appeared to increase nonlinearly with particle volume fraction and it reached a saturated value at electric field strength of 1 kV/mm. The storage modulus responses were 1728, 2592, 1996, 14053, and 8322 Pa for PI_03, Pth_U5/PI_03, Pth_U10/PI_03, Pth_U20/PI_03 and Pth_U30/PI_03 systems, respectively. At the higher electric field strength (2 kV/mm), the storage modulus response ($\Delta G'$) appeared to depend nonlinearly with the particle volume fraction. However, the storage modulus sensitivity value, defined as $\frac{\Delta G'(\omega)}{G'_0(\omega)}$, of polythiophene/polyisoprene blends Pth_U20/PI_03 system, attained a maximum G' sensitivity value of 110% at electric field strength of 2 kV/mm.

Our results suggest that at very low concentrations (Pth_U5/PI_03, Pth_U10/PI_03); the number of particles is too small and the distances between particles are too large to create a significant particle interaction [19]. The storage modulus responses of these systems are comparable to that of the crosslinked pure polyisoprene system (PI_03). At higher concentrations (Pth_U20/PI_03, and Pth_U30/PI_03) and when the distances between particles became smaller, we encountered stronger interparticle interactions [7, 19]. However, the electric field strength of 1 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 [19]. Thus, the storage modulus response of Pth_U30/PI_03 system become saturated and has approximately the same value as that of Pth_U20/PI_03 system. At the higher electric field strength of 2 kV/mm, it is sufficient to induce polarization in particles at high particle

concentrations. The storage modulus response showed a nonlinear dependent on the particle volume fraction and might reached saturation at volume fraction above 0.3.

Liu *et al.* (2001) [19] reported a similar effect for silicone/silica elastomer. They found that the enhancement of shear modulus was negligible below 8.0 vol%, but increased dramatically above this threshold concentration. At volume fraction above 55 vol%, the shear modulus decreased because the interparticle force decreased with the steric hindrance effect.

4.4.4 Time Dependence of the Electrorheological Response

Finally, we investigated the temporal characteristic of crosslinked polyisoprene (PI_03) and polythiophene/polyisoprene blends at particle concentration of 20 vol% (Pth_U20/PI_03), at various electric field strengths. The temporal characteristic of each sample was recorded in the linear viscoelastic regime at a strain of 1 %, and frequency of 1 rad/s. Figure 4.9(a) shows the change in G' of PI_03 system on electric field strength of 1 and 2 kV/mm during a time sweep test, in which an electric field was turned on and off alternately. At the electric field of 1 kV/mm, G' immediately increased and rapidly reached a steady-state value. Then, with the electric field off, G' decreased and nearly recovered its original value. Thus PI_03 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 overshoot to a large value on the first cycle followed by a irreversible decay with electric field off; and the steady state regime in which G' subsequently exhibited 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} . As shown in Table 4.2, the τ_{ind} decreases with increasing electric field strength; they are 107 and 75 sec at electric field strength 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 is essentially independent of the electric field strength, as shown in Table 4.2. The recovery time are 76 and 83 sec at electric field strength equal to 1 and 2 kV/mm, respectively. The independence of τ_{rec} on the field strength suggests that the strains induced were small such that the relaxations were

nearly the same. We also found that t_{ind} is independent of crosslink density or the elastic modulus, whereas t_{rec} decreases with higher crosslink density, as shown in Table 4.2. The independence of τ_{ind} with the crosslink density suggests that τ_{ind} depends more on electric field strength. The lower τ_{rec} required to relax with a higher crosslink density is because of higher elastic modulus or rigidity and hence a shorter relaxation time scale.

Figure 4.9(b) shows the temporal response of 20 vol% polythiophene/polyisoprene blends (Pth_U20/PI_03) at electric field strengths of 1 and 2 kV/mm, respectively. The Pth_U20/PI_03 is clearly an irreversible system at both of electric field strengths. Our result here may suggest that there are some irreversible interaction between polythiophene particles, perhaps due to hydrogen bonding between adjacent polythiophene particles and residual dipole moments inducing permanent interparticle interactions [9]. τ_{ind} decreases with increasing field strength. As shown in Table 4.2, τ_{ind} are 157 and 121 sec at electric field strength equal to 1 and 2 kV/mm, respectively. τ_{rec} is nearly independent of electric field strength. As shown in Table 4.2, τ_{rec} are 59 and 66 sec at electric field strength equal to 1 and 2 kV/mm, respectively.

4.5 Conclusions

In this study, electrorheological properties of polyisoprene and polythiophene/polyisoprene blends were investigated by examining the effects of crosslinking ratio, and polythiophene particle concentration on the dynamic moduli, G' and G'' , under the oscillatory shear mode at electric field strength various from 0 to 2 kV/mm. In pure PI systems, the storage modulus (G') increased but the loss modulus (G'') decreased with increasing crosslinking ratio. It exhibited a transition from a fluid-like to a solid-like behavior. The storage modulus (G') and the loss modulus (G'') of the uncrosslinked polyisoprene fluid exhibited no change with increasing electric field strength. Polyisoprene with the crosslinking ratios of 2, 3, 5 and 7, the storage modulus increased linearly with electric field strength. The

maximum G' sensitivity was found to be about 0.6 for the PI_03 system at electric field strength of 2 kV/mm; it is frequency independent.

Poly(3-thiophene acetic acid) particles were synthesized via an oxidative polymerization and blended with the PI_03 system. For the electrorheological properties of Pth_U/PI_03 blends, with the undoped polythiophene particle concentrations of 5, 10, 20, and 30 vol%, the dynamic moduli, G' and G'' of each polymer blends, were generally higher than those of pure polyisoprene due to polythiophene particles within the matrix acting as fillers; they can store or absorb the forces/stresses within the matrix. The storage modulus responses increased with electric field nonlinearly within the range of 0.1 to 2 kV/mm. This can be attributed to the polyisoprene and polythiophene particles 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 a maximum G' sensitivity values of 0.5, 0.35, 1.10 and 0.45 at particle concentrations of 5, 10, 20, and 30 vol% at the electric field strength of 2 kV/mm, respectively.

4.6 Acknowledgements

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Table 4.1 The crosslink density of pure polyisoprene

Systems	N_{DCP}/N_{PI}	Crosslink density (10^{-5} mol/cm ³)
PI 02	2.00	3.733 ± 0.312
PI 03	3.02	6.107 ± 1.000
PI 05	5.01	10.853 ± 0.625
PI 07	7.02	15.175 ± 1.750

Table 4.2 Induction time and recovery time of pure polyisoprene systems and polythiophene/polyisoprene blends

Samples	Electric field (kV/mm)	Induction time (τ_{ind})(s)	Recovery time (τ_{rec}) (s)	$\Delta G'_{ind}$	$\Delta G'_{rec}$
PI_03	1	107	76	195	188
	2	75	83	110	106
PI 05	2	73	74	202	175
PI 07	2	78	64	851	821
Pth_U20/PI_03	1	157	59	2257	35
	2	121	66	4794	80

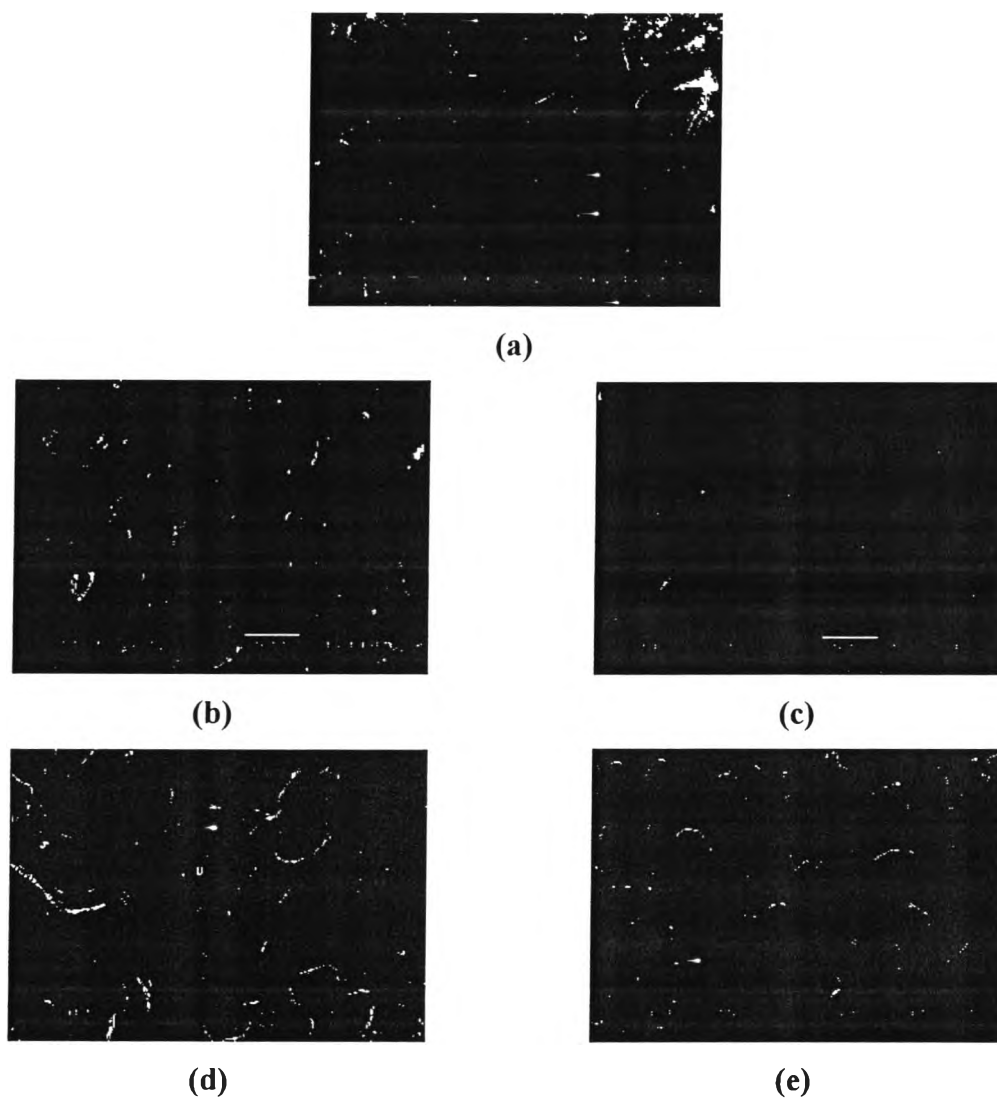
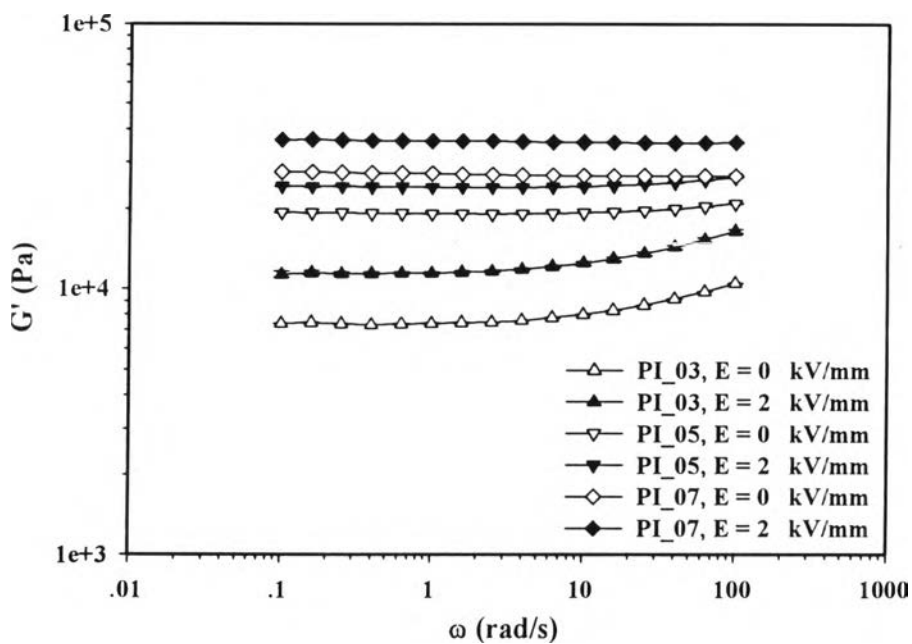
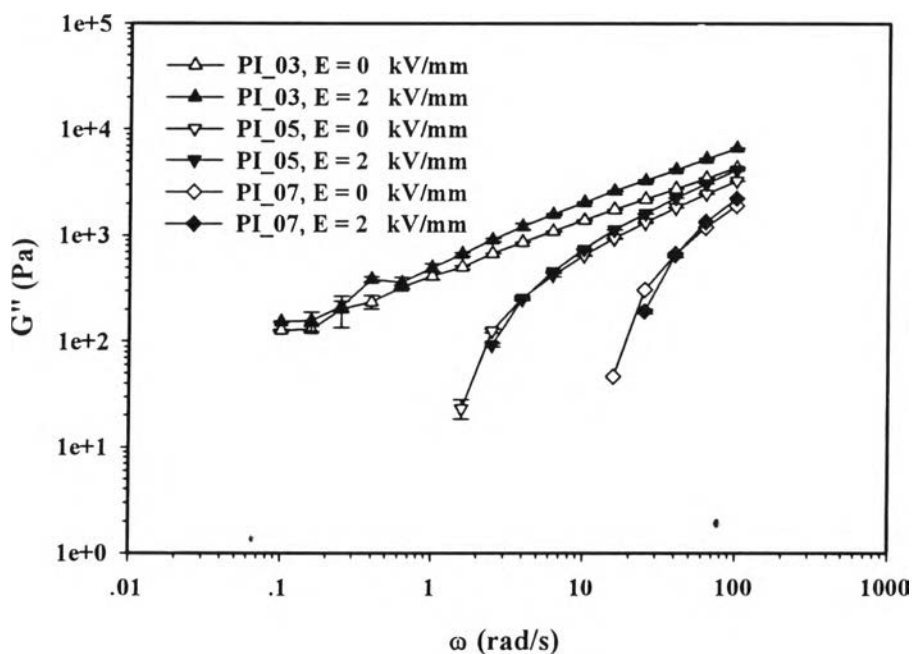


Figure 4.1 The morphology of polythiophene particles and polythiophene/polyisoprene blends: a) synthesized P3TAA at magnification of 1,500; b) Pth_U5/PI_03; c) Pth_U10/PI_03; d) Pth_U20/PI_03; and e) Pth_U30/PI_03 at magnification of 350.



(a)



(b)

Figure 4.2 Storage and loss moduli of polyisoprene systems at various crosslinking ratios vs. frequency, strain 1%, 27°C, and at electric field strengths 0 and 2 kV/mm: (a) storage modulus, $G'(\omega)$; (b) loss modulus, $G''(\omega)$.

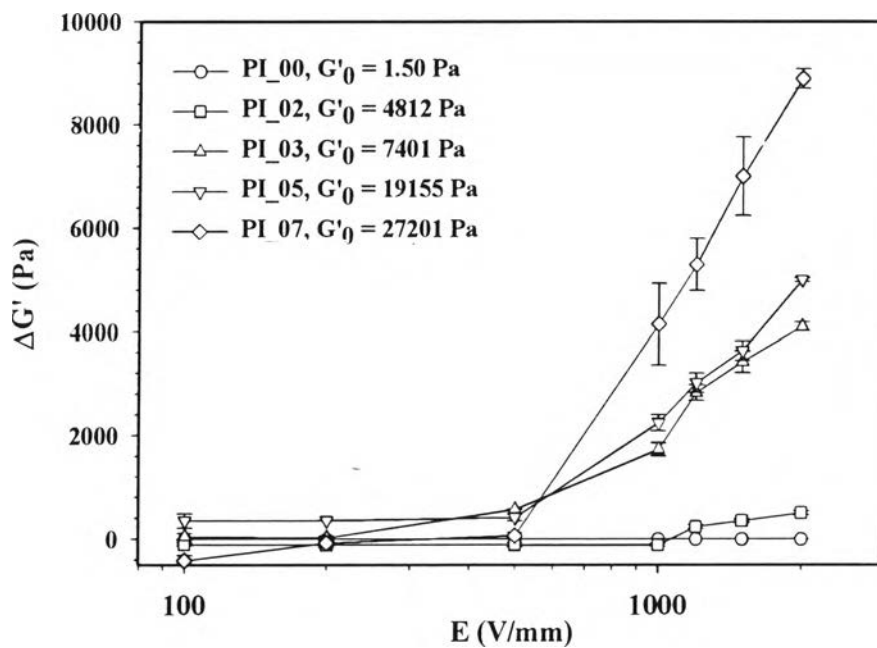


Figure 4.3 Storage modulus responses of the polyisoprene at various crosslinking ratios vs. electric field strength, at frequency 1 rad/s, strain 1%, (PI_00 system, strain 220%), and at 27°C.

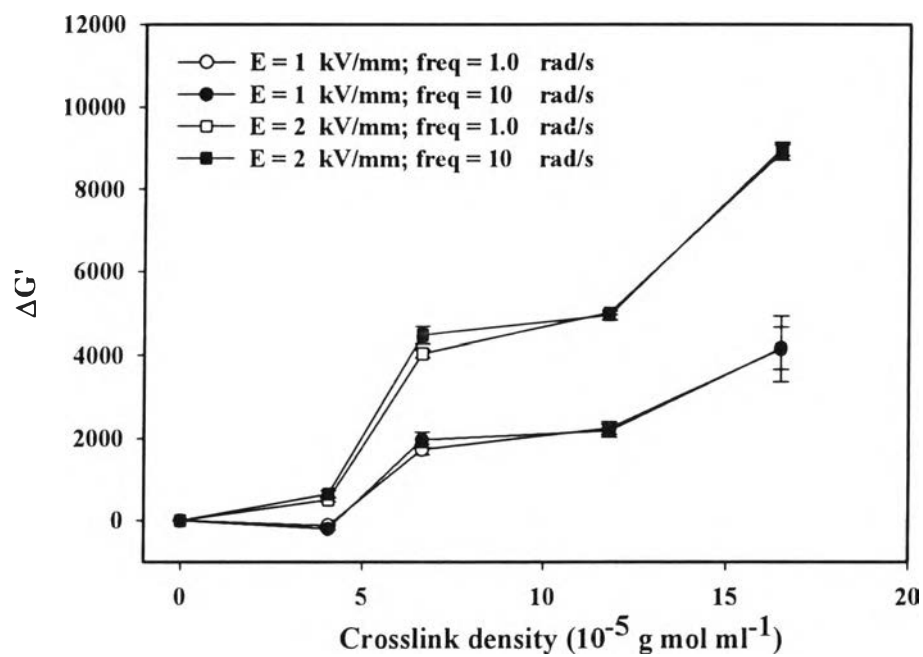
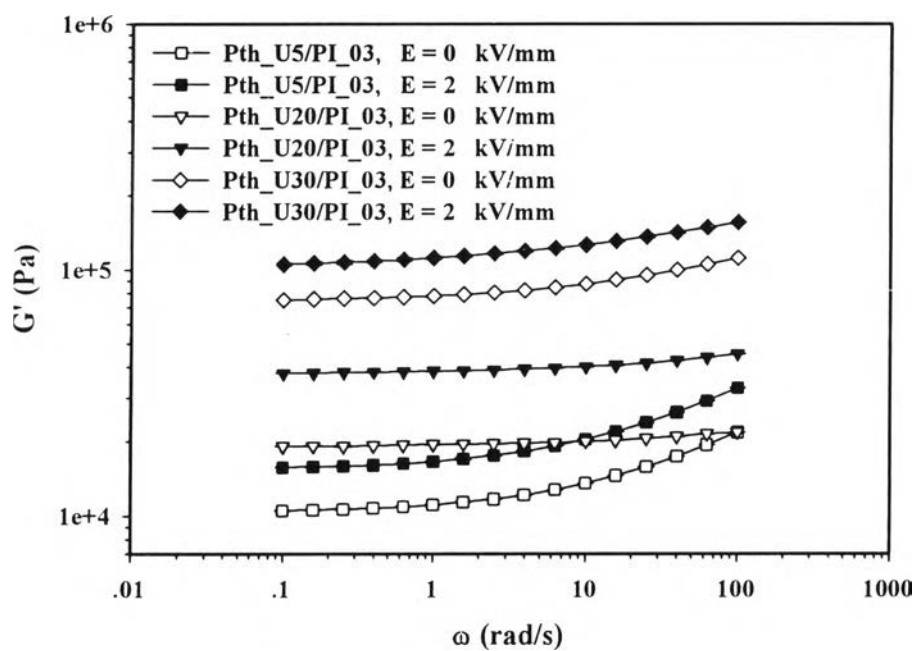
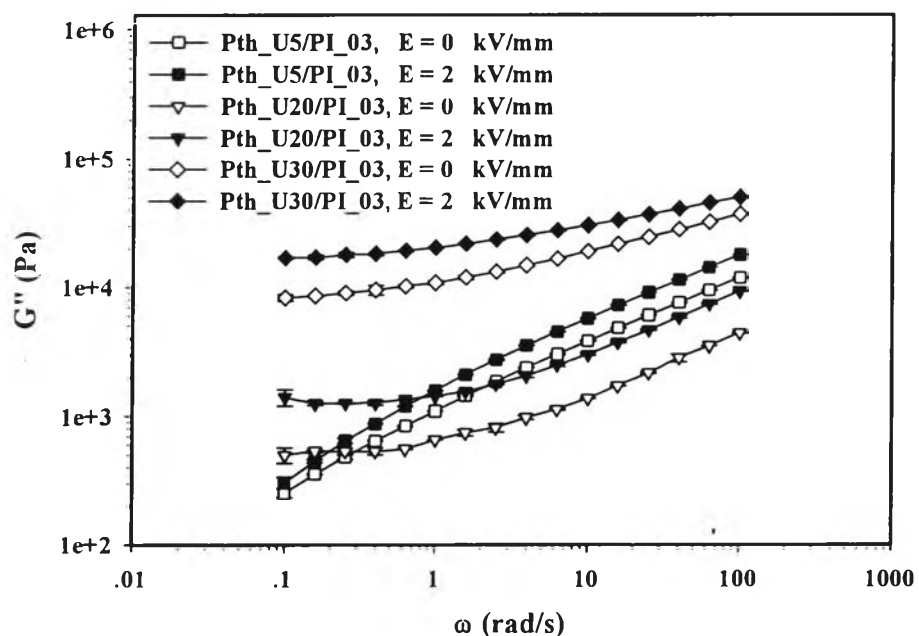


Figure 4.4 Storage modulus responses vs. crosslinking density at 27°C, various frequencies, and at electric field strengths of 1 and 2 kV/mm.



(a)



(b)

Figure 4.5 Comparison of the storage and the loss moduli of polyisoprene and polythiophene/polyisoprene blends (Pth_U/PI_03) at various particle concentrations (5,10, 20, and 30 vol.%), strain 1 %, 27°C, and at electric field strengths of 0 and 2 kV/mm: (a) storage modulus; G' , (b) loss modulus, G'' .

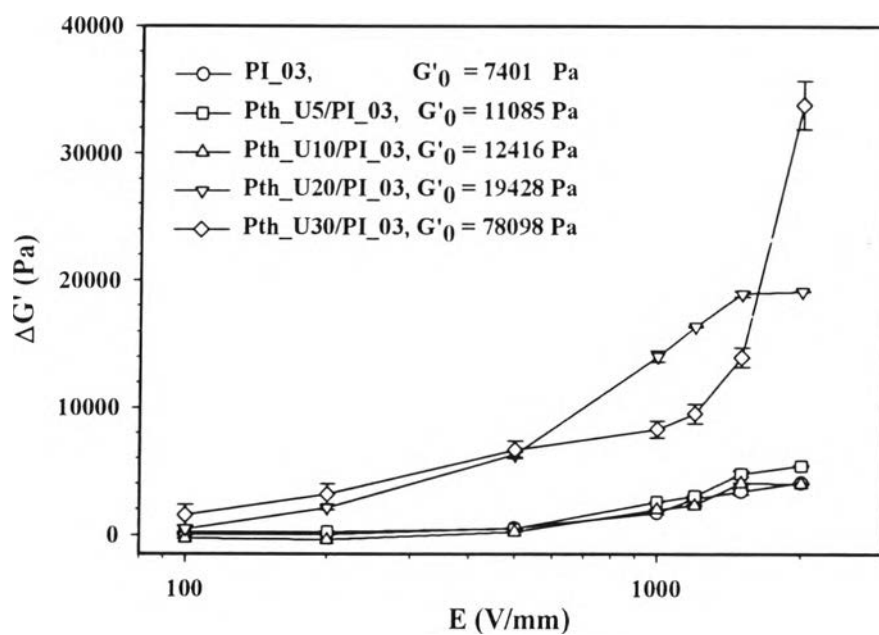


Figure 4.6 Storage modulus responses ($\Delta G'$) of the polythiophene/polyisoprene blends (Pth_U/PI_03) at various particle concentrations vs. electric field strength, at frequency 1 rad/s, strain 1 %, and at 27°C.

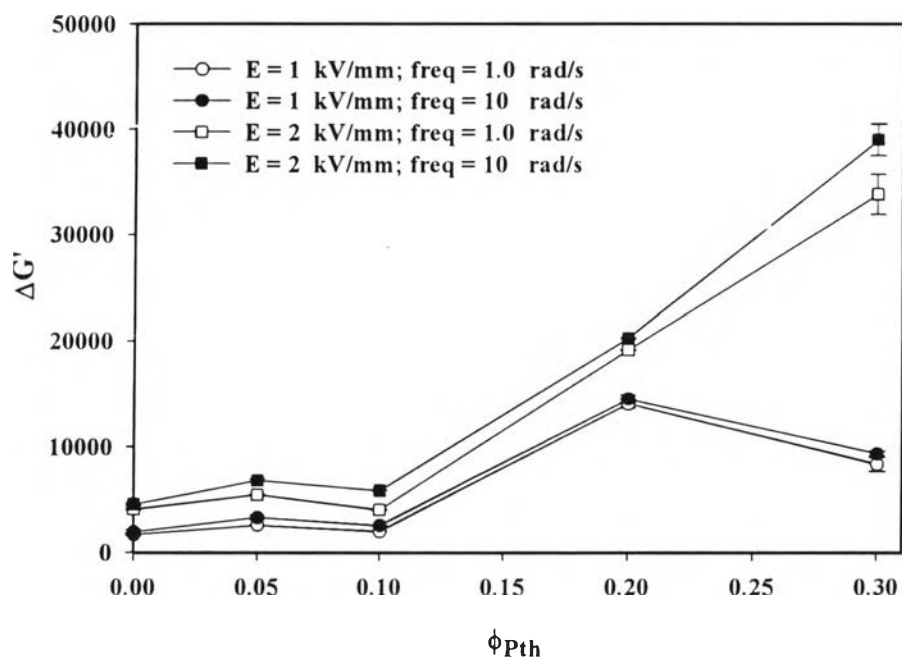


Figure 4.7 Storage modulus responses ($\Delta G'$) of the polythiophene/polyisoprene blends as functions of particle volume fraction, 27°C, of various frequencies, and at electric field strengths of 1 and 2 kV/mm.

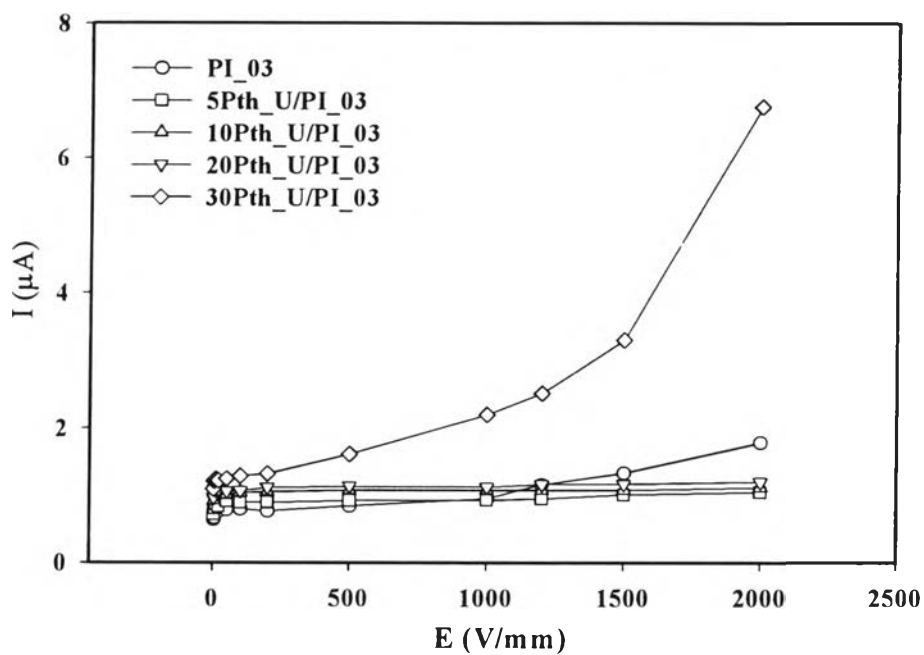
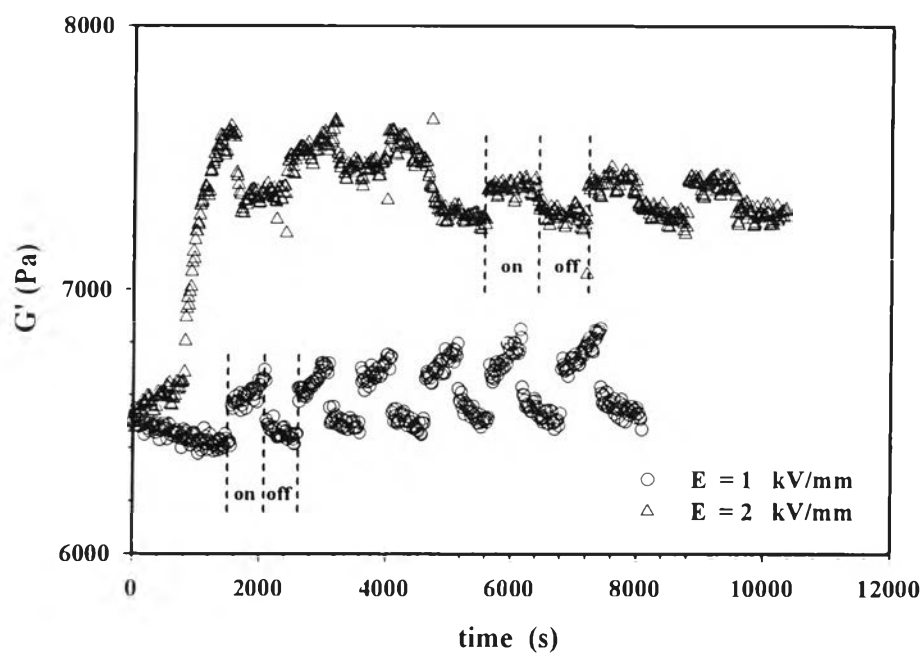
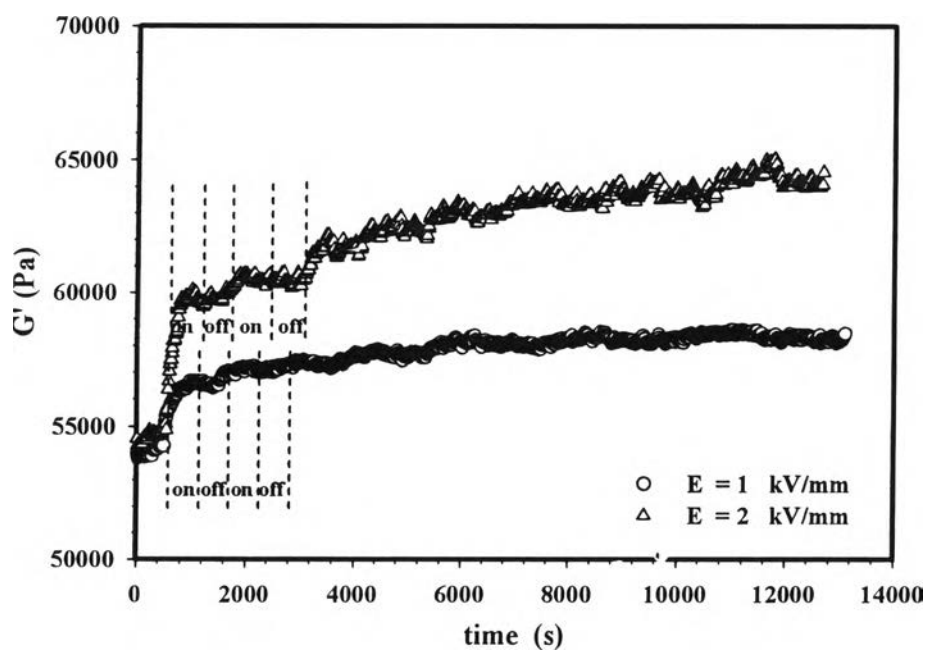


Figure 4.8 Current (I) vs. the applied electric field strength (E) of the polyisoprene system and polythiophene/polyisoprene blends system at various polythiophene particle concentrations, and at 27°C.



(a)



(b)

Figure 4.9 Temporal response of storage modulus (G') of: (a) PI₀₃ system at various electric field strengths (1 and 2 kV/mm); (b) Pth_U20/PI₀₃ system at various electric field strengths (1 and 2 kV/mm), and at temperature of 27°C.