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Using *in-situ* synchrotron x-ray diffraction to investigate phase transformation and lattice relaxation of a three-way piezo-phototronic soft material

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Abstract

A poly(vinylidene fluoride-co-trifluoro-ethylene) piezoelectric polymer is blended with nano particles of titanium oxide phthalocyanine to bridge photoconductive and piezoelectric effects. In this study, a system is examined by *in situ* synchrotron x-ray to test a three-way piezo-phototronic soft-material design. The sample is heated for *in situ* phase transformation characterization. The semi-crystalline poly (vinylidene fluoride-co-trifluoro-ethylene) polymer gradually transforms to an amorphous structure. A complementary piezoelectric experiment before and after the heating experiment shows that the piezoelectric performance is proportional to the phase ratio. Secondly, the system is examined to test its phototronic effect. Piezoelectric responses are measured by controlling the light illumination. The positive and negative controls of light illumination which validate this newly-designed system can be modulated by a three-way piezo-phototronic effect. *In-situ* synchrotron x-ray diffraction experiments are employed to measure the microstructure evolution as a function of applied voltage up to 800 V. We then

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turned off both the light and the applied voltage to examine the kinetic behavior of the system. There is orientation-dependent anisotropic relaxation. We compared the lattice-strain evolutions. Piezo-phototronic creep is found in the (110), but not the (310) planes.

Keywords: piezoelectric, piezo-phototronic, photoconductive, *in-situ* synchrotron x-ray diffraction, poly(vinylidene fluoride-co-trifluoroethylene), titanium oxide phthalocyanine

(Some figures may appear in colour only in the online journal)

1. Introduction

Piezo-phototronic devices enable a new direction for smart materials [1–3]. The concept is successfully employed on condensed materials [3–5], one-dimensional (1D) nanomaterial [6], and 2D materials [7]. To address the rising demand for flexible electronics and wearable devices, it becomes more and more important to develop new soft materials with piezo-phototronic properties. However, it is not trivial to integrate piezoelectricity, photonic excitation and semiconductor transport to couple three-way controls into soft materials.

Recently, Chang *et al* blended a semi-crystalline poly(vinylidene fluoride-co-trifluoro-ethylene) piezoelectric P(VDF-TrFE) polymer with nano particles of titanium oxide phthalocyanine (TiOPc) [8]. The TiOPc nano particles can harvest visible light to excite electrons. The band gaps of the PVDF-TrFE matrix between the lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals are modulated by these TiOPc nano particles subjected to light illumination. There is a dramatic improvement of piezoelectric properties, shown in both bulk performance and at lattice level [9].

Besides the aforementioned progress of developing new piezo-phototronic soft materials, the response time to the light illumination is another key parameter to advance the new system. However, this new material is still at an early stage. How to adjust and control the speed of electro-optical properties among the coupled fields, which interplay with the strain induced piezopotential, is still not clear. Hence, the objectives of the current study are to: (i) examine the phase-dependent piezoelectric performance by heating the sample; (ii) revisit the lattice-level responses subjected to the three-way piezo-phototronic controls, and (iii) examine the time-dependent relaxation behaviors of the P(VDF-TrFE).

2. Methods

The major challenges to obtain a desirable experimental environment were sample preparations and setup for the time-resolved *in situ* diffraction measurement with sufficient statistics. For the sample preparation, we blended the P(VDF-TrFE) copolymer and the TiOPc ($C_{32}H_{16}N_8OTi$) by mixing in dimethylacetamide (DMAC) solvent. The amount of TiOPc was 10 wt%. To achieve the best performance, this solution was stirred continuously for more than 24 h. To prepare the system in a format of thin film and to construct the device, a spin-coating technique was applied to coat the P(VDF-TrFE) and TiOPc mixture onto an indium-tin-oxide (ITO) coated glass slide. 50 μm films were formed at 65 °C on a hot plate

for two hours. The device of the P(VDF-TrFE) copolymer and the nano TiOPc on ITO was then annealed in a vacuum oven to evaporate the remaining solvent. The annealing processes include one step at 135 °C for 2 h and was followed by another at 70 °C for one hour. After the annealing process, the systems were poled for 2 h at 90 °C. Detailed information about the materials can be found in our earlier report [9].

The experiment was carried out at the beamline 13A of the National Synchrotron Radiation Research Center (NSRRC). The synchrotron x-ray was enabled to sample a greater gauge volume. A beam size of 1 mm in horizontal and 0.3 mm in vertical directions was capable of probing the polycrystal P(VDF-TrFE) matrix lying in different orientations. The P(VDF-TrFE)-TiOPc specimens were placed in a program-controlled device to heat the sample. *In-situ* measurements were conducted to study the phase transformation subjected to environmental temperature. The 2D diffraction patterns were simultaneously collected at a specific temperature. Unlike the diffraction spots from the preferred orientation seen in the other systems [10], uniform diffraction rings were observed in the systems [9]. The isotropic distribution of the diffraction intensity showed that there was no texture in our system. Hence, standard data reduction procedures were followed to reduce 2D diffraction rings into 1D diffraction profiles as a function of the applied voltage.

The results of where the phases were identified from the β -phase structure of P(VDF-TrFE) at room temperature to partial α -phase are shown in (figure 1(a)). A comparison was carried out between the intensity from the α -phase and β -phase and we quantified the piezo effect by measuring the d_{33} values to test the phase-dependent piezo effect. The phase ratio was quantified in (figure 1(b)). Similarly, an experiment was conducted at the beamline 13A of the National Synchrotron Radiation Research Center (NSRRC). The experimental configuration enabled us to apply a driving voltage and a control for with/without visible-light illumination. The Rayonix SX165 detector of the beamline 13A was enabled to complete each measurement within 2 min. Unlike the heating experiments, the environmental temperature was not changed. The P(VDF-TrFE)-TiOPc specimens were placed in a program-controlled device. *In-situ* measurements were conducted to study the piezoelectric responses subjected to applied voltage. The 2D diffraction patterns were simultaneously collected at specific applied voltage levels. Again, there were uniform diffraction rings observed in our systems [9]. The isotropic distribution of the diffraction intensity showed that there was no texture in our system subjected to applied voltage as well as light illumination. Hence, standard data reduction procedures were followed to reduce 2D diffraction

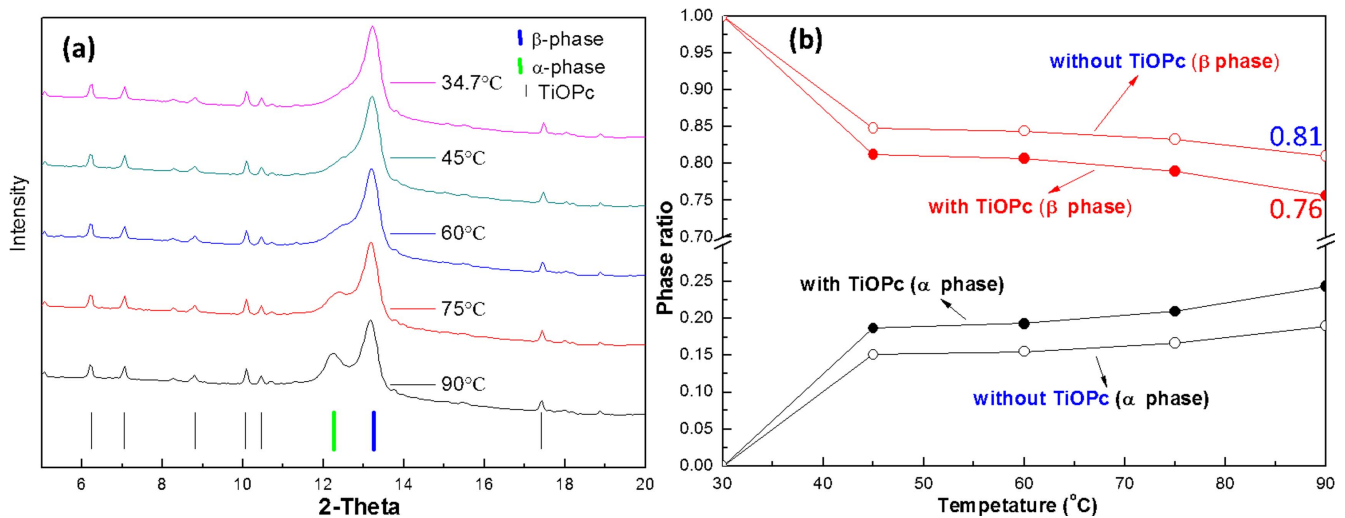


Figure 1. Diffraction evolution of the P(VDF-TrFE) subjected to heating: (a) Diffraction profiles of the 34.7 °C (pink), 45 °C (green), 60 °C (blue), 75 °C (red), and 90 °C (black). The diffraction peaks of α -phase, β -phase, and TiOPc diffraction peaks are marked with green, blue, and black legends, respectively. (b) The phase ratio for β -phase of the P(VDF-TrFE) with TiOPc (●) and without TiOPc (○). Similarly, the phase ratio for α -phase of the P(VDF-TrFE) with TiOPc (●) and without TiOPc (○).

rings into 1D diffraction profiles as a function of the applied voltage.

Referring to our earlier work [9], the (1 1 0) and (3 1 0) diffractions of the matrix were identified from the β -phase structure of P(VDF-TrFE). The diffraction results suggested that the matrix P(VDF-TrFE) systems have an all-trains (TTTT) conformation [11, 12]. Specifically, there were repeated units of a carbon back bone with two hydrogen and two fluorine atoms of the all-trains (TTTT) conformation as β -phase [13]. The all-trains (TTTT) conformation was formed by a net dipole moment pointing from relatively electro-negative fluorine to hydrogen [13]. The ensembles of the all-trains (TTTT) conformation collectively contributed to the piezoelectric property of the bulk P(VDF-TrFE).

To test the piezo-phototronic effect, the system which has been under the poling procedure was selected. Measurement was carried out and we controlled the environmental light illumination. An identical sample was measured subject to two conditions: one with light illumination and the other without light (for comparison). Diffraction data was collected at 0, 100, 300, 400, 500, 600, 700, and 800 Volts, respectively.

Final measurement was collected according to the aforementioned procedure at 800 V; both the light and the applied voltage were turned off. The samples had the identical configuration to the *in situ* synchrotron x-ray measurement setup. Measurement of the x-ray diffraction as a function of time was continued. With the fast data collection speed of the Rayonix SX165 detector, the relaxation behavior at a rate of every 2 min was measured.

3. Results

3.1. The phase-dependent piezo effects

To demonstrate the heating effect, the diffraction profiles at different temperatures are shown in (figure 1(a)). In the

beginning, there is the β -phase diffraction peak, marked by a blue legend, and TiOPc peaks, marked with black legends, respectively. Upon heating, there is a left shoulder shown underneath the β -phase diffraction peak, which is from the α -phase. The peak of the α -phase is marked with a green legend. To quantify the phase transformation from 34.7 to 90 °C, we resolve the diffraction intensity with an assumption of two-Gaussian-peaks. The peak intensity ratio is shown in (figure 1(b)) to show the temperature-dependent phase-transformation quantity. For comparison, we also carry out the same procedure on a P(VDF-TrFE) system, but without TiOPc. The temperature-dependent phase-transformation of the P(VDF-TrFE) system without TiOPc is also shown in figure 1(b). The ratio of the β -phase of the P(VDF-TrFE) system without TiOPc drops to 0.81 and that of the P(VDF-TrFE) system with TiOPc decreases to 0.76. Cheng *et al* also reported that the copolymer will go from the low-temperature (LT) ferroelectric phase to the high-temperature (HT) paraelectric phase [14].

Other piezoelectric tests are applied on identical systems of P(VDF-TrFE) with and without TiOPc as mentioned above, respectively. Before heating, the P(VDF-TrFE) system with TiOPc has a d_{33} value of 11.86 and that of the system without TiOPc is 17.4. The piezoelectric tests reflect the bulk performance. The P(VDF-TrFE) system containing TiOPc has a lower d_{33} value at 11.86 because TiOPc does not have piezoelectric properties. After heating up to 90 °C, both systems are cooled to room temperature. The d_{33} value of the P(VDF-TrFE) system with TiOPc decreases to 9.13 and that of the system without TiOPc decreases to 14.4. The d_{33} value of the heated P(VDF-TrFE) system with TiOPc becomes 77% of that of the identical system before heating. Similarly, The d_{33} value of the heated P(VDF-TrFE) system without TiOPc becomes 83% of that of the identical system before heating. Compared to figure 1(b), the performance change of

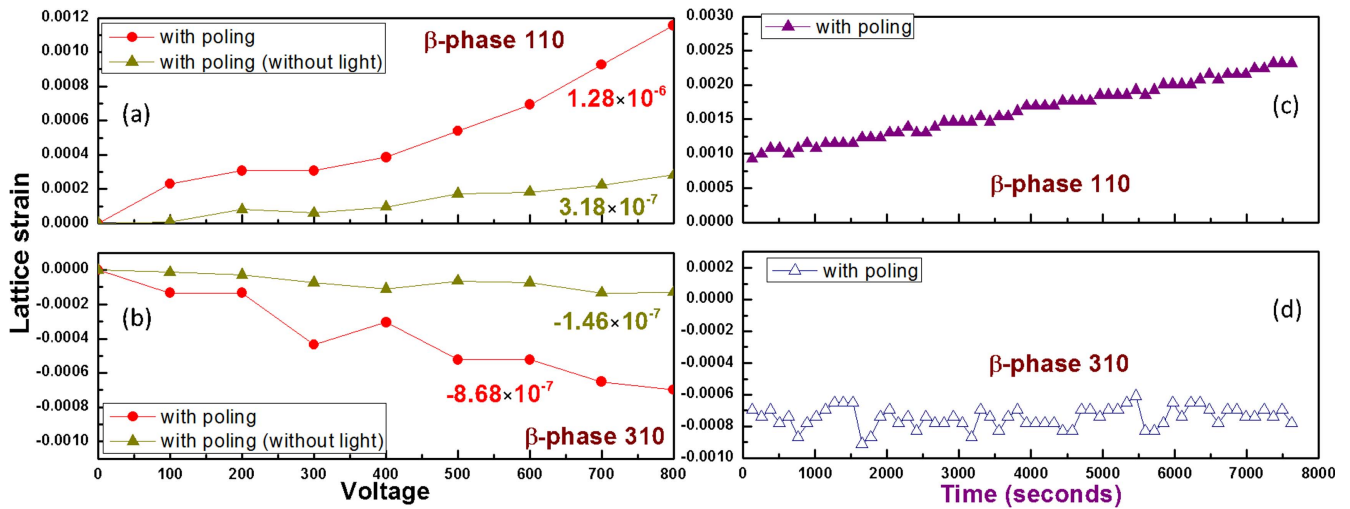


Figure 2. Lattice-strain evolution: (a) β -phase (1 1 0)-plane-lattice before light illumination (\blacktriangle) and after light illumination (\bullet); (b) β -phase (3 1 0)-plane-lattice before light illumination (\blacktriangle) and after light illumination (\bullet). Time-dependent lattice-relaxation behavior for (c) β -phase (1 1 0)-plane-lattice when both light and voltage are turned off (\blacktriangle). (d) β -phase (3 1 0)-plane-lattice when both light and voltage are turned off (\blacktriangle).

the piezoelectric effect is proportional to the β -phase ratio. Hence the performance decreases as the phase-ratio changes.

3.2. The piezo-phototronic effects

The lattice evolution of the measured d-spacing of (1 1 0) and (3 1 0) planes subjected to applied voltage are shown in (figures 2(a), (b)), respectively. Without light illumination, the data is shown by the triangles (\blacktriangle). The identical sample with light illumination is shown by the circles (\bullet). The (110) plane is more parallel to the polarized b -axis. Hence, the (1 1 0) lattice strain (\blacktriangle) in (figure 2(a)) is elongated subjected to the piezo effects. The (3 1 0) plane is more parallel to the perpendicular a -axis lattice strains (\blacktriangle) in (figure 2(b)), which is compressed accordingly. The applied-voltage-dependent lattice-strain evolution clearly shows the piezoelectric effect. If we compare the slopes before (\blacktriangle) and after (\bullet) the light illumination, the enhancement of the piezoelectric effect shows that the system with TiOPc clearly demonstrates the piezo-phototronic effect.

To test the piezo-phototronic effects, the identical system shown in figure 2 as (\blacktriangle) is illuminated by visible light as (\bullet). The results are shown in figure 2(a) as (\bullet) for (1 1 0) and figure 2(b) for (3 1 0), respectively. In figure 2(a), the slopes of (1 1 0) change from 3.18×10^{-7} (\blacktriangle) to 12.8×10^{-7} (\bullet). Similarly, the slopes of (3 1 0) change from -1.46×10^{-7} (\blacktriangle) to -8.68×10^{-7} (\bullet) in figure 2(b). To understand why there are stronger piezo effects in both (1 1 0) and (3 1 0) planes subjected to light illumination, our complimentary visible light absorbance spectra show different visible light absorbance [8, 15].

For piezoelectric materials, the strain is directly related to the electrical field. Our experimental results show that the strain of the composite can be dynamically controlled by light. The piezo-phototronic process involved here is discussed below. In this study, visible light absorbance spectra are important. The P(VDF-TrFE) system without any TiOPc

has very weak visible light absorbance. On the other hand, the P(VDF-TrFE)-TiOPc composite has an expanded absorbance band from the visible light to infrared. In our earlier work, the photosensitivity has been examined by the UV-vis absorbance spectra. The spectrum of the composite material was expanded in the 400 nm \sim 500 nm and 600 nm \sim 800 nm region because photon transfers its energy to the electrons. Additional electrons are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The gaps of the P(VDF-TrFE) and TiOPc blended composite from the lowest unoccupied (LUMO) to the highest occupied (HOMO) molecular orbitals decreases. When the systems are excited by light, the molecular orbitals of the P(VDF-TrFE) tuned by TiOPc allow more transfers of the local charges for piezoelectricity [8, 15]. Hence, the photo-sensitivity, reported here, has facilitated the aforementioned optical manipulation.

3.3. The time-dependent-relaxation behavior

After the test of the piezo-phototronic effects, the identical system for the results shown in (figure 2) is measured continuously, but with neither light nor any applied voltage. The samples are subjected to the identical configuration of the *in situ* synchrotron x-ray measurement setup. We continue to measure the x-ray diffraction as a function of time. The results are shown in (figure 2(c)) for β -phase (1 1 0) plane (\blacktriangle) and (figure 2(d)) for β -phase (3 1 0)-plane (\blacktriangle) every 2 min.

In figure 2(c), the β -phase (1 1 0) lattice strain at time zero, when both the light and the applied voltage are turned off (\blacktriangle), is very close to the value of the β -phase (1 1 0) without light illumination but at 800 V as shown in the final point (\blacktriangle) of figure 2(a). However, in figure 2(d) the β -phase (3 1 0) lattice strain at time zero (\blacktriangle) is very close to the value of the β -phase (3 1 0) with light illumination, but at 800 V as shown in the final point (\bullet) of figure 2(b). It clearly shows anisotropic behavior for time-dependent relaxation

from (1 1 0) to (3 1 0) orientations. The orientation-dependent anisotropy for the time-dependent-relaxation behavior is observed.

4. Discussion

Sample preparation procedures are critical. While mixing the P(VDF-TrFE) copolymer and TiOPc powder, the mixture must be continuously stirred for more than 24 h to ensure a uniformly blended state. If TiOPc powders are not uniformly distributed, the level of photo excitation could decrease. A careful microstructure investigation by using a scanning electron microscope (SEM) to check TiOPc distribution is required. Homogeneously distributed TiOPc is critical.

During the measurement of the piezo-phototronic effects, the experiment has to be controlled at a steady temperature to avoid thermal-induced lattice fluctuations. A steady-state environmental temperature control is necessary. Because both electricity and light illumination can heat up the sample, it is important to measure and to control the temperature of the system.

To modify the aforementioned temperature measurement, we conducted infrared thermography to check how uniform the temperature distribution is from the sample surface. We also measure how much time the specimen can reach a steady-state examination temperature. A steady state is reached for 10 min.

The limitation of the experiments is that we cannot describe the interface between the TiOPc powders and the P(VDF-TrFE) matrix. The interface certainly plays a very important role, which can significantly enhance the performance of the system. However, in this research, our protocol can qualitatively quantify the heating effect, the illumination effect, and the relaxation behavior at lattice level, respectively.

5. Summary

In summary, the *in situ* XRD techniques allow us to examine the piezo-phototronic effect at lattice level. The volume changes from β to α phases subjected to heating are quantified by comparing diffraction intensity evolutions. The phase ratio correlates to its bulk piezoelectric performance. The piezo-phototronic effects are revisited again in this study. Moreover, a control of light illumination was applied on the sample after being shined by the visible light. The anisotropic behavior of different lattice orientations suggests that the relaxation behavior has different kinetics. The results indicate a polarization direction dependent remnant effect.

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Author contributions

These authors accomplished this work together.

Conflicts of interest

The authors declare no conflict of interest.

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