



## CHAPTER V MANUSCRIPT

### **Electroactive Polydiphenylamine/Styrene-Isoprene-Styrene (SIS) Blends: Effects of Particle Concentration and Electric Field**

K. Thongsak<sup>1</sup>, A. Sirivat<sup>1,\*</sup>, and W. Lerdwijitjarud<sup>2</sup>

<sup>1</sup>*The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, 10330, Thailand.*

<sup>2</sup>*Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Sanamchandra Palace Campus, Nakhon Pathom 73000, Thailand.*

#### **Abstract**

Polymer blends between dedoped-polydiphenylamine (De\_PDPA) and Styrene-isoprene-styrene triblock copolymer with 19 %wt PS (D1114P, Kraton) were prepared to investigate their electrorheological (ER) properties. Polydiphenylamine was synthesized by the interfacial oxidative polymerization and dedoped with ammonium aqueous solution. ER properties were measured under a shear mode in the frequency range of 0.1-100 rad/s, at various electric fields strength of 0 to 2 kV/mm. At 27°C and 1 rad/s, storage modulus sensitivities ( $\frac{\Delta G'}{G'_0}$ ) of the blends with 0, and 5 %vol are small, but dramatically increase at concentration above 5 %vol, consistent with the increase in the dielectric constant dielectric constant. The sensitivities are reduced when the particle concentration is above 20 %vol (2 kV/mm) or 10 %vol (1 kV/mm). With increasing temperature, the storage modulus ( $G'$ ) of 20 %vol blend linearly increased up to the maximum value at 330 K, at 1 kV/mm and decreases beyond that. The blends of 20 and 30 %vol also show the similar behavior, the modulus increase to the maxima value at 310 and 350 K, and abruptly decrease above those temperatures. From the deflection testing of the

blends, the deflection response increases with increasing particle concentration up to 10 %vol blend and decreases at concentration higher than 10 %vol.

**Keywords:** Electrorheological properties, Styrene-Isoprene-Styrene, blockcopolymer, Polydiphenylamine, morphology, Dynamic moduli

\* Corresponding author.

*Email address:* [anuvat.s@chula.ac.th](mailto:anuvat.s@chula.ac.th), Tel: 662 218 4131, Fax: 662 611 7221

## Introduction

Electroactive materials are utilized in many forms such as artificial muscles, muscle/insect-like actuators, and robotics (Krause *et al.*, 2001) [1]. They have recently received much attention and continuously developed since these materials can converse electrical energy into mechanical energy. Electroactive polymers, belonging to a type of electroactive materials, offer novel characteristics such as light weight, flexibility, and high energy density. Elastomer, a dielectric material, is one type of electric-field-activated electroactive polymers. It is able to produce fast response, large strains and relatively high efficiency (Kornbluh *et al.*, 2002) [2].

Therefore, several elastomers have been used as the dielectric elastomer. Polyisoprene has many advantageous characteristics such as flexibility, low swelling in water, high tensile strength, good resilience, high tensile strength, and well behaved hysteresis, and etc. These characteristics are important to induce large actuation strain when polyisoprene is subjected to an electric field. Nevertheless, crosslinking is required to obtain those properties of polyisoprene (Puvaratvttana *et al.*, 2008) [3] through a difficult process. Thus, using styrene-isoprene-styrene triblock copolymer (SIS) is an interesting and alternative material. SIS is a thermoplastic elastomer, which is a composite material of two immiscible polymer phases. It also has hard and glassy domains of styrene acting as the reinforcing phase within the soft and rubbery isoprene matrix; therefore it can increase the modulus and the yield strength relative to those of polyisoprene alone. Moreover, SIS has

elastomeric properties of crosslinked rubber that can easily be processed by conventional processing such as melting or solvent casting (Winter *et al.*, 1993) [4].

Recently, the blending of a dielectric elastomer with a conductive polymer has been investigated towards many applications. For instances, the polyaniline-polyisoprene blend film for selective determination of  $H_2O_2$  detection biosensor (H. Xue *et al.*, 2001) [5], the blending of polyaniline/EPDM elastomer to improve thermal stability (Schmidt *et al.*, 2004) [6], a solid state actuator based on the PEDOT/NBR system (Cho *et al.*, 2006) [7], and the blended polythiophene/polyisoprene elastomer for the electroactive actuator application (Puvaratvattana *et al.*, 2008) [3] are just a few. There are many possible conductive polymers that can be used. Polydiphenylamine is an interesting conductive polymer since it has a molecular structure similar to polyaniline. It also can be easily synthesized by oxidative polymerization and easily doped with the acid solution of pH below 6.

In our work, we are interested in developing and testing blended polydiphenylamine/SIS thermoplastic elastomer for actuator applications. The mechanical properties, viscoelastic properties, and electrical properties will be investigated in terms of polydiphenylamine particle concentration and electric field strength.

## 2. Experimental

### 2.1 Materials

Diphenylamine, DPA (AR grade, Fluka), was used as a monomer. Hydrochloric acid, HCl (AR grade, Lab Scan), was used as an oxidant. Ammonium persulfate,  $(NH_4)_2S_2O_8$  (AR grade, Riedel-de Haën), was used as an initiator. Toluene,  $C_7H_8$  (Lab Scan, AR grade), was used as a solvent. Ammonium hydroxide solution,  $NH_4OH$ , (AR grade, Panreac), was used as a dedopant. Styrene-Isoprene-Styrene triblockcopolymer, SIS (D1114P (19 %wt PS), Kraton), was used as a polymer matrix.

### 2.2 Synthesis and doping of polydiphenylamine(PDPA)

Polydiphenylamine (PDPA) was synthesized through the interfacial polymerization according to Orlov *et al.*, (2005) [8] method. A 0.2 M solution of diphenylamine in toluene, a monomer solution, a 0.25 M solution of ammonium persulfate, a 1 M solution of HCl were prepared. The solutions were first cooled to  $-2 - 0^{\circ}\text{C}$  and then mixed momentarily. The reaction was carried out under intense stirring and temperature was kept at  $-2 - 0^{\circ}\text{C}$ , for 4 h. Reaction mixture was precipitated into a 5-fold excess of isopropyl alcohol, filtered and washed many times with distilled water to neutralize the reaction. After vacuum dried at  $27^{\circ}\text{C}$  for 24 h, the polymer obtained is a dark green powder.

The polymer was dedoped by stirring 1 g of polymers powder in a 20 ml of 1 M ammonium hydroxide solution and a 5 ml of ethanol over night, washed with ethanol/ $\text{H}_2\text{O}$  (3/1 (v/v)), and then vacuum dried at room temperature, the polymer obtained is a purple powder (Hua and Ruckenstein., 2003) [9].

### 2.3 Preparation of De\_PDPA/D1114P Blends Solution Casting

The blends were prepared by mechanical blending of De\_PDPA with an SIS triblock copolymer (D1114P) (Kunanuruksapong *et al.*, 2007) [10]. D1114P was dissolved in toluene and stirred for about 2 hours. Then De\_PDPA powder was added to obtain 10 % (w/v) toluene solution and further stirred for 24 h. The dispersion of particle was quite random. Concentrations of De\_PDPA in D1114P prepared were 5, 10, 20, and 30 %vol. The films were casting in a mold and left in air for the slow removal of the solvent, and then vacuum-dried to reduce stresses and residues at  $120^{\circ}\text{C}$  for 24 hours (winter *et al.*, 1993) [4].

### 2.4 Characterization and testing of De\_PDPA and the blends

The identification of functional groups of the D\_PDPA and De\_PDPA was investigated by a Fourier Transform Infrared spectrophotometer or FT-IR (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 PDPA particles were ground with a mortar, mixed with KBr at a ratio of PDPA:KBr = 1:20.

A thermal gravimetric analyzer (Perkin Elmer, TGA7) was used to study thermal stability, moisture content and decomposition temperature of De\_PDPA with the temperature scan from 30 to 800 °C at a rate of 10 °C/min. The sample was weighed in the range of 5-10 mg and loaded into a platinum pan.

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, model JSM-5200) to determine the morphology of D\_PDPA and De\_PDPA in powder forms, D1114P, and De\_PDPA/D1114P blends at various particle concentrations. The scanning electron micrographs of the conductive polymers and polymer blends were obtained by using an acceleration voltage of 15 kV with magnifications of 1500 and 2000 times.

The density of D\_PDPA and De\_PDPA was determined by using a ultrapycnometer (Ultrapycnometer 1000, V 2.4) with a small cell size. The polymers were firstly vacuum-dried for 24 h and then weighted at ambient temperature, and then loaded into the cell. Density determination was carried out 10 times for each sample for a run under the flow purge mode, the target gas pressure of 17 psi, and calibration volumes:  $V_{\text{added}} 12.4159 \text{ cm}^3$ ;  $V_{\text{cell}} 20.8093 \text{ cm}^3$ .

Particle sizes of D\_PDPA and De\_PDPA were determined by using a particle size analyzer (Malvern Instruments Ltd. Masterizer X Version 2.15). The lens used in this experiment was 45 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the standard size distribution.

Electrical conductivity of D\_PDPA, De\_PDPA, D1114P and De\_PDPA/D1114P blends was measured by using a custom-built two-point probe and a resistivity test fixture (Keithley 8009 resistivity test fixture) connected with a source power supplier (Keithley/ Model 6517A). The specific conductivity of De\_PDPA was carried out by using the two-point probe using the following Eq. (1):

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (1)$$

where  $\sigma$  is the specific conductivity (S/cm),  $\rho$  is the specific resistivity ( $\Omega \cdot \text{cm}$ ),  $R_s$  is the sheet resistance ( $\Omega/\text{sq}$ ),  $t$  is the thickness of sample pellet (cm),  $V$  is the applied

voltage (Voltage drop)(V),  $I$  is the measured current (A), and  $K$  is the geometric correction factor of the two-point probe meter which can be determined by using standard materials whose specific resistivity values are known, silicon wafer chips ( $\text{SiO}_2$ ). The correction factor was investigated by using following equation, (2):

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} \quad (2)$$

where  $\rho$  is the resistivity of a standard silicon wafer ( $\Omega \cdot \text{cm}$ ),  $R$  is the resistance of film ( $\Omega$ ). In the case of D1114P and De\_PDPA/D1114P blend films, the conductivity was carried out by using the resistivity testing fixture using the following Eq.(3):

$$\sigma = \frac{1}{\rho} = \frac{t \times I}{22.9 \times V} \quad (3)$$

where  $\sigma$  is specific conductivity (S/cm),  $\rho$  is the specific resistivity ( $\Omega \cdot \text{cm}$ ),  $t$  is the sheet resistivity ( $\Omega$ ),  $I$  is the measured current (A),  $V$  is the applied voltage (voltage drop) (V).

A melt rheometer (Rheometric Scientific, ARES) was used to measure electrorheological 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 the voltage input. The oscillatory shear strain was applied and the dynamic moduli ( $G'$  and  $G''$ ) were measured as functions of frequency, temperature, and electric field strength. Strain sweep tests were first carried out to determine the suitable strains to measure  $G'$  and  $G''$  in the linear viscoelastic regime. The appropriate strains of De\_PDPA/D1114P blends at 0, 5, 10, 20, and 30 %vol are 0.2, 0.2, 0.3, 0.1, and 0.3 %, respectively. The frequency sweep tests were carried out to measure  $G'$  of each sample as functions of frequency, temperature, and electric fields (0, 1, and 2 kV/mm). The deformation frequency was varied from 0.1 to 100 rad/s. Each sample was presheared at a low frequency (0.039811 rad/s), and then the electric field was applied for 30 minutes to ensure the formation of equilibrium polarization before the  $G'$  measurements. Experiments were carried out at the temperature of 27 °C and repeated at least two or three times. The effect of temperature in D1114P and De\_PDPA/D1114P blends was studied at various temperatures in the range of 27-117 °C. In the effect of electric field strength

the experiments were taken with various electric fields (0, 1, and 2 kV/mm). Temporal response measurements of the polymer blends were carried out at electric field strength 0 and 2 kV/mm.

Deflection of D1114P and the polymer blends were measured under various applied electric strengths. For each of films, one end of the sample was fixed with grip vertically in the chamber, which consisted of two electrodes and poly(dimethylsiloxane) with viscosity of 100 cP. The input DC field was generated by a DC power supply (Gold Sun 3000, GPS 3003D) and a high voltage power supply (Gamma High Voltage, UC5-30P) which delivered to a pair of copper electrodes various electric field strength from 25 to 600 V/mm. All of experiments were carried out at ambient temperature. A video recorder was used to record the displacement of the film made a model (Figure 5). The tip displacement was measured through a Scion Image (Beta 4.0.3) program.

### 3. Results and Discussions

#### 3.1 Characterization of De\_PDPA and De\_PDPA/D1114P blends

The FT-IR spectra of D\_PDPA and De\_PDPA were recorded to identify characteristic absorption peaks. The peaks of the polymers found are at  $3400\text{ cm}^{-1}$ ,  $3100\text{-}3000\text{ cm}^{-1}$ ,  $1595\text{-}1506\text{ cm}^{-1}$ ,  $1450\text{ cm}^{-1}$ ,  $1317\text{ cm}^{-1}$ , and  $812\text{ cm}^{-1}$ . These peaks are assigned to the N-H stretching of amine site; the C-H stretching of aromatic ring; the C=C stretching of aromatic ring; the C=N stretching; the C-N stretching at benzenoil ring; and the 1,4 disubstitute of benzene ring, respectively (Santana *et al.*, 2003 and Zhao *et al.*, 2005) [11-12]. The characteristic peak of the D\_PDPA and De\_PDPA is at  $3400\text{ cm}^{-1}$ ; the sharp peak of the N-H stretching is reduced in intensity as the doping mole ratio ( $N_{\text{HCl}}/N_{\text{monomer}}$ ) is increased. This can be attributed to the fact that the doped PDPA at a higher doping mole ratio has more counter ions (Cl<sup>-</sup>) available to attack the amine sites. The electron density at those sites is reduced, producing an attractive force between the counter ions and and H-atoms thus the stretching of N-H is consequently reduced.

The TGA thermogram of De\_PDPA indicates the degradation of De\_PDPA main chains beyond the temperature of  $440^{\circ}\text{C}$ .

De\_PDPA particle microstructure and the particle dispersion in D1114P matrix were observed using a scanning electron microscope (SEM) as shown in Figure 1 (a). The microstructure shows that the shapes of the De\_PDPA particles are quite irregular in shape and they cluster to each other. Figures 1 (b)-(e) show the De\_PDPA/D1114P blends with 5, 10, 20, and 30 %(v/v) of De\_PDPA; the micrographs show that the De\_PDPA particles are dispersed almost uniformly within the D1114P matrix.

The density of De\_PDPA is  $1.3156 \text{ g/cm}^3$  with a standard deviation of  $0.00061 \text{ g/cm}^3$ . This was determined through Ultracycrometer under flow purge mode at  $27^\circ\text{C}$ . The density determination was carried out 10 times for a run under the flow purge mode.

The particle size of the De\_PDPA was characterized by using a particle size analyzer which is around  $8.27 \mu\text{m}$  with a standard deviation of  $0.065 \mu\text{m}$ .

The specific conductivity was measured by a custom-built two point probe (Keithley, Model 6517A) for De\_PDPA and by using the resistivity testing fixture for De\_PDPA/D1114P blend films. The specific conductivity of De\_PDPA is  $2.89 \times 10^{-6} \text{ S/cm}$  with a standard deviation of  $3.15 \times 10^{-7}$ . The conductivity of De\_PDPA/D1114P blends with particle concentrations of 0, 5, 10, 20, and 30 %(v/v) are  $1.28 \times 10^{-19}$ ,  $2.24 \times 10^{-16}$ ,  $2.65 \times 10^{-15}$ ,  $2.25 \times 10^{-14}$ , and  $4.80 \times 10^{-14}$  with standard deviations of  $1.58 \times 10^{-20}$ ,  $1.06 \times 10^{-17}$ ,  $1.41 \times 10^{-16}$ ,  $5.36 \times 10^{-15}$ , and  $8.30 \times 10^{-15}$ , respectively.

### 3.2 Electrorheological Properties

#### *Effect of Temperature*

The effect of temperature on the rheological properties of the polymer blends between polydiphenylamine (De\_PDPA) and D1114P with concentration of 0, 5, 10, 20, and 30 %vol was investigated at electric field strengths of 0, 1, and 2 kV/mm with the temperature range between 300-390 K, frequency of 1.0 rad/s, and used strains as shown in Table 1. Figure 2(a)-(b) shows the storage moduli  $G'_{1\text{kV/mm}}$  and  $G'_{2\text{kV/mm}}$  vs. absolute temperature. In this experiment, we used one sample each for the  $G'_o$ ,  $G'_{1\text{kV/mm}}$  and  $G'_{2\text{kV/mm}}$  measurements. Without electric field applied,  $G'_o$



was measured successively at each temperature. Electric field was first applied on another sample for a period of 30 minutes before  $G'_{1\text{kV/mm}}$  and  $G'_{2\text{kV/mm}}$  were measured successively at each temperature.

From Figure 2(a) within the temperature range of 300-360 K, the storage modulus ( $G'_{1\text{kV/mm}}$ ) of each sample significantly changes with increasing temperature except those of the 20 and 30 %vol blends. The modulus ( $G'_{1\text{kV/mm}}$ ) of the 20 %vol blend increases linearly up to 330 K at electric field of 1 kV/mm, and gradually decreases after that. Moreover, at 330-360 K, the 20 %vol blend shows a greater storage modulus ( $G'_{1\text{kV/mm}}$ ) than those of the polymer blends of 30, 10, 5 and 0 %vol, respectively. This characteristic also appears under electric field strength 2 kV/mm. Figure 2(b) shows gradually increases ( $G'_{2\text{kV/mm}}$ ) with temperature of low particle concentration polymer blends: 0, 5, and 10 %vol at above 340 K. The modulus of highest particle concentration polymer blend (30 %vol) exhibits a higher modulus than the 20 %vol. For the 30 %vol blend, the modulus faintly increases below 310 K, but abruptly decreases above that. The 20 %vol blend modulus slightly increases up to 350 K then decreases dramatically beyond that temperature.

These results suggest that as more particles are added, the particle act as the filler which increases the storage moduli and the responses of the blends, but it affects the polystyrene network in the matrix also. The pure D1114P modulus increases above 320 K in plastic behavior regime (Sato *et al.*, 1996) [13]; it is related to microdomain of polystyrene segment which is still preserved at these immediate temperatures which are in a softened state. Therefore, the more added particle acts as plasticizer to reduce this effect of polystyrene at high temperature. As the distances between the particles become closer, the inter-particle interaction becomes stronger depending on the applied electric field. At the electric field strength of 2 kV/mm (Figure 2(b)), this is a strong enough electric field to increase the  $G'_{2\text{kV/mm}}$  of the 30 %vol blend. At 1 kV/mm (Figure 2(a)), the electric field is too weak to induce the inter-particle interaction for the 30 %vol blend to overcome the effect of filler on the storage modulus ( $G'_o$ ). In Figures 2(a) and (b), the maximum storage modulus occur at temperatures of 330, 310, and 350 K for 20 %vol blend at 1 kV/mm, 30 and 20 %vol blends at 2 kV/mm, respectively. Above the maximum temperature, the

matrix became more soft resulting in the decreases of the storage moduli and the response as the effect of particle concentration.

### *Effect of particle concentration*

The polymer blends between De\_PDPA and D1114P were investigated on the effect of De\_PDPA particle concentration on the electromechanical properties. The morphology of the dispersed phase is random. De\_PDPA concentrations of the blends are 0, 5, 10, 20, and 30 % vol. All experiments were carried out at the frequency of 1.0 rad/s, using strains as shown in Table 1.

Figure 3(a) shows the storage modulus response ( $\Delta G'$ ) vs. conductive polymer particle concentration at electric field strength 1 and 2 kV/mm, and at 27°C. The polymer blends exhibit linear increases in the storage modulus responses beyond 5 %vol of De\_PDPA particle concentration at the electric field of 2 kV/mm. At 1 kV/mm, the response appears to increase slightly. It can be seen the response is maximum at the particle concentration of 20 %vol.; it is equal to 20375 Pa. In Figure 3(b), the polymer blend sensitivity values ( $\Delta G'_{2\text{kV/mm}}/G'_0$ ) non-linearly increase with increasing particle concentration above 5%vol at 2 kV/mm. The sensitivity reaches the maximum value of 1.381 at 20 %vol and then decreases beyond that. At 1 kV/mm, the sensitivity slightly increases up to 0.2566 at 10 %vol and then slightly decreases beyond this concentration. In this figure, we also show the storage moduli ( $G'$ ) at each electric field. The moduli exhibit abrupt increases above 10 %vol of polymer concentration under applied electric field. For a small amount of particles added, the storage moduli ( $G'$ ) slightly change between 0-10 %vol. In this concentration range, the conductive polymer fillers induce only additional free volumes, the number of particles is too small resulting to the distances between particles are too large to create a significant particle interaction through the electric field-induced dipole moments. Therefore, the sensitivity is low at low particle concentrations. As more particles are added to the D1114P matrix, the dielectric constant is increased (Figure 3(c)) and the distances between particles become smaller and stronger inter-particle interactions result. The induced dipole moments can be thought of generating an equivalence of electric network strands which apparently increase the storage modulus response and sensitivity. The change in the

storage modulus response ( $\Delta G'$ ) is expected to be proportional the dielectric constant and applied electric square, as described by Shiga and coworkers [14]:

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

where  $\Delta G'$  is the storage modulus response,  $C$  is the volume fraction of particles,  $\varepsilon_m$  is the relative dielectric constant of matrix, and  $E$  is the applied electric field strength. For the polymer blend system at the highest particle concentration of 30 % vol, we obtain the highest  $G'_0$ . In this case, the effect of electric field is reduced since this system is elastically hardened by the added filler, and the phase separation may exist between the D1114P matrix and the conductive particles, and consequently a poor stress transfer occurs; additional increases in  $G'_{1\text{kV/mm}}$  and  $G'_{2\text{kV/mm}}$  with electric field are hindered. The decreases of the sensitivity occur beyond 10 and 20 %vol at electric field strengths of 1 and 2 kV/mm, respectively.

Kunanuruksapong *et al.*, (2007) [10] found the similar effect for poly(p-phenylene) particles and AR71 blends. They reported that the enhancement of shear modulus slightly occurred below 5 %vol, but increased abruptly above this concentration. The shear modulus appeared to decrease above 30 vol%, because the interparticle force decreased due to the steric hindrance effect of polymer particle. Shiga (1997) [14] reported the similar effect for poly(p-phenylene) and silicone elastomer blend. They found that the electroviscoelastic effect increased with increasing of particle content. They found that the enhancement of shear modulus was negligible below 8.4% vol.

### 3.3 Temporal response

D1114P and De\_PDPA/D1114P blends were studied for the temporal characteristic at electric field strengths 2 kV/mm. Each sample was tested in the linear viscoelastic regime at 27°C and at frequency of 1.0 rad/s, using the strains as shown in table 1. They were carried out in time sweep test in which the electric field was turned on and off alternately.

In Figure 4, the response of storage modulus ( $G'$ ) of De\_PDPA of the 20 and 30 %(v/v) blends appear to be reversible while 10 %De\_PDPA/D1114P shows an irreversible response. From the reversible systems, at electric field of 2 kV/mm,

$G'$  immediately increases and rapidly reaches a steady-state value. Then, with the electric field off,  $G'$  decreases but does not recover the original value. Subsequent applications of electric field in cycles, on and off, the response reaches steady state responses after durations of 9000 s for 20 %De\_PDPA/D1114P and 5000 s for 30 %De\_PDPA/D1114P. 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 decay with electric field off; and the steady state regime in which  $G'$  subsequently exhibits a reversible cyclic response. The time required for  $G'$  to reach the steady-state value on applying the field at steady state regime is called the induction time,  $\tau_{ind}$ . As shown in Table 2, the  $\tau_{ind}$  of 20 and 30 %DePDPA/D1114P are 886 and 597 sec. at electric field of 2 kV/mm. The time required for  $G'$  to decay towards its steady-state value when the electric field is turned off is called the recovery time,  $\tau_{rec}$ . From Table 2, these times are 886 and 906 sec. Both  $\tau_{ind}$  and  $\tau_{rec}$  are dependent on particle concentration of the blends,  $\tau_{ind}$  decreases with increasing particle concentration whereas  $\tau_{rec}$  increases with increasing of particle concentration, as shown in Figure 2. The dependence of  $\tau_{ind}$  on particle concentration suggests that in higher added particle system, the De\_PDPA particles are closer to each other resulting in a shorter time scale response under applied electric field. Whereas the higher  $\tau_{rec}$  value required to relax with higher particle concentration is because of some residual dipole moments of adjacent particles remain and interact with resulting in a longer relaxation time. Moreover, our result here may also suggest that there are some irreversible interactions between dedoped polydiphenylamine (De\_PDPA) particles, perhaps due to dipole bondings between adjacent De\_PDPA particles and residual dipole moments inducing permanent interparticle interactions (Chotpattananont *et al.*, 2004) [15].

### 3.4 Deflection response

Finally, Pure D1114P and De\_PDPA/D1114P bendings were observed in response to electric field. The samples were gripped between copper plates and immersed in poly (dimethylsiloxane). The positive current was applied to the copper plate as shown in Figure5. A video recorder was used to record the displacement of

the film made a model. The deflection distance in x axis ( $d$ ) and deflection length ( $l$ ) were measured through the analyzing program. The deflection angle was analyzed by calculating of arc tan between  $d$  and  $l$ .

Under external applied electric field strength, the free end samples bend toward to the positive site or the anode site by the interaction between electric field induced dipole moment of De\_PDPA particles and the anode site. Figure 6 shows the deflection distance of pure D1114P and the blends (De\_PDPA 10 and 30 %(v/v) blends). Both films deflections exhibit stepwise responses that increase depending on the electric field strength. From the figure, 10 %De\_PDPA/D1114P shows the highest response under electric field relative to others. Even though 30 %De\_PDPA/D1114P appears to start bending at a low electric field (75 V/mm), nevertheless the response becomes more poor than the 10 %(v/v) blend and pure D1114P since it has a lower deflection distance with increasing of electric field. The results suggest that the blend systems can respond to low electric field and deflect better than the pure system due to the interaction of conductive particles. However, the increasing of deflection is limited by the concentration of the conductive polymer. Adding more polymer particle affects the blend systems through a higher weight and a more rigidity resulting in the films which are harder to bend.

Figure 7 shows the dielectrophoretic force ( $F_d$ ) which can be calculated from the equation following:

$$F_d = F_e + mg \sin \theta \quad (5)$$

where  $m$  is the sample's weight (kg),  $g$  is the gravity ( $9.8 \text{ m/s}^2$ ),  $\theta$  is the deflection angle, and  $F_e$  is the load force or elastic force (N) from the field which was calculated through non-linear deflection theory by using the following equation [16, 17]:

$$F_e = \frac{dEI}{l^3} \quad (6)$$

where  $E$  is modulus of elasticity equal to  $2G'(1+\nu)$ ,  $G'$  is the shear modulus,  $\nu$  is poisson's ratio equal to 1/2 incompressible,  $I$  is the moment of inertia equal to  $t^3w/12$  which  $t$  is the sample thickness,  $w$  is the sample width,  $d$  is the deflection distance ( $d$ ), and  $l$  is the sample length.

The dielectrophoretic forces of the pure D1114P system and the blends system increase in stepwise fashions with increasing electric field. From the Figure 7, the true force can be calculate from the deflection distance is represented by filled symbols. Unfilled symbols represent the apparent force which is equal or lower than the true values.

In 2001, Feher *et al.* [18] detected the deflection and calculated dielectrophoresis force of PDMS containing  $\text{TiO}_2$  suspended in silicone oil between to parallel plate. They reported that the  $F_d$  is quadratically dependent on electric filed strength. This originates from the polarization of filled  $\text{TiO}_2$  under applied electric filed. In our work,  $F_d$  increases in a step-wise manner with the electric filed strength by polarization of De\_PDPA particles.. The response is at a maximum at the concentration of 10 %vol due the effect of De\_PDPA particles acting as a filler.

#### 4. Conclusion

In our study, the electrorheological properties of styrene-isoprene-styrene triblock copolymer with 19 %PS, D1114P and De\_PDPA/D1114P blends, were investigated at electric field strength varying from 0, 1, and 2 kV/mm. De\_PDPA was synthesized through the interfacial oxidative polymerization and then dedoped by ammonium hydroxide solution. The storage modulus response ( $\Delta G'$ ) increases beyond the concentration of 5 %vol De\_PDPA at an applied electric filed strengths of 1 and 2 kV/mm. However, the sensitivity is reduced at the high concentration, where the effect of electric field induced inter-particle interaction is strongly hampered by the increase in the storage modulus ( $G'_o$ ). Under temperature sweep, the response of 20 %vol at 1 kV/mm decreases after reaching the maximum via increasing temperature, in which the storage modulus ( $G'_o$ ) of the thermoplastic elastomer matrix is also reduced. Similar results also occur for the 20 and 30 %vol blends under the electric field strength of 2 kV/mm. The  $G'$  temporal responses, of the polymer blend systems of 20 and 30 %vol De\_PDPA, show a reversible behavior under applied electric field strength of 2 kV/mm. While the 10 %vol blend appears to be an irreversible system. This is due to dipole bondings between adjacent De\_PDPA particles and residual dipole moments inducing permanent inter-particle interactions.

The bending response was observed by measuring the deflection distance. For pure D1114P and the blends, the response and force increase stepwise under electric field. The response and calculated force increase with increasing particle concentration up to 10 %vol and then decrease at the concentration higher than 10 %vol.

## 5. Acknowledgements

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**Table 1** Rheological properties of D1114P and DePDPA/D1114P blends at 27°C, frequency 1.0 rad/s, under various electric field strengths

%v/v of De PDPA	% Strain	$G'_0$ (Pa)	$G'_{1kV/mm}$ (Pa)	$\Delta G'_{1kV/mm}$ (Pa)	$\Delta G'_{1kV/mm}/G'_0$	$G'_{2kV/mm}$ (Pa)	$\Delta G'_{2kV/mm}$ (Pa)	$\Delta G'_{2kV/mm}/G'_0$	$\sigma$ (S/cm.)
0	0.2	36579.1	31841.1	-	-	32130.6	-	-	$2.24 \times 10^{-19}$
5	0.2	37325.3	39554	2228.7	0.0597	39508.3	2183.0	0.0585	$2.65 \times 10^{-16}$
10	0.3	29329.9	36857.0	7527.1	0.2566	41654.3	12324.4	0.4202	$2.25 \times 10^{-15}$
20	0.1	88769.9	109145	20375.1	0.2295	212085	12331.1	1.3891	$4.80 \times 10^{-14}$
30	0.3	200060	218055	17995	0.0899	439275	239215	1.1957	$1.28 \times 10^{-14}$

All of materials were tested at frequency = 1 rad/s, strain 0.1% and, temperature = 27°C

$G'_0$  is the storage modulus without electric field

$G'_{1kV/mm}$  and  $G'_{2kV/mm}$  are the storage modulus at 1 and 2 kV/mm.

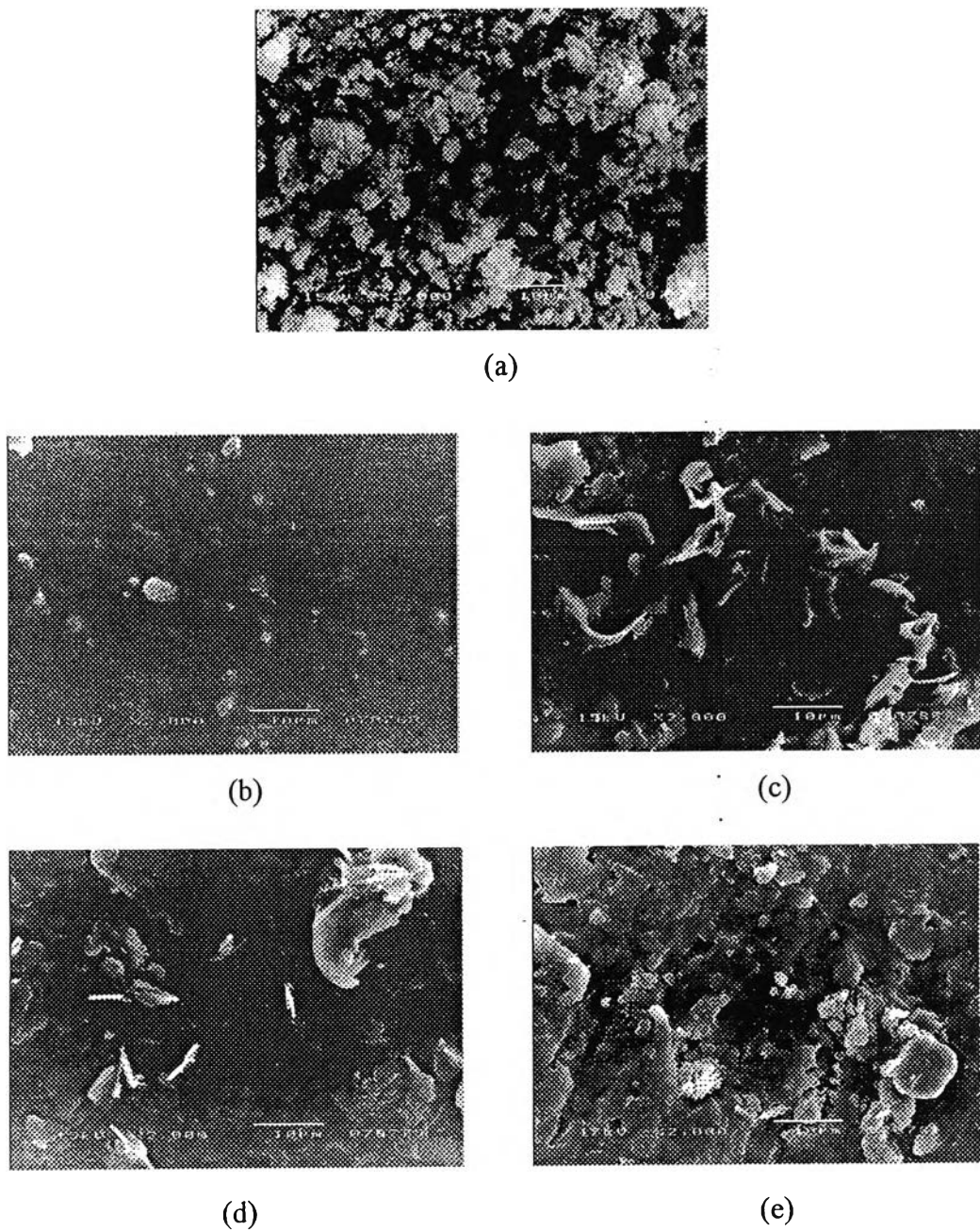
$\Delta G'_{1kV/mm}$  and  $\Delta G'_{2kV/mm}$  are the storage modulus response defined as  $G'_{1kV/mm} - G'_0$  and  $G'_{2kV/mm} - G'_0$ .

$\Delta G'_{1kV/mm}/G'_0$  and  $\Delta G'_{2kV/mm}/G'_0$  are the sensitivity of the storage modulus at electric field strength of 1 and 2 kV/mm.

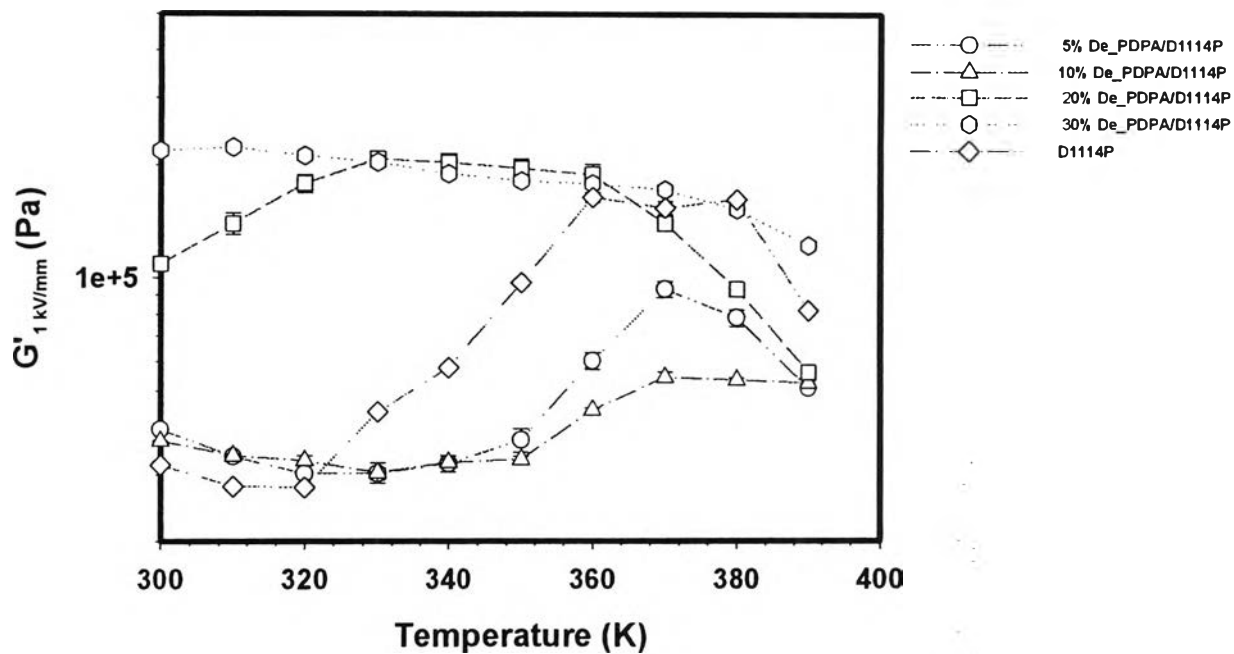
$\sigma$  is the electrical conductivity of polymer

**Table 2** Induction times and recovery times at 27°C of D1114P and De PDPA/D1114P blends

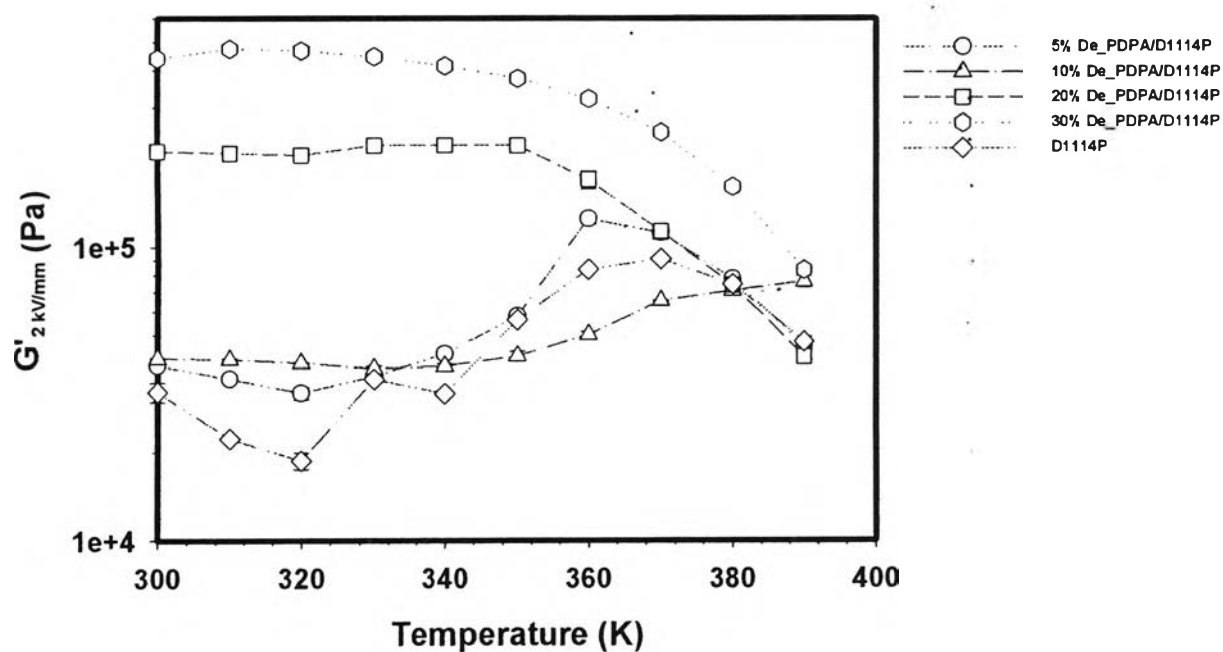
Samples	Electric field	First induction time	Saturated induction time	First recovery time	Saturated recovery time	First $\Delta G'_{ind}$	Saturated $\Delta G'_{ind}$	First $\Delta G'_{rec}$	Saturated $\Delta G'_{rec}$
	(kV/mm)	( $\tau_{ind}$ ) (s)	( $\tau_{ind}$ ) (s)	( $\tau_{rec}$ ) (s)	( $\tau_{rec}$ ) (s)	(Pa)	(Pa)	(Pa)	(Pa)
D1114P	2	-	-	-	-	-	-	-	-
5%DePDPA/D1114P	2	-	-	-	-	-	-	-	-
10%DePDPA/D1114P	2	679	-	-	-	3142	-	-	-
20%DePDPA/D1114P	2	917	886	908	886	143200	154208	120740	159535
30%DePDPA/D1114P	2	905	597	896	906	158368	76001	79927	81838



**Figure 1** SEM micrograms at magnification of 2000. 15 kV: (a) De\_PDPA; (b) 5%De\_PDPA/D1114P; (c) 10%De\_PDPA/D1114P; (d) 20%De\_PDPA/D1114P; (e) 30 %De\_PDPA/D1114P.

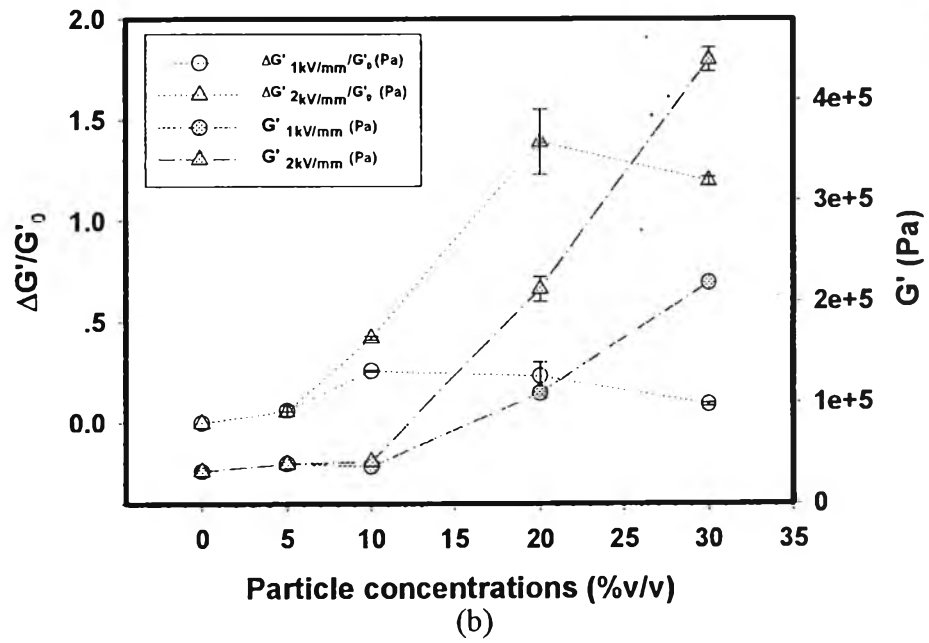
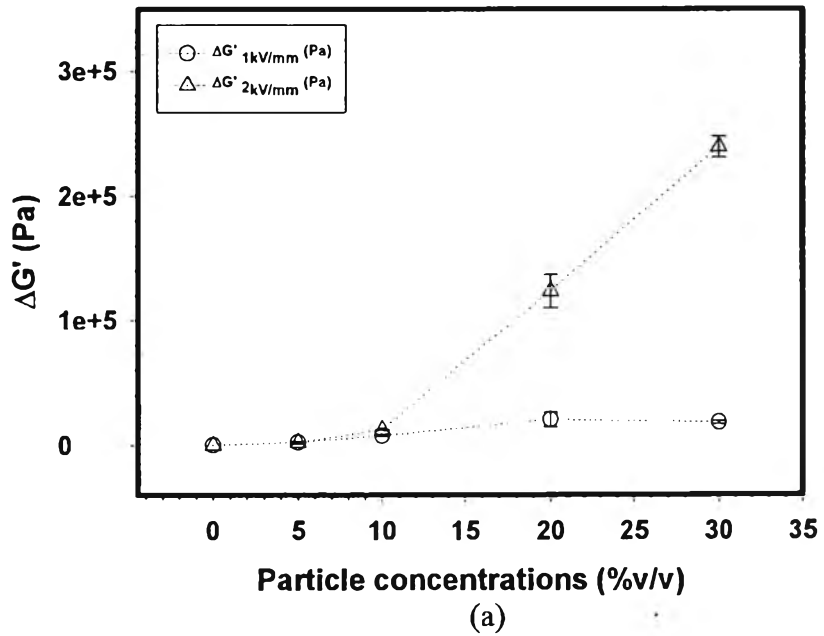


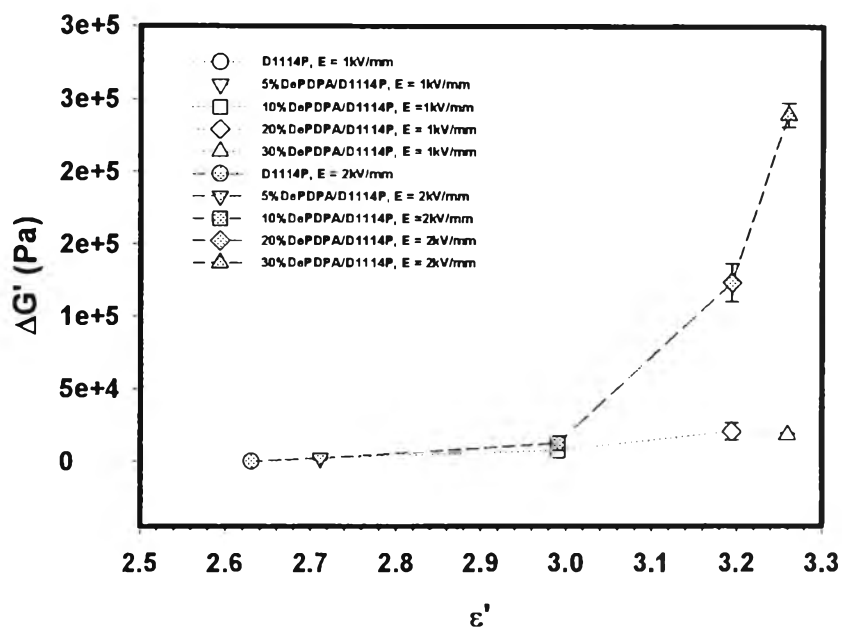
(a)



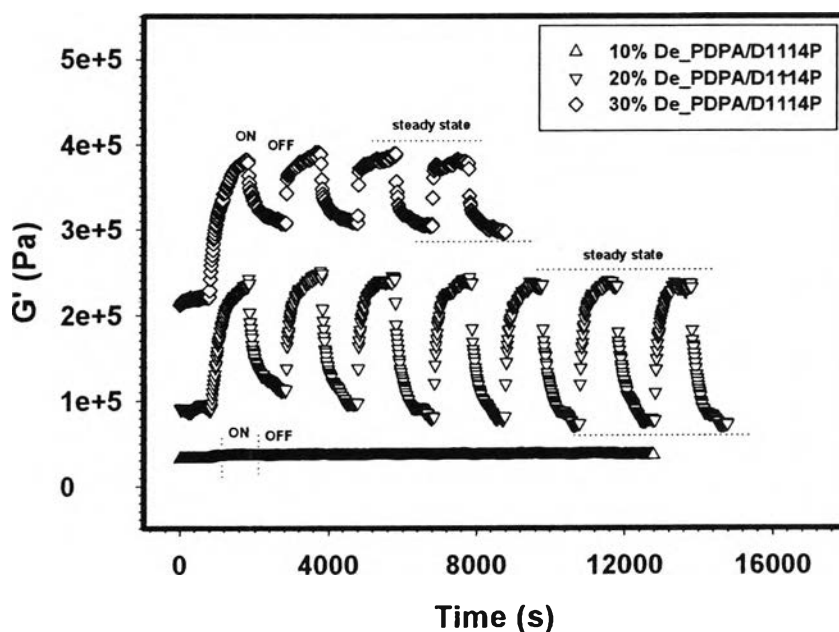
(b)

**Figure 2** Effect of temperature on storage modulus ( $G'$ ) of D1114P and De\_PDPA/D1114P blends, at frequency 1 rad/s: (a) the storage modulus at  $E = 1$  kV/mm at various temperatures for one sample at all temperatures tested; (b) the storage modulus at  $E = 2$  kV/mm at various temperatures for one sample at all temperatures tested.

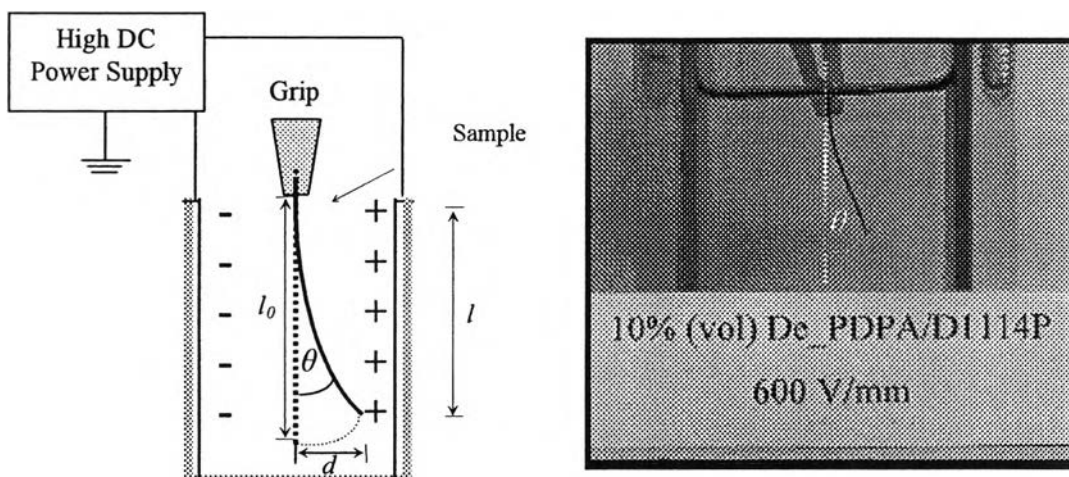




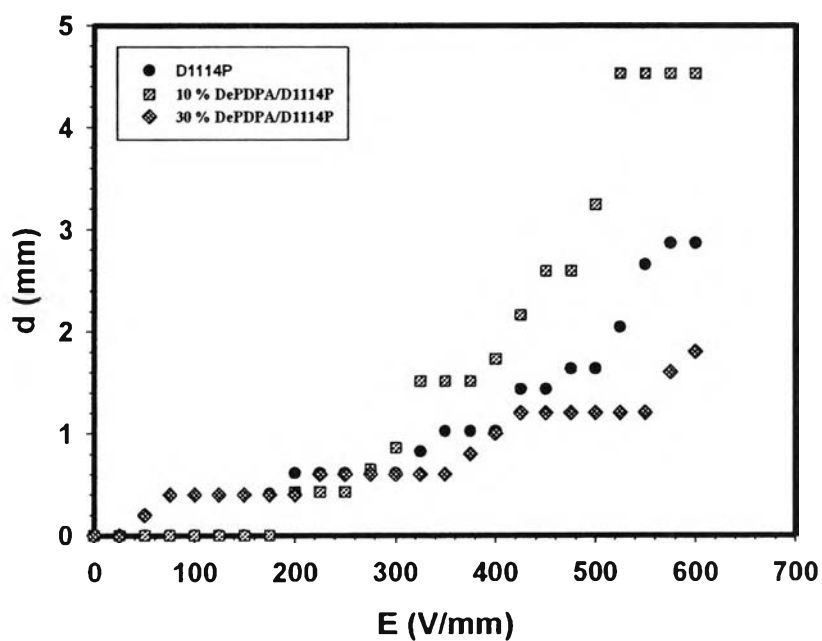
**Figure 3** Effect of particle concentration of De\_PDPA in D1114P, at 27 °C, frequency of 1 rad/s on: (a) the storage modulus response ( $\Delta G'$ ) at  $E = 1$  and 2 kV/mm; (b) the storage modulus sensitivity ( $\Delta G'/G'_0$ ) at  $E = 1$  and 2 kV/mm and storage modulus of De\_PDPA/D1114P blends; (c) storage modulus response ( $\Delta G'$ ) at frequency of 1 rad/s versus relative dielectric constant ( $\epsilon'$ ) at various particle concentrations, 27°C, frequency of 20 Hz.



**Figure 4** Temporal response of storage modulus ( $G'$ ) of 10, 20, and 30 %vol. De\_PDPA/D1114P, parallel plate, strain 0.3, 0.1, and 0.3 %, respectively, film diameter 25 mm, frequency 1.0 rad/s, electric field ( $E$ ) 2 kV/mm, 27°C.



**Figure 5** Deflection of one free end sample cantilever beam.



**Figure 6** Deflection distances of D1114P and De\_PDPA/D1114P blends at various electric field strengths calculated through the Non-Linear Deflection theory.

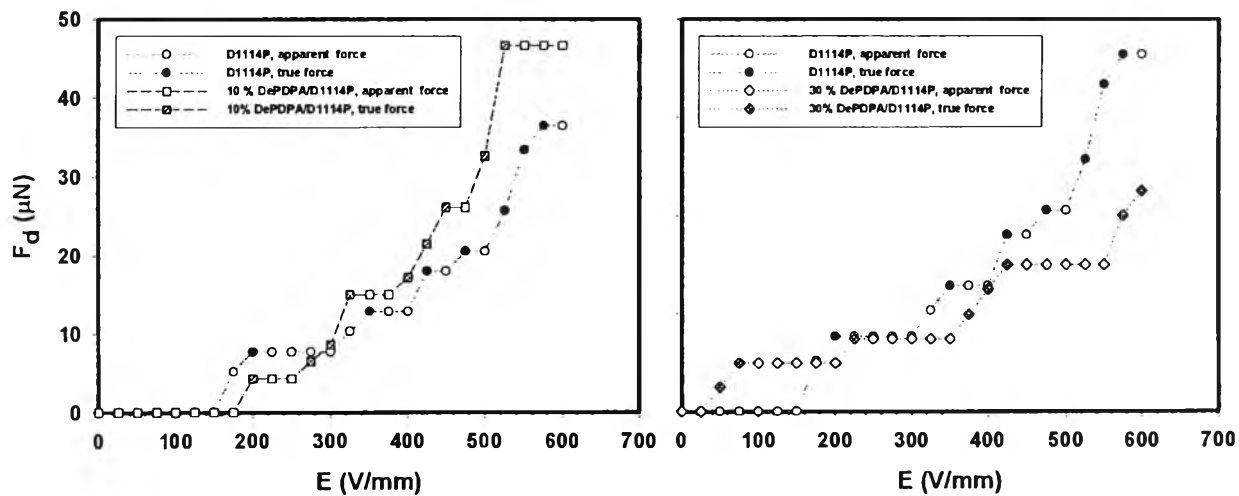


Figure 7 Dielectrophoretic forces of D1114P and De\_PDPA/D1114P blends at various electric field strengths calculated through Non-Linear Deflection theory.