



CHAPTER IV
POLY(P-PHENYLENE) AND ACRYLIC ELASTOMER BLENDS
FOR ELECTROACTIVE APPLICATION

Abstract

Polymer blends between poly(p-phenylene) PPP and an acrylic rubber (Nipol AR71) were fabricated in order to tailor their electromechanical properties towards electroactive 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 AR71 depend on the temperature and electric field strength; the storage modulus (G') monotonically increase with increasing electric field. The storage modulus sensitivity ($\frac{\Delta G'}{G'_0}$) increases with electric field strength and attains maximum values of 64% at the $E = 2$ kV/mm. For the polymer blends with the undoped particle concentrations of 5, 10, 20, 25, 30 and 40 vol%, the dynamic moduli, G' and G'' of each blend, are higher than those of pure AR71. Their storage modulus sensitivity ($\frac{\Delta G'}{G'_0}$) increases with electric field strength; it attains a maximum value about 97% at $E = 2$ kV/mm. The effect of temperature, on electrorheological properties of pure AR71 and polymer blends, is studied between 27-77 °C. The storage modulus increases linearly with temperature with the slope proportional to the effective strand density.

Keywords: Electroactive polymer, Poly(p-phenylene), Acrylic Elastomer, Dynamic moduli

Introduction

Electroactive materials have been continuously developed for a variety of applications such as muscle/insect-like actuators, robotics, drug release, and etc. One type of electroactive materials is the electroactive polymer [1]. Electroactive polymers (EAPs) offer promising and novel characters: lightweight, high energy density, and high flexibility; they are material candidates for muscle-like actuators. Dielectric elastomers belong to a type of electric-field-activated electroactive polymers that are capable of producing large strains, fast response, and relatively high efficiency [1]. In particular, an acrylic elastomer is a dielectric material which has many advantageous characters over other dielectric polymers: inexpensiveness, flexibility, low swelling in water, high tensile strength, good resilience, and high respond under electric field [2, 3]. These characteristics are desirable properties required to induce large actuation strains when subjecting a material to an electric field.

Recently, incorporation of a conductive polymer into a dielectric elastomer forming a composite has been of interest. Shiga *et al.* [4] studied the electroviscoelastic effect of the polymer blend between poly(p-phenylene) and silicone elastomer. They mixed the poly(p-phenylene) particles with silicone elastomer solution. They controlled the morphology of disperse phase by applied the electric field to polymer solution. They found that the storage and loss modulus sensitivity ($\Delta G'$ and $\Delta G''$) were increased linearly with the volume fraction of poly(p-phenylene) particles but the volume fraction of particles below 8.4 vol% could not produce the electroviscoelastic responded. Shiga and coworker had studied the effect of morphology of the disperse phase. The result show that in the case of the random dispersed the storage modulus increasing linearly with increasing of electric field but these relation did not linearly in the case of the straight line structure. The effect of temperature on the electroviscoelastic response was studied by Shiga, the result show that the electroviscoelastic effect starts over 50 °C and attains maxima at 110 °C. From the results that studied by Shiga, we expect that the conductive polymers can offer a variety of benefits to the host elastomer: variable conductivity, improved thermal stability, and mechanical properties. Examples are a polyanilene-

polyisoprene composite for biosensor application [5], a polyanilene-EPDM composite [6], and TiO₂ embedded in PDMS gels for actuator application [7].

In our work, we are interested in poly(p-phenylene)/Nipol AR71 elastomer blends as candidates for artificial muscles or actuators. The thermal properties, electrical properties, and electrorheological properties were investigated in terms of poly(p-phenylene) particle concentration, temperature, and electric field strength.

Experimental

Materials

Benzene solution (AR grade, Thai aromatic Co.,LTD) was used as the monomer. Aluminium chloride, AlCl₃ (AR grade, Riedel-delHean) was used as the oxidant. Cupric chloride, CuCl₂ (AR grade, Fluka-Aldrich) was used as the catalyst. The sulphuric acid dopant, H₂SO₄ (AR grade, Fluka-Aldrich) was used as received. Acrylic elastomers Nipol AR71 (Commercial grade, Zeon Polymix Advance Co.,LTD) were used as the polymer matrix.

Synthesis Poly(p-phenylene) and preparation of Polymer Blend

We followed the poly(p-phenylene) synthesis procedure of Kovacic [8] using benzene, AlCl₃, and CuCl₂. The reaction was carried out under nitrogen in a 3-neck flask equipped with a paddle stirrer. After the dropwise addition of benzene (1 mole) and aluminum chloride (0.5 mole), cupric chloride (0.5 mole) was introduced into the solution. Temperature was raised up to 35-37°C, and the reaction was allowed to proceed for 3 hours. Then the solution was cooled to 5°C and filtered with 18% HCl solution. The obtained poly(p-phenylene) powder was washed with boiling 18% HCl solutions until the washing solutions were colorless. The poly(p-phenylene) powder was finally washed with hot water until the washings had a pH of 7.0. After drying at 27°C under vacuum for 12 hours, the final obtained product was in the form of a finely divided, light brown solid powder. Great care was taken to avoid contamination from moisture [9-11]. We following the doping procedure of poly(p-phenylene) from previous work [12]. A suspension of dried poly(p-phenylene) powder in sulphuric acid was prepared in a sealed flask. The mole of sulphuric acid (N_{acid}) was varied vs. the mole of monomer ($N_{monomer}$). $N_{acid} : N_{monomer}$ values chosen were 1:100, 1:10, 1:1, 10:1 and 100:1. The mixture was

stirred for 2 hour, at temperature of 5°C, under nitrogen atmosphere. The doped poly(p-phenylene) was filtered out by a funnel. After drying at 27°C under vacuum for 12 hr, the obtained products were dark brown powders whose color depended on the degree of doping.

The blends were prepared by mechanical blending of Poly(p-phenylene) with an acrylic elastomer. We dissolved 7 cm³ of acrylic elastomer (Nipol AR71) in 70 cm³ of acetone and stirred for about 10 hours. Then we added PPP powder and stirred the mixture over night. The dispersion of particle is randomly. Concentrations of PPP in AR71 prepared were 5, 10, 15, 20, 25, 30, and 40% vol. We cast the sheets in a mold and left them in a vacuum oven to remove bubbles at 27°C for 24 hours.

Characterization and Testing

The undoped and doped poly(p-phynylene) (PPP) were characterized by a FT-IR spectrometer in order to identify their functional groups. The FT-IR spectrometer (Thermo Nicolet, Nexus 670) was operated in the absorption mode with 32 scans and a resolution of ± 4 cm⁻¹, covering a wavenumber range between 400 to 4,000 cm⁻¹, using a deuterated triglycine sulfate detector. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized PPP was intimately mixed with dried KBr at a ratio of PPP:KBr = 1:20

The UV-Visible spectra of undoped and doped Poly(p-phynylene) were recorded with a UV-Vis absorption spectrometer (Perkin-Elmer, Lambda 10). Measurements were taken in the reflectance mode in the wavelength range between 200-900 nm. Synthesized PPP was grinded into a fine powder and put into a sample holder. The scan speed was 100 mm/min, and a slit width of 5.0 nm using a deuterium lamp as the light source.

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to determine the amount of moisture content and the decomposition temperatures of undoped and doped poly(p-phenylene) at various mole ratios of dopant to poly(p-phenylene) with the temperature scan from 30 to 900°C, and with a heating rate of 10°C/min. The samples were weighted in the range of 5-10 mg and loaded into a platinum pan, and then heated it under a nitrogen gas flow.

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, model JSM-5200) to determine the morphology of poly(p-

phenylene) in powder forms and PPP/AR71 blends at various particle concentrations. The scanning electron micrographs of poly(p-phenylene) and polymer blends were obtained by using an acceleration voltage of 20 kV with magnifications of 350 and 1500 times.

X-rays diffraction patterns as recorded by a diffractometer (Phillips PW 1830/00 No.DF 1241) between angles of 5-35° were used to study the atomic arrangements and the degree of crystallinity of undoped poly(p-phenylene) and doped poly(p-phenylene). Samples were prepared in a pellet form from the compression.

Particle sizes of poly(p-phenylene) were determined by using a particle size analyzer (Malvern Instruments Ltd. Masterizer X Version 2.15). The lenses used in this experiment were 30 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 was measured by a meter which consists of two probes making contact on a surface of film sample. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The applied voltage and the current change in the linear Ohmic regime were converted to the electrical conductivity of polymer using equation (1) as follows:

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

where σ is specific conductivity (S/cm), ρ is the specific resistivity ($\Omega \cdot \text{cm}$), R_s is the sheet resistivity (Ω), I is the measured current (A), K is the geometric correction factor, V is the applied voltage (voltage drop) (V), and t is the pellet thickness (cm).

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials where specific resistivity values were known; we used silicon wafer chips (SiO_2). In our case, the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was calculated by equation (2) as follow:

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

where K is the geometric correction factor, ρ is the known resistivity of standard silicon wafer ($\Omega \cdot \text{cm}$), t is the film thickness (cm), R is the film resistance (Ω), and I is the measured current (A).

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 the 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 strains to measure G' and G'' in the linear viscoelastic regime. The appropriate strain was determined to be 0.1% for pure AR71 and for the undoped poly(p-phenylene) blended with AR71 matrix, respectively. 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. Before each measurement, pure AR71 and poly(p-phenylene)/AR71 blends samples were presheared at a low frequency (0.039811 rad/s), and then the electric field was applied for 13 minutes to ensure the formation of equilibrium polarization before the G' and G'' measurements. Experiments were carried out at the temperature of 27 °C and repeated at least two or three times. The effect of temperature was studied at various temperatures between 27-77°C for pure AR71 and polymer blend PPP/AR71 at 30%vol. The temporal response experiments were carried out at 1 and 2 kV/mm for pure AR71 and the polymer blend PPP/AR71 at 30%vol.

Results and Discussion

Characterization of Poly(p-phenylene)

A FT-IR spectrum of the undoped poly(p-phenylene) was taken to identify the characteristic absorption peaks [10]. The characteristic peaks of undoped poly(p-phenylene) are at 3,025-3,020 cm^{-1} , 1,477 cm^{-1} , 1,000 cm^{-1} , 805 cm^{-1} , 757 cm^{-1} , and 693 cm^{-1} . These peaks can be assigned to the C-H stretching of benzene ring; the double sides p-substitute stretching of benzene ring; the C-C stretching of benzene ring, and the single side p-substitute stretching, respectively [10]. A FT-IR spectrum of the doped poly(p-phenylene) was taken to identify the characteristic absorption peaks [12]. The characteristic peaks of doped poly(p-phenylene) are at 1,530 cm^{-1} , 1,080 cm^{-1} and 810 cm^{-1} . These peaks can be assigned to the double sides p-substitute stretching of benzene ring after doping, and the C-C stretching of benzene ring after doping, respectively [12]. The most important peak are the C-C stretching of benzene ring and the single side p-substitute stretching at 1477 and 805 cm^{-1} , respectively. After the doping process, these peaks shift to higher wavelengths [13].

UV-visible absorption spectra of undoped poly(p-phenylene) in powder form show a reflectance peak at 350 nm corresponding to the π - π^* transition of the benzoid ring [13]. After doping, the reflectance peak of the π - π^* transition of the benzoid ring shifts to 300-400 nm [14].

The TGA thermogram of undoped poly(p-phenylene) shows a degradation peak at 700 °C corresponding to the backbone degradation [8]. The highly doped poly(p-phenylene) thermogram shows two degradation steps at 220 °C and 700 °C; they can be referred to the short chain and the long chain degradations, respectively. The acrylic elastomers Nipol AR71 thermogram shows a degradation peak at 300°C.

The average particle diameter of poly(p-phenylene) is approximately 46 μm with standard deviation of 2 μm . Highly doped and undoped poly(p-phenylene) particle microstructure was observed using a scanning electron microscope (SEM). Figures 1 (a)-(b) show the shapes of the undoped and the doped poly(p-phenylene) particles; they are quite irregular in shape. Figure 1 (c), of the polymer blend between AR71 and 30 vol% undoped poly(p-phenylene), shows that particles are dispersed uniformly within the AR71 matrix.

The X-ray characteristic peaks of undoped poly(p-phenylene) are at 2θ equal to 19.58, 22.48, and 27.94, with corresponding d-spacings of 4.5301, 3.9518, and 3.1907 Å, respectively. The d-spacing at 19.58° can be referred to the length of a phenyl unit; the ring is nearly planar and completely of para substitution. After doping, the new peak has not been detected but the peaks shift to higher 2θ values, and the peak intensity decreases. The d-spacings slightly decreased which suggests that the structures are more closely packed [15, 16].

The specific conductivity of undoped and doped PPP and polymer blends was measured by a custom-built two point probe (Keithley, Model 6517A). The specific conductivity of undoped PPP is 5.28×10^{-6} S/cm with a standard deviation of 4.86×10^{-7} S/cm. The specific conductivity of doped PPP at $N_{\text{acid}} : N_{\text{monomer}}$ equal to 1:100, 1:10, 1:1, 10:1, and 100:1 are 1.07×10^{-6} , 1.56×10^{-6} , 3.48×10^{-5} , 3.31×10^{-4} , and 1.30×10^{-3} S/cm with standard deviations of 1.66×10^{-7} , 7.24×10^{-7} , 2.86×10^{-6} , 4.78×10^{-5} , and 2.26×10^{-5} S/cm, respectively.

Electrorheological Properties

Effect of Concentration

Effect of poly(p-phenylene) concentration on the rheological properties of polymer blends between poly(p-phenylene) and AR71 was first investigated. The morphology of disperse phase is randomly. Poly(p-phenylene) concentrations of the blends are 0, 5, 10, 20, 25, 30, and 40% vol. Figure 2(a) shows the storage modulus (G') vs. frequency at electric field strengths of 0 and 2 kV/mm and at strain equal to 0.1%. G'_0 and $G'_{2\text{kV/mm}}$ increase linearly with increasing particle concentration. The linearity of G'_0 vs. concentration ends at 20% vol; beyond this concentration the increase is nonlinear. For $G'_{2\text{kV/mm}}$ the linearity extends up to the maximum concentration of 40%. In this figure, we also show the storage modulus response $\Delta G'_{2\text{kV/mm}}$ vs. concentration. It can be seen that the response is maximum at 30% vol; it is equal to 107,770 Pa. The corresponding sensitivity value is 0.971, as also tabulated in Table 1. The mixing of poly(p-phenylene) particles into AR71 leads to the increases in both G' and G'' with and without electric field. The increasing of G'_0 can be attributed to the effect of particles acting as fillers. The corresponding

increase in G'' can be attributed to the induced free volume and the fact that the interface of the particles and the matrix is poor.

Figure 2(b) shows the relation between the response $\Delta G'_{2\text{kV/mm}}$ and the sensitivity $\Delta G'_{2\text{kV/mm}}/G'_o$ vs. G'_o of the pure AR71 and various polymer blends. The storage modulus sensitivity values at electric field strength of 2 kV/mm are 61.7, 23.8, 30.6, 71.0, 76.3, 97.1, and 14.3% for pure AR71, and blends of 5, 10, 15, 20, 25, 30, and 40 vol%. The sensitivity first decreases with G'_o , then rises towards a maximum, and then decreases monotonically with the particle concentration greater than 30 % vol. The initial decrease in the G' response suggests that a very soft matrix can be readily activated with electric field. For a small amount of particles added, the fillers induce only additional free volume, the number of particles is too small, and 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 concentration. As more particles are added to the matrix, the distances between particles become smaller and stronger interparticle interactions result. Physically, the induced dipole moments can be thought of generating an equivalence of electric network strands which increase the storage modulus response and sensitivity. The maximum $\Delta G'_{2\text{kV/mm}}$ and $\Delta G'_{2\text{kV/mm}}/G'_o$ occurs with the material system AR71:30_un. For the material system with the highest particle concentration of 40 % vol corresponding to the highest G'_o , the effect of electric field appears to diminish since this system is presumably hardened without electric field applied, and the phase separation may exist between the matrix and the particles, and consequently a poor stress transfer; an additional increase in G' with electric field is hampered.

Shiga *et al.* [4] was found the similar effect for poly(p-phenylene) and silicone elastomer blend. The electroviscoelastic effect increased with increasing of particle content. They found that the enhancement of shear modulus was negligible below 8.4% vol. Liu *et al.* [17] 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. Krause *et al.* [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. Chotpattananont *et al.* [18] found that the storage and loss moduli of a polymer blend between polythiophene and polyisoprene increased with increasing polythiophene concentration.

Effect of Temperature

The effect of temperature on the rheological properties of the pristine elastomer [AR71] was investigated next at electric field strengths of 0 and 2 kV/mm with the temperature range between 300-350 K. Figure 3(a) shows G'_{\circ} and $G'_{2\text{kV/mm}}$ vs. absolute temperature. Here we used one sample each for the G'_{\circ} and $G'_{2\text{kV/mm}}$ measurements. Without electric field applied, G'_{\circ} was measured successively at each temperature. Electric field was first applied on another sample for a period of 10 minutes before $G'_{2\text{kV/mm}}$ was measured successively at each temperature. We can see that the storage moduli increase linearly with temperature, in conformation with the classical network theory [19]:

$$G' = \nu k_B T \quad (3)$$

where k_B is Boltzmann's constant, T is the absolute temperature [K], and ν is number of strands per unit volume [$1/\text{cm}^3$]. Since the elastomer was unmodified and no crosslinks existed, the linear dependence of G'_{\circ} and $G'_{2\text{kV/mm}}$ on T presumably stems from physical entanglements. G' at 2 kV/mm is higher than that without electric field at any temperature investigated, as a result of the dipole-dipole interactions created by the electric field within the matrix. In addition, we may note that the slope of G'_{\circ} is lower than that of $G'_{2\text{kV/mm}}$. Eq. (3) implies that ν of the blend with electric field applied is larger than at without electric field. .

Figure 3(b) shows $\Delta G'_{2\text{kV/mm}}$ and $\Delta G'_{2\text{kV/mm}}/G'_{\circ}$ of pure AR71 as functions of G'_{\circ} for the experiments of Figure 3(b). Both functions increase monotonically with G'_{\circ} . The effects of electric field strength and temperature on the electrorheological properties of a polymer blend of AR71 and poly(p-phenylene) 30

vol% or AR71:30_un, was investigated next in the range of electric field strength between 0-2 kV/mm, and in the range of temperature between 300-350 K. Figure 4(a) shows G'_o and $G'_{2kV/mm}$ vs. temperature. Experiments were carried out using the same procedure as that of the data of Figure 3(a). With the presence of poly(p-phenylene) particles, G'_o and $G'_{2kV/mm}$ increase linearly with temperature, consistent with the relation of Eq. (3). Here, ν with electric field is slightly higher than that of ν without electric field. Figure 4(b) shows $\Delta G'_{2kV/mm}$ and $\Delta G'_{2kV/mm}/G'_o$ of pure AR71 as functions of G'_o for the experiment of Figure 2(b). While $\Delta G'_{2kV/mm}$ increases monotonically with G'_o , $\Delta G'_{2kV/mm}/G'_o$ decreases. Shiga *et al.* [4] reported that the temperature could lead to increased the electroviscoelastic effect of polymer blends. From their results the polymer blends had electroviscoelastic effect start accelerated at over 50 °C and attain maxima at 110 °C. They explained that the effect of increasing of the storage modulus come from the point-dipole approximation model. This effect comes from the raising of dielectric permittivity by increasing the temperature.

Time Dependence of the Electrorheological Response

Finally, we investigated the temporal characteristic of pure AR71 and the polymer blend at particle concentration of 30 vol% (AR71:30_un), at electric field strengths 1 and 2 kV/mm. The temporal characteristic of each sample was recorded in the linear viscoelastic regime at a strain of 0.1 %, and frequency of 1 rad/s.

Figure 5 shows the change in G' of pure AR71 system at electric field strengths 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 fields of 1 or 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 its original value. Subsequent on and off on electric field produces steady state responses after a duration of about 10,000 sec. 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 an 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 is called the induction time, τ_{ind} . As shown in Table 2, the τ_{ind} increases with increasing electric field strength; they are 120 and 395 sec at electric field strengths equal to 1 and 2 kV/mm, respectively. The time required for G' to decay towards its steady-state value when the electric field is turned off is called the recovery time, τ_{rec} . It is essentially independent of the electric field strength, as shown in Table 2. The recovery time are 72 and 97 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 notably small such that the relaxations were nearly the same.

Figure 6 shows the temporal response of AR71 and PPP 30 vol% blends (AR71:30_un) at electric field strengths of 1 and 2 kV/mm, respectively. After some initial period with electric field on and off, the AR71:30_un appears to be a reversible system at both of electric field strengths. Our result here may suggest that there are some irreversible interactions between poly(p-phenylene) particles, perhaps due to dipole bondings between adjacent poly(p-phenylene) particles and residual dipole moments inducing permanent interparticle interactions. τ_{ind} increases with electric field strength; as shown in Table 4.2, τ_{ind} are 103 and 497 sec at electric field strengths equal to 1 and 2 kV/mm, respectively. On the other hand, τ_{rec} is nearly independent of electric field strength; as shown in Table 2, τ_{rec} are 94 and 180 sec at electric field strength equal to 1 and 2 kV/mm, respectively.

Conclusions

In this study, electrorheological properties of poly(p-phenylene)/AR71 blends were investigated by examining the effects of poly(p-phenylene) particle concentration and temperature on the dynamic modulus, G' , under the oscillatory shear mode at electric field strength varying from 0 to 2 kV/mm. In the pure AR71 system, the storage modulus (G') increases with increasing electric field strength. We suggest this result to be related to the number of electrical strands created by electric field-induced dipole moments. The storage modulus sensitivity ($\Delta G'_{2kV/mm}/G'_0$) of the polymer blends with the concentrations of 0, 5, 10, 15, 20, and 25 increases linearly with electric field strength 0 kV/mm. The maximum storage modulus

sensitivity is about 97% for the AR71:30_un system at electric field strength 2 kV/mm.

The effect of temperature is to increase the storage modulus of pure AR71 and poly(p-phenylene)/AR71 linearly. For pure AR71 and AR71:30un systems, in conformity with the classical rubber elasticity, the effect of temperature and electrical strands induce an increase in G' linearly with temperature. With PPP particles present, the effect of electrical strands induced becomes more dominant.

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References

- [1] S. Krause, K. Bohon, *Macromolecules* 34 (2001) 7179–7189.
- [2] R. Kornbluh, R. Perlrine, Q. Pei, S. Oh, J. Joseph, *Proceedings of The first World Congress on Biomimetics*, 2002.
- [3] Z. Shen, H. Xue, Y. Li, *Synth. Metals* 124 (2001) 345–349.
- [4] T. Shiga, *Advances in Polymer Science*, vol. 134/20, Springer-Verlag, Berlin, 1997, pp. 133–163.
- [5] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, *J. Chem. Soc.* 578 (1977) 911–923.
- [6] B. Francis, M. Rawiso, *Synth. Metals* 69 (2005) 85–97.
- [7] A.A. Berlin, *J. Polym. Sci.* 55 (1962) 105–120.
- [8] P. Kovacic, A. Kyriakis, *J. Am. Chem. Soc.* 85 (1969) 2238–2242.
- [9] P. Kovacic, F.W. Koch, *J. Am. Chem. Soc.* 28 (1963) 1864–1869.
- [10] P. Kovacic, R.M. Lange, *J. Am. Chem. Soc.* 28 (1962) 1960–1966.
- [11] P. Kovacic, C. Wu, *J. Polym. Sci.* 47 (1960) 540–544.

- [12] P. Hiamtup, MS Thesis, Silpakorn University, 2002, pp. 22–23.
- [13] S. Geetha, D.C. Trivedi, *Synth. Metals* 148 (2005) 891–900.
- [14] J. Oguma, K. Akagi, H. Shirakawa, *Synth. Metals* 101 (1999) 86–103.
- [15] W.V. Evans, R. Pearson, D. Braithwaite, *J. Am. Chem. Soc.* 63 (1994) 1024–1030.
- [16] B. Yu, H. Li, *Mater. Sci. Eng. A325* (2002) 463–490.
- [17] B. Liu, T.M. Shaw, *J. Rheol.* 45 (2001) 641–657.
- [18] D. Chotpattananont, A. Sirivat, A.M. Jamieson, *Colloid Polym. Sci.* 282 (2004) 357–365.
- [19] M. Rubinstein, R.H. Colby, *Polym. Phys.* (2003) 298–300.

Table 1 Rheological properties of polymer blends of PPP and acrylic elastomer (Nipol, AR71)

%v/v of PPP	G'_0 (Pa)	$G'_{2kV/mm}$ (Pa)	G''_0 (Pa)	$G''_{2kV/mm}$ (Pa)	$\Delta G'_{2kV/mm}$ (Pa)	$\Delta G''_{2kV/mm}$ (Pa)	$\Delta G'_{2kV/mm}/G'_0$	$\Delta G''_{2kV/mm}/G''_0$	σ (S/cm.)
0	9959	16105	1124	2206	6146	1082	0.617	0.962	2.35E-12
5	21375	26478	2707	2897	5103	190	0.238	0.065	3.53E-12
10	27250	34979	2565	3918	7729	1353	0.306	0.527	8.73E-12
20	39859	68158	5316	9798	28299	4482	0.710	0.843	1.03E-11
25	68353	120490	10825	18503	52137	7678	0.763	0.415	4.28E-11
30	115420	218750	15111	28564	107770	13453	0.971	0.890	8.95E-11
40	343330	396960	42644	50312	49800	7668	0.143	0.179	1.01E-09

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

G'_0 , and G''_0 are the storage and loss moduli without electric field

$G'_{2kV/mm}$, and $G''_{2kV/mm}$ are the storage and loss moduli at 2 kV/mm.

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

$\Delta G''_{2kV/mm}$ is the loss modulus response defined as $G''_{2kV/mm} - G''_0$

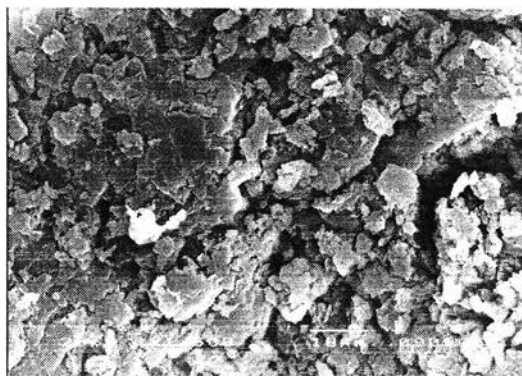
$\Delta G'_{2kV/mm}/G'_0$ is the sensitivity of the storage modulus

$\Delta G''_{2kV/mm}/G''_0$ is the sensitivity of the loss modulus

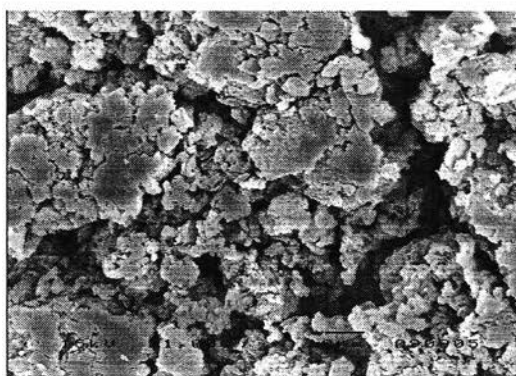
σ is the electrical conductivity of polymer

Table 2 Induction time and recovery times at 27°C of AR71 matrix and AR71:30_un

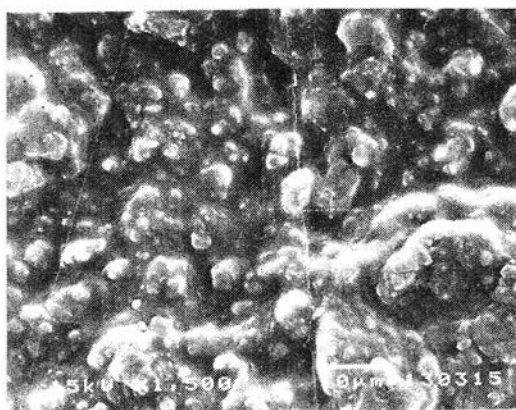
Samples	Electric field	First induction time	Saturated induction time	First recovery time	Saturated recovery time	First $\Delta G'_{ind}$	Saturated $\Delta G'_{ind}$	First $\Delta G'_{rec}$	Saturated $\Delta G'_{rec}$
	(kV/mm)	(τ_{ind}) (s)	(τ_{ind}) (s)	(τ_{rec}) (s)	(τ_{rec}) (s)	(Pa.s)	(Pa.s)	(Pa.s)	(Pa.s)
Pure AR71	1	451	120	97	72	2,490	578	256	374
Pure AR71	2	487	395	132	97	4,795	1,115	802	922
AR71:30 un	1	602	103	443	94	6,374	2,819	2,410	1,771
AR71:30 un	2	518	497	437	180	43,910	63,270	24,140	49,650



(a)

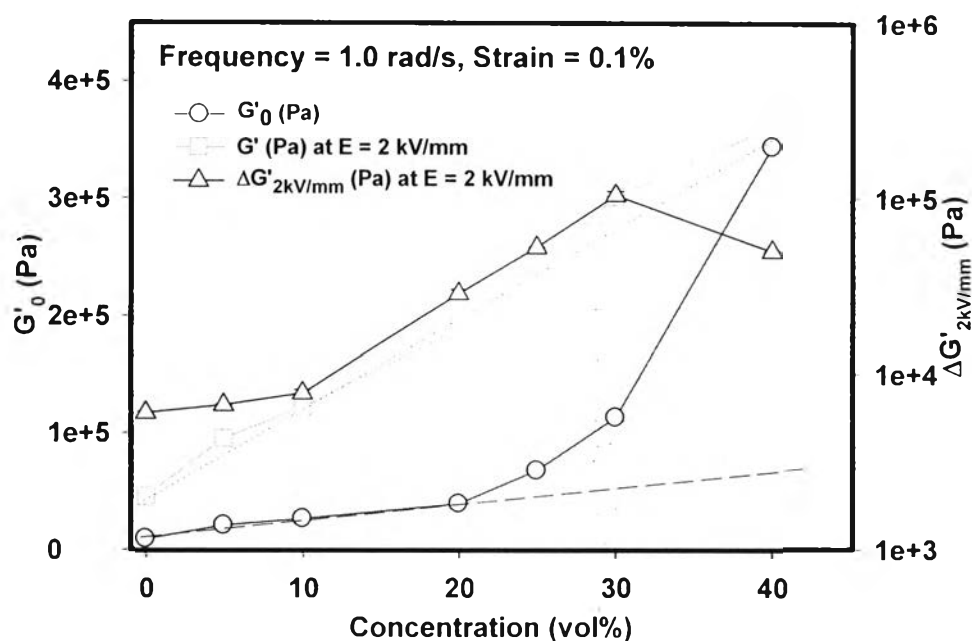


(b)

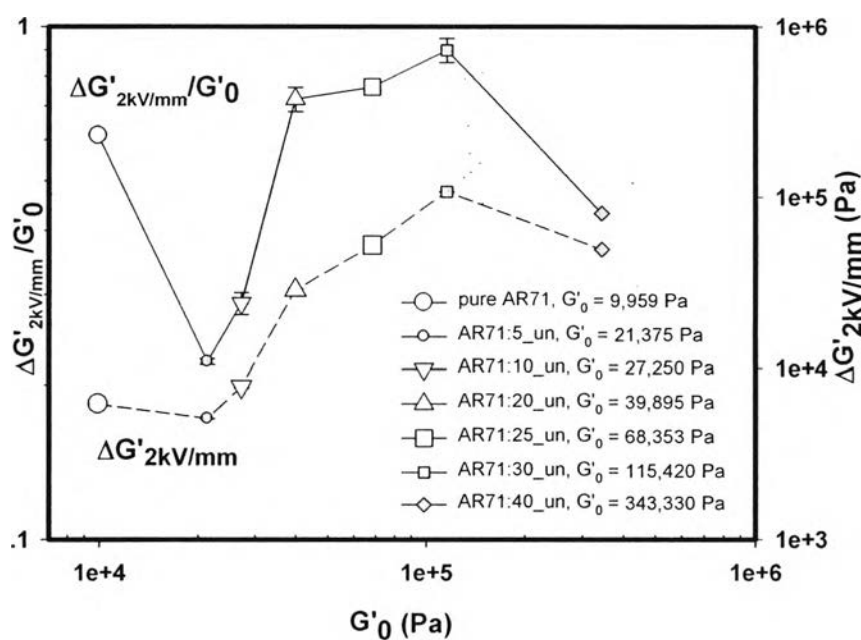


(c)

Figure 1 The morphology of poly(p-phenylene) particles and the poly(p-phenylene)/AR71 blend: a) synthesized undoped PPP at magnification of 1,500; b) synthesized doped PPP, at $N_{\text{acid}}: N_{\text{monomer}} = 100:1$, and at magnification of 1,500; and c) AR71:30_un blend at magnification of 1500.

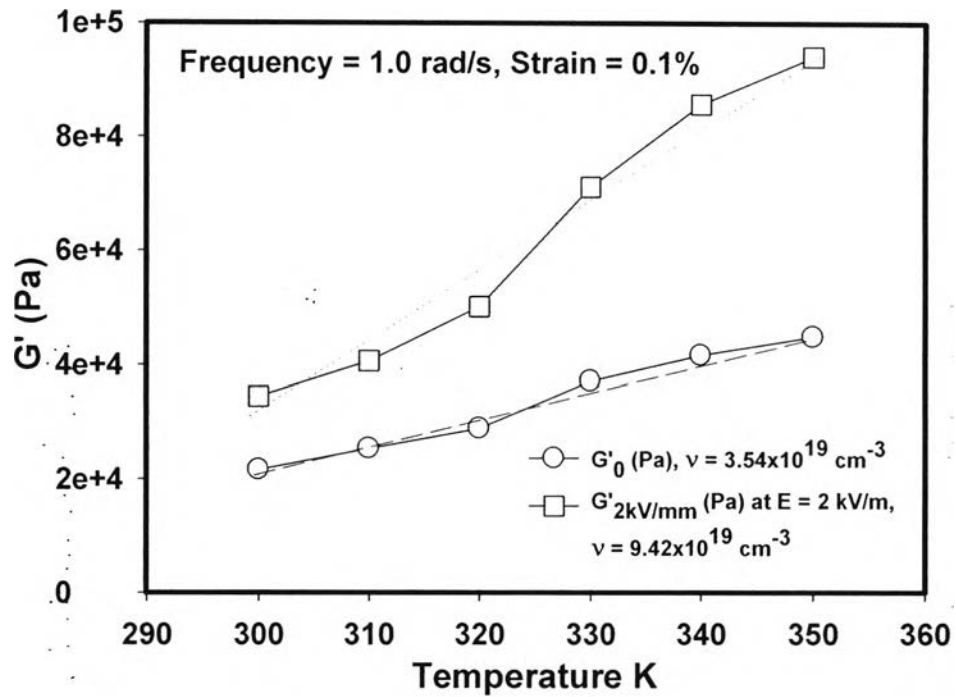


(a)

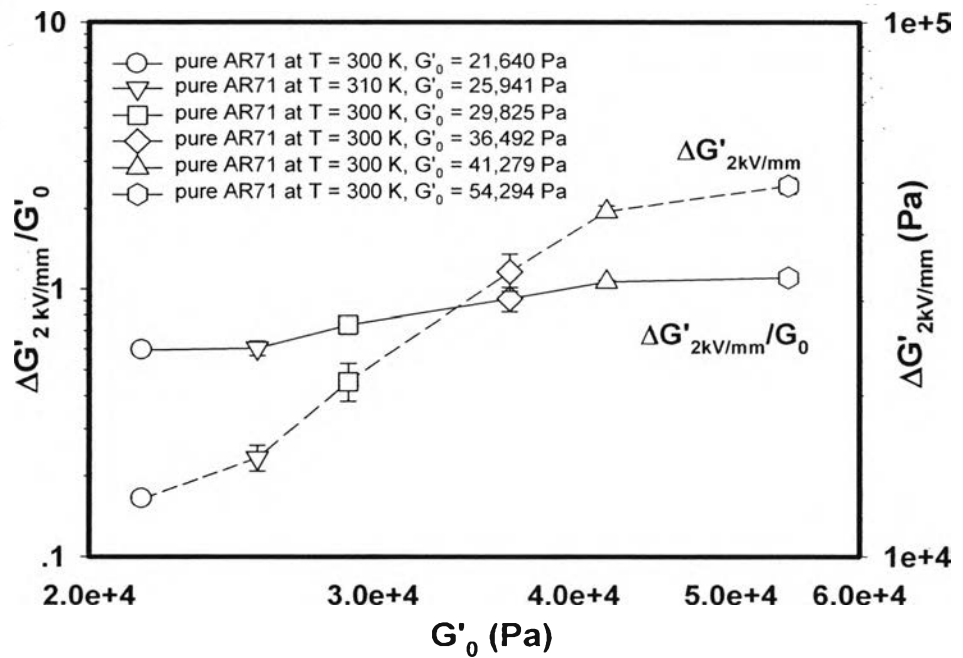


(b)

Figure 2 Effect of concentration of particle on: (a) the storage modulus responses ($\Delta G'$) at $E = 1$ and 2 kV/mm and storage modulus at $E = 0$ (G'_0) and 2 kV/mm (G'_0); and (b) the storage modulus sensitivity ($\Delta G'/G'_0$) vs. G'_0 , and the storage modulus response $\Delta G'$ at $E = 2$ kV/mm ($\Delta G'_{2kV/mm}$) vs. G'_0 .



(a)



(b)

Figure 3 Effect of temperature for the pure matrix on: (a) the storage modulus (G') at $E = 0$ and 2 kV/mm at various temperatures for one sample at all temperatures tested; (b) the sensitivity of storage modulus ($\Delta G'/G'_0$) vs. G'_0 and the storage modulus response $\Delta G'$ at $E = 2 \text{ kV/mm}$ ($\Delta G'_{2\text{kV/mm}}$) vs. G'_0 .

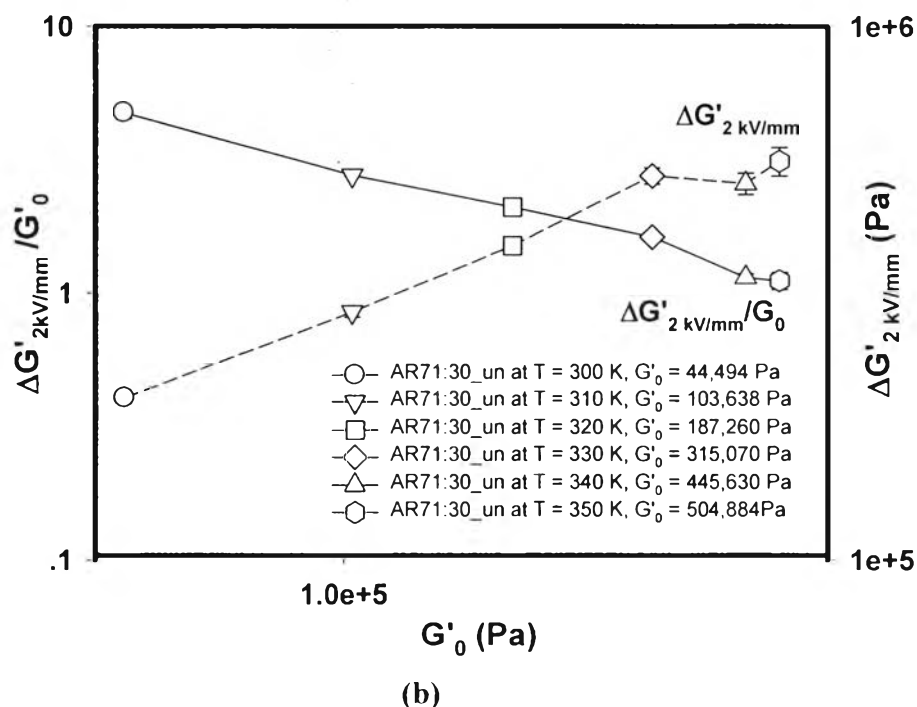
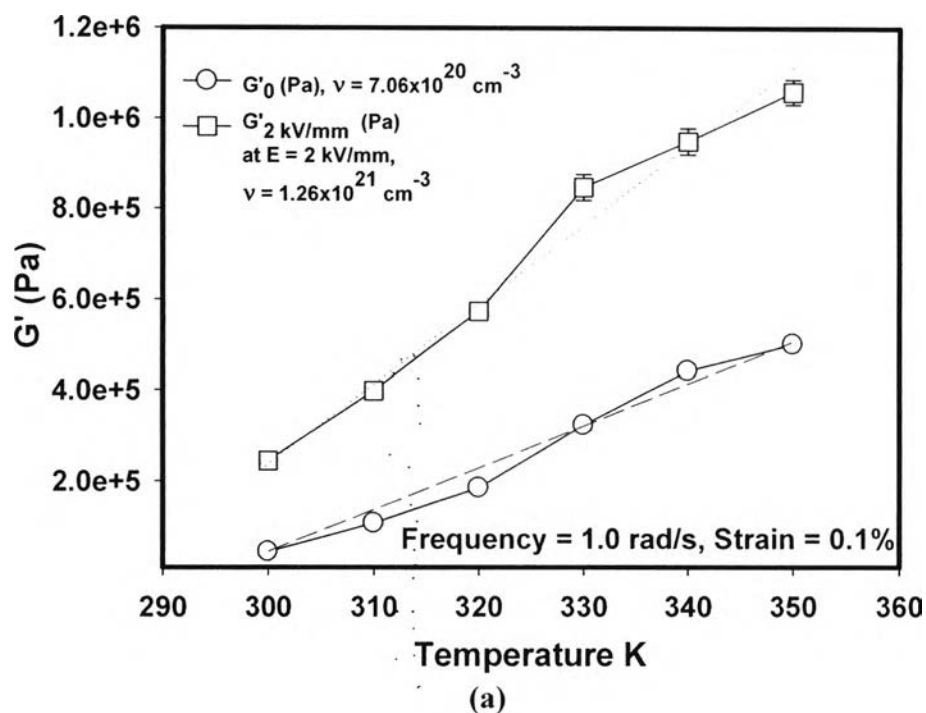


Figure 4 Effect of temperature of the polymer blend between AR71 and undoped PPP at 30% v/v (AR71:30_un): (a) the storage modulus (G') at $E = 0$ and 2 kV/mm at various temperatures using one sample for all temperatures tested; (b) the sensitivity of storage modulus ($\Delta G'/G'_0$) vs. G'_0 and the storage modulus response $\Delta G'$ at $E = 2 \text{ kV/mm}$ ($\Delta G'_{2 \text{ kV/mm}}$) vs. G'_0 .

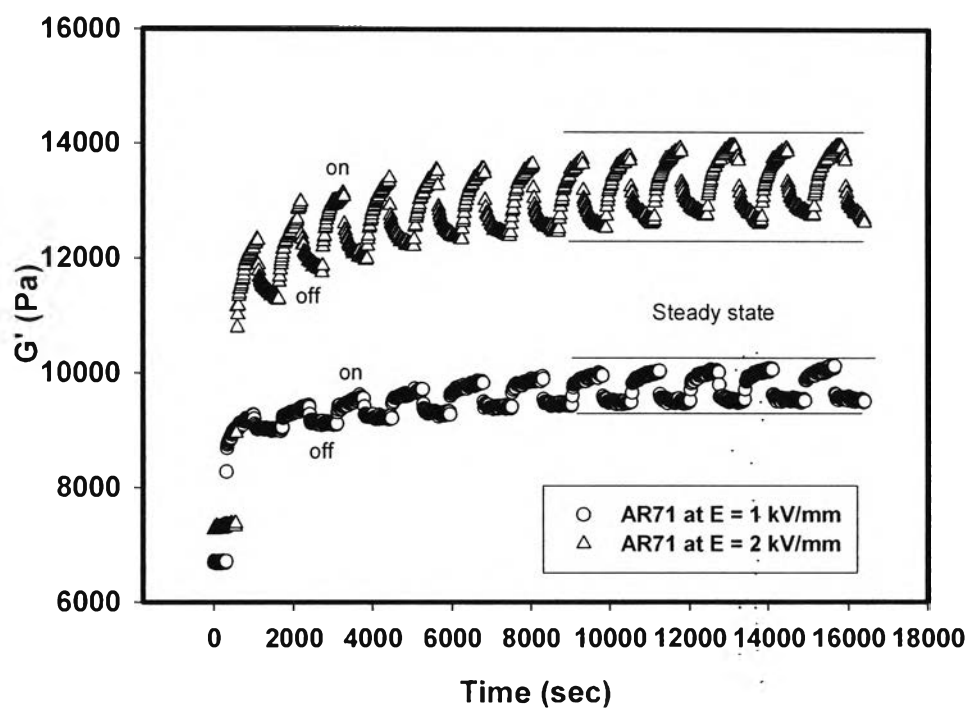


Figure 5 Temporal response of the storage modulus (G') of AR71 matrix at electric field strengths of 1 and 2 kV/mm, frequency 1.0 rad/s, strain 0.1%, and at 27 °C.

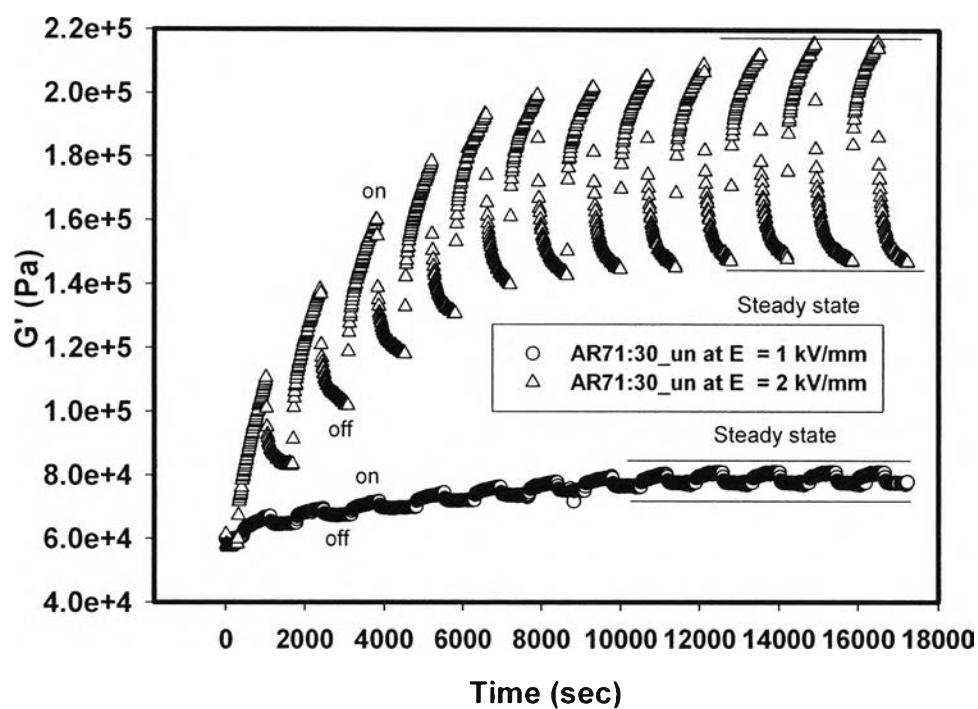


Figure 6 Temporal response of storage modulus (G') of the polymer blend between AR71 and undoped PPP at 30% v/v (AR71:30_un) at electric field strengths of 1 and 2 kV/mm, frequency 1.0 rad/s, strain 0.1%, and at 27 °C.