

**CHAPTER IV**  
**ELECTROMECHANICAL RESPONSE OF**  
**POLYTHIOPHENE/ACRYLONITRILE-BUTADIENE RUBBER AS AN**  
**ARTIFICIAL MUSCLE**

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**Abstract**

Acrylonitrile-butadiene rubber (NBR) and blends of poly(3-thiopheneacetic acid)/ acrylonitrile-butadiene rubber, NBR/P3TAA, were prepared to investigate electrorheological properties, dielectric properties, and electrical conductivities. Electrorheological properties were carried out under an oscillatory shear mode in range of frequency from 0.1 to 100 rad/s at various electric field strengths from 0 to 2 kV/mm at fixed temperature of 27°C to observe the effects of acrylonitrile content (ACN) in the pure rubbers and particle concentration in the blends. For pure NBR, the storage modulus,  $G'$ , increases with increasing electric field strength. The storage modulus response ( $\Delta G'$ ) are correlated with the dielectric constants ( $\epsilon'$ ) to study the effect of ACN content. With increasing ACN content, the modulus linearly increases with dielectric constants. With the conductive polymer particles added to the highest ACN content rubber matrix, both the modulus and the dielectric constants of blend film increase.

*Keywords:* Electrorheological properties; Dielectric properties; Acrylonitrile-butadiene Rubber; Poly(3-thiopheneacetic acid)

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## 1. Introduction

There are many kinds of materials are used as artificial muscle such as pneumatic actuators, shape memory alloys (SMA), electroactive ceramics. However, those kinds of materials have a number of disadvantages. The most recent approach for this application is electroactive polymers (EAPs). An attractive characteristic of EAPs is their ability to emulate the operation of biological muscle with high fracture toughness, large actuation strains, and inherent vibration damping [1]. Dielectric elastomers are outstanding EAPs being capable of producing large strains, fast and high electromechanical responses are promising for advanced electromechanical and dielectric applications [1, 2]. The principle operation of dielectric elastomer follows the electrostatic model of actuation described by Pelrine et al. [2]. The response of the polymer is directly proportional to the square of the applied electric field and proportional to dielectric constant.

Acrylonitrile-butadiene rubber (NBR) is one type of elastomers having excellent resistance to petroleum products. With increasing ACN content, their properties will change such as the molecules become more polar and the electrical permittivity of the rubber increases. NBR also has quite good miscibility with conductive polymers [3].

One of conductive polymers is polythiophene.. A substituted Poly(thiophene) at 3- and/or 4-position of the thiophene ring not only confers processability to poly(thiophene)s but can also be used to modify their properties [4].

The presence of fillers and other electrically conductive additives in elastomers have been observed to change electrical, dielectric, and mechanical properties along with morphology [3, 5, and 6]. The incorporation of the conductive materials into dielectric elastomers is widely studied in analogous to both magnetorheological (MR) and electrorheological (ER) fluid. Lokander and Stenberg (2003) studied MR of NBR having different acrylonitrile contents and the blends of NBR with iron particles [7]. The mechanical properties under the influence of electric field, dynamic viscoelasticity, was also investigated by using doped poly(3-hexylthiophene), (P3HT), blended to a silicone elastomer [8]. Shiga (1997) reported the ER effect of

the PMACo particles in silicone gel; the increase in the elastic modulus induced by an electric field is 4 kPa with the particle volume fraction more than 25%. When the particles were incorporated in the rubber matrix, under electric field the interaction between particles occurred [9].

In our previous work, many matrix systems were used to investigate on electrorheological (ER) properties in several parameters such as the effect of electric field strength, particle concentration, and operating temperature on electromechanical responses of poly (dimethyl siloxane)(PDMS) networks containing camphorsulfonic acid (CSA) doped-polyaniline (PANI) particles [10]. ER properties of PDMS gel and PPV/PDMS blends were studied including the effect of particle electrical conductivity [11]. The pure crosslinked polyisoprene elastomers and polythiophene/polyisoprene blends were also investigated [12]. The effect of temperature on Poly (p-phenylene) and an acrylic rubber blends were studied [13]. In this study, NBR having various ACN contents were chosen as matrices because of their polarity properties and the incorporation of poly(3-thiopheneacetic acid) which have high polarity.

In our work, we are interested in elastomeric actuator materials, Acrylonitrile-butadiene rubber containing a conductive polymer, Poly(3-thiopheneacetic acid), to be used as artificial muscles. The effects of the acrylonitrile content in acrylonitrile-butadiene rubber, and particle concentration on electrorheological properties and dielectric properties of pure rubbers and the blends are investigated.

## **2. Experimental**

### *2.1. Materials*

#### *2.1.1. Synthesis Poly(3-Thiopheneacetic acid)*

3-thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer. Anhydrous ferric chloride,  $\text{FeCl}_3$  (AR grade, Riedel-de Haën), was used as the oxidant. Chloroform,  $\text{CHCl}_3$  (AR grade, BDH), and methanol,  $\text{CH}_3\text{OH}$  (AR grade,

CARLO ERBA) dried over molecular sieve for 24 hours under the nitrogen atmosphere and then distilled, were used as solvents. The perchloric acid dopant,  $\text{HClO}_4$  (AR grade, AnalaR) was used as the dopant. Sulfuric acid,  $\text{H}_2\text{SO}_4$  was used to protect the oxidative decomposition of monomer. Diethyl ether and deionized water were used to extract materials. Sodium hydroxide,  $\text{NaOH}$  was used as the hydrolyzing agent.

### 2.1.2. Acrylonitrile-butadiene rubbers (NBR)

Several commercial grades of Acrylonitrile-butadiene rubber (NBR) [Nipol NBR<sup>®</sup> DN101L, Nipol NBR<sup>®</sup> DN 2850, Nipol NBR<sup>®</sup> DN401L (Zeon Advanced Polymix, Thailand), Krynac<sup>®</sup> 3345 F, and Krynac<sup>®</sup> X7.50 (Lanxess) having bound acrylonitrile contents and specific gravities of 42.3%;1, 28%;0.97, 18.5%;0.94, 33%0.97, and 26.5%;0.99 respectively, were used as the polymeric matrices.

## 2.2. Polymerization Procedure

### 2.2.1. Preparation of 3-Thiophene Methyl Acetate (TMA)

The reaction was by the oxidative-coupling polymerization according to the method of Kim *et al.* (1999) [14]. 10.0 g of 3-thiopheneacetic acid was refluxed for 24 hours in 50 ml of dry methanol with 1 drop of concentrated  $\text{H}_2\text{SO}_4$  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  $\text{MgSO}_4$ , and then filtered. The diethyl ether was evaporated from the filtrate by a rotating evaporator. TMA product was obtained.

### 2.2.2. Synthesis of Poly(3-Thiophene Methyl Acetate) (PTMA)

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 was 4:1 in all cases. The reaction was carefully maintained at  $0\text{ }^{\circ}\text{C}$  ( $\pm 0.5\text{ }^{\circ}\text{C}$ ) for 24 hours. The reaction mixture was precipitated by pouring into a large

excess amount of methanol (1 L). The product was repeatedly washed with methanol and deionized water to obtain PTMA.

### 2.2.3. *Synthesis of Poly(3-Thiopheneacetic acid) (PTAA)*

PTMA was hydrolyzed by adding 0.5 g of PTMA in 50 ml of 2.0 M NaOH solution and heating for 24 hours at 100 °C. The mixture was filtered, neutralized and precipitated with a dilute HCl solution (~0.5 M) to obtain the polymer product. The P3TAA was washed several times with deionized water before vacuum drying at room temperature for 2 days. PTAA were ground with mortar and passed through a 38 µm sieve to control the particle size.

### 2.3. *Preparation of Pure Acrylonitrile-butadiene rubber*

Crude acrylonitrile-butadiene rubbers were purified by dissolving in CHCl<sub>3</sub> (AR grade, BDH) and coagulating in methanol, and then they were subsequently dried (Vallim *et al.*, 1999) [6]. Purified rubbers were dissolved in CHCl<sub>3</sub> to obtain rubber solution prior casting into films thickness around 1 mm. Then they were placed in atmosphere at room temperature overnight and taken into vacuum to remove remaining solvent.

### 2.4. *Preparation of the PTAA/Acrylonitrile-butadiene rubber blends*

The blends were prepared by mechanical blending of doped and undoped synthesized polythiophene at various particle concentration (5%, 10%, 15%, 20%, and 30%vol./vol.) into acrylonitrile-butadiene rubbers. The solutions were magnetically stirred for ~24 hr at 27 °C. Bubbles were removed in atmosphere at room temperature of 27 °C overnight prior casting into the films. Then they were taken into vacuum to remove remaining solvent.

### 2.5. *Characterization methods*

A Fourier transform infrared spectrometer (Thermo Nicolet, Nexus ±4 cm), covering a wavenumber range of 4000–400 cm<sup>-1</sup> and using a deuterated triglycine

sulfate detector was used to characterize conductive polymer. The samples were prepared by grinding the conductive polymer particles and with KBr (Carlo Erba Reagent) at a ratio of P3TAA:KBr = 1:20 and then the mixtures were compressed into pellets. For acrylonitrile-butadiene rubbers and polymer blends, they were characterized in order to identify their structures in different types by using a Horizontal Attenuated Total Reflectance accessory (HATR) with equipped with ZnSe.

Nuclear Magnetic Resonance;  $^1\text{H-NMR}$  (Varian Unity Inova) were recorded at  $25 \pm 1$  °C by using a 500 MHz to characterize synthesized conductive polymer. Deuterated dimethyl sulfoxide was used as the standard solvent.

The particle sizes of P3TAA powder was determined by using a particle size analyzer (Malvern, Master Sizer X).

Thermogravimetric/differential thermal analyzer (Perkin Elmer, Pyris Diamond) with the temperature scan from 30 to 800°C at a heating rate of 10°C/min under  $\text{N}_2$  atmosphere were used in order to characterize the synthesized polythiophene, pure acrylonitrile-butadiene rubber, and polythiophene/acrylonitrile-butadien rubber blends.

Scanning electron microscope (JOEL, model JSM-5200-2AE) was used to determine the morphological structure of the conductive polymers and polymer blend morphology. The samples in pellet form were cut into small pieces and adhered on a brass-stub by using an adhesive tape. Then, they were coated with a thin layer of gold by using JFC-1100E ion-sputtering device prior to observation.

Custom-built two-point probe electrometer (Keithley, Model 6517A) was used to determine electrical conductivity of conductive polymer (25 mm diameter and 0.2 mm thickness) prepared by molding with a hydraulic press. The relation  $\sigma = (1/Rt)(1/K) = (I/Vt)(1/K)$  was used to calculate specific conductivity, where  $t$  is the pellet thickness,  $I$  is current change,  $V$  is apply voltage (voltage drop) 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 applied voltage was plot versus the current change to determine the linear ohmic regimes of each sample. The applied voltage and the current change in this linear ohmics regime were converted to the electrical conductivity of polymer using above relation.

The resistivity testing fixture (Keithley, Model 8009) connected to a source meter (Keithley, Model 6517A) was also used to determine the electrical conductivity of matrix materials and the blended films. It is a constant voltage source and the resultant current was read under the atmospheric pressure, 54-60% relative humidity, and 24-25°C. The volume resistivity ( $\rho_v$ ) of matrixes was calculated following the ASTM standard D257,  $\rho_v = K_v R/t$ , where  $K_v$  is the effective area of the guarded electrode for the particular electrode arrangement employed (22.9 cm<sup>2</sup>),  $t$  is the pellet thickness, and  $R$  is the volume resistance is ohms. The conductivity of blend polymers and polymer matrices were calculated by using this relation  $\sigma = 1/\rho_v = (t_c \times I)/(22.9 \times V)$ , where  $t_c$  is the pellet thickness,  $I$  is the resultant current,  $V$  is the applied voltage (voltage drop).

Dielectric measurements were carried out in the frequency range 20 Hz up to 600 kHz under applied voltage 1 volt at  $27 \pm 0.5$  °C by using an LCR meter type (HP, 4284A) which was connected with and controlled by the melt rheometer (Rheometric Scientific, ARES) fitted with a custom-built copper parallel plate fixture (diameter of 25 mm). The samples were covered with silver conductive paint (Electrolube) to protect unreliable data from air that were entrapped in the samples.

A melt rheometer (Rheometric Scientific, ARES) was used to measure electrorheological properties. It is fitted with a custom-built copper parallel plate fixture (diameter of 25 mm). A DC voltage was applied with a DC power supply (Instek, GFG 8216A), which can deliver electric field up to 4 kV. A digital millimeter (Made, model) 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 firstly carried out to determine the appropriate strain to measure  $G'$  and  $G''$  in

the linear viscoelastic regime. The strain was 0.1% which it was used in frequency sweep tests in various frequency and electric field strength.

Bending measurements were carried out by using DC power supply (Goldsen, GPS 30035) connected with an amplifier (Gamma High Voltage, UC5-30P) supplying high DC positive current to copper electrodes (30 mm long, 30 mm wide, and 1.0 mm in thickness, the distance between the electrodes is 10 mm). The apparatus were set as shown in Fig. 6. Specimens were immersed in silicone oil having viscosity 100 cP between a pair of parallel copper electrode plates. The Specimens width is 5 mm, and thickness is 0.6 mm. All the measurements were carried out at ambient temperature. The electric response of the specimens was recorded by a video camera, and the deflection was analyzed by a digital image software (Sciion Image).

### 3. Results and Discussion

#### 3.1. Characterization of poly(3-thiopheneacetic acid), (P3TAA) and poly(3-thiopheneacetic acid)/Acrylonitrile-butadiene rubber, (P3TAA)/NBR, blends

The peak of FT-IR spectrum of PTMA, at 3000-2800  $\text{cm}^{-1}$  can be assigned to the stretching vibration of the C-H band on the thiophene ring. Absorption band at 1735-1750  $\text{cm}^{-1}$  is due to the C=O stretching vibrations; the peak at 1432  $\text{cm}^{-1}$  is an evidence of the thiophene ring stretching vibration, and at 1300-1200  $\text{cm}^{-1}$  for C-O the stretching vibration. Therefore, the oxidative polymerization of 3-thiophene methyl acetate is confirmed [15]. The characteristic peaks of P3TAA are found at 3200-3000  $\text{cm}^{-1}$  and assignable to the stretching vibration of the C-H bond on the thiophene ring; at 3000-2800  $\text{cm}^{-1}$ , they represent the aliphatic C-H bonds; at 1700  $\text{cm}^{-1}$ , the C=O stretching vibration; at 1400  $\text{cm}^{-1}$ , the thiophene ring stretching vibration; and at 1300-1200  $\text{cm}^{-1}$ , the C-O stretching vibration. The most characteristic feature in this spectrum is the extremely broad O-H absorption occurring in the region from 3400 to 2400  $\text{cm}^{-1}$  [14].

P3TAA/NBR blends were characterized by using FT-IR equipped with HATR. The data showed the wavenumber of the blends that were a combination between



NBR and P3TAA. When P3TAA were added to the NBR matrix, the wavenumber around  $3400\text{ cm}^{-1}$  which represent the  $-\text{OH}$  group of poly(3-thiopheneacetic acid) was detected at the blend films. This wavenumber is higher for the blends having higher P3TAA compositions. However, the IR spectrum cannot be used to observe a significant shift of the peak of the blended films to infer the interaction between P3TAA and NBR.

The structure of P3TAA was characterized by using  $^1\text{H-NMR}$  to identify successful synthesis of poly (3-thiopheneacetic acid).  $^1\text{H-NMR}$  spectra of these polymers were in agreement with the expected structures: P3TMA  $\delta$  7.26-7.3 ppm (m, thiophene ring proton, 1H), 3.68 ppm (s, thiophene ring  $-\text{CH}_2-$ , 2H), 3.66 ppm (s,  $-\text{CH}_3$ , 3H). P3TAA, (DMSO) 12.60 ppm (s,  $-\text{COOH}$ , 1H), 7.55-7.28 ppm (m, thiophene ring proton, 1H), 3.80-3.37 ppm (m, thiophene ring  $-\text{CH}_2-$ , 2H). The position at 12.6 ppm is the important feature peak of poly(3-thiopheneacetic acid) in order to identify that the structure can be changed from poly(3-thiophene methyl acetate) to poly(3-thiopheneacetic acid) because this peak disappears in case of poly(3-thiophene methyl acetate) [14].

The TGA thermogram of undoped P3TAA indicates three transitions:  $30-120^\circ\text{C}$ ,  $120-300^\circ\text{C}$  and  $450-650^\circ\text{C}$ ; they refer to the losses of water and residue solvent, the side chain degradation, and the backbone degradation, respectively [16]. Acrylonitrile-butadiene rubbers have a better thermal stability whose main transition temperature starts at  $415^\circ\text{C}$ .

P3TAA/NBR blends were characterized by using a thermogravimetric/differential thermal analyzer under nitrogen gas. When P3TAA were more added to NBR, the thermogram of the blended samples shows a decomposition temperature around  $230^\circ\text{C}$  being the decomposition temperature of side chain of P3TAA. As more P3TAA are added, the decomposition temperature are in between P3TAA and NBR. From these data, we can imply that NBR rubber enhances the thermal stability of P3TAA.

The particle size of the P3TAA was characterized by using a particle size analyzer which is around  $20\ \mu\text{m}$  with a standard deviation of 0.131. It was confirmed by SEM photograph of Fig. 3(a).

The morphology of blended films was characterized to observe the dispersion of the particles, as shown in Fig. 3(b)-(d). From the photographs, the P3TAA particles are moderately dispersed in NBR matrix.

The electrical conductivity of undoped P3TAA is approximately  $5 \times 10^{-6}$  S/cm with standard deviation of  $2.73 \times 10^{-6}$  S/cm. The electrical conductivities of pure NBR is around  $3.31 \times 10^{-10}$  S/cm with standard deviation of  $7.71 \times 10^{-11}$  S/cm. When more P3TAA particles are added to the NBR matrix, the electrical conductivity increases; at the highest concentration (30%vol./vol.) it is  $4.02 \times 10^{-9}$  S/cm with standard deviation of  $8.97 \times 10^{-10}$  S/cm .

### *3.2. Dielectric Properties of Pure Acrylonitrile-butadiene Rubber and Poly(3-thiopheneacetic acid)/ Pure Acrylonitrile-butadiene Rubber, (P3TAA)/NBR, Blends*

#### *3.2.1. Effect of Acrylonitrile Content (ACN)*

Effect of acrylonitrile content (ACN) on dielectric properties of pure acrylonitrile-butadiene rubber, NBR1, NBR2, NBR3, NBR4, and NBR5 having acrylonitrile contents of 42.5%, 33%, 28%, 18.5%, and 26.5% including carboxylic 7%, respectively, was investigated under in the frequency range 20 Hz up to 600 kHz, applied voltage of 1 volt, at a fixed temperature of 27°C. Fig. 2(a) shows the dielectric constants ( $\epsilon'$ ) of the pure NBR increase with ACN content. The dielectric constant of NBR having highest ACN content (NBR1) at frequency 20 Hz is 14 and the lowest ACN content (NBR4) is 7.8. When increasing the frequency ( $> 10^4$  Hz), the dielectric constants decrease, NBR1 shows a higher drop relative to others. These results suggest that the increase in  $\epsilon'$  due to the increase in  $C\equiv N$  dipoles, leading to an increase in the orientation polarization which diminishes when the frequency is more than  $10^4$  Hz [5].

#### *3.2.2. Effect of Particle Concentration*

NBR1 is the matrix containing poly(3-thiopheneacetic acid) at various particle concentrations 5%, 10%, 15%, 20%, and 30%vol./vol.. From Fig. 2(b), the dielectric constants increase with particle concentration when the frequency is lower

than  $10^2$  Hz. The dielectric constant of blend system having the highest concentration at the frequency 20 Hz is 48.92, and it decrease with increasing frequency. In the blend system, the dielectric constant increases because adding conductive particles to NBR causes the interfacial polarization to increase. It was suggested that in heterogeneous polymer blends, the dielectric constants of the polymers are influenced by the interfacial effects [17]. From Fig. 2(b), the dielectric constant of 30 %vol. concentration system sharply drops relative to others when frequency is more than  $10^2$  Hz. This may be due the higher particle interactions; the particles lose ability to be polarized by electric field. The addition of different concentrations to the blend leads to different effects on the dielectric constant. In the system having high the conductive concentration, it means that the system has small portion of polar section ( $C\equiv N$ ), hence the effect of orientation polarization of the 30%vol./vol. is less than 20 %vol./vol. system which have more NBR section.

### *3.3. Electrorheological Properties of Pure Acrylonitrile-butadiene Rubber and Poly(3-thiopheneacetic acid)/ Pure Acrylonitrile-butadiene Rubber, (P3TAA)/NBR, blends*

#### *3.3.1. Effect of Acrylonitrile Content (ACN)*

Electrorheological properties on pure NBR was characterized by using a melt rheometer under electric field strength varying from 0 to 2 kV/mm, at a fixed temperature of 27°C. Strain sweep tests were firstly carried out to determine the suitable strain to measure  $G'$  and  $G''$  in the linear viscoelastic regime the linear regime which was 0.1 % strain. Then frequency sweep test were carried out to measure storage modulus,  $G'$  and loss modulus,  $G''$  of each sample as functions of frequency by varying from 0.1 to 100 rad/s after preshear at low frequency (0.04 rad/s). Fig. 2. shows the storage modulus response which is defined as  $\Delta G' = G'_E - G'_o$  where  $G'_E$  is the storage modulus under electric field, and  $G'_o$  is the storage modulus without electric field, vs. electric field strength, which can be compared with the electrostatic model of actuation as described by Perline [2]. The equation in this model can be written as:

$$p = \epsilon_0 \epsilon_r E^2 \quad (1)$$

where  $\epsilon_0$  and  $\epsilon_r$  are the permittivity of free space and the relative permittivity of polymer, respectively, and  $E$  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;  $\Delta G' \propto E^\alpha$ ,  $\alpha = 2$ . From Fig. 2(a) shows the storage modulus responses ( $\Delta G'$ ) of pure rubber increase with electric field strength ( $E$ ). From  $\Delta G' \propto E^\alpha$  relation,  $\alpha$  of pure NBR having various ACN content, NBR1, NBR2, NBR3, NBR4, and NBR5, is 0.66, 0.66, 0.61, 0.60, and 0.79, respectively when  $0.05 \text{ kV/mm} < E < 1.2 \text{ kV/mm}$ . As an electric field is applied, electrical dipole moments are generated and the electrostatic interactions between the polymer chains are induced leading to an intermolecular interaction acting like an electrical network. 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  $G'(\omega)$  [18]. In addition, a voltage differential between the electrodes is known to create electromagnetic forces that act to pull the electrodes together. 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 [2].

### 3.3.2. Effect of Particle Concentration

P3TAA/NBR1 blends at various P3TAA particle concentrations, 5, 10, 15, 20, and 30 %vol., were investigated in the range between 0-2 kV/mm. For blend system being insulating material containing conductive particles, the Maxwell-Wagner Model was proposed by Klingenberg *et al.* (1996) [19]. Fig. 2(b) shows the storage modulus ( $G'$ ) of each polymer blend system generally increases with increasing electric field strength as:  $\Delta G' \propto E^\alpha$ ,  $\alpha$  of each blend system is 0.25, 0.33, 0.33, 0.35, and 0.49 for the particle concentrations of 5, 10, 15, 20, and 30 %vol., respectively. The relation between the storage modulus response and the electric field strength can be compared with the power law behavior in Maxwell-Wagner Model as:  $\Delta G' \propto E^\alpha$ , in which  $\alpha$  is equal to 2. For the blend system, the effect of the electric field strength to the modulus response is less than the model in which the

interaction between particles was calculated by assuming the center-to-center distance of the adjacent spheres. The deviation from the quadratic dependence on electric field at low concentration is due to the distances between particles too large to create a significant particle interaction [21]. At high concentrations, the deviation might be a result from the nonlinear conduction as proposed by Atten *et al.* (1994) [20], and the steric hindrance [21]. They suggested that the electric field between particles can become so large such that dielectric breakdown strength of continuous phase is exceeded. Fig. 4 shows the relation between particle concentration with the storage modulus response, at low electric field (0.1, 0.2 kV/mm), at low concentration of particles (<15%vol./vol) the modulus linearly increases with concentration following the relation  $\Delta G' \propto \Phi^\beta$ ,  $\beta$  at electric field strength 100 and 200 V/mm is 0.31 and 0.23, respectively for  $0 < \Phi < 0.15$ . This results from the number of particles is too small and the distances between particles are too large to create a significant particle interaction [21]. The increase in the modulus results from P3TAA particles behaving as fillers in the matrix. However, as P3TAA particles are added more than 15%vol./vol., the modulus sharply increases with particle concentration. At high electric field (1.0, 2.0 kV/mm), the particles have a greater influence on the modulus relative to low electric field. When P3TAA particles are added to NBR1, the modulus first decreases at 5 vol.%, then it increases towards a maximum (20 %vol./vol.);  $\beta$  of each system is 0.63 and 0.81, respectively. At the higher electric field strength of 1 kV/mm, induced polarization interactions are more effective amongst particles at high particle concentrations. The initial decrease in the modulus responses suggests that it might occur from the cancellation of dipoles of P3TAA which try to align along an electric field and the distances between particles are too large to interact with each other so they act as fillers which induce an additional free volume, instead of enhance the storage modulus [13].

Shiga [8] found the similar effect for poly(*p*-phenylene) and silicone elastomer blends. The storage modulus response increased with increasing particle content; it was negligible below 8.4 vol.%. Chotpattananont *et al.* (2004) [16] found that the storage and loss moduli of a polymer blend between polythiophene and silicone oil increased with increasing polythiophene concentration. However, at high

concentration, the storage modulus is not quite responsive to electric field due to the steric hindrance effect. Liu and Shaw (2001) showed the enhancement of shear modulus of silicone/silica ER elastomers was negligible below 8.0 vol %, but increased dramatically above threshold concentration [21]. At volume fraction above 55 vol%, the shear modulus decreased because the interparticle force decreased with the steric hindrance effect.

### 3.4. *Electrorheological Properties and Dielectric Properties of Acrylonitrile-butadiene Rubber, NBR and Poly(3-Thiopheneacetic acid)/ Acrylonitrile-butadiene Rubber, P3TAA/NBR, blends*

#### 3.4.1. *Pure NBR*

In Fig. 5(a),  $\epsilon'$  increases with increasing ACN content.  $\Delta G'$  at frequency 1.0 rad/s and 0.1 % strain linearly increases with  $\epsilon'$  at low (0.1 and 0.2 kV/mm) and high (1 kV/mm) electric field strength, consistent with the electrostatic model of actuation which the actuation pressure is proportional to dielectric constant as described by Perline *et al.* (2000) [2].

#### 3.4.2. *Poly(3-Thiopheneacetic acid)/ Acrylonitrile-butadiene Rubber*

Electrorheological properties on P3TAA/NBR blends in which the conductive polymer particles were added to the rubber (NBR1) with 5, 10, 15, 20, and 30 %vol./vol., P3TAA\_5/NBR1, P3TAA\_10/NBR1, P3TAA\_15/NBR1, P3TAA\_20/NBR1, and P3TAA\_30/NBR1, respectively. Fig. 5(b) shows the correlation between the storage modulus response ( $\Delta G'$ ) and the dielectric constant ( $\epsilon'$ ) at 20 Hz of the blends. The storage modulus response ( $\Delta G'$ ) nonlinearly increases with increasing dielectric constant. The storage modulus response sharply increases beyond the particle concentration 15 %vol. This result suggests that the interfacial polarization is influential to the electrorheological property according to the results from Hao *et al.*, (1998) [22]. In Fig. 2(b),  $\epsilon'$  of the blends in Maxwell-Wagner region (<100 Hz) increases with increasing conductive particle [17]. As more P3TAA particles are added to NBR, the mismatch between their conductivities

occurs resulting in the interfacial polarization. As this mismatch increases, the interaction between particles increases, leading to the modulus increase [22].

### 3.5. Time Dependence of the Electrorheological Response

The temporal characteristics of pure NBR1 and P3TAA\_20/NBR1 blend at electric field strengths 1.2 kV/mm were investigated. The temporal characteristic of each sample was recorded in the linear viscoelastic regime at a strain of 0.1% and at frequency of 1.0 rad/s. Table 1 shows the induction and recovery times of the samples. They were detected during a time sweep test, in which an electric field was turned on and off alternately. The response of storage modulus,  $G'$  of pure NBR system can be divided into two regimes: the initial regime in which  $G'$  rapidly overshoots to a large value,  $\Delta G'$  is 23470 Pa, on the first cycle followed by an irreversible decay. The time required for  $G'$  to reach the steady-state value on applying the field is called the induction time,  $\tau_{ind}$ . For NBR1,  $\tau_{ind}$  is 1000 s. The time required for  $G'$  to decay towards its steady-state value when the electric field is turned off is called the recovery time,  $\tau_{rec}$ . It takes longer time to decay to the steady-state,  $\tau_{rec}$  is 1500 s; however, it does not recover its initial state. The response decreases only by 1460 Pa. As the electric field is turned on again, the response slightly increases until reaching the steady-state. From the temporal response of the pure rubber system, when the electric field is applied to the rubber the dipole of  $C\equiv N$  segment align themselves along the electric field. When the electric field is turned off, some dipole moments remain due to the interaction between  $C\equiv N$ , lead to irreversible of the modulus. Berlepsch *et al.*, (1989) studied a stretched copolymer of acrylonitrile and methylacrylate. They found that their samples showed an appreciable piezoelectric activity [23]. Eid and El-Nashar (2006) investigated the relaxation time of polymer blend between NBR and EPDM, they found that the relaxation time increased slightly by the addition of NBR to the EPDM. The relaxation time could be associated with those orientations of small aggregates caused by the movement of the main chain [5].

P3TAA\_20/NBR1 is also an irreversible system. Table 1 shows the modulus response and  $\tau_{ind}$  of the first cycle are 209920 Pa and 1500 s, respectively, both are larger than those of the pure NBR1 system. The blend system takes more time to decay to the steady-state when electric field is turned off. This result suggests that there are some irreversible interactions between polythiophene particles, perhaps due to hydrogen bonding between adjacent polythiophene particles, and the residual dipole moments inducing permanent interparticle interactions [12].

### 3.6. Bending Response

Pure NBR1 and P3TAA\_10/NBR1 bendings were observed in response to electric field. The samples were clamped between copper plates and immersed in silicone oil. The positive current was applied to the copper plate as shown in Fig. 6. The electric deflection responses of the samples were recorded by a video camera as shown in Fig. 7. The bending angle was analyzed by calculating  $\arctan$  of the ratio between deflection distance ( $a$ ) and sample length ( $l$ ). Fig. 8 shows the bending angle of pure NBR1 and the bending angle increases with the electric field. For NBR1 system, it increases linearly with electric field, whereas for the blend system it slightly increases at low electric field ( $<500$  V/mm) and then sharply increases at applied electric field 500 V/mm. From the result, the blend system requires a higher electric field to bend until it touches the copper at the ground side plate. However, the bending angle of the blend in low field ( $<200$  V/mm) is higher than that of the pure system. For the bending angle results, data suggest that the blend system can respond to low electric field better than the pure system due to the interaction of conductive particles. The blend system has a higher weight and rigidity, so it requires a higher electric field to bend and touch the plate. Fig. 9 shows the electric force ( $F_E$ ) which was calculated from the equation following:

$$F_E = mg \sin \theta + P_E(\theta) \quad (2)$$

where  $m$  is the sample's weight (kg),  $g$  is the gravity ( $9.8 \text{ m/s}^2$ ),  $\theta$  is the bending angle, and  $P_E$  is the load force (N) from the field which was calculated from [24]:



$$P_E = \frac{3Ela}{l_o^3} \quad (3)$$

where E is Yong's modulus equal to  $2G'(1+\nu)$ , G' is the shear modulus,  $\nu$  is posson's ratio equal to 1/2 incompressible, I is the moment of inertia equal to  $2/3C^3W$  which C is the sample thickness, W is the sample width, a is the deflection distance (a), and l is the sample length.

From Fig. 9, the electric force of the pure system increases linearly with electric field whereas the blend system is a nonlinear system. The pure NBR requires a lesser force than the blend system because the pure rubber system is more flexible than the blend system. However, as the electric field increases, the blend system generates lesser  $F_E$  relative to the pure NBR; this might be due to the particle interactions with electric field effect.

#### 4. Conclusions

In this study, electrorheological properties and dielectric properties of acrylonitrile-butadiene rubber (NBR) and poly(3-thiopheneacetic acid)/Acrylonitrile-butadiene rubber blends, P3TAA/NBR, were investigated at electric field strength varying from 0 to 2 kV/mm. Poly(3-thiophene acetic acid) particles were synthesized via an oxidative polymerization.

For the pure NBR system, the storage modulus responses ( $\Delta G'$ ) increase with increasing electric field strength around 0.7 order magnitude. With increasing ACN content,  $\Delta G'$  slightly increases. However, some pure system becomes more complicated with the addition of the carboxylic group inside polymer chain so the ACN is not the only parameter that has to be concerned with. For the correlation between the storage modulus ( $\Delta G'$ ) and dielectric constant ( $\epsilon'$ ) in pure system the modulus increases linearly with dielectric constant

P3TAA/NBR blend systems, particle of P3TAA were added to NBR with particle concentrations of 5, 10, 15, 20, and 30 %vol. the storage modulus responses

( $\Delta G'$ ) increase with particle concentration due to those particles interacting with each other under electric field. However, the modulus becomes saturated at the electric field strength of 1 kV/mm. The storage modulus increases with increasing electric field strength upto 0.3 order magnitude.  $\Delta G'$  is nonlinearly correlated with  $\epsilon'$ . The storage modulus of the blends increases nonlinearly at high particle concentrations above 15%vol. because of the particle interaction.

For the temporal response, both systems are irreversible systems because they have remaining dipole interaction in the systems when the electric field is turned off.

The bending response was observed by calculating from bending angle and electric force. In pure rubber system (NBR1), the response and force increase linearly with electric field. For the blend system, the response and the force are nonlinear with electric field.

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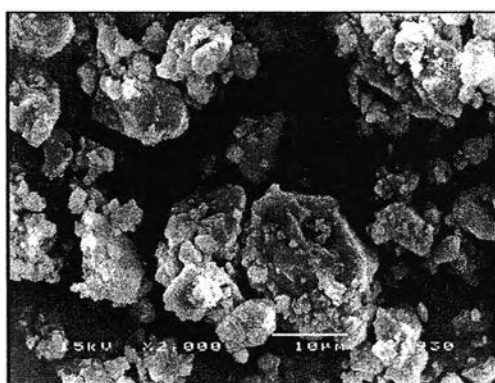
### **References**

- [1] Bar-Cohen Y. *Electroactive Polymer (EAP) Actuators as Artificial Muscles: Reality, Potential, and Challenges*. 2nd ed. The International Society for Optical Engineering, Washington; 2004.
- [2] Perline R, Kornbluh R, Joseph J, Heydt R, Pei Q, Chiba S. *Mater Sci Eng C* 2000;11:89-100.
- [3] Yong KC, Foot PJS, Morgan H, Cook S, Tinker AJ. *Eur Polym J* 2006;42: 1716-1727.
- [4] Li Y, Vamvounis G, Holdcroft S. *Macromolecules* 2001;34:141-143.

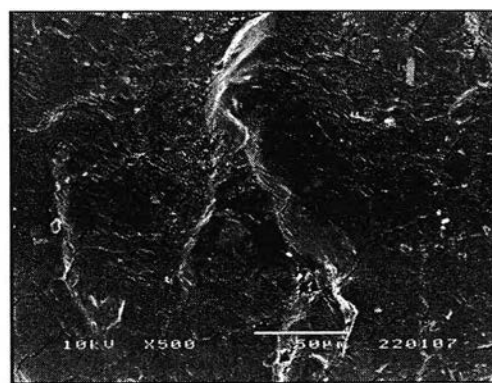
- [5] Eid MAM, El-Nashar DE. *Polym-Plast Technol* 2006;45:675–684.
- [6] Vallim MR, Felisberti MI, De Paoli M-A. *J Appl Polym Sci* 2000;75:677–84.
- [7] Lokander M, Stenberg B. *Polym Test* 2003;22:245–251.
- [8] Shiga T, Okada A, Kurauchi T. *Macromolecules* 1993;26:6958-6963.
- [9] Shiga T. *Adv Polym Sci* 1997;134:133-163.
- [10] Hiamtup P, Sirivat A. *Am Soc of Mech Eng Mat* 2005;100:301-304.
- [11] Naimlang S, Sirivat A. *Am Soc of Mech Eng Mat* 2005;100:305-308.
- [12] Puvanattvattana T, Chotpattananont D, Hiamtup P, Niamlang S, Sirivat A, Jamieson AM. *React Funct Polym* 2006;66:1575–1588.
- [13] Khunanuruksaphong R, Sirivat A. *Mater Sci Eng A*, submitted for publication.
- [14] Kim B, Chen L, Gong J, Osada Y. *Macromolecules* 1999;32:3964-3969.
- [15] Senadeera GKR. *Curr Sci* 2005;88:145-148.
- [16] Chotpattananont D, Sirivat A, Jamieson AM. *Colloid Polym Sci* 2004;282:357–365.
- [17] George S, Varughese KT, Thomas S. *J Appl Polym Sci* 73 (1999) 255–270.
- [18] Krause S, Bohon K. *Macromolecules* 2000; 34:7179–7189.
- [19] Parthasarathy M, Klingenberg DJ. *Mater Sci Eng* 1996;R17:57-103.
- [20] Atten P, Foulc J-N, Felici N. *Int J Mod Phys B* 1994;8:2731–2745.
- [21] Liu B, Shaw TM. *J Rheol* 2001;45:64–657.
- [22] Hao T, Kawai A, Ikazaki F. *Langmuir* 1998;14:1256-1262.
- [23] Berlepsch H, Kiinstler W, Wedel A, Danz R, Gei D. *J Polym Sci Pol Chem* 1972;10:3457-3467.
- [24] Timoshenko SP, Goodier JN. *Theory of elasticity*. 3rd ed. Auckland: McGraw-Hill; 1970, 41–46.

**Table 1** Induction time and recovery time at electric strength 1.2 kV/mm of the pure NBR system and P3TAA\_10/NBR1 blends

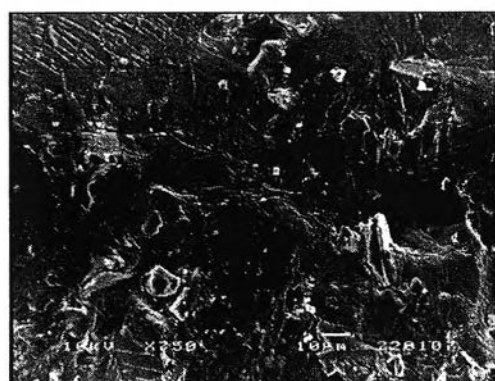
Sample	Induction time ( $\tau_{ind}$ ) (s)	Reduction time ( $\tau_{rec}$ ) (s)	$\Delta G'_{ind}$ (Pa)	$\Delta G'_{rec}$ (Pa)
NBR1	1000	1500	23470	1460
P3TAA_20/NBR1	1500	3000	209920	4010



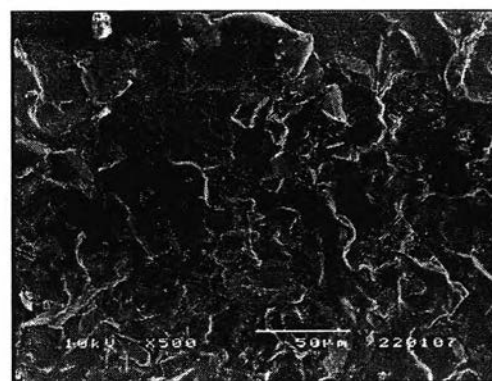
(a)



(b)



(c)



(d)

Fig. 1. SEM photographs of: (a) undoped poly(3-thiopheneacetic acid) at magnification 2000; (b) P3TAA\_5/NBR1 at magnification 500; (c) P3TAA\_20/NBR1 at magnification of 500; (d) P3TAA\_30/NBR1 at magnification of 500.

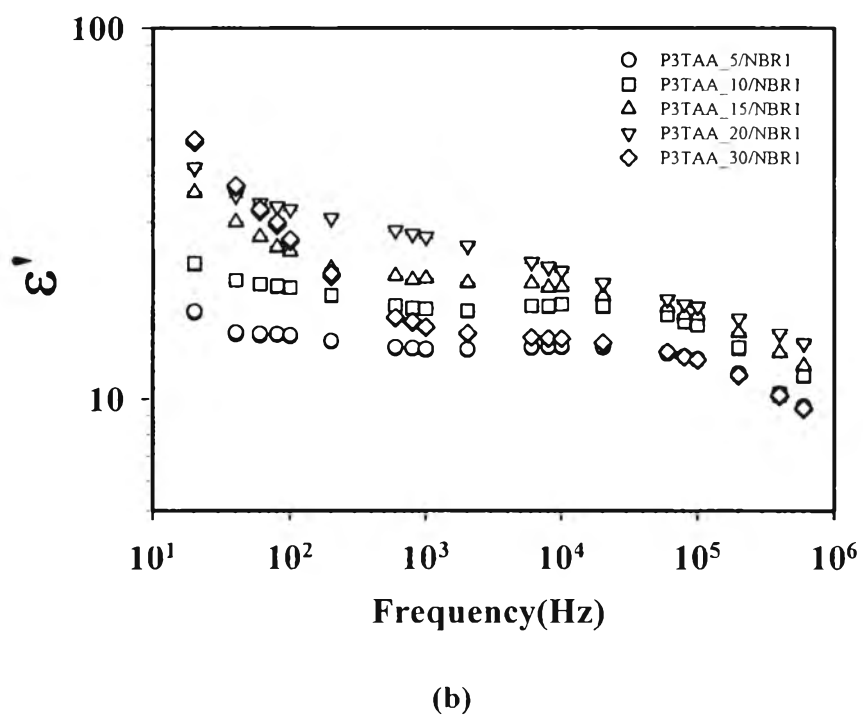
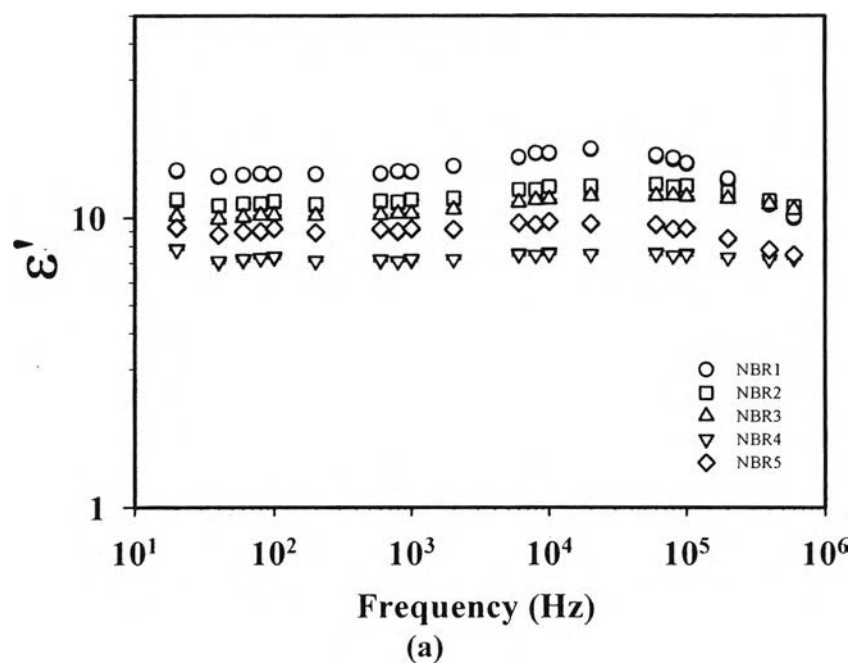
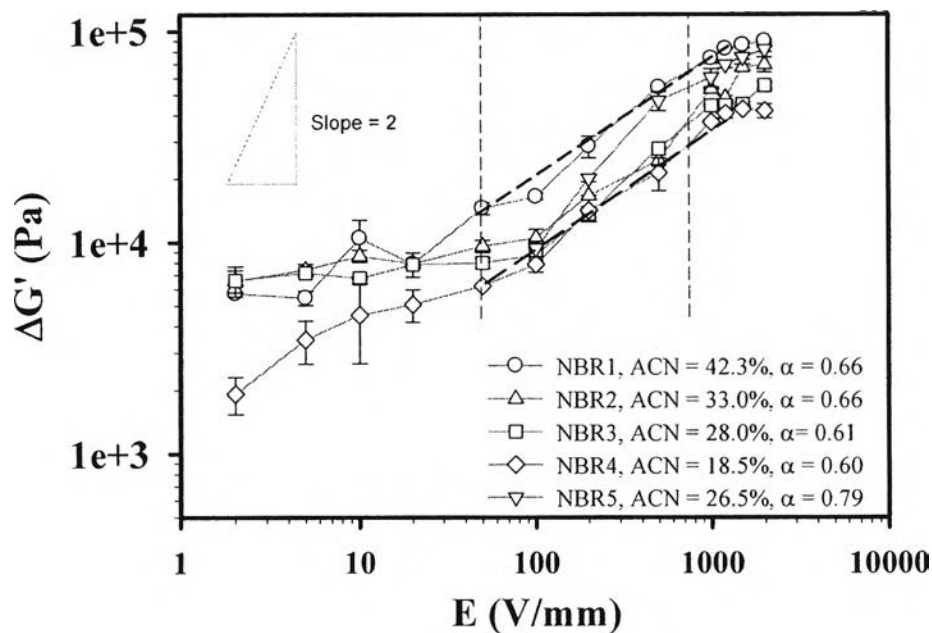
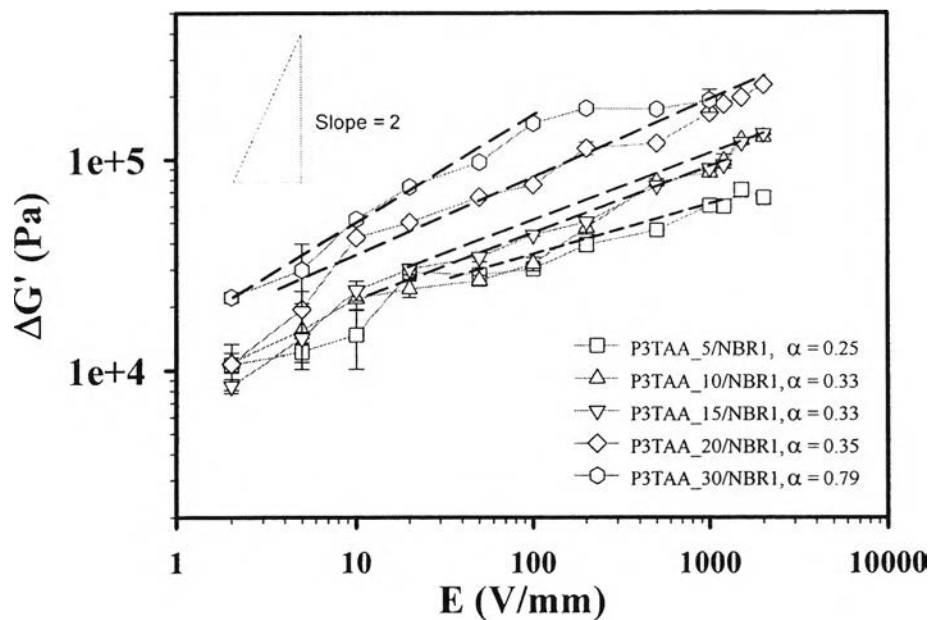


Fig. 2. Comparison of the dielectric constant ( $\epsilon'$ ) of pure NBR and P3TAA/NBR1 vs. frequency at applied voltage of 1.0 volt, temperature  $27 \pm 0.5$  °C, gap range 0.7 – 1.0 mm: (a) pure NBR; (b) P3TAA/NBR blends.



(a)



(b)

Fig. 3. Comparison of the storage modulus response ( $\Delta G'$ ) of pure NBR and P3TAA/NBR1 at various particle concentrations (5%, 10%, 15%, 20%, and 30%vol.) at frequency 1.0 rad/s vs. electric field strength, strain 0.1%, temperature  $27 \pm 0.5$  °C, gap range 0.7- 1.0 mm: (a) pure NBR; (b) P3TAA/NBR1.

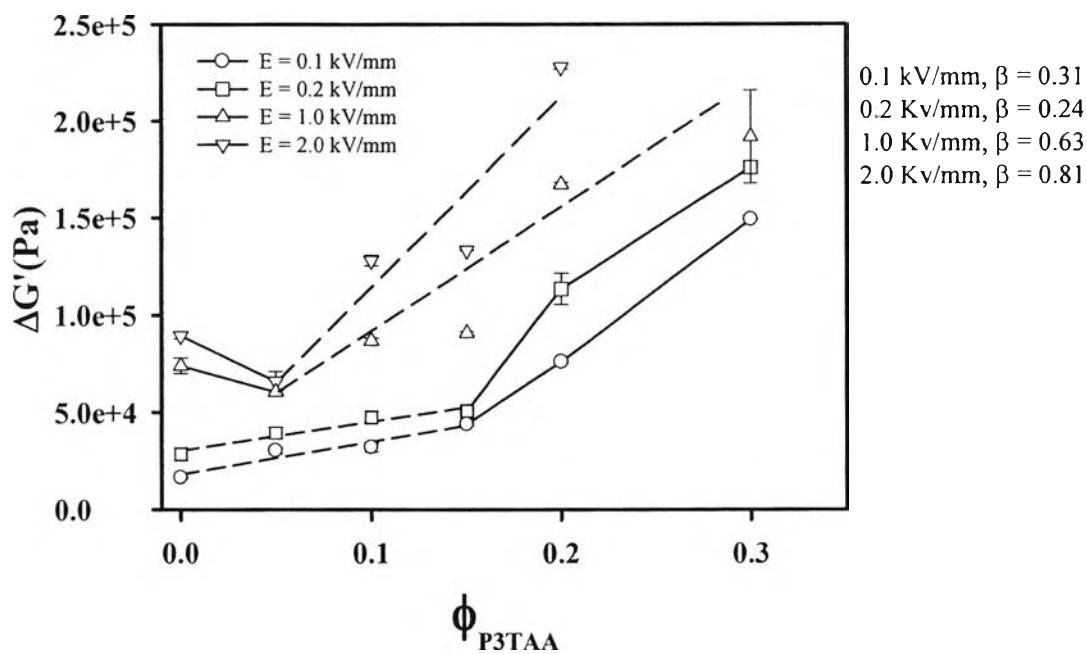
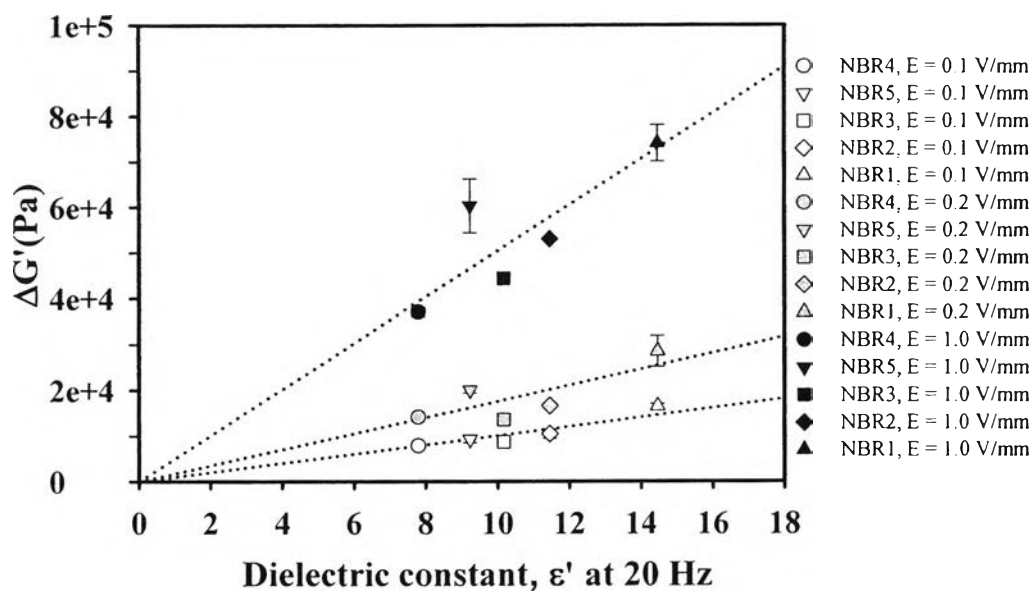
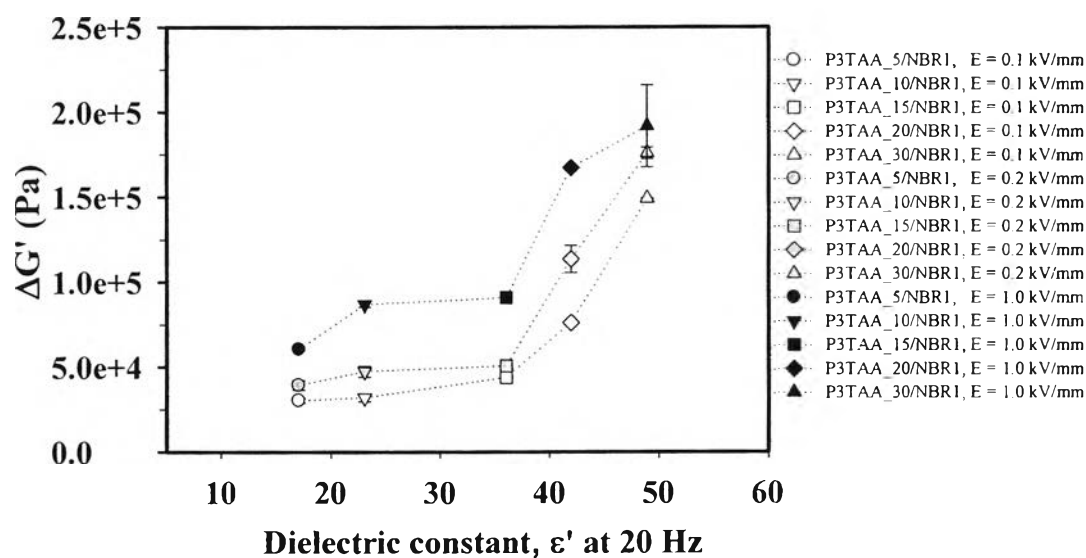


Fig. 4. Comparison of the storage modulus response ( $\Delta G'$ ) of pure NBR and P3TAA/NBR1 blends at various electric field strengths (0.1, 0.2, and 1 kV/mm) vs. particle concentration ( $\phi = 0, 5, 10, 15, 20,$  and  $30$  %vol.) frequency 1.0 rad/s, strain 0.1%, temperature  $27 \pm 0.5$  °C, gap between 0.7 to 1.0 mm.



(a)



(b)

Fig. 5. Storage modulus responses at frequency 1.0 rad/s, strain 0.1%, and various electric field strength (0.1, 0.2, and 1 kV/mm) of pure NBR and P3TAA/ vs. dielectric constant, at 20 Hz, applied voltage of 1 volt, 27 °C, and gap range from 0.7 to 1.0 mm: (a) pure NBR; (b) P3TAA/NBR1 at various particle concentrations (5%, 10%, 15%, 20%, and 30%vol.).



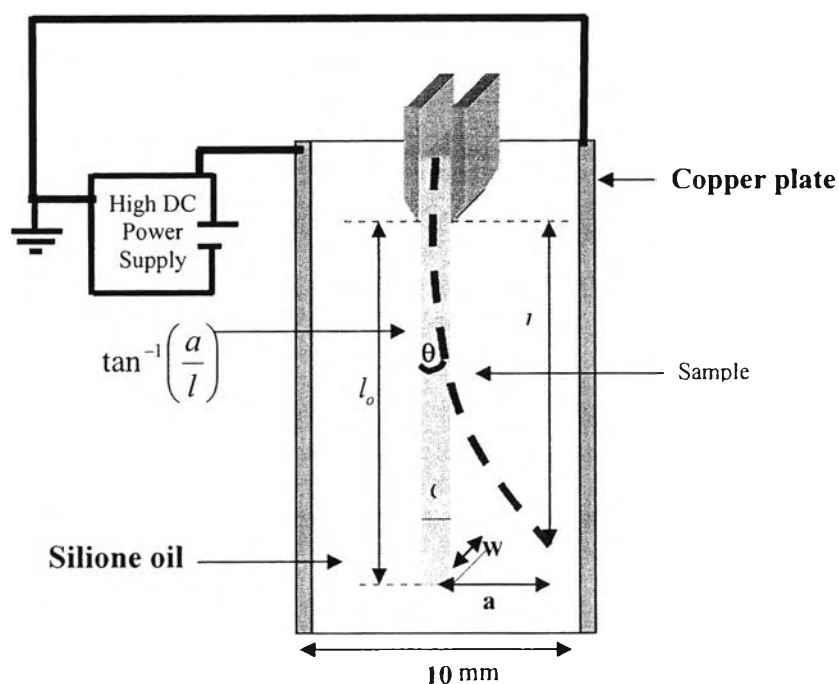


Fig. 6. Schematic diagram of the bending response measurement of pure NBR1 and P3TAA\_10/NBR1 films suspended vertically in a silicon oil bath and sandwiched between copper plates (30 mm long, 30 mm wide, and 1.0 mm in thickness, the distance between the electrodes is 10 mm) in acrylic box. A DC electric field was applied horizontally at ambient temperature, which causes a deflection distance ( $a$ ) of the film from its original position to a new position (dash line).

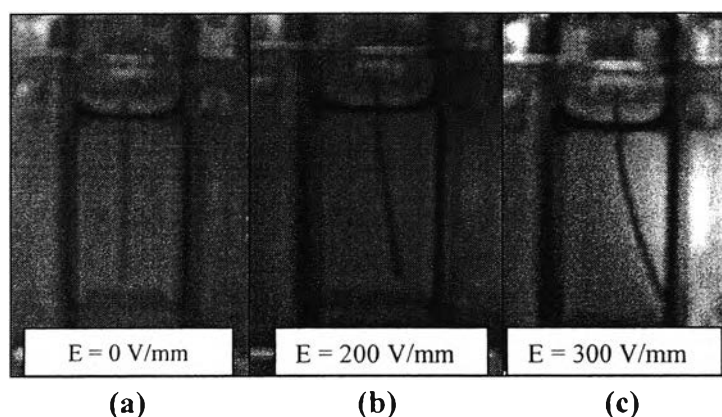


Fig. 7. Bending response pictures of pure NBR1 at various applied voltages at ambient temperature: (a)  $E = 0$  V/mm; (b)  $E = 200$  V/mm; (c)  $E = 300$  V/mm. Size of pure NBR sample 0.6 mm thick, weight 0.1515 g, width of 5.55 mm.

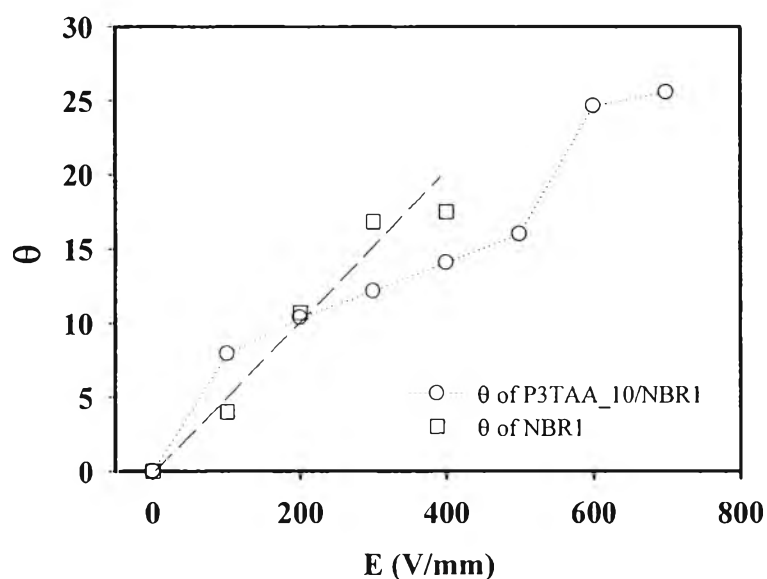


Fig. 8. Bending angle of pure NBR1 and P3TAA\_10/NBR1 vs. electric field strength at ambient temperature. Size of pure NBR sample is 0.6 mm thick, with the weight 0.1515 g; for P3TAA\_10/NBR1, it is 0.5 mm thick, weight of 0.1356 g, both samples have a width of 5.55 mm.

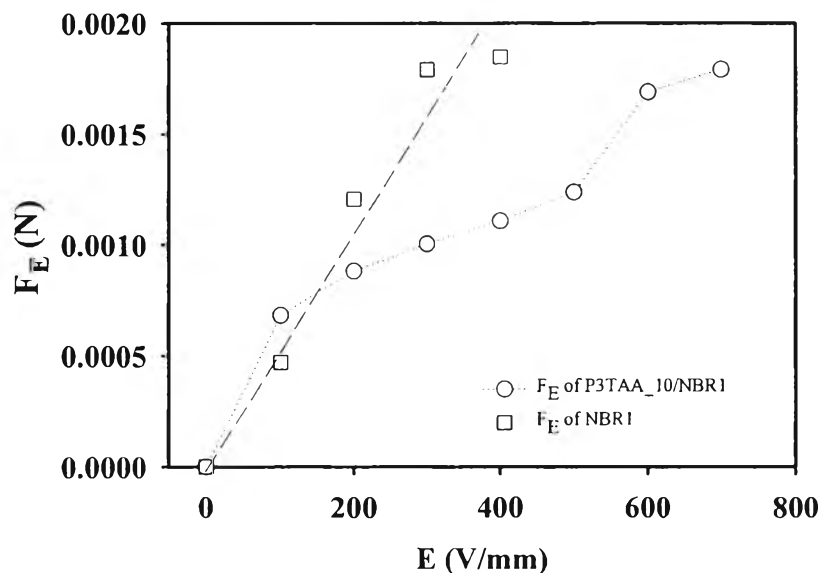


Fig. 9. Electric force of pure NBR1 and P3TAA\_10/NBR1 vs. electric field strength at ambient temperature. Size of pure NBR sample is 0.6 mm thick, with the weight 0.1515 g; for P3TAA\_10/NBR1 it is 0.5 mm thick, weight of 0.1356 g, both samples have a width of 5.55 mm.