

Improving Ferro- and Piezo- Electric Properties of Hydrogenized Poly(vinylidene fluoride-trifluoroethylene) Films by Annealing at Elevated Temperatures^{*}

Jian Wang^a, Zhong Li^{a, b}, Yuan Yan^c, Xiao Wang^a, Yun-chuan Xie^{a**} and Zhi-cheng Zhang^{a**}

^a Department of Applied Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, School of Science, Xi'an Jiaotong University, Xi'an 710049, China

^b College of Material Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, China

^c School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Abstract After annealing the solution cast P(VDF-TrFE) films at elevated temperatures, which were synthesized *via* a full hydrogenation process from P(VDF-CTFE) with a composition of VDF/TrFE = 80/20 (mol%), a series of P(VDF-TrFE) films were fabricated in present work. The crystalline and ferroelectric phases of the films were carefully characterized and their dielectric, ferroelectric and piezoelectric properties were systematically investigated. The improved crystalline and ferroelectric phases in the films induced by annealing at elevated temperatures are responsible for the significant improved electric properties of the films. The optimized annealing temperature is found to be 130 °C and the best performance including the highest dielectric constant of 12.5 at 1 kHz, the largest maximum polarization of 11.21 $\mu\text{C}/\text{cm}^2$ and remnant polarization of 7.22 $\mu\text{C}/\text{cm}^2$, the lowest coercive electric field of 56 MV/m, and the highest piezoelectric coefficient of -25 pC/N is observed.

Keywords: P(VDF-TrFE); P(VDF-CTFE); Hydrogenation; Annealing; Electrical properties.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) based ferroelectric polymers have attracted considerable attention owing to their unique piezoelectric, pyroelectric and ferroelectric properties and excellent mechanical flexibility since the ferro- and piezo- electricity of PVDF were initially reported by Kawai in 1969^[1]. That allows them to be widely utilized in piezoelectric devices including nonvolatile memories, integrated circuits, stationary power generators, and miniature capacitors for telecommunication^[2–6]. Comparing with the traditional electroactive ceramics, piezoelectric polymers possess advantages such as high mechanical elasticity, high electrical breakdown strength, ease of film fabrication, low cost, and self-healing ability, although their piezoelectricity is only one tenth of ferroelectric ceramics^[7, 8]. Among the known five types of crystal phases of PVDF, β -PVDF with all-trans chain conformation possesses the highest polarity, thus the best ferro- and piezo- electric properties

^{*} This work was financially supported by the National Natural Science Foundation of China (Nos. 51103115, 50903065 and 51573146), Fundamental Research Funds for the Central Universities (Nos. XJJ2013075 and extd2015003), International Science & Technology Cooperation Program of China (No. 2013DFR50470), Natural Science Basic Research Plan in Shaanxi Province of China (Nos. 2013JZ003 and 2015JZ009), and National Basic Research Program of China 973 (No. 6132620101).

^{**} Corresponding authors: Yun-chuan Xie (解云川), E-mail: ycxie@mail.xjtu.edu.cn

Zhi-cheng Zhang (张志成), E-mail: zhichengzhang@mail.xjtu.edu.cn

Received November 27, 2015; Revised December 27, 2015; Accepted January 4, 2016

doi: 10.1007/s10118-016-1782-8

after polarization^[2, 3, 9]. To fabricate PVDF films in β -phase, either mechanical rolling or stretching followed by polarizing under a very high electric field has to be utilized^[10, 11]. As a result, the high piezoelectricity obtained in PVDF piezoelectric films is only able to remain below the processing temperature, which is usually below 100 °C for the conversion of the polymer chains from thermodynamically stable α -phase into β -phase.

Besides of the mechanical processing methods, chemically copolymerizing VDF with other monomers such as trifluoroethylene (TrFE) and tetrafluoroethylene (TFE) is another effective way to turn the chain conformation of PVDF from non-polar α -phase to polar β -phase^[12, 13]. The ferroelectric properties of poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) were firstly disclosed by Tamemoto in 1979^[14]. The polar β -phase could only be detected in P(VDF-TrFE)s containing TrFE over 20 mol% regardless of the fabrication procedure^[7, 8]. The remnant polarization (P_r) of P(VDF-TrFE) is found to be about 10 $\mu\text{C}/\text{cm}^2$ for the sample of VDF/TrFE = 75/25 (mol%)^[15]. The introduction of TrFE results in the appearance of a ferro- to para- electric (F-P) phase transition (or Curie transition, T_c) associated with the polymer chain conformation change from all-trans to trans-gauche^[16–18]. F MAS and ^1H - ^{19}F CP/MAS NMR spectra of P(VDF-TrFE) (75/25 mol%) show that VDF and TrFE in the copolymer chain is connected with each other in head-to-tail sequence ($-\text{CF}_2\text{CH}_2-\text{CF}_2\text{CFH}-$)^[19]. In contrast to PVDF, P(VDF-TrFE) in β -phase could be prepared by annealing process at a temperature between the Curie and melting points where the molecular chains lying perpendicular to the lamellar plane rotate thermally around the chain axis on the crystal lattice^[20]. However, ferroelectric P(VDF-TrFE) copolymers suffer from the low productivity, high cost and high hazard of TrFE although they possess the processing advantage.

Recently, in an effort to overcome the major shortcomings of TrFE (high price and hazards), several two-step processes involving the catalysed hydrogenation of poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE)) have been developed to synthesize TrFE containing PVDF based copolymers^[21–30]. More detailed investigation has shown that the VDF and TrFE in hydrogenized terpolymers are mostly in head-to-head connection, which is different from the head-to-tail connection in direct terpolymers. Therefore, the energy storage properties of hydrogenized P(VDF-TrFE-CTFE) terpolymer are lower than those of direct terpolymer with the consistent composition^[28–31], since the head-to-head connection of VDF and TrFE may partially eliminate the dipoles contribution of VDF to the copolymer. More recently, we showed that the ferro- and piezoelectric properties of the P(VDF-TrFE) bearing 20 mol% TrFE synthesized from the full hydrogenation of P(VDF-CTFE) were rather close to those of the copolymerized P(VDF-TrFE) (VDF:TrFE = 75:25 in mol%)^[32]. The simulated results showed that, comparing with the copolymerized P(VDF-TrFE), the hydrogenated P(VDF-TrFE) possessed lowered twisted angle between sequences containing every four VDF units and more evenly distributed electro-withdrawing C—F bonds and electro-donating C—H bonds on the opposite sides of the polymer chain. That may compensate the negative polarity contribution of TrFE connected with VDF in H—H connection of hydrogenized P(VDF-TrFE). Although it has been well accepted that annealing at elevated temperatures is an effective way to realize more perfect ferroelectric phase and achieve high ferro- and piezoelectric performance in direct P(VDF-TrFE)^[20–23], how to improve the dielectric performance of hydrogenated P(VDF-TrFE) copolymers by annealing process has barely been reported. Considering the low cost, facile synthesis process and high application potential of hydrogenized P(VDF-TrFE) together with the structure difference between the direct and hydrogenized copolymers, the influence of annealing temperature on the crystalline, F-P transition, dielectric, ferroelectric and piezoelectric properties of the hydrogenized P(VDF-TrFE) bearing 20 mol% TrFE is carefully investigated. The optimized annealing condition is obtained and may provide guidance for the fabrication and application of this type of excellent piezoelectric films.

EXPERIMENTAL

Materials

P(VDF-CTFE) (80/20 mol%) was purchased from China Bluestar Chengrand Chemical Co. Ltd.. Tetrahydrofuran (THF) is dried from sodium and distilled before use. All the chemicals are commercially available and used as received. P(VDF-TrFE) with 20 mol% TrFE was synthesized from an environmental

process as described in the reference^[26–28]. ^1H - and ^{19}F -NMR conducted on a Bruker AM-300 in acetone- d_6 with 0.05 vol% TMS as internal standard is used to confirm the composition and structure of P(VDF-TrFE). The assignment of the ^1H -NMR peaks is as follows, 5.3–5.7 (m, 1H, $-\text{CF}_2\text{CFH}-$), 2.6–3.6 (m, 2H, $-\text{CF}_2\text{CH}_2\text{CF}_2-$, H-T), 2.2–2.5 (m, 2H, $-\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2-$, H-H). The ^{19}F -NMR peaks are assigned as follows, -92.36 ($-\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2-$, VDF-VDF, H-T), -93.16 to -96.46 ($-\text{CHFCH}_2\text{CF}_2\text{CH}_2\text{CF}_2-$, TrFE-VDF, H-H and $-\text{CH}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2-$, VDF-VDF-VDF, H-H-T), -112.68 to -116.52 ($-\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CHF}-$, VDF-TrFE, H-H and $-\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2-$, VDF-VDF, H-H), -122.79 to -123.50 ($-\text{CF}_2\text{CHFCH}_2\text{CHFCH}_2-$, TrFE-TrFE-VDF, H-T-T), -130.94 to -131.50 ($-\text{CF}_2\text{CHFCH}_2-$, VDF-TrFE, H-H), and -200 ($-\text{CF}_2\text{CF}_2\text{CHFCH}_2\text{CF}_2-$, VDF-TrFE, H-H).

Fabrication of P(VDF-TrFE) Films

The films about 10–20 μm in thick were prepared *via* casting the polymer solution in dimethylformamide (DMF) onto glass substrate or a quartz slide, and marked as ‘as-cast’ films. After removing the solvent completely, the obtained films were annealed at elevated temperatures from 70 $^\circ\text{C}$ to 160 $^\circ\text{C}$ (marked as ‘A-70’, ‘A-80’, *etc.*) for 24 h before being peeled off. For electric characterizations, gold electrodes (thickness 80 nm, area = 0.069 cm^2) were sputtered on both surfaces of the polymer films with a JEOL JFC-1600 auto fine coater (Japan).

Characterization

X-ray diffraction (XRD, RIGAKU D/MAX-2400, Rigaku Industrial Corporation, Japan) was utilized to characterize the crystal structures and crystallinity of P(VDF-TrFE) films, and the wavelength of the X-ray was 0.1542 nm (Cu $\text{K}\alpha$ radiation, 40 kV, 100 mA, and 10 K/min). Fourier transform infrared spectroscopy (FTIR, 27 FTIR spectrometer, Bruker Corporation, Germany) was used to characterize the crystalline structure and chain conformation of P(VDF-TrFE) films. Differential scanning calorimetric (DSC) curves were obtained on a Netzsch DSC 200 PC instrument (Netzsch, Germany) in a nitrogen atmosphere at a heating rate of 10 K/min during the first heating circle. The dielectric responses of different P(VDF-TrFE) films as a function of frequency and temperature were obtained on an Agilent 4284 LCR meter. The electric displacement-electric field (D-E) hysteresis loops at room temperature were obtained on a Premiere II ferroelectric tester from Radiant Technologies, Inc., where AC electric fields ranging from 25–500 MV/m were applied across polymer films with a triangular waveform at a frequency of 10 Hz. Piezoelectric values (d_{33}) were recorded on a ZJ-4A static piezoelectric analyser presented by Chinese Academy of Sciences.

RESULTS AND DISCUSSION

Crystalline Properties of P(VDF-TrFE) Films Annealed at Elevated Temperatures

The crystalline properties of P(VDF-TrFE) films annealed at different temperatures were characterized with XRD, FTIR and DSC. The normalized FTIR absorption spectra are shown in Fig. 1. All the copolymer films exhibit typical β and γ phase absorption bands at 505 cm^{-1} , 810 cm^{-1} , 843 cm^{-1} , and 1290 cm^{-1} , while typical α phase absorption bands are not observed at 530 cm^{-1} , 614 cm^{-1} , 764 cm^{-1} , 795 cm^{-1} and 976 cm^{-1} . Since both molecular chains of β and γ phase possess TTTT conformation, that means the crystal regions in all the P(VDF-TrFE) (80/20) films are in β -, γ -phases or the mixture of them^[33]. Because it has little change in crystal phase structure, annealing the films at elevated temperatures leads to no visible change on the absorption intensity.

To deeply understand the conformation from crystallographic view, XRD is used and the data are shown in Fig. 2. When the annealing temperatures are 70, 80 and 90 $^\circ\text{C}$, two peaks at 18.4 $^\circ$ and 19.6 $^\circ$ are observed as indicated in Fig. 2 after peak fitting. The sharp peak at 19.6 $^\circ$ is from the ferroelectric β phase associated with the all-*trans* conformation and represents the Bragg diffraction of (110)/(200) of β phase^[15]. However, peaks are at 18.4 $^\circ$ and 19.9 $^\circ$, indicating that the as-cast, and A-70 to A-90 films also show the character of γ phase.

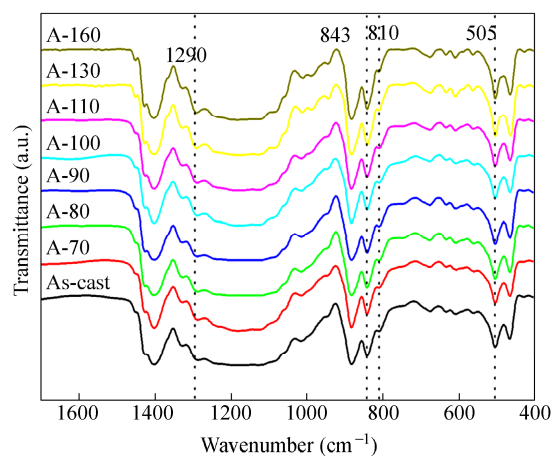


Fig. 1 FTIR spectra of P(VDF-co-TrFE) films annealed at elevated temperatures

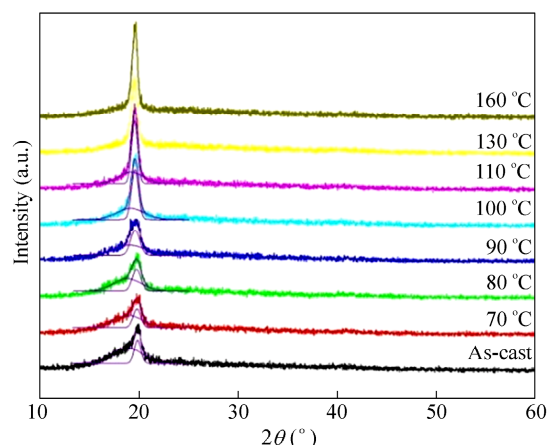


Fig. 2 X-ray diffraction patterns of copolymer films annealed at elevated temperature

As the annealing temperature increased to 100 °C, only a sharp peak at 19.6° referring to the ferroelectric β phase was observed for A-100 to A-160 films. And the vanishing peak of 18.4° indicates that γ phase disappeared in high temperature annealed samples.

DSC has been found to be an effective technique to characterize the different crystal phases of P(VDF-TrFE), which is particularly powerful for distinguishing γ -phase from β -phase^[33]. As shown in Fig. 3, two peaks including a broad one at 110 °C and the other sharp one at 146 °C are observed in the as-cast sample, which are attributed to the F-P transition (T_C) and melting point (T_m) of β -P(VDF-TrFE), respectively. The rather broad temperature range of T_C indicates that the ferroelectric phase is rather imperfect and the grains are dispersed in a large size range. After annealing at elevated temperatures below 110 °C, a much sharper peak and increased ΔH_C are obtained at about 10 K higher than the annealing temperature as shown in Fig. 3. But no visible change has been observed on the peak at 146 °C corresponding to T_m . That means annealing at the temperature below 110 °C could improve the formation of larger ferroelectric domains rather than improve the crystalline properties of P(VDF-TrFE). The highest T_C (~120 °C) and ΔH_C are obtained for the sample A-110 annealed at 110 °C. Annealing the samples at even higher temperatures (~130 °C and 160 °C) would lead to the melting and recrystallization of the crystal grains. As a result, the peak at 146 °C is significantly sharpened and the height is improved, which means both the crystallinity and crystal size are increased. That agrees very well

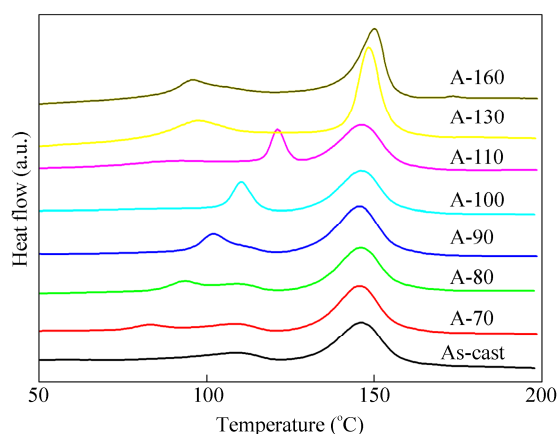


Fig. 3 DSC curves of copolymer films annealed at various temperatures

with the XRD results. However, T_C is reduced to 90 °C and ΔH_C is decreased as well, which means annealing temperature over T_C is not favourable for the improvement of ferroelectric phase. Therefore, annealing the sample at the melting point may lead to the formation of larger crystal domains and the improved crystallinity. Subsequently, annealing the sample at about 110 °C would benefit the formation of ferroelectric grains in large scale. That should be the promising annealing procedure of the hydrogenized P(VDF-TrFE) (VDF/TrFE = 80/20 mol%) sample.

Dielectric Properties Measured at Varied Frequencies and Temperatures

Figure 4 shows the dielectric properties of the films annealed at elevated temperatures as a function of testing frequency. Comparing with the as-cast film, annealed samples possess gradually increased dielectric constant (ϵ_r) as a function of the annealing temperature. When the annealing temperature is less than 90 °C, the increment is relatively small. However, when the annealing temperature is raised to over 100 °C, ϵ_r of the samples is significantly increased as shown in Fig. 4(a). For example, ϵ_r of as-cast, A-90 and A-130 films at 1 kHz is 8.8, 10.1 and 12.5, respectively. Further increasing the annealing temperature over 110 °C shows little influence on the dielectric properties. It has been well accepted that PVDF-based fluoropolymers under low electric field at frequency below 100 kHz have been well recognized to originate from both the dipoles alignment in amorphous phase in rubber state and the weak swing of crystal phase^[34]. As frequency increases from 100 kHz to 1 MHz, the contribution of crystal phase is vanishing for the delay of the swing of crystal phase than the applied electric field characterized with a sharp increment of the dielectric loss at this frequency range. As discussed above, annealing the samples at temperatures below T_C would improve the content and grain size of the ferroelectric phase slightly, which is responsible for the gradually elevated dielectric constant. However, the contribution is not significant since the increment of the ferroelectric phase is small and the overall crystallinity is not changed. When the annealing temperature is raised up to 110 °C, both the ferroelectric phase and crystalline properties of the films are dramatically improved as confirmed by both XRD and DSC results. That may explain the quickly enhanced dielectric performance. Besides of the increased ϵ_r , annealing at higher temperatures results in slightly improved dielectric loss at $1 \times 10^2 - 1 \times 10^6$ Hz as well as indicated in Fig. 4(b).

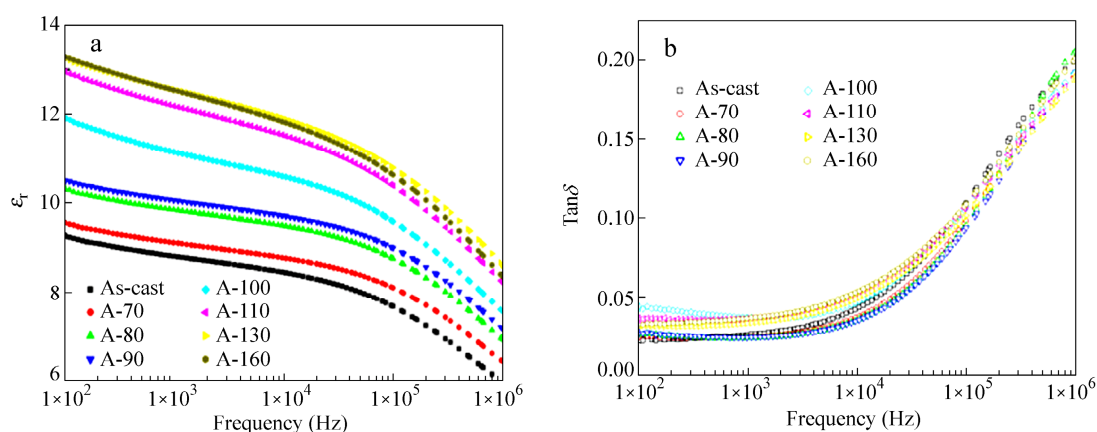
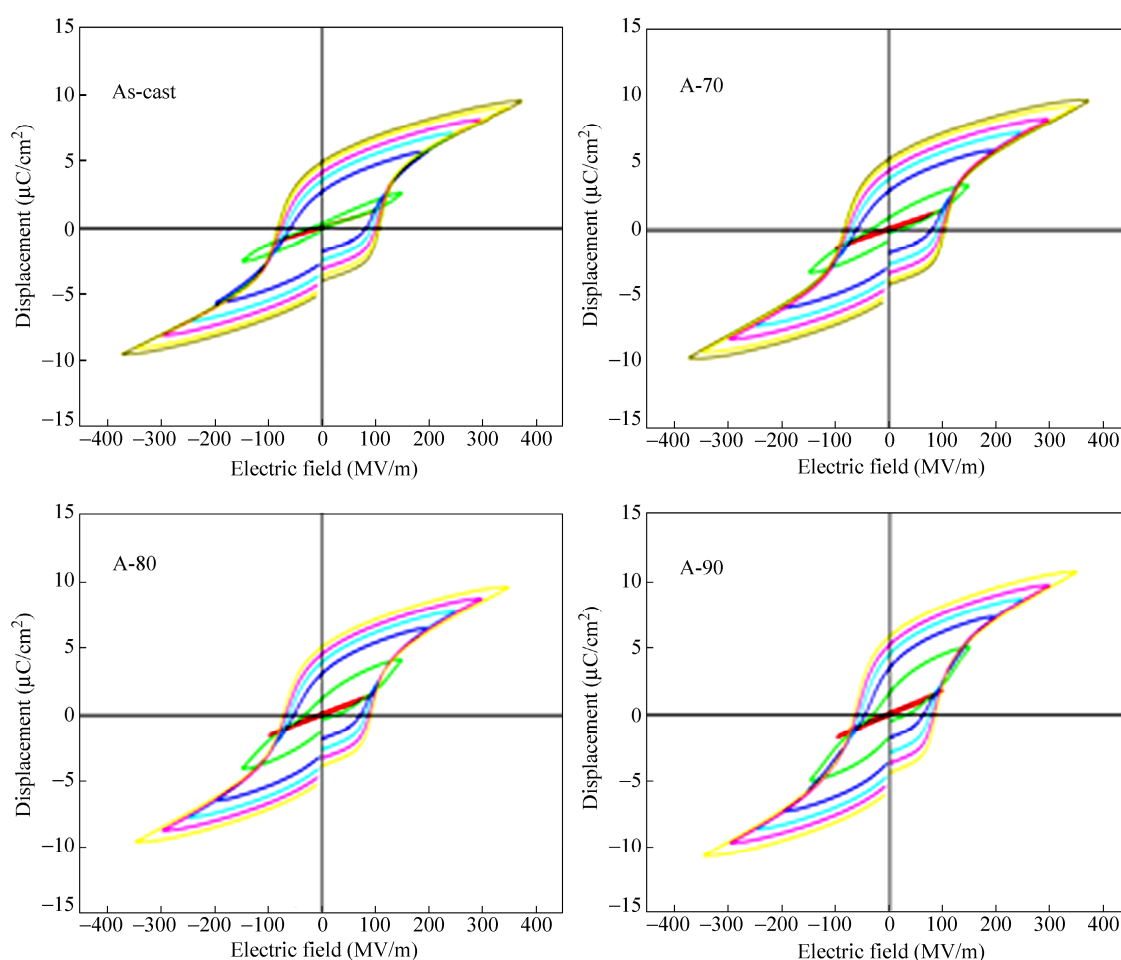


Fig. 4 Dielectric constant (a) and loss (b) of P(VDF-co-TrFE) copolymer films annealed at different temperature as a function of testing frequency

Ferroelectric Properties under High Electric Field

D-E hysteresis loops have been well utilized as a direct and powerful technique to characterize the ferroelectric properties of the materials, where a number of very useful characteristic parameters including the maximum polarization (P_m), remnant polarization (P_r) and coercive electric field (E_c) could be obtained. Figure 5 represents the D-E loops of all the eight samples measured under 10 Hz elevated electric field with an increment step of 25 MV/m. When the field is below the E_c , all the samples exhibit linear like loops, which means the ferroelectric phase has not been oriented yet. When the external electric field is increased to be over E_c , the ferroelectric

grains starts to orient along the electric field and contribute quickly increased displacement. As a result, the loops start widening and turning into rectangle shape, which is the typical loop structure of normal ferroelectric samples. As a function of the elevated electric field, all the samples show the similar changing trend but the value of the characteristic parameters is varied. Taking the D-E loops measured under 300 MV/m field as examples, P_m , P_r and E_c of the samples annealed at evaluated temperatures are presented in Fig. 6. The as-cast film possesses the highest E_c of 76 MV/m. As annealing temperature increases, E_c is decreasing gradually and the lowest E_c of 56 MV/m is observed for the samples annealed at 110–130 °C. Annealing at higher temperatures (~160 °C) leads to elevated E_c (~68 MV/m). E_c is a critical field where the alignment force provided by the external field on the ferroelectric grains is equal to the coupling forces among ferroelectric domains. Apparently, the ferroelectric grains in large scale possess larger overall polarity and the alignment force under the consistent electric field would be bigger. If the coupling force is regarded as a constant, the field required to overcome the coupling force (namely E_c) for the larger ferroelectric domains should be much smaller than that of the grains in smaller size. As well discussed above, the samples annealed at elevated temperatures exhibit continuously improved ferroelectric phase and grains, which should be responsible for the lowered E_c . Annealing at temperatures over its melting point would destroy the crystalline structure and the sample may recrystallize as temperature decreases, which favours the formation of large crystal grains but not helpful for the generation of large ferroelectric grains. That may explain the higher E_c observed for the sample A-160.



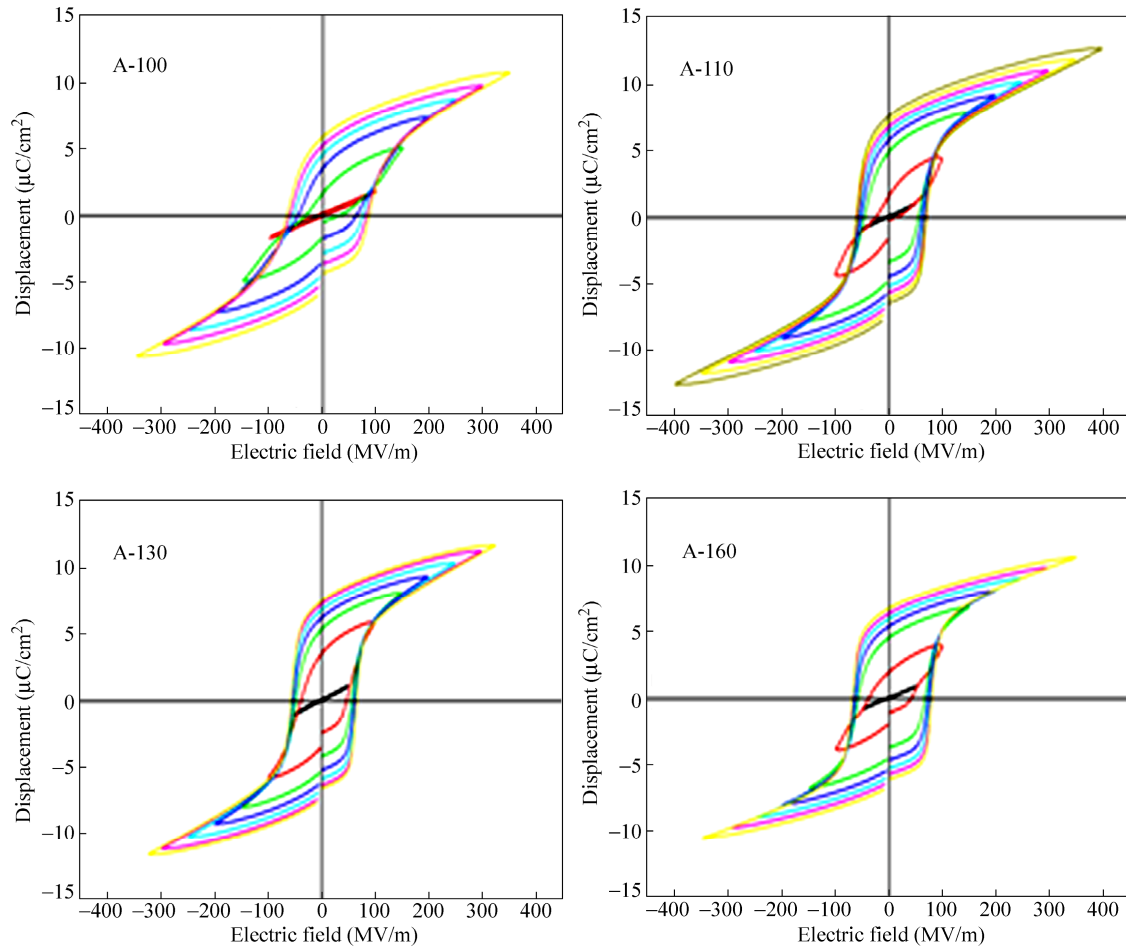


Fig. 5 D-E loops of P(VDF-co-TrFE) films annealed at elevated temperatures as a function of polarizing electric field

The conclusion could be further confirmed by the P_m and P_r as presented in Fig. 6. As annealing temperature increases, both P_m and P_r obtained under the consistent electric field are increasing gradually and reach the maximum values (P_m of $11.21 \mu\text{C}/\text{cm}^2$ and P_r of $7.22 \mu\text{C}/\text{cm}^2$) for the samples annealed at 130°C . Further increasing the annealing temperature results in the reduced P_m and P_r , which coincide very well with the E_c results. P_m represents the maximum polarization of the films under the polarizing electric field, which is the polarization contribution sum of both the amorphous and crystalline phases. Under 300 MV/m , the elevated P_m against the annealing temperature indicates that thermally treating the samples at higher temperatures may help to improve the overall polarity in the samples. XRD and DSC results have well proved that it is mostly from the transferring of randomly distributed dipoles in amorphous phase to the well-organized dipoles in crystalline phase. Besides of the contribution to overall polarity of the samples, the transition of small dipoles to large polar grains is also responsible for the improved remnant polarization measured at the zero electric field. P_r represents the irreversible polarization retained in the films once the external polarizing field is reduced to zero, which is mostly attributed to the strong coupling force among the adjacent high polar ferroelectric grains. The distance between neighbored grains would be reduced as ferroelectric phase content increases, which is favourable for the improvement of coupling force between them. Meanwhile, the larger ferroelectric grains possess higher polarity and favour the enhancement of coupling force as well. Therefore, the more perfect ferroelectric phase formed under elevated annealing temperatures is responsible for the improved coupling force among ferroelectric grains thus the increased P_r .

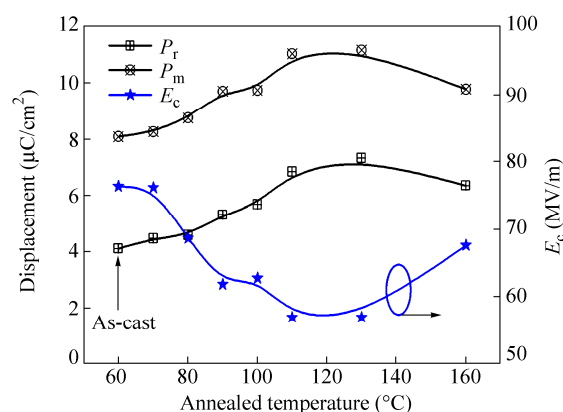


Fig. 6 Maximum polarization (P_m), remnant polarization (P_r) and coercive electric field (E_c) obtained from the D-E loops under 300 MV/m electric field

Piezoelectric Properties

Direct P(VDF-TrFE) copolymers have been well known and investigated as excellent electrets materials thanks to their rather high remnant polarization retained in the films after being polarized under high electric field. A number of piezoelectric parameters have been utilized to characterize the piezoelectric properties of the electrets. In present work, piezoelectric coefficient (d_{33}) is utilized to characterize the piezoelectric performance of the films annealed at varied temperatures. Besides of the ferroelectric nature of the materials, the piezoelectric performance of the electret shows strong dependence on the polarizing conditions as well. All the films were polarized at room temperature under elevated electric fields starting from 50 MV/m with an increment step of 25 MV/m for one circle and d_{33} of all the polarized films is presented as a function of polarizing electric field. As shown in Fig. 7, all the films exhibit the similar piezoelectric coefficient increasing trend as the polarizing electric field increases. After polarizing under electric field below 50 MV/m, a rather low d_{33} is observed in all the samples since the electric field is not sufficient for orienting the ferroelectric domains. Starting from 50 MV/m, d_{33} is increasing quickly and linearly against the increasing polarizing field and reaches the maximum value at 125–175 MV/m depending on the annealing temperature of the samples. Further increasing the polarizing field leads to little increment of d_{33} .

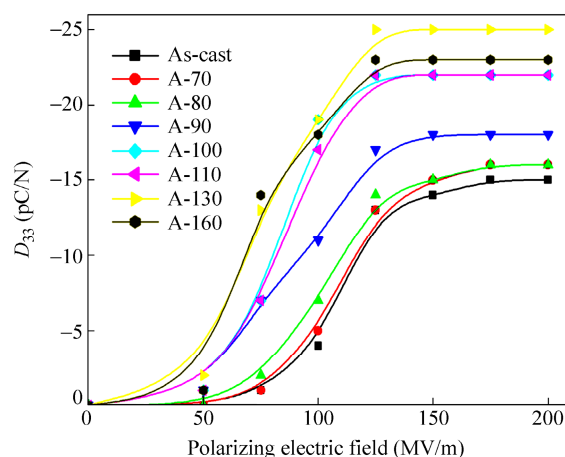


Fig. 7 Piezoelectric coefficient (d_{33}) of copolymer films annealed at elevated temperatures as a function of polarizing electric field

For the as-cast sample and samples annealed at lower temperatures (~ 70 , 80 and 90 °C), relatively high polarizing field is required to achieve the maximum d_{33} , which may be attributed to the imperfect ferroelectric grains in small size formed at low temperatures. As the annealing temperature increases to over 90 °C, the lowest polarizing field is reduced to about 125 MV/m thanks to the improved ferroelectric phase and increased grain size as discussed above. That agrees very well with the results of E_c as discussed above. The maximum d_{33} of all the films shows close dependence on the annealing temperature. Generally, the higher annealing temperature leads to the increased d_{33} from -15 pC/N to -25 pC/N and the highest d_{33} of -25 pC/N is observed for the samples annealed at 110 – 130 °C, which coincides very well with the P_r results as discussed above. For PVDF based electrets, the piezoelectric properties are mostly relying on the remnant polarization retained in the films after the polarization field is removed, which is the key for bounding static charges on the surfaces of the film. Apparently, annealing at the temperatures between their T_c and T_m is an effective way to improve the more perfect ferroelectric phase thus to achieve the best piezoelectric performance in the resultant P(VDF-TrFE) films. The highest d_{33} of -25 pC/N observed in the optimized film is rather close to the stretched PVDF piezoelectric film and the direct P(VDF-TrFE) films. However, the hydrogenized P(VDF-TrFE) piezoelectric films show obvious advantages including the low cost, the facile processing conditions and rich material resource comparing with the other two materials. That allows them to be widely accepted and utilized in massive devices in the industry.

CONCLUSIONS

By annealing at elevated temperatures, the dielectric, ferro- and piezo- electric properties of the hydrogenized P(VDF-TrFE) films have been finely tuned. The improved ferroelectric phase content with the assistance of annealing is responsible for the significant improved electric properties. Below the melting temperature of the crystalline phase, the higher annealing temperature leads to continuously increased dielectric, ferro- and piezo- electric properties. The optimized annealing temperature is found to be 130 °C, which is right between T_c and T_m of the materials, and the highest dielectric constant of 12.5 at 1 kHz, the largest P_m of 11.21 $\mu\text{C}/\text{cm}^2$ and P_r of 7.22 $\mu\text{C}/\text{cm}^2$, the lowest E_c of 56 MV/m, and the highest d_{33} of -25 pC/N are obtained. With respect to its low cost, facile fabrication conditions as well as the rich material resource, the hydrogenized P(VDF-TrFE) copolymer with a composition of VDF/TrFE = $80/20$ (mol%) is a most promising piezoelectric polymer and has a rather high application potential in energy transfer areas.

REFERENCES

- 1 Kawai, H., Jpn. J. Appl. Phys., 1969, 8: 975
- 2 Lovinger, A.J., Jpn. J. Appl. Phys., 1985, 24: 18
- 3 Herbert, J.M., Glass, A.M. and Wang, T.T., "The application of ferroelectric polymers", New York, Chapman & Hall, 1988
- 4 Nalwa, H.S., "Ferroelectric polymers", New York, Marcel Dekker, 1995
- 5 Kang, S.J., Park, Y.J., Hwang, J., Jeong, H.J., Lee, J.S., Kim, K.J., Kim, K.C., Huh, J. and Park, C., Adv. Mater., 2007, 19: 581
- 6 Lee, J.S., Prabu, A.A., Chang, Y.M. and Kim, K.J., Macromol. Symp., 2007, 13: 249
- 7 Naber, R.C.G., Tanase, C., Blom, P.W.M., Gelinck, G.H., Marsman, A.W., Touwslager, F.J., Setayesh, S. and Leeuw, D.M.D., Nat. Mater., 2005, 4: 243
- 8 Fukada, E., Ferroelectrics, 1995, 171: 1
- 9 Dillon, D.R., Tenneti, K.K., Li, C.Y., Ko, F.K., Sics, I. and Hsiao, B.S., Polymer, 2006, 47: 1678
- 10 Lovinger, A.J., Polymer, 1981, 22: 412
- 11 Satyanarayana, K.C. and Bolton, K., Polymer, 2012, 53: 2927

- 12 Davis, G.T., Broadhurst, M.G., Lovinger, A.J. and Furukawa, T., *Ferroelectrics*, 1984, 57: 73
- 13 Lovinger, A.J., Johnson, G.E., Bair, H.E. and Anderson, E.W., *J. Appl. Phys.*, 1984, 56: 2412
- 14 Yagi, T. and Tatemoto, M., *Polym. J.*, 1979, 11: 429
- 15 Ohigashi, H., Omote, K. and Gomyo, T., *Appl. Phys. Lett.*, 1995, 66: 3281
- 16 Yagi, T., Tatemoto, M. and Sako, J., *Polym. J.*, 1980, 12: 209
- 17 Furukawa, T., Johnson, G.E., Bair, H.E., Tajitsu, Y., Chiba, A. and Furukawa, E., *Ferroelectrics*, 1981, 32: 61
- 18 Tashiro, K., Tadokoro, H. and Kobayashi, M., *Ferroelectrics*, 1981, 32: 167
- 19 Aimi, K., Ando, S., Avalle, P. and Harris, R.K., *Polymer*, 2004, 45: 2281
- 20 Ohigashi, H., Kagami, N. and Li, G.R., *J. Appl. Phys.*, 1992, 71: 506
- 21 Ibos, L., Bernès, A. and Lacabanne, C., *J. Ferroelectrics*, 2015, 320: 15
- 22 Kim, J.H. and Khang, D.Y., *Eur. Polym. J.*, 2014, 59: 78
- 23 Wahid, M.H.M., Sa'ad, S.Z., Sarip, M.N., Gan, W.C. and Abd. Majid., W.H., *J. Adv. Mater. Res.*, 2013, 812: 60
- 24 Lu, Y.Y., Claude, J., Neese, B., Zhang, Q.M. and Wang, Q., *J. Am. Chem. Soc.*, 2006, 128: 8120
- 25 Moggi, G. and Bonardelli, P., *J. Polym. Sci., Part B: Polym. Phys.*, 1984, 22: 357
- 26 Tan, S.B., Li, J.J. and Zhang, Z.C., *Macromolecules*, 2011, 44: 7911
- 27 Liu, E.Q. and Zhang, Z.C., *Acta Polymerica Sinica (in Chinese)*, 2010, (8): 1087
- 28 Tan, S.B., Liu, E.Q., Zhang, Q.P. and Zhang, Z.C., *Chem. Commun.*, 2011, 47: 4544
- 29 Lu, Y.Y., Claude, J., Zhang, Q.M. and Wang, Q., *Macromolecules*, 2006, 39: 6962
- 30 Wang, Z.M., Zhang, Z.C. and Chung, T.C.M., *Macromolecules*, 2006, 39: 4268
- 31 Zhang, Z.C., Meng, Q.J. and Chung, T.C.M., *Polymer*, 2009, 50: 707
- 32 Xia, W.M., Xu, Z., Zhang, Z.C. and Li, H.Y., *Polymer*, 2013, 54: 440
- 33 Zhang, Q.P., Xia, W.M., Zhu, Z.G. and Zhang, Z.C., *J. Appl. Polym. Sci.*, 2013, 217: 2094
- 34 Sencadas, V., Lanceros-Mendez, S., Serra, R.S.I., Balado, A.A. and Ribelles, J.L.G., *Eur. Phys. J.E.*, 2012, 85: 41