Local Evaluation of Piezoelectricity of Polyester Polymer Processed with Microwave Heating

Jun TAKARADA^{*,1}, Yifu TANG^{*}, Takaaki TONE^{*}, Kohei TAKATANI^{*}, Shingo TANAKA^{*}, Yoshihiko NISHIZAWA^{**}, Masamichi ANDO^{**}, Daisuke MANAI^{***}, Masayuki KABATA^{***}, Tomoya MIZUMORI^{***}, Makoto KUSUNOKI^{***}, Takanori MATSUYAMA^{***} andYoshiro TAJITSU^{*}

(Received September 24, 2020; Accepted December 17, 2020)

Dipoles of novel polyester polymer film were oriented by instant heating with high power microwaves in order to obtain the polymer with piezoelectricity. Response displacement indicating the piezoelectricity was confirmed from results of measuring the applied voltage dependencies by piezoresponse force microscopy. The reason is that the fundamental wave component of response displacement is about 10 times larger than the second harmonic component of response displacement. However, it was also confirmed that the area observing the piezoelectric response was local. The amplitude of the response displacement in an area shifted a few mm from an origin area was 1/10 times smaller than that in the origin area with large piezoelectric response. In addition, it was confirmed that there were a few particles whose piezoelectric response was larger than other particles in the area where large displacement response was obtained. Microwave processing has the capability to partially orient the polyester polymer.

1. Introduction

Piezoelectric polymers have attracted attention with the advent of polyvinylidene fluoride (PVDF)¹⁾. The piezoelectric polymers are now widely recognized as the key material of wearable device sensors²⁻⁵⁾. However, the upper limit temperature of the polymer is less than 80°C, which hinders the practical development. In the past several decades, the research for piezoelectric polymers to replace PVDF has been focused on imide^{3,6)}, urea⁷⁻¹⁰⁾ and lactic acid^{7,11-14)} based polymers. In order to exhibit the ferroelectricity, the dipoles in the molecules chain in the crystallites wrapped amorphous must be oriented by the external electric field. It is necessary for PVDF to break the hydrogen bond pinning the dipole in the molecule chain and the dipole is switched only by the internal rotation of the molecular chain. In other words, the external electric field must change the space position of the molecule stabilized by the Coulomb force of the dipole, the hydrogen bond, the molecular interaction with covalent bond,

Keyword : Microwave Heating, Piezoresponse Force Microscopy, Polyester Polymer

- * Department of Electrical and Electronic Engineering, Kansai University, 3-3-35, Yamate-cho,Suita-city, Osaka, 564-8680, Japan
- ** Murata Manufacturing Co., Ltd., 2288, Oshinohara, Yasucity, Shiga, 520-2393, Japan
- *** Osaka Organic Chemical Ind., Ltd., 18-8, Katayama-cho, Kashiwara-city, Osaka, 582-0020, Japan
 takarada@kansai-u.ac.jp

DOI : https://doi.org/10.34342/iesj.2021.45.1.28

and the intermolecular interaction including van der Waals force. However, PVDF crystals are known to be stabilized by van der Waals forces, because the Coulomb forces are almost balanced. Therefore, the thermal resistance is low, and the ferroelectricity deteriorates significantly at around $140^{\circ}C^{15}$. When trifluorinated ethylene (TrFE), which disturbs the structure of the crystal, is randomly inserted into the molecule chain, the intermolecular distance of vinylidene fluoride (VDF) / TrFE copolymer with mol% ration of 55/45 become larger than that of PVDF. The different crystal phase becomes stable (paraelectric phase) at low temperature, and the ferroelectricity disappears at Curie point of 80°C, because the Coulomb force of the dipole-dipole interaction becomes small. The structure of the crystal was verified from the experimental result of an endothermic peak in a thermal analysis¹⁶⁻¹⁸⁾, Curie-Weiss law related to temperature characteristics in dielectric constant^{17, 19-21)}, a rapid disappearance of the remnant polarization^{19,20}, and a large change in lattice spacing²⁰⁻²². The balance of each energy such as PVDF is a miracle in the case of a complex structure of polymer. The dipoles associated with the molecular chain cannot be effectively switched and aligned in one direction although many researchers have expended to select molecular structures in imide and urea polymers. Therefore, there was no emergence of ferroelectric polymers exceeding the thermal resistance of PVDF. Therefore, in this research, we set the following goals.

- · Avoid strong hydrogen bonds.
- · Control the influence of Coulomb force.

- Secure a certain ordered region where ferroelectricity is expressed.
- Stabilize the molecule by hydrogen bonding after dipole orientation to increase thermal resistance.

We will develop a novel polyester polymer that combine dipolar orientation and stabilization by inserting fluorine groups into side chain molecules with high degree of freedom instead of main chain molecules with low freedom as shown in Fig. 1. The hydrogen bond between the dipoles of the polyester polymer is smaller than that of PVDF because the end of the side chain of the polyester polymer has a carbonyl group in addition to the methyl and the fluorine group. However, it is not easy to orient the dipole in the direction of the electric field due to the hydrogen bonding although the dipole is in the side chain. Therefore, we tried to control the Coulomb force by applying energy of 10 kJ/mol order to the sample by high power microwave irradiation to break the hydrogen bond. Furthermore, we try to orient the fluorine group in the region by applying a DC voltage. The origin of the orientation of this polyester polymer is the rotation of the side chain while the origin of orientation of PVDF is the rotation of the main chain. Therefore, the degree of freedom of dipole rotation of this polymer is higher than that of PVDF. In addition, this polymer has more amorphous components than PVDF. Based on the above, this polymer was selected in this study. We aim at orientating the dipole in the region with certain ordered amorphous particles around crystals by the local and instant heating and cooling. We succeeded in securing a certain ordered region to express the piezoelectricity because the piezoelectric response voltage was confirmed in the local region from the measurement result of Piezoresponse Force Microscopy (PFM). In addition, this polyester polymer has a thermally stable structure since the melting point of this polyester polymer is 200°C or more.

2. Orientation processing of polyester polymer film by microwave heating

High voltage application is required to orient the film. Polarization reversal could not be observed from DE loop of the film as shown in Fig. 2 although an electric field exceeding the coercive electric field of PVDF was applied to the sample.

Therefore, we tried to heat the polymer rapidly with high power microwave and simultaneously applied high DC voltage to orient the molecules in the polymer. The origin of the orientation of this polymer is the rotation of the side chain.



Fig.1 Chemical structure of (a) PVDF and (b) Polyester polymer.



Fig.2 D-E curve of polyester polymer shown in Fig.1(b).

However, the dispersion frequency of its orientation polarization is considered to be sufficiently lower than the frequency of microwaves. Therefore, dipoles cannot follow the microwave AC electric field, and the orientation does not change with the microwave AC electric field. The temperature rises locally and instantaneously due to the dielectric loss of atomic polarization and electronic polarization although dipoles cannot be followed. The dipoles are oriented by a static electric field while giving a rapid temperature change by superimposition. Few example of microwave heating have been applied to heating polymers although microwave heating has been used to sinter ceramics²³⁾. Local heating by microwaves can instantly break hydrogen bonds between molecules in this polymer. While the total amount of thermal energy given to the sample by microwaves is the same as that by normal heat treatment, the heat absorption and radiation rate by microwaves are faster than that by normal heat treatment. In addition, microwave heating can prevent the crystallization of the sample compared to normal heat treatment that conducts heat from outside the sample because microwaves heat the inside of the sample uniformly.

Figure 3 shows a microwave heating and applying DC voltage system that has been applied to the polylactic acid film in previous research²⁴⁾. The microwave used for heating is 2.4 GHz. A magnetron was used to generate high power microwaves. The magnetron can oscillate high intensity and stable microwaves. Microwaves are output from the magnetron in a rectangular waveguide. Microwaves transmitted in the



Fig.3 Manufacturing apparatus applying microwave and DC voltage to polyester polymer²⁴.

rectangular waveguide are converted to ones transmitted in a coaxial line with an input impedance of 50 Ω because microwaves transmitted in coaxial line are easier to form a bias-T, couplers, a resonant and a load termination part in the processing system than microwaves transmitted in the rectangular waveguide. For the high power transmission, radius of the center conductor of the coaxial line is 10 mm. The microwaves are input to the sample through a power monitoring coupler and a bias voltage application bias-T.

Figure 4 (a) shows the film and the conductor formed by the finite element method (FEM) simulation model that exactly represents resonant and input part in the microwave heating system. The film is nipped and transported by a conductor roller. The conductor roller is a $\lambda/2$ resonator, a microwave whose amplitude amplified ten through hundred times by the resonator is applied to the film. Figure 4 (b) shows the FEM calculation result of the resonant electric field strength at 2.4 GHz when the microwave power of 300 W is input. The 7 MV/m electric field strength was applied to the film²⁴⁾. Therefore, a polymer with small loss tangent can be heated rapidly. The measured dielectric loss tangent of the sample was 0.003. The sample absorbs the power about 2 W and replaces the power with thermal energy when the sample receives the power of 600W. The power consumption actually measured was also 1 to 2W. When the conductive roller moves the sample at 5 mm/s in the width direction with a width of 0.1 mm at which the sample contacts the roller, the sample contacts the roller during 20 ms and obtains the energy of 40 mJ by microwave. The film thickness of the sample and the length of contact between the sample and the roller are 20 μ m and 30 mm, respectively. Assuming that the sample has a specific heat and density of a common polymer, the temperature of the microwave incident area can increase from



Fig.4 FEM simulation (a) model and (b) result of resonant electric field amplitude at 2.4 GHz inputting the microwave power of 300 W²⁴.

150 to 300 K during 20 ms. Actually, some of the sample is melted when the microwave is incident to the sample. In addition, the energy given by microwaves per mol of the monomer can be 20 - 40 kJ/mol. The energy can cut hydrogen bond. The heat instantaneously generated by the microwave is absorbed by the conductive roller, and the sample is instantaneously cooled. This rapid temperature change prevents complete crystallization of the polymer and creates a space in which crystal defects and molecules move. At the same time, we aim to orient the molecules by applying a DC voltage. The normal orientation process is performed while the sample is warmed by thermal conduction from the heater. On the other hand, the proposed orientation process is performed while the microwave directly heats the sample. The crystal phase of the sample changes when the same thermal energy as the proposed orientation process is applied during the normal orientation process. In normal process, the crystallization is promoted and the molecule is fixed, and the dipole cannot be aligned with only high DC voltage. In proposed process, high DC voltage can align the dipole with the help of the microwave.

3. Evaluation of Piezoelectricity of Polyester polymer

According to the requirements mentioned in Chapter 1, we synthesized a polymer whose main component is a molecule having a carbonyl group and a fluorine group at the end of the side chain as shown in Fig. 1 (b). The main component was copolymerized with a molecule having a carbonyl group and a methyl group at the end of the side chain as a softener. The molar ratio of each molecule having a fluorine group m and molecule having a methyl group n is 4:1. A film was fabricated by solvent casting. The film size and thickness were 5.0×5.0 mm² and 20 µm, respectively. The sample film was set in the production apparatus shown in Fig. 3, and a microwave of 600 W was input to the film. At the same time, a DC voltage of -2 kV was applied to the sample. The topographic and piezoelectric image of the 2 \times 2 µm² region were observed by

atomic force microscopy (AFM) and PFM. In previous study, the author has observed the local polarization reversal phenomenon of P(VDF/TrFE) film by PFM^{25} . Thus, the orientation of the particles in the polyester polymer film was observed by PFM. The scan in contact with the surface was performed with a conductive cantilever with a spring constant and a resonant frequencies of 0.1 N/m and 37 kHz, respectively. A voltage with a frequency of 10 kHz was applied to the sample. The applied voltage amplitude Figure 5 shows topographic images before and after the microwave and DC processing. The surface roughness before and after the processing are 2.26 and 225 nm, respectively. The particles are region surrounded by the white line in Fig. 5. The particle sizes are about 20 through 30 nm and 100 through 200 nm, respectively. The particles grow about 10 times by the processing.

Figure 6 shows the response displacement images obtained in the area of Fig. 5(b) (Area 1). Figures 6(a) and 6(b)show fundamental wave amplitude images of displacement when voltage amplitudes 2 and 5 V were applied. Figures 6(c)and 6(d) show the second harmonic amplitude images of displacement. The response displacement amplitude increases as the applied voltage amplitude increases. In addition, the width of the maximum and the minimum value of the displacement amplitude also increase. This result suggests the occurrence of piezoelectricity in the local area of this film. However, there are regions that cannot measure piezoelectric response when the observed position changes.

Figure 7 shows the topographic and displacement response images of an area a few mm away from Area 1 (Area 2). The fundamental wave amplitude of the displacement response and the width of the maximum and minimum values shown in Fig. 7(b) and 7(c) are smaller than those shown in Fig. 6(a) and 6(b). The second harmonic amplitude of the displacement shown in Fig. 7(d) and 7(e) can hardly measure the response due to noise. Next, the sample was turned upside down, and microwave and DC voltage of -2 kV are applied to the sample. Figure 8 shows the topographic and displacement response images on the top surface of two samples. Figures 8 (a)-(c)show the topographic, displacement amplitude and phase images before turning the direction in which the voltage was applied, and Figs. 8 (d)-(f) show those after turning the direction in which the voltage was applied (Area 3). The displacement response is reversed since the average value of the phase calculated from the displacement phase images shown in Figs. 8 (c) and 8 (f) is 20.9 and -167.8 degrees, respectively.



Fig.5 Topographic images (a) before and (b) after the microwave and DC processing.



Fig.6 Microscopic images in region with large amplitude of response voltage: (a) and (b) displacement response images of fundamental wave amplitude applying voltage amplitude of 2 and 5 V, (c) and (d) displacement response images of second harmonic amplitude applying voltage amplitude of 2 and 5 V.



Fig.7 Microscopic images in region with small amplitude of response voltage: (a) Topographic image, (b) and (c) displacement response images of fundamental wave amplitude applying voltage amplitude of 2 and 5 V, (d) and (e) displacement response images of second harmonic amplitude applying voltage amplitude of 2 and 5 V.

Figures 9 (a) and (b) show topographic data and the fundamental wave amplitude changing the applied voltage at the location described by the white solid line in Area 1. The response voltage become locally large for the particles on the surface located in the region of 0.70 to 0.90 μ m. This result suggests that the microwave processing locally orients the



Fig.8 Microscopic images on the top surface of two samples: (a)-(c) one sample images before turning direction in which DC voltage of -2 kV was applied, (d)-(f) another sample images after turning direction in which DC voltage of -2 kV was applied, (a) and (d) topographic images, (b) and (e) displacement response amplitude images, and (c) and (f) displacement phase images.



Fig.9 Line plot at the location described by the solid line in Figure 5 (b): (a) Topographic Height, (b) fundamental wave amplitude changing the applied voltage.

particles on the surface. In addition, the base response voltage increases with the increase of the applied voltage. This result suggests that the microwave processing orients the particles inside the film.

The plots described by triangles in Figs. 10 (a) and (b) indicate the average value of the response voltage in Fig. 9(b) when the applied voltage is changed. The average value was calculated from the voltage value between 0.70 and 0.90 μ m on the particle with particularly large response voltage mentioned above. The fundamental and second harmonic components of the average voltage are fitted by the first and second order functions to the applied voltage as shown in Figs. 10(a) and 10(b), respectively. The fundamental average voltage is larger than the second one. Figure 10(c) shows the applied voltage dependency of the average value of the cosine component of the response voltage in Area 3. The average value was calculated from the response voltage value on solid white line described in Fig. 8(d). The top surface response after microwave processing with -2 kV applied to the top



Fig.10 Average value of response voltage changing applied voltage in Area 1-3: (a) Fundamental wave in Area 1 and 2, (b) second harmonic component in Area 1 and 2, and (c) Fundamental wave in Area 3.

surface has a positive correlation with the applied voltage. On the other hand, the top surface response after microwave treatment with -2 kV applied to the bottom surface has a negative correlation with the applied voltage. Therefore, it assumes that these responses are piezoelectric responses due to the orientation of the polyester polymer processed by microwave heating. However, there are also the region with almost no voltage dependence in one film, as shown in Fig. 7. The plots described by circles in Figs. 10(a) and 10(b)indicate the average value of the response voltage of the particles on the line shown in Fig. 7(a) when the applied voltage is changed. The slopes of fundamental and second harmonic components in the region with large response are 13.2 and 9.9 times larger than those in the region with small response, respectively. From the result, microwave processing partially orients this polyester polymer. Areas 1 and 3 selected regions that passed just in the center of the roller where the microwave processing was performed. Area 2 selected a region that passed a few mm outside from the center. The reason for selection is that the intensity of the microwave electric field generated in the center of the roller is the strongest from the finite element analysis result. It is possible that the piezoelectricity has increased due to the effect of thermal energy from microwaves, however detailed verification has not yet been achieved. The evaluation of dependence of processed location is a future issue.

We aim to uniformly orient this polyester film by microwave

heating, and to create a macro piezoelectric polymer film in the future although it is limited to partially orienting this polyester-based polymer in this report. It is considered that the piezoelectricity was obtained only in some small regions and some particles since the crystallization of the sample has progressed as a whole. We planned to rotate the dipole side chain of the amorphous region. However, there were no defects or spaces in which the side chains could rotate because many ordered crystals were formed. The piezoelectricity will be obtained by changing the processing speed and microwave power since the temperature change rate was still slow.

4. Conclusions

Dipoles of polyester polymer film were oriented by instant heating with high power microwaves in order to obtain the polymer with piezoelectricity. The displacement response indicating the piezoelectricity was confirmed as a result of measuring the piezoelectricity with Atomic Force Microscope. The reason is that the fundamental wave component of response displacement is about 10 times larger than the second harmonic component of response displacement. However, it was also confirmed that the area observing the piezoelectric response was local. The amplitude of the response displacement in an area shifted a few mm from an origin area was 1/10 times smaller than that in the origin area with large piezoelectric response. In addition, it was confirmed that there were a few particles whose piezoelectric response was larger than other particles in the area where large displacement response was obtained. Microwave processing has the capability to partially orient the polyester polymer.

References

- H. Kawai: The Piezoelectricity of Poly (vinylidene Fluoride). Jpn. J. Appl. Phys., 8 (1969) 975
- 2) Y. Tajitsu: Biomedical applications of electroactive polymer actuators, ed. E. Smela, p.357, Wiley, New Jersey (2009)
- 3) T. Sekitani, T. Yokota, U. Zschieschang, H. Klauk, S. Bauer, K. Takeuchi, M. Takamiya, T. Sakurai, T. Someya: Organic Nonvolatile Memory Transistors for Flexible Sensor Arrays. Science, **326** (2009) 1516
- Y. Tajitsu, Piezoelectric and electrostrictive polymers, ed. F. Carpi, p.509, Springer, Berlin (2016)
- 5) S. Kundu, D. Maurya, M. Clavel, Y. Zhou, N. N. Halder, M. K. Hudait, P. Banerji and S. Priya: Integration of lead-free ferroelectric on HfO₂/Si (100) for high performance nonvolatile memory applications. Sci. Rep., 5 (2015) 8494
- K. Tanimoto, Y. Tajitsu: Shear piezoelectricity of optically active polysuccinimides. Jpn. J. Appl. Phys., 54 (2015) 10NF02-1
- E. Fukada: History and Recent Progress in Piezoelectric Polymers. IEEE Trans. Ultrason. Ferroelectr. Freq. Control, 47 (2000) 1277

- Y. Takahashi, S. Ukishima, M. Iijima, and E. Fukada: Piezoelectric properties of thin films of aromatic polyurea prepared by vapor deposition polymerization. J. Appl. Phys., 70 (1991) 6983
- A. Kubono, M. Murai, and S. Tasaka: High Piezoelectric Activity in Nonpoled Thin Films Prepared by Vapor Deposition Polymerization. Jpn. J. Appl. Phys., 47 (2008) 5553
- 10) M. Morimoto, Y. Koshiba, M. Misaki, and K. Ishida: Polyurea spin-coated thin films: Pyro- and piezoelectric properties and application to infrared sensors. Jpn. J. Appl. Phys., 54 (2015) 04DK13
- 11) Y. Tajitsu: Fundamental Study on Improvement of Piezoelectricity of Poly(*l*-Lactic Acid) and Its Application to Film Actuators. IEEE Trans. Ultrason. Ferroelectr. Freq. Control, 60 (2013) 1625
- 12) M. Ando, H. Kawamura, H. Kitada, Y. Sekimoto, T. Inoue, and Y. Tajitsu: Pressure-Sensitive Touch Panel Based on Piezoelectric Poly(L-lactic acid) Film. Jpn. J. Appl. Phys., 52 (2013) 09KD17
- 13) M. Yoshida, T. Onogi, K. Onishi, T. Inagaki, and Y. Tajitsu: High piezoelectric performance of poly (lactic acid) film manufactured by solid-state extrusion. Jpn. J. Appl. Phys., 53 (2014) 09PC02
- 14) J. Takarada, T. Kataoka, K. Yamamoto, T. Nakiri, A. Kato, T. Yoshida, and Y. Tajitsu: Fundamental Study on Vibration in Edge Face of Piezoelectric Chiral Polymer Film. Jpn. J. Appl. Phys., **52** (2013) 09KE01
- P. Herchenröder, Y. Segui, D. Horne, and D. Y. Yoon: Ferroelectricity of Poly (Vinylidene Fluoride): Transition Temperature. Phys. Rev. Lett., 45 (1980) 2135
- 16) T. Yagi, M. Tatemoto and J. Sako: Transition Behavior and Dielectric Properties in Trifluoroethylene and Vinylidene Fluoride Copolymers. Polymer J., 12 (1980) 209
- 17) T. Yamada, T. Ueda and T. Kitayama: Ferroelectric-toparaelectric phase transition of vinylidene fluoridetrifluoroethylene copolymer. J. Appl. Phys., 52 (1981) 948
- 18) K. Koga and H. Ohigashi: Piezoelectricity and related properties of vinylidene fluoride and trifluoroethylene copolymers. J. Appl. Phys., 59 2142 (1986)
- 19) T. Furukawa, M. Date, E. Fukada, Y. Tajitsu and A. Chiba: Ferroelectric Behavior in the Copolymer of Vinylidenefluoride and Trifluoroethylene. Jpn. J. Appl. Phys., **19** (1980) L109
- 20) Y. Tajitsu, A. Chiba, T. Furukawa, M. Date and E. Fukada: Crystalline phase transition in the copolymer of vinylidenefluoride and trifluoroethylene. Appl. Phys. Lett., 36 (1980) 286
- 21) A. J. Lovinger, G. T. Davis, T. Furukawa and M. G. Broadhurst: Crystalline forms in a copolymer of vinylidene fluoride and trifluoroethylene (52/48 mol%). Macromolecules, 15 (1982) 323
- 22) K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani and H. Tadokoro: Structure and ferroelectric phase transition of vinylidene fluoride-trifluoroethylene copolymers: 2. VDF 55 % copolymer. Polymer J., 25, (1984) 195
- 23) H. Takahashi, Y. Numamoto, J. Tani, K. Matsuta, J. Qiu1 and S. Tsurekawa: Lead-Free Barium Titanate Ceramics with Large Piezoelectric Constant Fabricated by Microwave Sintering. Jpn. J. Appl. Phys., 45 (2006) L30
- 24) J. Takarada, Y. Tang, Y. Nishizawa, M. Ando, and Yoshiro Tajitsu: Surface charge dependence on load in amorphous stereocomplex poly(lactic acid) electrets processed with microwave heating. Jpn. J. Appl. Phys., 59 (2020) SPPE02
- 25) J. Takarada, H. Sato, and A. Furukawa: Domain switching of ferroelectric polymer film using piezoelectric force microscopy. Jpn. J. Appl. Phys., 54 (2015) 10NA17