

Polar Phase Formation and Piezoelectricity of PVDF by Hot-pressing under Electrostatic Intermolecular Interactions

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Electronic Supplementary Information

Abstract Piezoelectric poly(vinylidene fluoride) (PVDF) has received considerable attention due to its ability of interconverting mechanical into electric energies and potential applications in wearable electronics. To achieve piezoelectricity, it is important to simultaneously control the formation of polar phases, crystallinity, and dipole alignments in PVDF-based films. Here we demonstrate that piezoelectricity can be obtained by directly hot-pressing PVDF films sandwiched between chitosan or cellulose films. The electrostatic interactions between PVDF and chitosan or cellulose enabled an exceptional high content of polar phases (β - and γ -phases) up to 90% and a measured piezoelectric charge coefficient d_{33} of up to -30 pC/N. This study provides a simple and low-cost approach for obtaining piezoelectric PVDF films used for sensors, actuators, and energy harvesters.

Keywords Poly(vinylidene fluoride); Piezoelectricity; Electrostatic interactions; Hot-pressing

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INTRODUCTION

Since the discovery of piezoelectricity in poly(vinylidene fluoride) (PVDF) in 1969,^[1] piezoelectric polymers have received considerable attentions for applications in wearable sensors, actuators, and energy harvesters due to their flexibility, low-cost and biocompatibility.^[2–5] Analogous to ceramic ferroelectrics, the best piezoelectric polymers were found in ferroelectric polymers, in which the piezoelectricity can be described by an electrostriction model,^[6] i.e., the piezoelectric coefficient d_{33} is written as $d_{33}=2Q_{33}\epsilon P_r$, where Q_{33} is the electrostriction coefficient, ϵ is the permittivity and P_r is the permanent polarization. As Q_{33} and ϵ are almost constants for an individual ferroelectric polymer,^[7] it is thus essentially important to increase P_r to fabricate piezoelectric films from ferroelectric polymers with good piezoelectric performances. PVDF is a semicrystalline polymer with at least four different crystalline polymorphs which are assigned to α -, β -, γ -, and δ -phases.^[8,9] The α -phase is the most thermodynamically stable phase and is easy to fabricate. However, α -phase PVDF is paraelectric due to its alternating trans (T) and gauche (G) molecular

conformations and anti-parallel alignment of polymer chains in unit cells. To achieve a non-zero P_r , it is necessary to convert the nonpolar α -phase into polar phases such as β -, γ -, and δ -phase.^[10] This has been achieved by mechanical stretching or compressing,^[11–14] and exploring intermolecular interactions.^[15–19] In order to maximize the numbers of dipole moments on the surfaces of films, some post-processing methods, such as electric poling,^[20–22] epitaxial growth^[23–25] and geometrical confinement,^[26–28] have been developed to effectively control the alignment of dipole moments, which is perpendicular to the chains of PVDF. Therefore, the current processing procedures of piezoelectric PVDF films are very complex. Considering the widely potential applications of piezoelectric polymers, it is a long-standing challenge to fabricate piezoelectric PVDF films with a simply and low-cost method.

In this study, we report a simple yet effective method for producing PVDF films with high content of polar phases and excellent piezoelectric performances. PVDF homopolymer is selected here because of its higher Curie transition temperature (close to the melting point of PVDF) compared to PVDF-based copolymers such as poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)), poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) and poly(vinylidene fluoride-co-tetrafluoroethylene) (P(VDF-CTFE)).^[29,30] Typically,

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PVDF films dominated by α -phase were firstly produced with a solution casting method. The films were sandwiched between chitosan or cellulose films and subjected to hot pressing. As the chitosan or cellulose chains bear plenty of hydroxyls^[31] and/or amino groups,^[32] we expect that electrostatic interactions such as hydrogen bonds can be formed between the hydroxyl groups (and/or amino groups) and CF_2 groups in PVDF chains.^[33,34] In such a way, polar phases may be obtained when PVDF films are crystallized under pressing and electrostatic interactions. Indeed, we found that the content of polar phases including β - and γ -phases can raise up to 90%, while the crystallinity maintains at about 40%. The measured piezoelectric charge coefficient d_{33} was found to be about -30.0 pC/N, which is comparable to PVDF films obtained by stretching and electric poling.

EXPERIMENTAL

Materials

PVDF powders with weight-average molecular weight of 5.34×10^5 g/mol were purchased from Sigma Aldrich. *N,N*-dimethylformamide (DMF) was purchased from Sinopharm Chemical Reagent Co., Ltd. Chitosan (CS) and hexafluoroisopropanol (HFIP) were purchased from Macklin Co., Ltd. Cellulose nanocrystals (CNC) were purchased from ScienceK Co., Ltd. All the reagents and solvents were used as received without further purification.

Preparations of PVDF Films

Free-standing PVDF films were firstly prepared. Briefly, PVDF powders were dissolved in DMF at a concentration of 100 mg/mL. The solutions were cast on a clean cover glass at room temperature and then put into a vacuum oven pre-heated to 110 °C. After 3 h, the samples were removed from the oven. Free-standing films were thus obtained by peeling off the films supported on cover glasses with a tweezer. The thickness of the obtained free-standing PVDF films is measured to be about 50.0 μm .

Before preparation of CS films, CS powders were dissolved in HFIP at a concentration of 5.0 mg/mL. The solution was dropped into clean petri dishes at room temperature. After HFIP was evaporated at room temperature (about 36 h), free-standing CS films were obtained by taking out from petri dishes. Similarly, CNC powders were dispersed in deionized water at a concentration of 50.0 mg/mL. Free-standing films of CNC were obtained by evaporating water at room temperature.

Before hot pressing, a piece of free-standing PVDF film was sandwiched between a pair of CS or CNC films. A pair of glass sheets were then used to protect the assembled films. The assembled films protected by glass sheets were subsequently clamped with a metal clip with an applied pressure of about 0.1 MPa and put into a vacuum oven which was preset at different temperatures. Before removing, the vacuum oven was naturally cooled to room temperature. In order to determine the main cause of phase shift is electrostatic interactions between PVDF and CS/CNC rather than other reasons such as pressure, only clean glass plates are used for hot pressing.

Characterization

Fourier transform infrared spectroscopy (FTIR) data were

obtained in the range of 400–4000 cm^{-1} using an infrared spectrometer (VERTEX 70, BRUKER), with 32 scans at a resolution of 2 cm^{-1} . Wide-angle X-ray diffraction (WAXD) measurements were performed using an X'Pert Pro diffractometer (PANalytical, Holland) with a $\text{Cu-K}\alpha$ radiation source at $\lambda = 0.154$ nm. The thermal characteristics were investigated by differential scanning calorimetry (DSC) measurement under atmospheric pressure using a DSC 2010 instrument (TA Instrument, USA) at a heating and cooling rate of 10 °C/min under N_2 atmosphere.

In order to study the piezoelectric performance of PVDF films, commercially available indium tin oxide (ITO) coated polyethylene terephthalate (PET) films (0.7 cm $\times$ 1.7 cm) were used as bottom and top electrodes. To avoid sliding triboelectric effects, the ITO was adhered to the films by electrically conductive double side tapes (Nisshin EM Co., Ltd.). The devices were finally sealed with polyimide tapes. A homemade piezoelectric test setup was used to apply periodic forces with a compressive cylindrical radius of 0.5 cm to the samples and to measure the output charge signals by using an oscilloscope (Tektronix TDS 2024B) connected to a charge amplifier (Vkinging Co., LTD., VK103). Typically, the frequency of applied force is 5.0 Hz.

RESULTS AND DISCUSSION

The processing procedure of piezoelectric PVDF films is schematically shown in Fig. 1(a). Briefly, free-standing PVDF films were sandwiched between a pair of CS or CNC films and subjected to hot-pressing in vacuum. Due to the presence of plenty of hydroxyl groups on the surfaces of CS and CNC films (and amino groups on CS), we expect that electrostatic interactions such as hydrogen bonds can be formed between CF_2 groups in PVDF chains and CS (or CNC) films, as shown in Fig. 1(b). Therefore, polar phases may be induced in PVDF films when crystallized. Meanwhile, the dipoles may be aligned to be parallel to the normal direction of films since they are perpendicular to PVDF chains.^[35] For convenience, PVDF hot-pressed between CS films are labeled as CS-P-CS, PVDF hot-pressed between CNC films as CNC-P-CNC, and PVDF hot-pressed between glass films as Glass-P-Glass in the following context.

To verify the interactions between the CF_2 groups in PVDF and the hydroxyl groups in CS or CNC, we compared the FTIR spectra of the as-prepared PVDF films and CS-P-CS films obtained at 180 °C for 3 h. As shown in Fig. 2(a), an absorption band at 1179 cm^{-1} which is attributed to the CF_2 stretching mode of PVDF,^[33] can be clearly observed in the as-prepared PVDF films. The absorption band shifts to 1168 cm^{-1} in the PVDF films sandwiched between CS. In addition, absorption bands at 3025 and 2985 cm^{-1} which are attributed to the ν_{as} ($-\text{CH}_2$) and ν_{s} ($-\text{CH}_2$) vibrational bands of PVDF,^[36] can be observed in the as-prepared PVDF films as shown in Fig. 2(b). The absorption band shifts to lower wavenumber direction after PVDF films hot-pressed between CS/CNC. The shift of absorption peak toward lower wavenumber indicates the interactions between PVDF and CS/CNC. However, there was no shift of absorption bands in PVDF film hot-pressed between glass sheets. These interactions may result from the electrostatic interactions such as hydrogen bonds between CF_2 groups in PVDF and hydroxyl and/or amino groups in CS.^[37]

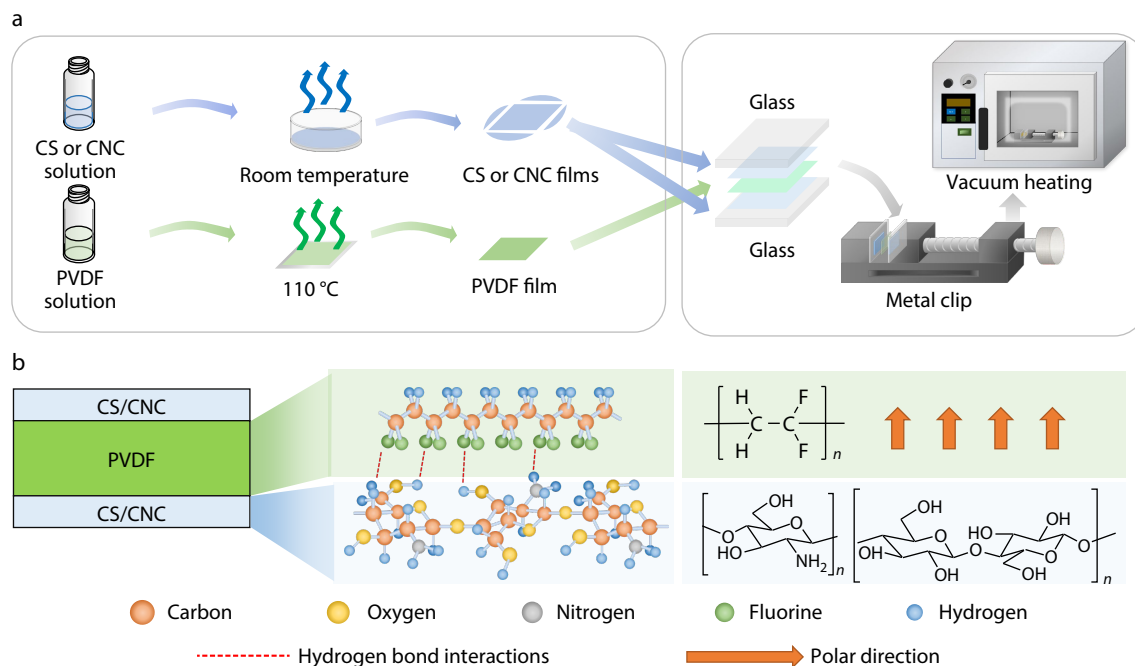


Fig. 1 The Schematic diagram for (a) the fabrication process and (b) the electrostatic interaction between PVDF and CS/CNC and chemical formula of related materials.

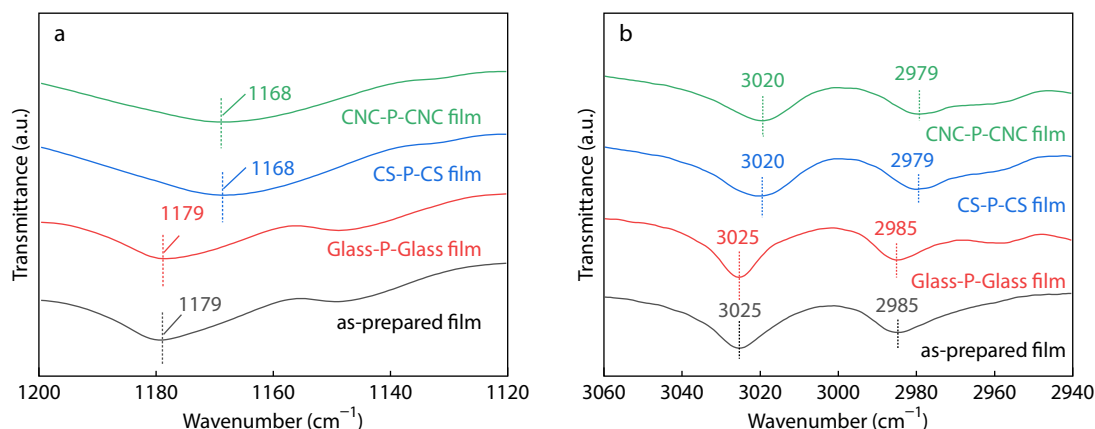


Fig. 2 FTIR spectra of (a) the as-prepared PVDF film and PVDF films obtained by pressing against CS films/CNC films/glass sheets after 3 h in the region of 1120–1200 cm^{-1} , and (b) the as-prepared PVDF film and PVDF films obtained by pressing against CS films/CNC films/glass sheets after 3 h in the region of 2940–3060 cm^{-1} .

To investigate the effects of hot-pressing temperatures on the phase transitions, the FTIR spectra of PVDF films obtained by pressing at different temperatures for 3 h are shown in Fig. 3(a). All the characteristic absorption bands of α -phase (615, 766, 795, 855, 975, 1149, and 1211 cm^{-1}) are observed when the temperature is lower than 160 $^{\circ}\text{C}$.^[38] The characteristic absorption bands of β -phase (840 and 1275 cm^{-1}) and γ -phase (813, 833, 1116, and 1231 cm^{-1}) are very weak. These results indicate that α -phase dominates the PVDF films obtained by pressing at 150 and 160 $^{\circ}\text{C}$. With the increase of pressing temperatures, the characteristic absorptions bands of α -phase are weakened. Meanwhile, the characteristic absorptions bands of β - and γ -phases are strengthened, indicating the increase of contents of β - and γ -phases as a function of pressed temperature. Note that the

band at 840 cm^{-1} is attributed to both β - and γ -phases. We evaluate the content of electroactive β - and γ -phases (F_{EA}) by the following equation:^[38]

$$F_{\text{EA}} = \frac{A_{\beta/\gamma}}{(K_{\alpha}/K_{\beta/\gamma})A_{\alpha} + A_{\beta/\gamma}} \quad (1)$$

where A_{α} (α -phase) and $A_{\beta/\gamma}$ (β/γ -phase) represent the absorption band intensities at 766 and 840 cm^{-1} , respectively. K_{α} and $K_{\beta/\gamma}$ are the absorption coefficients at the respective wavenumbers. The values of K_{α} and $K_{\beta/\gamma}$ are 6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2 \cdot \text{mol}^{-1}$, respectively.^[39] The calculated results are shown in Fig. 3(d). Apparently, the content of β - and γ -phases sharply increases from 6.9% at 160 $^{\circ}\text{C}$ and saturates at $\approx 93\%$ at 180 $^{\circ}\text{C}$.

The structures of the hot-pressed PVDF films were further characterized by WAXD, as shown in Fig. 3(b). The presence of

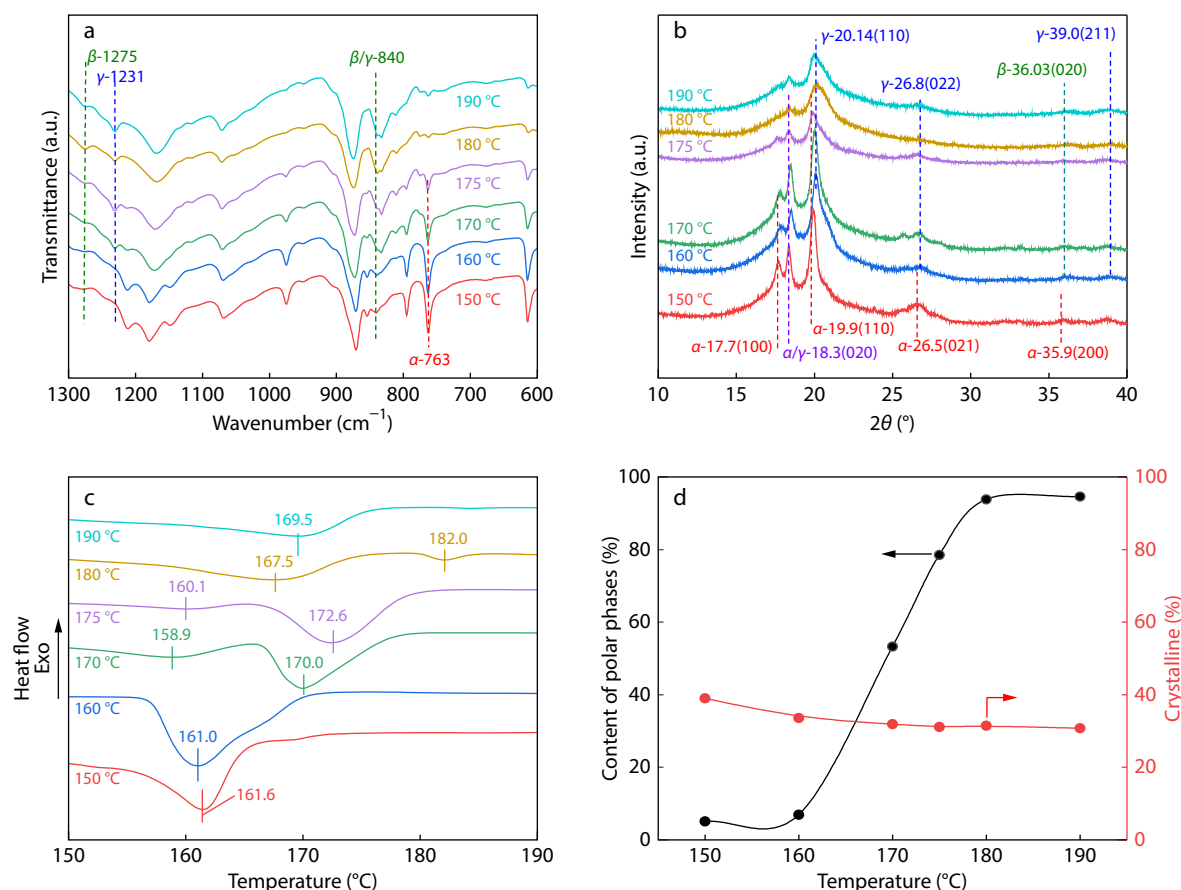


Fig. 3 Structural characterizations of PVDF films obtained by pressing against CS films at different temperatures. (a) FTIR, (b) WAXD, and (c) DSC results. (d) Content of polar phases (β - and γ -phases) and crystallinity calculated from (a) and (c).

diffraction peaks at $2\theta=17.7^\circ$, 18.3° , 19.9° , 26.5° , and 35.9° , which can be indexed to (100), (020), (110), (021), and (200) planes of α -phase,^[40,41] respectively, confirms that non-polar α -phase is dominant in the PVDF films pressed at 150 °C. When the pressing temperature is increased to 160 °C, a diffraction centering at $2\theta=20.1^\circ$ which can be attributed to either (110/200) planes of β -phase or (110/101) planes of γ -phase, is superimposed to the diffraction peaks of α -phase. This indicates part of the α -phase transform to β - and γ -phases. However, it is difficult to identify the specific crystalline forms because the diffraction peaks of β - and γ -phase are too close. When the pressing temperature increased to 180 °C, the diffraction peaks characterizing α -phase almost disappear, indicating the nearly complete transformation.

In order to study the thermal behaviors of PVDF films treated at different temperatures, DSC measurements were performed and shown in Fig. 3(c). When the pressed temperatures are lower than 160 °C, the melting temperature (T_m) is around 161 °C, confirming that these films are dominated by α -phase. When the pressed temperature exceeds 170 °C, the main T_m peak moves to a higher temperature centering at 170 °C. This means that most parts of the α -phase were transformed into γ -phase.^[30] When the pressing temperature exceeds 180 °C, two main T_m peaks are observed at 167.5 and 182 °C, meaning that the crystalline regions of PVDF films are mixture of β - and γ -phases.^[40] To determine the degree of

crystallinity (χ_c) in the hot-pressed PVDF films, Eq. (2) is used as follows:

$$\chi_c (\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (2)$$

where ΔH_m is the measured melting enthalpy and ΔH_m^0 (104.5 J/g) is the melting enthalpy of 100% crystallized PVDF.^[42] The calculated results are shown in Fig. 2(d). Apparently, the crystallinity slightly decreased from 39.0% at 150 °C to 30.8% at 190 °C.

We also prepared PVDF films with the CS-P-CS system at 180 °C for different time, i.e., 0, 0.5, 1.0, 2.0, and 3.0 h. The corresponding FTIR spectra of PVDF films are shown in Fig. 4(a). As seen, all the characteristic absorption bands of α -phase are observed before hot-pressing (0 h). The characteristic absorption bands of β - and γ -phase are very weak. These results indicate that α -phase dominates the PVDF films before hot-pressing. After hot pressing for 1 h, the characteristic absorption bands of α -phase are weakened. Meanwhile, the characteristic absorptions of β - and γ -phases are strengthened, indicating that the polar phases formation in crystalline regions of PVDF progress with time. When the time of hot pressing reaches 2 h, the characteristic absorption bands of α -phase almost disappear and the characteristic absorption bands of β - and γ -phases appear. It means that the polar phase becomes prominent in PVDF after hot-pressing at 180 °C for 2 h. By cal-

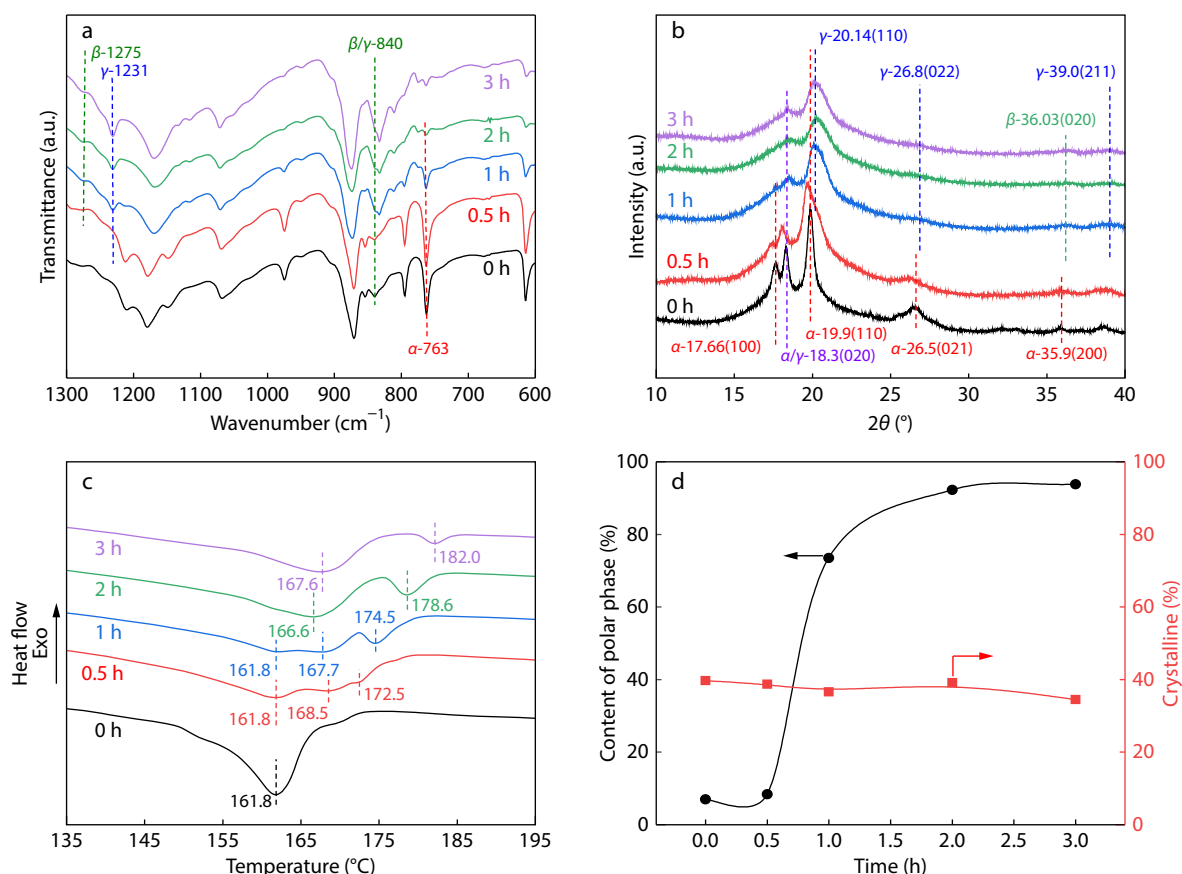


Fig. 4 Structural characterizations of PVDF films obtained by pressing against CS films at different times. (a) FTIR, (b) WAXD, and (c) DSC results. (d) Content of polar phases (β - and γ -phases) and crystallinity calculated from (a) and (c).

culating the content of polar phases using Eq. (1), we found that the content of polar phases increases from 8.4% for 0.5 h to 93.8% for 3 h, as shown in Fig. 4(d).

The results of WAXD of PVDF films obtained by pressing at 180 °C for different time are shown in Fig. 4(b). For PVDF films pressed for 0 h, only the characteristic diffraction peaks of α -phase are observed. When the pressing time lasts 1 h or more, the diffraction peaks at $2\theta=19.9^\circ$ shift to 20.1° , indicating the nearly complete phase transformation from α - to β - or γ -phase.

The DSC results of PVDF films pressed at 180 °C for different time are shown in Fig. 4(c). Before hot pressing, PVDF film has only one T_m centered at 161.8 °C. For samples pressed for 0.5 h, the T_m at 161.8 °C is gradually weakened. Meanwhile, two shoulder T_m peaks centered at 168.5 and 172.5 °C are observed, indicating that both β - and γ -phases appear in the crystallization regions of PVDF films. When the processing time exceeds 2 h, only two T_m peaks appear at 166.6 and 178.6 °C are observed, meaning the almost complete transformation of α -phase into β - and γ -phases. The crystallinity was calculated and shown in Fig. 4(d). As seen, the crystallinity slightly fluctuated between 39.7% to 34.5%.

To verify the versatility of the methods, we replace the CS with CNC films. The FTIR spectra of PVDF films obtained at different temperatures for 3 h are shown in Fig. 5(a). As seen, all the characteristic absorption bands of α -phase are observed when the temperature is 150 °C. The characteristic absorp-

tion bands of β -phase and γ -phase can also be observed. By increasing the pressed temperature to 170 °C, the characteristic absorptions of β - and γ -phases are enhanced. With the further increase of temperature, the spectra contain almost only the characteristic absorptions of β - and γ -phases. These results indicate that the β - and γ -phases dominated in the PVDF film after hot-pressing at 170 °C for 3 h. Apparently, the content of β - and γ -phases sharply increases from 38.1% at 150 °C and saturates at 92.5% at 170 °C, as shown in Fig. 5(d). The structures of PVDF hot-pressed between CNC films were also characterized by WAXD, as shown in Fig. 5(b). The presence of diffraction peaks at $2\theta=17.7^\circ$, 18.3° , 19.9° , 26.5° , and 35.9° indicates the existence of α -phase in the PVDF films pressed at 150 °C. When the pressing temperature increased to 170 °C or more, the diffraction peak at $2\theta=19.9^\circ$ shifts to 20.1° , indicating the phase transformation from α -phase to β - or γ -phases. We found that the critical temperature is about 170 °C. This fact is also manifested by the results of DSC measurements shown in Fig. 5(c). When the temperature of hot-pressing was lower than 160 °C, the T_m of PVDF films is around 160.9 °C, indicating that the films are dominated by α -phase. When the pressed temperature exceeds 170 °C, the T_m peaks presence at 167.8 and 181 °C, indicating a mixture of β - and γ -phases. The calculated crystallinities are shown in Fig. 5(d). Apparently, the crystallinity slightly fluctuates from 39.1% at 150 °C to 38.4% at 190 °C.

In order to prove that the phase change mainly comes from

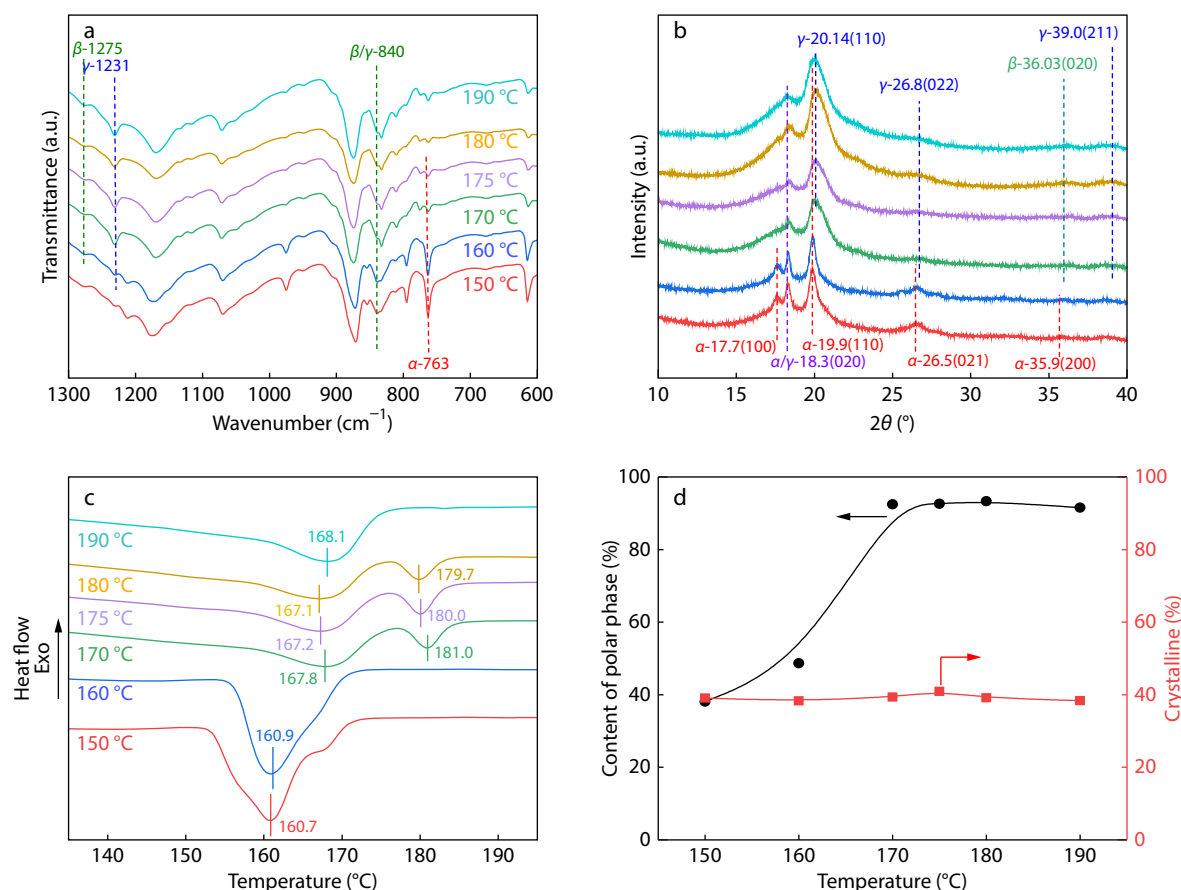


Fig. 5 Structural characterizations of PVDF films obtained by pressing against CNC films at different temperatures. (a) FTIR, (b) WAXD, and (c) DSC results. (d) Content of polar phases (β - and γ -phases) and crystallinity calculated from (a) and (c).

the interaction between CS/CNC and PVDF rather than the influence of pressure or other factors, PVDF films were hot-pressed between glass for different temperature. The FTIR spectra of PVDF films hot-pressed between glass obtained at different temperatures for 3 h are shown in Fig. S1(a) (in the electronic supplementary information, ESI). As can be seen, all the characteristic absorption bands of α -phase are observed when the temperature from 150 °C to 190 °C. The characteristic absorption bands of β - and γ -phases are weak no matter what hot-pressing temperature are used. These results indicate that α -phase dominates the PVDF films when PVDF is hot-pressed between glass. By calculating the content of polar phases using Eq. (1), the content of polar phase decreases with the increase of hot-pressing temperature from 15.2% at 150 °C to 0.7% at 190 °C, as shown in Fig. S1(b) (in ESI). This means that polar phases cannot be created by hot pressing between the glass plates and the interaction between CS/CNC and PVDF is the main reason of phase change during hot-pressing.

The electromechanical testing confirms the piezoelectricity and quantifies the piezoelectric coefficients of the hot-pressed PVDF films. For the measurements, we applied periodic compressive forces to the thin films and measured output charges *via* the electrodes stuck on the films. As shown in Fig. 6(a), when the external periodic forces are applied, a periodic charge signal with the same frequency (5.0 Hz) is immediately observed.

The response time, which is characterized by the half-width of output charge peaks, is about 30.0 milli-second (ms).

To quantify the piezoelectric charge coefficient d_{33} , the output charge densities were measured as a function of time with different input forces. For PVDF films obtained by pressing at 180 °C for 3 h with CS, the charge density increases from 0.81 nC/cm² to 1.60 nC/cm² when the input force is increased from 3 N to 21 N (Fig. 6b). Similarly, the charge density increases from 0.45 nC/cm² to 1.18 nC/cm² for PVDF films pressed with CNC (Fig. 6c). The changes of output charge densities as a function of applied forces are plotted in Fig. 6(d), from which the d_{33} is calculated based on the following equation:^[43]

$$d_{33} = \frac{P \cdot A_2}{F} \quad (3)$$

where P is the charge density, F is the applied force, and A_2 is the compressed area. The calculated d_{33} values for CS-P-CS and CNC-P-CNC are about -30.2 and -29.8 pC/N, respectively. These values are comparable to literature reports for PVDF obtained by stretching and subsequent electrical poling (d_{33} = -13 pC/N to -28 pC/N).^[44] In order to comparison, PVDF piezoelectric sensors produced by Tektronix Electronic Equipment Co., Ltd. were purchased for testing. The charge densities of this sample are shown in Fig. S2(a) (in ESI), when the external force increases from 5 N to 21 N, the charge density increases from 0.18 nC/cm²

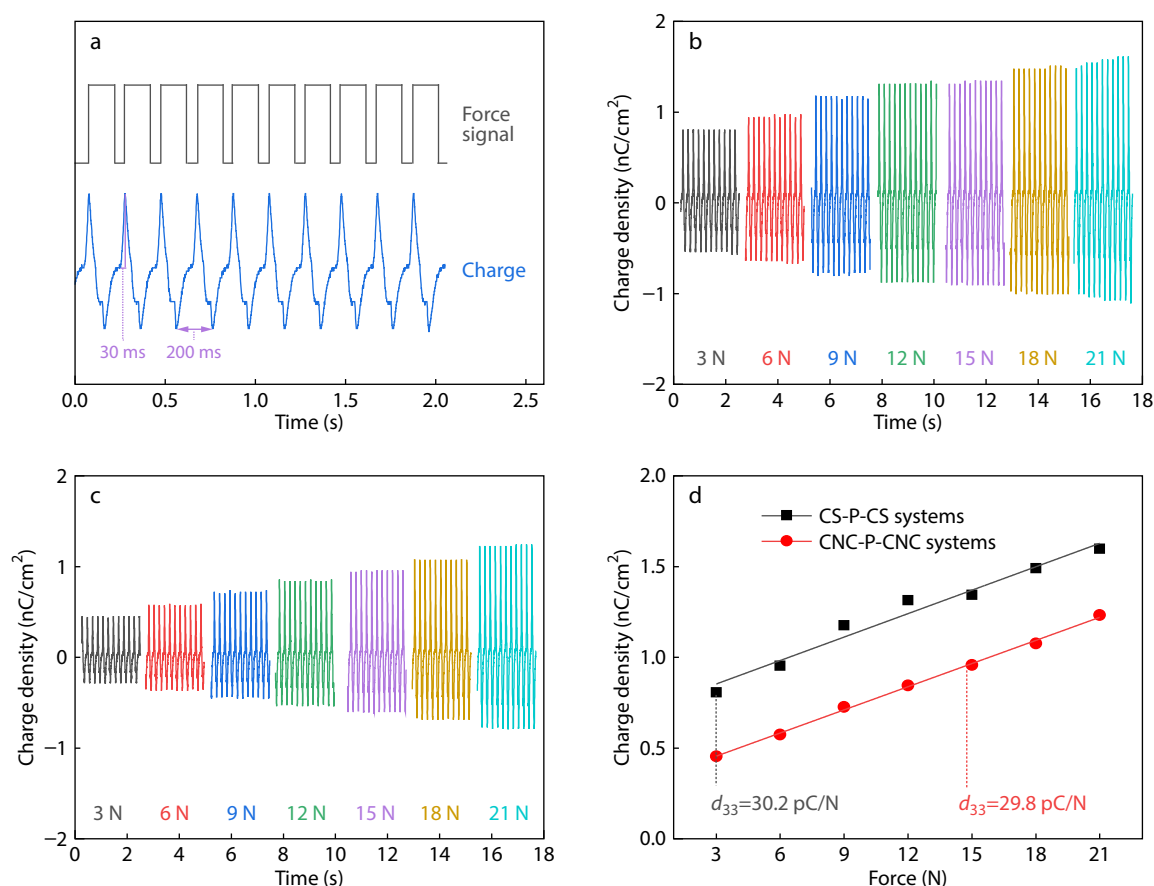


Fig. 6 Piezoelectric characterization of the samples. (a) Schematic diagram of the applied force signals and the measured output charge signals of PVDF films; (b) The output charge densities of PVDF films obtained from CS-P-CS systems under different applied forces; (c) The output charge densities of PVDF films obtained from CNS-P-CNS systems under different applied forces; (d) The measured output charge densities of PVDF films as a function of applied pressures, from which the piezoelectric coefficients d_{33} are calculated.

to 0.65 nC/cm^2 . The calculated d_{33} for PVDF piezoelectric sensor is about -20.3 pC/N (Fig. S2b in ESI).

CONCLUSIONS

In summary, we successfully fabricated PVDF films with high content of polar phase (up to $\approx 93\%$) by taking advantages of hot-pressing and interfacial interactions between PVDF and chitosan or cellulose films. The crystalline forms of PVDF films have been changed from nonpolar α -phase to polar phase (β - and γ -phases). The crystallinity, however, maintains constant of about 40%. The measured piezoelectric charge coefficient d_{33} were found to be about -30.0 pC/N , which is comparable to PVDF films obtained by stretching and electric poling.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/>

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