

FABRICATION AND CHARACTERIZATION OF
MULTIFUNCTIONAL BIO-INSPIRED COMPOSITES

by

Zhe Xu



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To my family

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MULTIFUNCTIONAL BIO-INSPIRED COMPOSITES

by

ZHE XU, MS

DISSERTATION

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This dissertation concentrates on a comprehensive study on bio-inspired (“Nacre”-like) composite materials. It involves the design and fabrication approaches and characterize properties of composite materials including meta-ceramic brick-and-mortar composites and piezo-polymer matrix ceramic reinforced composites. Hybrid composites of layered brittle-ductile constituents assembled in brick-and-mortar architecture are promising for applications requiring damage-tolerance. Mostly, polymer mortars has been considered the ductile layer, however, low stiffness of polymers does not efficiently transfer the shear force between hard ceramic bricks. Theoretical models point to metals as a more efficient mortar layer. However, infiltration of metals into ceramic scaffold is non-trivial, given the low adhesion between metals and ceramics. We report on an alternative approach to assemble brick-and-mortar metal-ceramic composites by using electro-less plating of nickel on alumina micro-platelets, which are subsequently aligned by magnetic field, taking advantage of paramagnetic properties of nickel. The assembled nickel-coated ceramic scaffold is then sintered using spark plasma sintering (SPS). We report on materials and mechanical properties of the composite. The fabricated metal-ceramic composite shows a

rising R-curve fracture behavior. The results show that this is a promising approach toward development of damage-tolerant metal-ceramic composites.

Hybrid materials of inorganic-organic phases in which each phase provides different functionality are attractive candidates for achieving multi-functionality. Using a layer-by-layer approach, we fabricated sheets of piezoelectric polymer P(VDF-TrFE) reinforced by aligned sub-micron thick platelets of single crystal sapphire. The as-fabricated films were transparent and piezoelectric, exhibited ductility up to ~330%, and tensile toughness of up to 26 J/g. In addition, we investigated the effect of thermal annealing of the polymer on the crystallinity of the polymer phase and its effect on the mechanical and piezoelectric properties of the fabricated films. Thermal annealing resulted in improvement of the elastic modulus and piezoelectric properties of the films. PVDF and its co-polymers piezoelectric polymers in film and nanofiber forms are increasingly used for sensing, actuation and energy harvesting. Given the semi-crystalline structure of these polymers, their electromechanical coupling behavior changes with thermomechanical processing. This research reports on the evolution of the mechanical properties, piezoelectric properties and morphology of P(VDF-TrFE) piezoelectric polymer thin films fabricated by spin-coating during thermal annealing and drawing, studied via tensile test, polarized optical microscopy, X-ray diffraction, polarized FTIR, and piezoresponse force microscopy (PFM). The results show that annealing and drawing process result in 10 and 13 times improvement in the elastic modulus and ultimate strength of the films, respectively. In addition, the piezoelectric constant and electromechanical coupling improves by 30% and more than 17 times, respectively. These changes are accompanied by 65% increase in the percentage of the crystallinity of the semi-crystalline piezoelectric films.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

With rapid technological development in our modern world, we are about to experience the fourth industrial revolution, Robotization. This means robots and other types of machines that have artificial intelligence help human beings complete certain tasks. Because of the massive usage of machines, it inevitably raises serious issues and concerns. Currently our population is suffering from heavy environmental issues globally, for instance the PM 2.5 issue in major cities in China, caused by uncontrolled traditional fuel consumption and a highly increasing rate of vehicle emission. All these facts are driving researchers to both take advantage of new clean energy, like wind and solar energy, and develop robust, ductile and lightweight materials in order to reduce traditional fuel consumption that could create serious negative consequences. In this dissertation, I mainly focus on development of composite materials that have robust, tough, low density and multi-functional properties.

Until now, composite materials have been widely used in industrial fields, such as the aerospace industry, vehicles, wind turbines, and compressed gas storage. The Boeing 787 Dreamliner is an outstanding example involving the application of composite materials where approximately 50% of body of the plane is covered with carbon laminated composite material, which is one of the fiber reinforcement polymer composite that has superior in-plane mechanical properties. In order to encourage the growth of the composite material industry, the *Institute for Advanced Composites Manufacturing Innovation* (IACMI) was established by the US Department of Energy's Advanced Manufacturing Office, in 2015.

In this dissertation, I will demonstrate two different types of bio-inspired composites that are inspired by nacre in red abalone shells. One of reasons that I devoted myself to this research is its unique “brick-and-mortar” structure that gives this material extraordinary multifunctional properties, such as simultaneous high fracture toughness and high strength.

In Figure 1.1., the Ashley plot effectively reveals the relation between fracture toughness and elastic modulus among various materials including the structured nacre in seashells and unstructured monolithic rock (calcite). Chemically, there is no obvious differences between these two because nacre is made of 95% aragonite (calcium carbonate) and 5% organic soft material[1, 2], chitin, and the rock contains 100% calcium carbonate, that leads to both materials having the same range of elastic modulus. On the other hand, in terms of the resistance to existing defect, the fracture toughness of nacre in seashell is about 100 times higher than that of rock.

Besides facts from experimental data, numerous scientists and researchers conducted a series of studies in order to properly interpret potential mechanisms that hides inside this attractive specimen. There are several popular theoretical modals about fracture mechanism and toughening mechanism, for example, platelets pull-out model referring the fact that when the aspect ratio of platelets is lower than the critical value so that polymer matrix yields first; tension-shear chain model indicating that the main load is carried by platelets and is transferred to the neighboring platelets though soft matrix by shear and the “composition-structure-property” diagram revealing asymmetrical and non-uniform stress distribution within the overlapped platelets [3-6].

But among all these previous theories, still some key factors are not being considered, such as the role of vertical mortar in the composite. The vertical “mortar” is significant for raising the peak strength in the composite. In Ritchie *et al.*’s study[7], most of the factors are comprehensively

included; It also offers the fabrication fundamentals about the metallic-matrix ceramic reinforced “Nacre”- like composite materials. The optimal combination is that strong ceramic bricks that have a large aspect ratio when compared to “mortar”, or small aspect ratio bricks combined with very strong “mortar” materials. In conclusion, the application of metallic mortar material significantly increases the robustness and fracture toughness of the composite that has a “brick-and-mortar” structure.

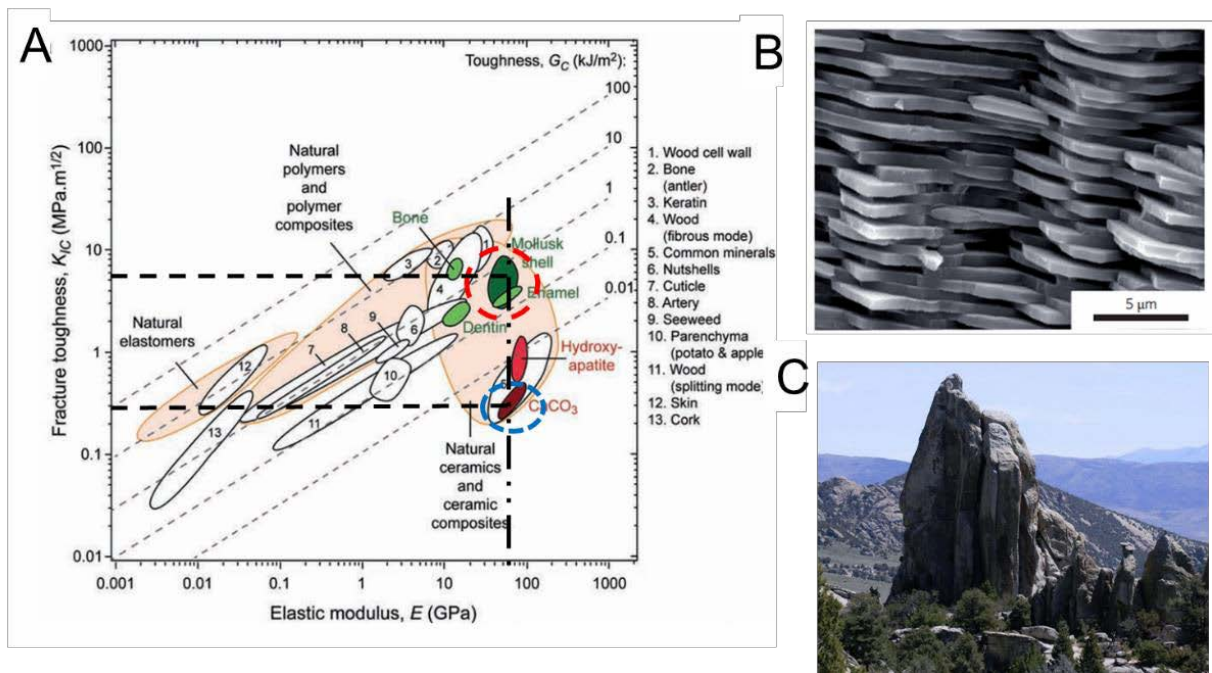


Figure 1.1. **(A)** the Ashby plot reveals the fracture toughness(K_{IC}) as a function of elastic modulus (E) among the various types of materials including nacre (red dash circle and monolithic Calcium carbonate ($CaCO_3$) (blue dash circle) [8, 9], **(B)** the high magnification SEM image of “layer-by-layer” structure in Nacre[2], **(C)** the photography of giant rock in City of Rock National Reserve[10].

Another fact about these natural materials is that they usually have multi-functionalities. For example, bone is not only a robust and tough material but also has the piezo-electricity. Obviously, the robustness and toughness come from the hierarchical structure, in another aspect the soft

constituent, such as single collagen fibrils[11], existing between adjacent inorganic platelets contributes the piezoelectric phenomenon. The piezoelectricity is often recognized by its electromechanical coupling efficiency that enables sensing and actuation functionalities. In order to assemble the piezo polymer ceramic composite, I demonstrated the “layer-by-layer” approach which is a versatile technique that can precisely control the thickness of polymer films in chapter 4. The piezo-electric polymer (polyvinylidene fluoride and its copolymer poly[(vinylidenefluoride)-co- trifluoroethylene]) play a significant role in sensing, actuation and in the energy harvesting field, and its electromechanical coupling behavior can be modified via thermal and mechanical processing. I conducted a research study that shows the morphological properties of this piezo polymer can be manipulated in order to increase its elasticity and strength along with its electromechanical coupling efficiency.

1.2 Background

1.2.1 Electro-less plating technique

The electro-less deposition technique was accidentally invented by Brenner and Riddell in 1946 [12]. “Electro-less” means that there is no external electrode involved in the process, but it does involve the electron transfer. In the technique, an anode refers to the metal salt in the solution, and the cathode reaction takes place on the surface of the substrate (surface of ceramic platelets in this work). Electrons are provided via the reducing agent (sodium hypophosphite, NaH_2PO_2). This technique was first popularly used among artists to, for example, create metallic coating on glass and wood. Later, electro-less deposition was widely used in more practical applications because some of its unique features are not shared with other techniques. For instance having no limitations

about the shape of surfaces to be coated and materials, highly efficient use of metallic material and having thin coating layer when compared with other conventional metal deposition techniques. On the basis of previous reports, a wide range of metallic materials can be yielded via electro-less plating including nickel, copper, gold, cobalt, palladium, and silver as well as their alloys with phosphate and boron.

There are multiple steps involved in electro-less plating, which include cleaning, surface modification, sensitization, catalyzing, and activation; and the water rinsing step is necessary between each steps. Since no strong covalent bond can be formed between ceramic and metal, the interface adhesion property has become an important concern. One of the promising solutions is to roughen the surface in order to increase the adhesion via mechanical friction and entrapment. However based on the previous study, etching the single crystal alumina platelets will compromise the properties of platelets dramatically [13].

Without involving the etching process, the surface functioning steps are quite critical, and include sensitization and activation. Fundamentally these two steps are designed to seed a very thin layer of active material, such as palladium in this case. This thin catalyzed surface on alumina platelets will provide the large amount of nucleation sites so that the nickel islands grow near them in the high density (Figure 1.2.). On the other hand, the reason that rinsing steps are significant is because the chemical residues, such as deoxidizers, from previous steps can create the inactive spots that will block the electro-less deposition initiation. The size, density and distribution on surfaces of electro-less deposited nickel is obvious depending on the time span of merging in nickel bath solution, however this discussion about these factors is not topics included in this dissertation.

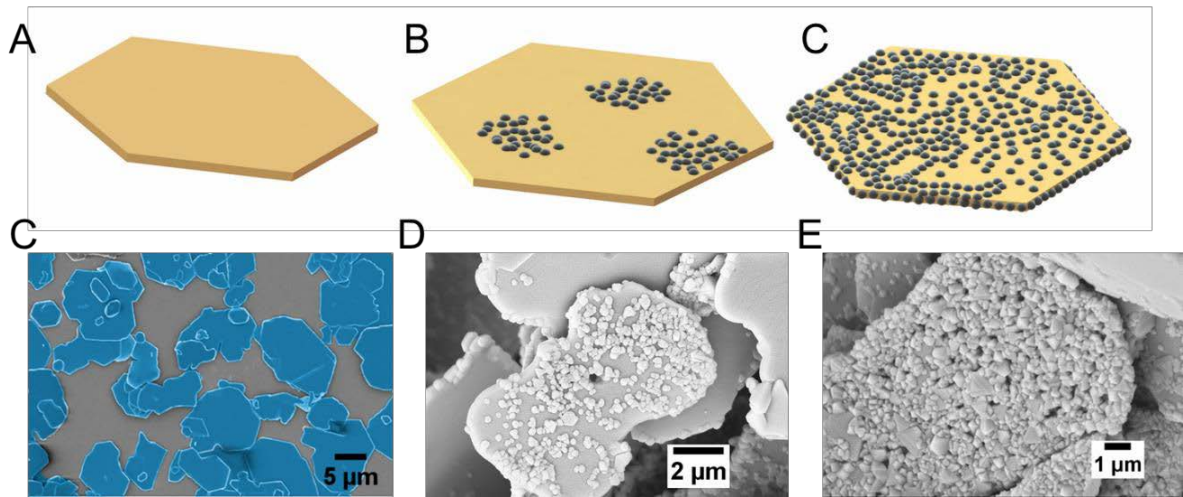


Figure 1.2. Basic steps of electroless deposition. (A) - (C) the schematic diagrams of electroless deposition, (A) the raw platelet, (B) the nickel islands form near nucleation sites, (C) the nickel island grows continuously and forms the film (D) finally. (C) - (D) the actual SEM images show the growth process of nickel corresponding to (A) - (C), respectively.

1.2.2 Piezoelectricity

Piezoelectricity has drawn the attention of researchers for about a century. In 1880, the fact that some certain crystals can generate a charge on their surface when compressed was claimed by Pierre and Jacques Curie, and Brother Curie is the first scientists who discovered the piezoelectricity. Later on, in 1946, Walter Guyton Cady wrote the first book, piezoelectricity, that provides the fundamental understanding about the piezoelectric behavior[14]. The sonar is the first practical application on the basis of piezoelectricity.

The relationship between piezoelectric, ferroelectric and pyroelectric can be explained by the crystal structures. Overall, all the ferroelectric crystals can be classified as pyroelectric and all pyroelectrics belong to the piezoelectric category. Ferroelectricity usually disappears above the Curie temperature (T_c), and above T_c the material is in a para-electric state that obeys the Curie-

Weiss law. Below T_c , the material has spontaneous polarization and will produce a hysteresis loop, shown in Figure 1.3.

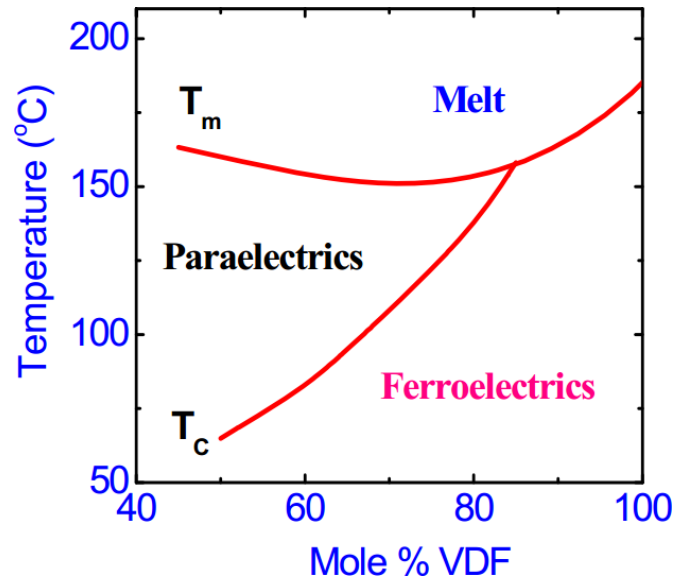


Figure 1.3. PVDF-TrFE phase diagram[15].

Piezoelectric effect is the appearance of an electrical potential or voltage when mechanical stress is applied on a material, shown in Figure 1.4. The piezoelectric effect is a reversible process that has two responses allowing the material to convert mechanical energy to electrical energy and vice versa[16]. The primary effect, known as the direct effect that is caused when a force subjected on a piezoelectric material generates a charge on its surface. The secondary effect is named the indirect effect. This is when a voltage applied across a piezoelectric material leads to a mechanical deformation. Both effects are widely used in different applications, for example, the indirect piezoelectric effect is used in production of ultrasonic sound waves[17]. electroactive property[18], beside piezoelectricity, which is another reason why this type of polymer has drawn a bulk of attractions.

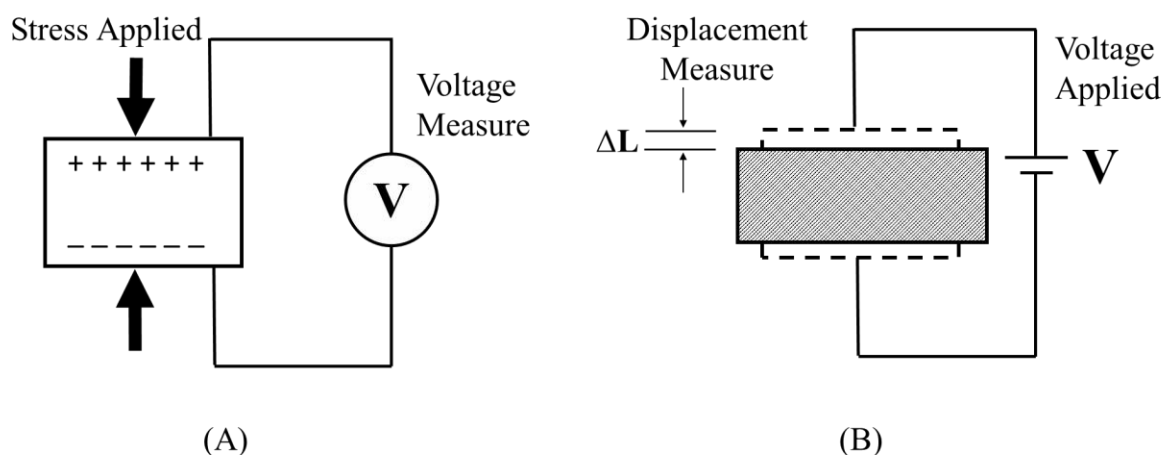


Figure 1.4. **(A)** the direct piezoelectric effect and **(B)** the in-direct effect.

1.2.3 PVDF and its copolymer (PVDF-TrFE)

Piezoelectric materials are an important candidate of multifunctional material, and are widely used as high voltage and power sources[19], sensors[20, 21], actuators[22], piezoelectric motors, and even in surgery[23]. Some of the piezoelectric materials exist in nature [24-26] such as wood, silk and bone. Also, some synthetic ceramics are also piezoelectric [27], for example, Barium titanate (BaTiO_3), Lead zirconate titanate (PZT), and Zinc oxide (ZnO). These piezoelectric ceramics are currently exploited in industries due to their high piezo response [28-30](PZT: $\sim 400 \text{ pC/V}$; BaTiO_3 : $\sim 100 \text{ pm/V}$). On the other hand, they also have their own disadvantages. For instance they are all brittle materials, and have low engineering strain (less than 0.1-3%). On the contrary, the piezoelectric polymers have demonstrated a great potential to achieve stretchability and flexibility. Among all piezoelectric polymers[31-33], such as Nylon-11, polylactic acid (PLLA) and poly (lactic-co-glycolic acid) (PLGA), poly (vinylidene fluoride) (PVDF) and its copolymer (polyvinylidene fluoride trifluoroethylene) (PVDF-TrFE) have the best piezoelectric performance, PVDF, a semi-crystalline polymer, is a non-conjugated linear fluorinated

hydrocarbon that consists of a repeating $-\text{CH}_2-\text{CF}_2-$ units. The CH_2-CF_2 unit of PVDF has the net dipole moment that point from the electronegative fluorine atom to the electropositive hydrogen atom. It presents four distinct polymer phases, including β -phase (polar), α -phase (non-polar), γ -phase (polar) and δ -phase (polar), relating to the different carbon chain conformations. All Trans zig-zag or TTTT conformation is assigned to be β -phase (also referred to as phase I), which shows the highest piezoelectric effect among all four crystal phases (Figure 1.5. (A) and (C)). Another important phase is α -phase (phase II) that has ‘trans-gauche’ or TGTG conformation, and it is the most thermodynamically stable and easily obtainable crystal phase in PVDF. The dipole moment of α crystallites has the opposite direction leading to the zero net polarization (Figure 1.5. (B) and (D)). The γ -phase (phase III) is intermediate between α - and β -phase, consisting of a T3GT3G conformation. A fourth polymorph of PVDF is the δ -phase (phase II) which is the α -phase that has the polarization, with basically the same molecular unit cell but a varying symmetry. Currently the most of research interests are focused on the first three phases.

One of the downfalls of utilizing PVDF as a ferroelectric material is the fact that it does not easily crystallize into the ferroelectric β -phase without specialized processing such as uniaxial drawing. If PVDF is polymerized with TrFE, the result is a copolymer PVDF-TrFE. The extra fluorine atoms in the chain reduce the influence of the head to head and tail to tail defects. This effect increases the crystallinity of the copolymers to about 80%, after the copolymer films have been annealed at 135°C for at least one hour. If the TrFE content is higher than 18%, then the PVDF-TrFE copolymer will crystallize with the same chain conformation as the β -PVDF. The β -phase of this copolymer can be improved by mechanical stretching and electric poling[34].

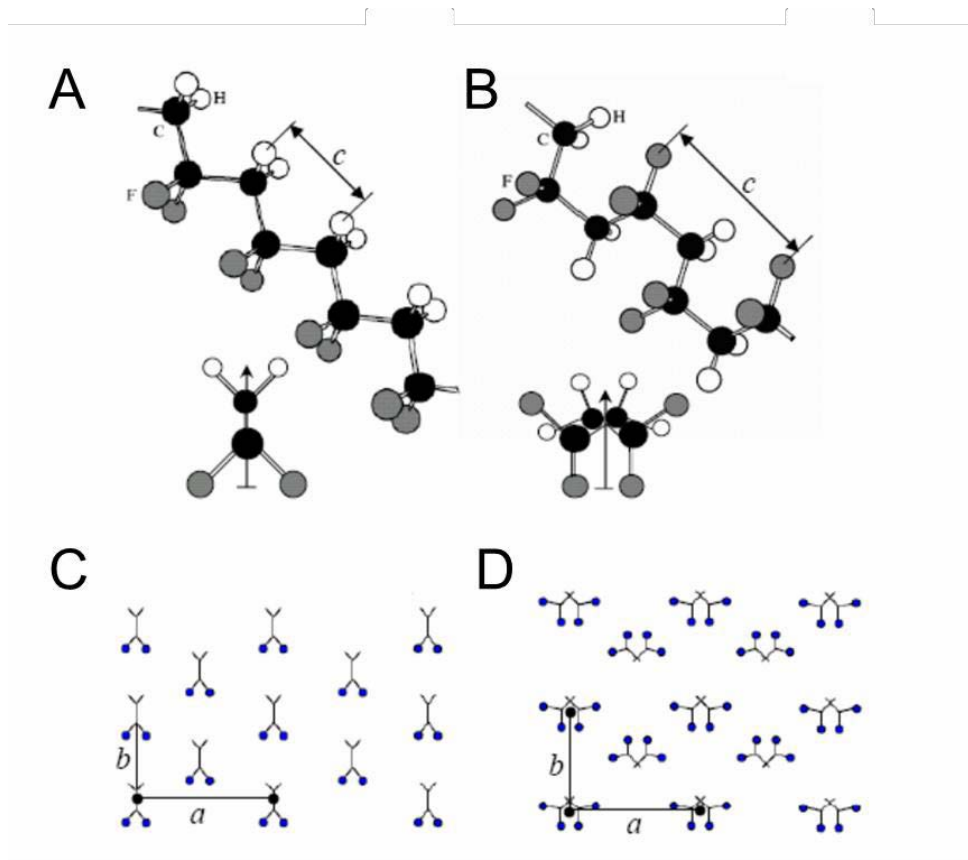


Figure 1.5. Diagram of crystalline forms of PVDF **(A)** in the all-trans conformation (inset, end view of a chain); **(B)** in the alternating trans-gauche conformation (inset, end view of a chain); **(C)** end-on view of the crystal structure of the ferroelectric β phase, composed of close-packed all-trans chains; **(D)** end-on view of the crystal structure of the paraelectric α phase, composed of close-packed trans-gauche chains[35].

CHAPTER 2

EXPERIMENTS AND METHODS

2.1 Fabrication and characterization of polymer-matrix ceramic-reinforced composite

2.1.1 Materials

Sapphire platelets used in cosmetics were purchased from Rona Flair (Rona Flair White Sapphire, Product No. 1.17751, >99% purity). Methanol was purchased from Sigma Aldrich (CAS number 67-56-1, $\geq 99.9\%$ purity) and the ethanol was purchased from Fisher Scientific (200 proof, CAS Number 64-17-5). The ATES ((3-Aminopropyl) triethoxysilane, 99%, CAS Number 919-30-2) was purchased from Sigma Aldrich. P(VDF-TrFE) was obtained from Piezotech S.A.S, France. DMF (N,N-Dimethylformamide), which was used as solvent for the P(VDF-TrFE), was obtained from Sigma Aldrich (CAS 68-12-2). Acetone (BDH, Cat No. BDH1101-1LP) was used to dilute the mixture of PVDF-TrFE and DMF.

2.1.2 Sapphire platelets solution

To prepare the sapphire platelets, 15 ml of DI water was mixed with 5 ml of methanol (3:1 volume ratio) in a beaker. To this mixture, 2 ml ATES was added and stirred on top of the magnetic plate using a magnetic stirrer for about 1 hour. After being thoroughly mixed, 0.79 g of sapphire platelets was added to the beaker, followed by ultra-sonication for 5 minutes. This mixture was then stirred for 30 minutes using the magnetic stirrer at a temperature of 40 °C. Once this step was completed, the solution was centrifuged with pure ethanol two times. Finally, the sapphire platelets were mixed with ethanol in a proportion such that the final solution contained 1% sapphire platelets and

99% ethanol by volume. Two milliliters of this solution was then withdrawn using a syringe and added drop-wise to a beaker filled with DI water. The platelets formed a thin layer on the surface of the water. This beaker was then subjected to ultrasonication for 20 to 30 minutes in order to obtain a homogenous Langmuir film at the interface of air and water.

2.1.3 Preparation of P(VDF-TrFE)

To obtain a total of 10 g of 10% P(VDF-TrFE) solution, 1 g of P(VDF-TrFE) was placed inside a small glass bottle to which 9 mg of DMF was added using a glass pipette. This mixture was stirred on a hot plate magnetic stirrer for 10 hours under 70 °C until the solution looked clear.

2.1.4 Preparation of layered composite material

To prepare the layered composites, a layer-by-layer (LBL) process was employed involving spin-coating process for the P(VDF-TrFE) and dip-coating process for the alumina platelets. For spin coating of the polymer, the following parameters were used: $S_1 = 3000$ rpm, $T_1 = 20$ seconds, $S_2 = 3000$ rpm, $T_2 = 20$ seconds, where S and T are angular speed and the duration, respectively. The Teflon substrate was used as the main substrate for all samples. The Teflon substrate was attached onto a glass slide, and the entire substrate (Teflon and glass slide) was fixed onto the spin-coater disc by using the double-sided tape. About 0.4 ml of the 15% P(VDF-TrFE) solution was drawn from a syringe and loaded on top of the Teflon substrate. After the spin-coating was completed, the P(VDF-TrFE) layer on the substrate was placed in a vacuum oven at 100 °C for 2 minutes in order to eliminate the solvent (DMF) and air-bubbles. To coat the alumina platelets, the substrate containing spun-coated polymer film was slowly dipped into the water beaker containing alumina platelets on its surface, and was then slowly taken out. The alumina platelets were adsorbed onto

the surface of the substrate. Subsequently, the substrate was placed inside the oven for ~15 minutes at 60 °C to completely evaporate any water content. Samples with thicknesses from ~5 µm to 40 µm were obtained based on number of layers and thickness of the polymer film.

2.1.5 Fourier transform infrared spectroscopy (FTIR)

FTIR data was collected by using the built-in ATR module on Nicolet is50 spectrometer (Thermo Scientific, Marietta, OH).

2.1.6 X-ray Diffraction (XRD)

XRD analysis was performed by Rigaku Ultima III XRD (Rigaku Corp., Tokyo, Japan) with Cu K α source ($\lambda = 0.15418$ nm). The X-ray angle varied between 10 degree to 60-degree with the resolution of 0.05 degree and 3-degree per minute of scanning speed. The calculation of percentage of crystallinity was conducted using JADE 7(MDI, material data Incorporated).

2.1.7 DSC(Differential scanning calorimetry)

DSC was performed using a Differential Scanning Calorimeter Q2000 (TA instrument). The testing procedure has one loop including the heating process and cooling process. It started from a heating process that increased the temperature from -50 °C to 200 °C at a heating rate of 10 °C per minute. The sample stayed at 200°C for 5 minutes, and then it was cooled at a rate of 20 °C per minute.

2.1.8 *in situ* SEM tensile test

The micro-tensile test *in situ* SEM was performed using a MTII/FULLAM SEMTester (MTI Instruments, Inc.) inside a LEO 1530 VP FE-SEM (LEO Electron Microscopy Ltd).

2.1.9 *ex situ* tensile test

Tensile tests were performed using a FAVIMAT tensile tester (Textechno H. Stein GmbH & Co. KG). The tensile samples (length ~150 mm and width ~2-3 mm) were cut from the fabricated sheets. The final tensile test sample was fixed onto a paper frame (20 mm × 20 mm) with 10 mm gauge length.

2.1.10 Piezo-response force microscopy (PFM)

The PFM imaging and local piezo-response measurements (PFMRamp) were performed by MFP-Bio-3D AFM (Asylum Research). The conductive AFM probe used in the PFM experiments was HQ: NSC14/CR-AU, with a resonance frequency of 160 kHz and a force constant of 5 N/m. The sample used for PFM imaging and PFMRamp were placed on a conductive substrate, which was grounded. A standard AR-PPLN calibration samples (Periodically Poled Lithium Niobate, Asylum Research) was used as the reference sample

2.1.11 Electrical poling procedure

For electric poling, a thin layer of Cr/Au was deposited on both sides of the composite films by e-beam evaporation at room temperature. The coated sample was connected to a high voltage source (Gamma High Voltage Research). For electric poling, an electric field of 100 MV/m and duration of 30 minutes was used.

2.1.12 Focused ion beam (FIB) and TEM imaging

Characterization of films was conducted using high-resolution transmission electron microscopy (TEM, JEOL 2100F at 200 kV). The sample was prepared using a NanoLab dual-beam focused

ion beam - scanning electron microscope system (FIB/SEM, FEI Nova 200). A thin slice was cut out perpendicular to the film surface, and therefore perpendicular to the sapphire platelets, and attached to TEM copper grid (Omniprobe® lift-out grid, Ted Pella Inc.). To protect sample during further FIB polishing, SiO₂ and Pt layer was deposited on the film surface – the top of film slice. The final polishing was performed at 5-10 kV to assure the least film damage down to the thickness ~100 nm. The cross-section images of the films were acquired using SEM (FEI Nova 200 and Zeiss-LEO 1530) after the cross-section was cut and polished using the FIB.

2.2 Fabrication and characterization of polymer thin film

2.2.1 Materials

P(VDF-TrFE) (70/30) copolymer powder was purchased from Piezotech S.A.S, France. DMF (N,N Dimethylformamide), which was used as solvent for the P(VDF-TrFE), was obtained from Sigma Aldrich (CAS 68-12-2). Acetone (BDH, Cat No. BDH1101-1LP) was used to dilute the mixture of P(VDF-TrFE) and DMF solution.

2.2.2 Preparation of films

P(VDF-TrFE) solution was prepared according to protocol reported previously [36]. Briefly, P(VDF-TrFE) 70/30 powder, DMF and acetone with weight ratios of 15:60:25 were used to prepare the solution. First P(VDF-TrFE) powder was added to DMF and mixed with magnetic stirrer on hotplate at 70 °C for at least 8 hours. Finally, acetone was added to the solution and stirred without heating for several hours until the solution attained uniform viscosity and clear appearance. The thin layer of P(VDF-TrFE) was prepared using spin-coating process. A 2-inch

silicon wafer as substrate of film was fixed onto the spin-coater disk (VTC-50A, MTI Corporation). Spin-coating was carried out at speed of 2000 rpm for 40 seconds. The P(VDF-TrFE) thin film was peeled off from the silicon wafer and cut to proper size for different experiments.

2.2.3 Stretching and annealing process

The 5-mm wide as-fabricated films were fixed on U-shape cardboard frames with 10 mm gap. Cardboard frame was cut after mounting the sample on the tensile machine grips right before stretching. Polymer films were stretched to desired elongation (50%, 100% or 200%) using tensile machine (Instron, MA) with 10 %/min crosshead speed, followed by load-control unloading step with 0.5 N/min rate. Then, stretched sample was fixed onto a new frame and transferred for annealing process. Annealing was performed at 135 °C for 2 hours in a vacuum oven (Model 281A, Fisher Scientific). During the annealing process, both ends of the sample were clamped tightly at a constant length. The surfaces of samples remained free from any constrain other than the tensile stress in the uniaxial stretched direction [37].

2.2.4 FTIR – XRD spectroscopy

The FTIR data was collected using the built-in ATR module on Nicolet is50 spectrometer (Thermo Scientific, Marietta, OH). The wide-angle X-ray powder diffraction pattern of P(VDF-TrFE) film (CuK α , wavelength of 0.154 nm) was obtained using GADDS BRUKER-AXS MWPC 3-thiracle X-ray Diffractometer in the range of 2θ from 5° to 43°. The crystallinity was calculated based on the relative areas under the deconvoluted amorphous and crystalline peaks fitted by using Gaussian peak shapes. The orientation of the crystalline phase P(VDF-TrFE) was determined based on the

azimuthal scans of the 2D diffraction peak at $2\theta \approx 20^\circ$. The alignment of crystals was quantified for comparison purposes between different fabrication conditions as FWHM, corresponding to the full-width at half-maximum value of the crystalline peak.

2.2.5 DSC (Differential scanning calorimetry)

DSC was performed using a Q2000 DSC (TA instrument). The testing procedure includes heating process and cooling process. It started from a heating process that increased the temperature from -50°C to 170°C at a heating rate of 10°C per minute. The sample stayed at 170°C for 5 minutes, and then the sample was cooled at a rate of 10°C per minute.

2.2.6 Tensile test

Tensile tests were performed using Model 5848 Instron machine. The tensile samples were cut from as-fabricated film that made on 2-inch silicon wafer by spin-coating method. The final tensile test sample was fixed onto a paper frame ($20\text{ mm} \times 20\text{ mm}$) with 20 mm gauge length gap. Tensile test strain rate was set to 10 %/min.

2.2.7 Optical microscopy with cross polarizers

Polarized optical images were obtained using an Olympus BX51 with fixed angle cross polarizer (model U-AN-2 and U-PO3).

2.2.8 Piezoresponse force microscopy (PFM)

The PFM Ramp measurement was conducted by MFP-3D-BIO (Asylum research, Santa Barbara, CA). The cantilever conductive AFM probe used in the PFM experiments was HQ: NSC14/CR-AU, with a resonance frequency of 160 kHz and a force constant of 5 N/m. The sample used for

PFMRamp were placed on a conductive substrate which was grounded. A standard AR-PPLN calibration samples (Periodically Poled Lithium Niobate, Asylum Research) was used as the reference sample.

2.3 Fabrication and characterization of Nickel ceramic composite

2.3.1 Electro-less deposition of nickel on ceramic platelets

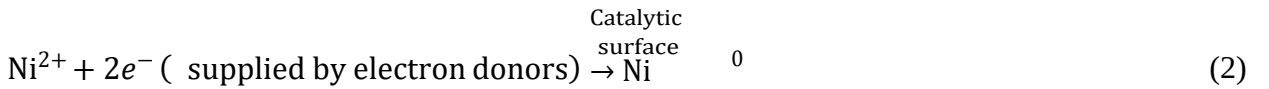
For electro-less deposition of Ni on ceramic platelets, four different solutions were used including alumina storage solution, alumina sensitization solution, alumina activation solution and nickel bath solution. If there is not specific notification, all chemicals used in this section were all purchased from Sigma-Aldrich Co. LLC, US. The solution of alumina storage contained 8 g/L NaOH and 40 g/L Na_3PO_4 . The alumina sensitization solution contained 0.1 M Tin dichloride (SnCl_2) and 0.1 M Tin tetrachloride. The alumina activation solution contained 0.25 g/L PdCl_2 and 10 mL/L HCl. The solution for nickel bath contained 20 g/L NiCl_2 , 20g/L NaH_2PO_3 and 35 g/L NH_4Cl , with pH between 9 and 10 regulated by 100 g/L potassium hydroxide (KOH) solution. The alumina surface treatment involved three solutions above except nickel bath. In this step, the alumina platelets (Rona Flair White Sapphire, >99% purity) were treated by each solution for different duration (details presented in table of electro-less Ni deposition scheme), then rinsed by DI water for 30 seconds twice after each solution, and the solution-usage sequence of these three solution was followed by alumina storage solution, sensitization solution and activation solution, later the surface treated platelets were stored in DI water, available to conduct the nickel deposition. In nickel deposition, ~0.5 g pre-treated platelets were placed statically at the bottom of a 500 ml beaker containing 10 ml DI water. Then, 10 ml nickel bath solution was gradually added.

After 30 minutes, the entire solution in the beaker was removed, the Ni-coated platelets were rinsed with DI water. The final Ni-coated platelets were collected and stored in DI water for subsequent steps of composite preparation.

At the beginning of the electro-less plating, the alumina micro-platelets were soaked in the alumina storage solution in order to produce the catalytic ceramic surface [10]. Rinsing by distilled water is required between steps. Next, the platelets were transferred to the micro-centrifuge tube containing the sensitization solution for at least half day, and then to this solution the activation solution was added and was kept for same duration. During these steps, the corresponding chemical reaction is:



The tin ions stabilize the palladium ions onto the catalytic platelet surface. The activation step is also used to remove the layer formed by the sensitization agent with Hydrochloric acid (HCl). Finally, the platelets were completely soaked in an aqueous Nickel bath solution with pH between 9 and 10, regulated by potassium hydroxide (KOH) solution. Metal ions (Ni^{2+}) were reduced to metal (Ni^0) by the action of chemical Sodium hypophosphite (NaH_2PO_2), which are simply electron donors. The main metallizing reaction is:



During the progress of metallization, nickel islands are formed around nucleation sites on the surface of the micro-platelets. These islands keep growing until their boundaries merge and become a layer of nickel. In the meantime, the hydrogen bubbles are formed vigorously during the process.

Table 2.1. Electro-less nickel deposition diagram.

Table:Electro-less Ni Deposition Scheme				
Step	Solution	Action/Purpose	Duration	Note
1	Alumina Storage Solution	Stock	~ 0.5 day	
2	DI Water	Rinse	30 s each time	Raw platelets was rinsed by DI water two time in a row.
3	Sensitization Solution	Surface Sensitize	~ 0.5 day	
4	DI Water	Rinse	30 s each time	All rinse steps are identical.
5	Activation Solution	Surface Activate	at least 3 hrs	
6	DI Water	Rinse	30 s each time	
7	Nickel Bath Solution	Metallizing	~ 30 mins	see details in experimental section.

2.3.2 Magnetic-assisted assembly of layered scaffold

To initiate the magnetic-assisted assembly, the mixture of 2% alginate solution and Ni-coated platelets was well-mixed and poured into a cylinder container with 12.5 mm diameter. The weight of the platelets in the mixture was adjusted by the final height of the cylindrical as-cast scaffold. We found out that approximately 10 g of platelets create ~10 mm in height as-cast composite in the container. The solution for assembling layered scaffold was the mixture of coated platelets and 2% alginate solution (FMC BioPolymer, Philadelphia, PA, US). The platelets in the solution were mixed by a vortex mixer (Fisher Scientific, US) for 5 minutes, then placed statically in order to degas. Subsequently, the entire solution was placed in a home-built magnetic assisted assembly setup for 24~48 hours. A pair of Neodymium magnetic bar (3 inch in length, ½ inch in width and ¼ inch in thickness, grade N45) were used to provide a uniform magnetic field for aligning all platelets. The rotation speed was set to 1rpm for entire magnetic-assisted alignment process. When

all platelets settled at the bottom of the container, the cross-linker (2% CaCl_2 solution) was added into the mixture for 24 hours. At the end of the process, the extra cross-linked alginate was cut off by a sharp blade, and was separated from the rest of the sample.

2.3.3 Spark plasma sintering (SPS) process

SPS process was conducted using a model 10-4 SPS machine from Thermal Technology LLC, Santa Rosa, CA, USA. The fully cross-linked scaffold was carefully trimmed to a cylinder with 18~19 mm in diameter by a sharp blade in order to fit the graphite die. The scaffold was placed inside a 20 mm diameter graphite die, wrapped with a thin graphite foil. Two graphite punches were inserted from top and bottom to seal the scaffold. Two graphite foils were also placed between punches and the scaffold for easy removal after sintering. Samples were sintered at 1050 °C or 1250 °C with a heating rate of 100 °C/min and a pressure of 60 MPa. The temperature was measured by a pyrometer targeting at a pre-cut hole on the die. The pre-cut hole was in the center of the die, 5 mm away from the inner wall. The holding time was 10 minutes and the environment in the vacuum was set at a pressure of 4 Pa.

2.3.4 Specimen preparation of fracture toughness measurement

In order to characterize the fracture resistance of the metal-ceramic composite, fracture toughness measurements were conducted on three-point bending beam with a pre-fabricated notch. The beam had a span (~9.8 mm) to width (~2.5 mm) ratio of approximately four according to ASTM standards (E1820-08). Prior to experiments, the pristine pellets were sectioned to individual beams with approximate dimensions (length ~ 15 mm, width ~ 2.5 mm and thickness ~1.25 mm). The samples were polished with ultra-fine polishing process with the various grade of diamond paste

(particle size 10 μm , 5 μm , 3.5 μm , 1.5 μm and 0.25 μm). Specimens for fracture toughness test were sectioned by a diamond saw (Allied techcut diamond saw cutting tool, model Techcut 4”), and then grinded sequentially with BIJ-684 diamond (5 μm , 1 μm and 0.5 μm) lapping paste (Kent Supplies). Pre-notches on SENB (single-edge notched beam) specimens were generated by the diamond saw, then continuously sharpened by a razor blade. Dimensions of the specimen was based on the ASTM E 1820 standard.

2.3.5 Energy dispersive X-ray spectrometer (EDS)

The elemental composition of the samples was investigated using an energy dispersive X-ray spectrometer (EDS), integrated into a scanning electron microscope (SEM, Zeiss-LEO Model 1530), and operated at accelerating voltage of 20 kV. The EDS analysis on the polished cross-section of the sample provided the element identification and distribution information and mapping of the composite samples.

2.3.6 Calculation of the porosity of the composite

Individual composite beams were sectioned from raw composite pellet, and were polished into regular shape. In the next step, their dimension and weight was precisely measured. The entire beam was soaked into high concentration HCl acid to etch away Nickel contained inside the composite. To ensure that Ni was removed from the sample, the etching process lasted over 48 hours, and the acid was changed in every 10 hours. By comparing the weight loss of the composite before and after the acid treatment, the weight ratio of nickel was acquired. The density of bulk nickel and alumina is 8.908 g/ml and 3.98 g/ml, respectively. The porosity of the composite can be estimated according to the following equations:

$$m_{composite} = m_{nickel} + m_{ceramic} \quad (3)$$

$$m_{nickel} = \rho_{nickel} \times V_{nickel}, \quad m_{ceramic} = \rho_{ceramic} \times V_{ceramic} \quad (4)$$

$$Porosity = \frac{V_{composite} - V_{nickel} - V_{ceramic}}{V_{composite}} \times 100 \quad (5)$$

CHAPTER 3

BIOINSPIRED BRICK-AND-MORTAR CERAMIC-METAL COMPOSITE FABRICATED BY ELECTRO-LESS PLATING AND SPARK PLASMA SINTERING

3.1 Introduction

During the process of evolution in nature, species and living organisms often craft sophisticated multifunctional materials with unique structures to enable them to adapt to living in various environments, capture preys, and defense themselves from predators [8, 37]. Various materials have been studied for bioinspiration from nature including gecko foot hair [38], bone [39], beetle exocuticle [40] and smashing predator stomatopod (*odontodactylus scyllarus*) [41], among others. “Nacre” in abalone shell with hierarchical “brick-and-mortar” structure is the one of these materials that has been exploited in theoretical and experimental field successfully and profoundly [2, 42]. Mostly, polymer mortars have been considered as the ductile layer, however, low stiffness of polymers does not efficiently transfer the shear between hard ceramic bricks. Theoretical models point to metals as a more efficient mortar layer [4-7]. There have been several attempts in order to build the “nacre-like” composite with alumina platelets and metallic mortars [43-45]. However, there are several outstanding challenges: first, the low weight percentage of ceramic contents; secondly, the high porosity of composite caused by the high viscosity of the molten metal that cannot infiltrate into a ceramic scaffold completely; thirdly, the large size of ceramic platelets. We report on an alternative approach to assemble brick-and-mortar metal-ceramic composites by using electro-less plating of nickel on alumina micro-platelets (Figure 3.1.). The nickel-coated micro-platelets are subsequently aligned by a magnetic field, taking advantage of paramagnetic

properties of nickel. In the final step, the assembled nickel-coated ceramic scaffold is sintered using spark plasma sintering (SPS).

Table 3.1. The progress involving “Nacre”-like composite in last two decades [3, 38-47].

	Year	Reference	Elastic Modulus (GPa)	Ultimate Strength (MPa)	Fracture Toughness (MPa m ^{0.5})	Composite Components	Structure
1	2005	Li et al	21.4	109	N/A	Nano clay+ agarose	Nacre-like
2	2005	Sue et al	4.7	98	3	Clay+Nylon-6	Nacre-like
3	2007	Meyers et al	60-70	300-500	8±3	Natural Shell	Nacre-like
4	2007	Kotov et al	13	150	N/A	Clay+PVA	Nacre
5	2008	Studart et al	9.6	315	N/A	Alumina platelets+chitosan	Nacre-like
6	2008	Ritchie et al	N/A	200	30	Alumina + PMMA	Nacre-like
7	2009	Ritchie et al	N/A	300	40	Alumina+ Al-Si	Nacre-like
8	2010	Gauckler et al	5.3±0.9	34.3±1.8	N/A	Alumina+ maleic anhydride polypropylene	Nacre-like
9	2013	Walter et al	25	320	N/A	Clay+cellulose	Nacre-like
10	2015	Barthelat et al	7±1.2	72.5	N/A	Alumina platelets+chitosan	Nacre-like
11	2015	Walter et al	40	200	N/A	Nano clay+ PVA	Nacre-like
12	2015	Studart et al	45	200	8.5	Alumina+PMMA	Nacre-like
13	2016	Li et al	11	280	N/A	Alumina+ cyanate ester	Nacre-like
14	2016	Ritchie et al	N/A	238±17	10	Alumina+ Nickel	Nacre-like
15	2017	Ikkala et al	25	220	3.4	Clay+PVA	Nacre-like

Electro-less metal deposition, or autocatalytic plating, is defined as a metallic coating by a controlled chemical reduction. Electro-less plating does not require power supplies, electrical contacts and other apparatus and it creates less porous layers. This process is widely used for printed circuits and corrosion resistance coatings [54]. On the other hand, since super thin metallic layers can be coated on the catalytic surface, and technically there is no limitation about shapes of surfaces to be coated, the process has been used to build ultra-stiff, low-density micro-lattice

structures [55, 56]. In this study, nickel plating also provides magnetic property that can be utilized effectively to align micro-platelets in “nacre-like” composite.

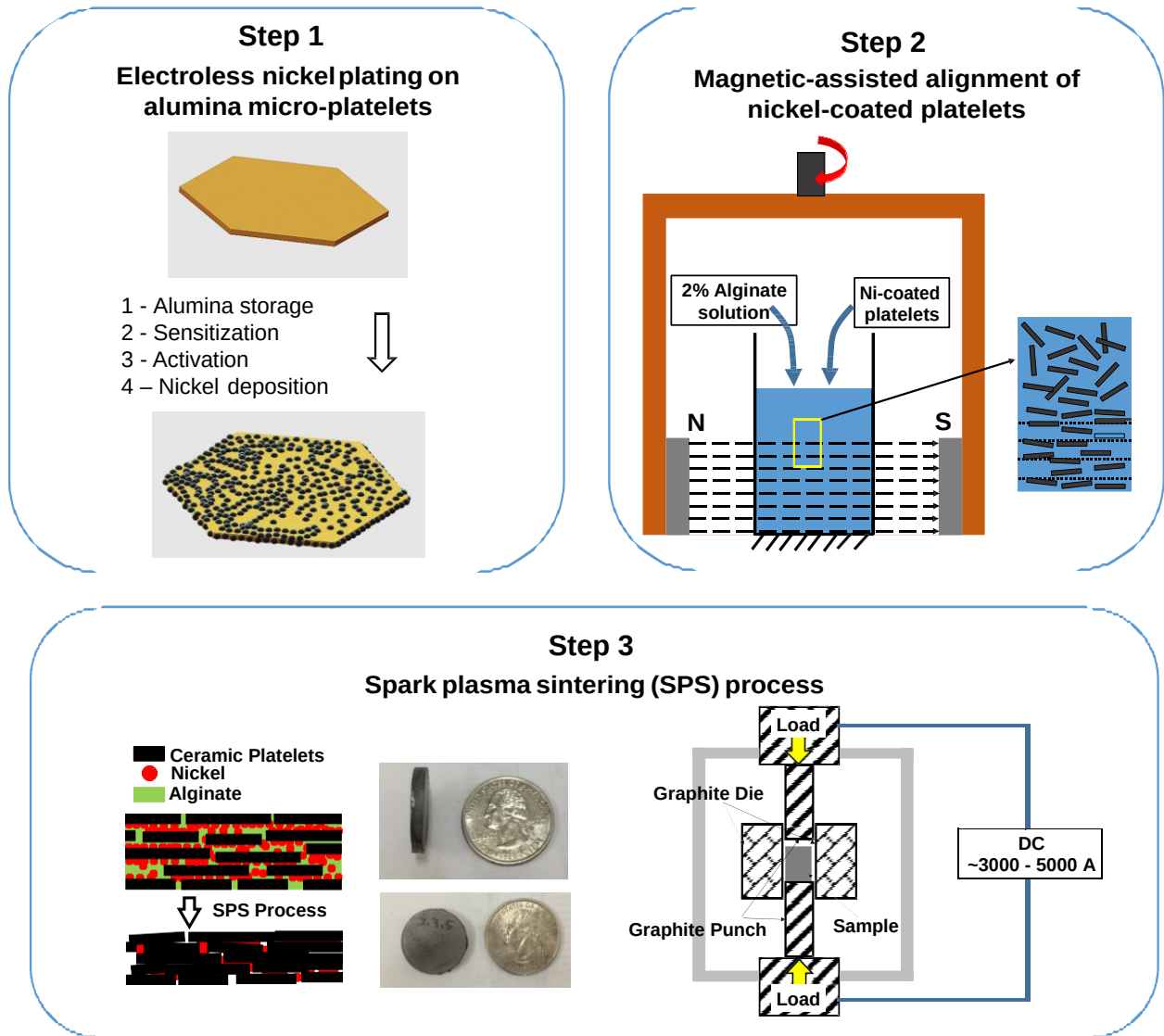


Figure 3.1. Processing route for fabrication of brick-and-mortar ceramic-metal composite. The three main steps include: electro-less nickel plating on alumina micro-platelets; magnetic-assisted alignment of nickel-coated micro-platelets; and spark plasma sintering process.

3.2 Results and Discussion

The process route is schematically shown in Figure 3.1. For fabrication of layered brick-and-mortar composite, we used commercially available alumina micro-platelets, with a thickness of ~ 500 nm, and in-plane dimension of ~ 6 μm . More details on these micro-platelet is given in our previous publications [1, 48]. These micro-platelets have similar geometry to aragonite platelets in natural nacreous of seashells. Electro-less plating is often performed on metal surfaces. Electro-less plating on ceramic surfaces is a more challenging and involved process compared to plating on metallic and even polymeric surfaces. There are commercially available kits and processes for plating of nickel on large ceramic surfaces (for example, RTM process from TRANSENE company, Inc., MA, US), however, these processes often require surface roughness on the order of several microns, for example the RTM process requires that ceramic materials show surface roughness of at least 0.5 micron.

We used a modified version of the commercially available process for plating of nickel on alumina. Since nickel is plated on the surface of the non-conductive alumina micro-platelets, surface treatment is necessary to create the catalytic ceramic surface. Surface treatment requires three steps including alumina storage, sensitization, and activation. To coat alumina micro-platelets, we made a series of customized solutions including three surface treatment solutions, and the final metal plating solution. Using these solutions the platelets were coated with nickel at room temperature. Detailed recipe is provided in the experimental section. Figure 3.2. shows SEM images of the original ceramic micro-platelets (without Ni coating), as well as intermediate step during nickel plating in which discontinuous nickel islands were plated on the surface of ceramic platelets. With further plating full coverage of the nickel on the micro-platelets was obtained.

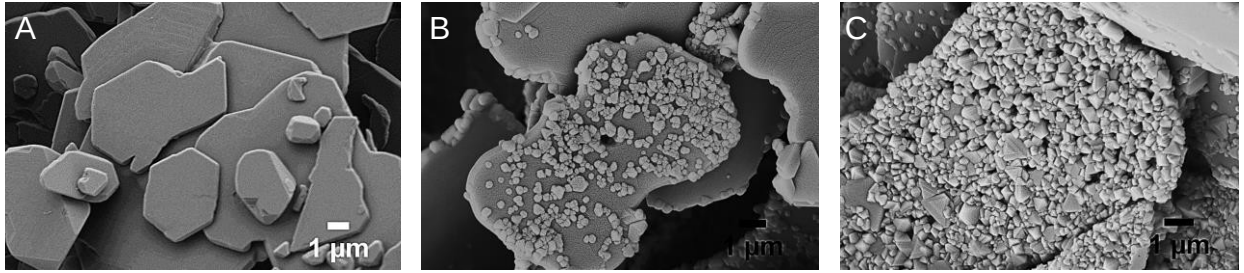


Figure 3.2. Electro-less plating of nickel on alumina micro-platelets. SEM images of **(A)** the original ceramic micro-platelets (without Ni coating); **(B)** Intermediate step shows the discontinuous nickel islands plated on the surface of ceramic platelets (the reaction time was ~10 mins); **(C)** Full coverage of the nickel on the micro-platelets (the reaction time was ~30 mins).

After coating the platelets, the next step is aligning the platelets in layered architecture. Several processes can be used for this purpose, including freeze-casting, layer-by-layer (LBL) process, vacuum filtration, and magnetic-assisted alignment[49, 50]. Freeze-casting and magnetic-assisted alignment often result in large-scale alignment of the platelets. LBL process and vacuum filtration often produce free-standing films. In this article, we used magnetic-assisted alignment. Often time for magnetic-assisted alignment, iron-oxide nanoparticles are used to functionalize non-magnetic platelets. Here, we took advantage of paramagnetic properties of Ni, and the electro-plated Ni coating was used to align the platelets. To constrain the Ni-coated platelets in organized layered architecture, 2% alginate solution was used as the support in the magnetic-assisted alignment process. To initiate the magnetic-assisted assembly, the mixture of 2% alginate solution and Ni-coated platelets was well-mixed and poured into a cylinder container. Alginate offers several advantages in this process. First, it is transparent, and hence motion of the micro-platelets under magnetic field can be observed during the process; secondly, the high viscosity of alginate reduces the sedimentation rate of the platelets, which allows the platelets to get well-aligned by magnetic

field; finally, the alginate solution can be immediately cross-linked by a cross-linker such as calcium chloride. This final step in the magnetic alignment process freezes the aligned platelets in their position, until the sintering process permanently restrains them in their aligned orientation. Figure 3.3. A shows an optical image of the as-fabricated composite after magnetic-assisted alignment process. Samples with several centimeters in dimension were fabricated using this method. Figure 3.3. C shows the SEM cross-section images of the as-fabricated composite. The Ni-coated platelets are fairly aligned and uniformly distributed in the composite.

After the magnetic alignment process, the spark plasma sintering (SPS) process was applied on the green body. The processed details are elaborated in material and method section. Cross-linked alginate is burnt during the SPS process. Based on initial trials, two different temperatures were selected for the SPS process, 1050 °C and 1250 °C. These temperatures were selected to be below the melting temperature of Ni, ~ 1455 °C. Figure 3.3. B shows an optical image of the composite after SPS process. Applied pressure in the SPS process significantly reduces the porosity of the composite, and the thickness of the samples reduces accordingly. Each SPS processed sample was obtained by placing together 2-3 pellets from the magnetically-aligned green bodies. Figure 3.3. D shows the SEM cross-section images of the SPS processed composite. The alignment of the platelets from green body was mostly preserved in the SPS process and more compact samples were obtained.

The density of the composites processed at 1250 °C and 1050 °C was ~3.26 g/cm³ and ~2.72 g/cm³, respectively. To quantify the weight ratio of each component in the composite, a piece of composite sample was sectioned and submerged in highly concentrated hydrogen chloride acid to completely etch away the Ni. Results show that ~4.2% wt. and ~17.7% wt. nickel was contained

in the composite processed in 1250 °C and 1050 °C, respectively. To identify the chemical constituents in the composite, we performed energy-dispersive X-ray spectroscopy (EDS). Figure 3.4. A shows the chemical elements map overlaid on the SEM image (Figure 3.4. B) for a composite processed at 1250 °C. The individual color maps for Ni and Al are shown in Figure 3.4. C and 3.4. D. The corresponding EDS spectrum is shown in Figure 3.4. E. The gold signal is from the coating on the sample before SEM imaging. Overall, Ni does not show uniform distribution between the alumina platelets. Ni was found between some of the platelets, however, it seem some of the Ni was forced out from between the platelets, possibly due to high pressure applied during SPS process.

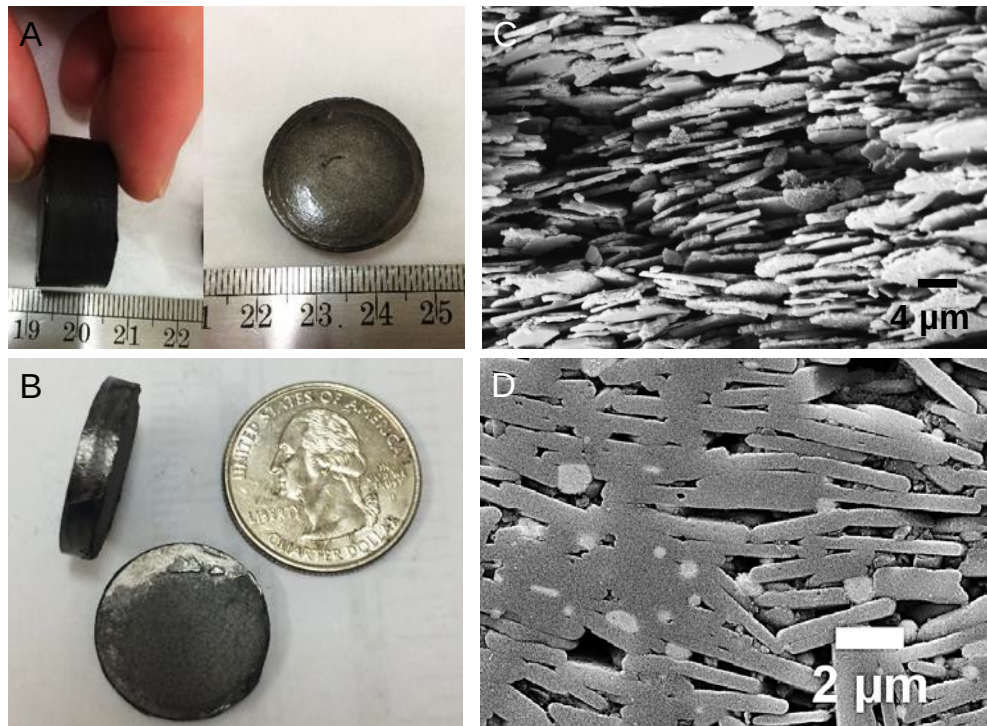


Figure 3.3. (A) Optical image of the as-fabricated composite after magnetic-assisted alignment process; (B) The final composite pellet processed by spark plasma sintering process. (C) and (D) are the SEM cross-section images of the as-fabricated composite shown in A and the final composite (processed at 1250 °C) shown in B, respectively.

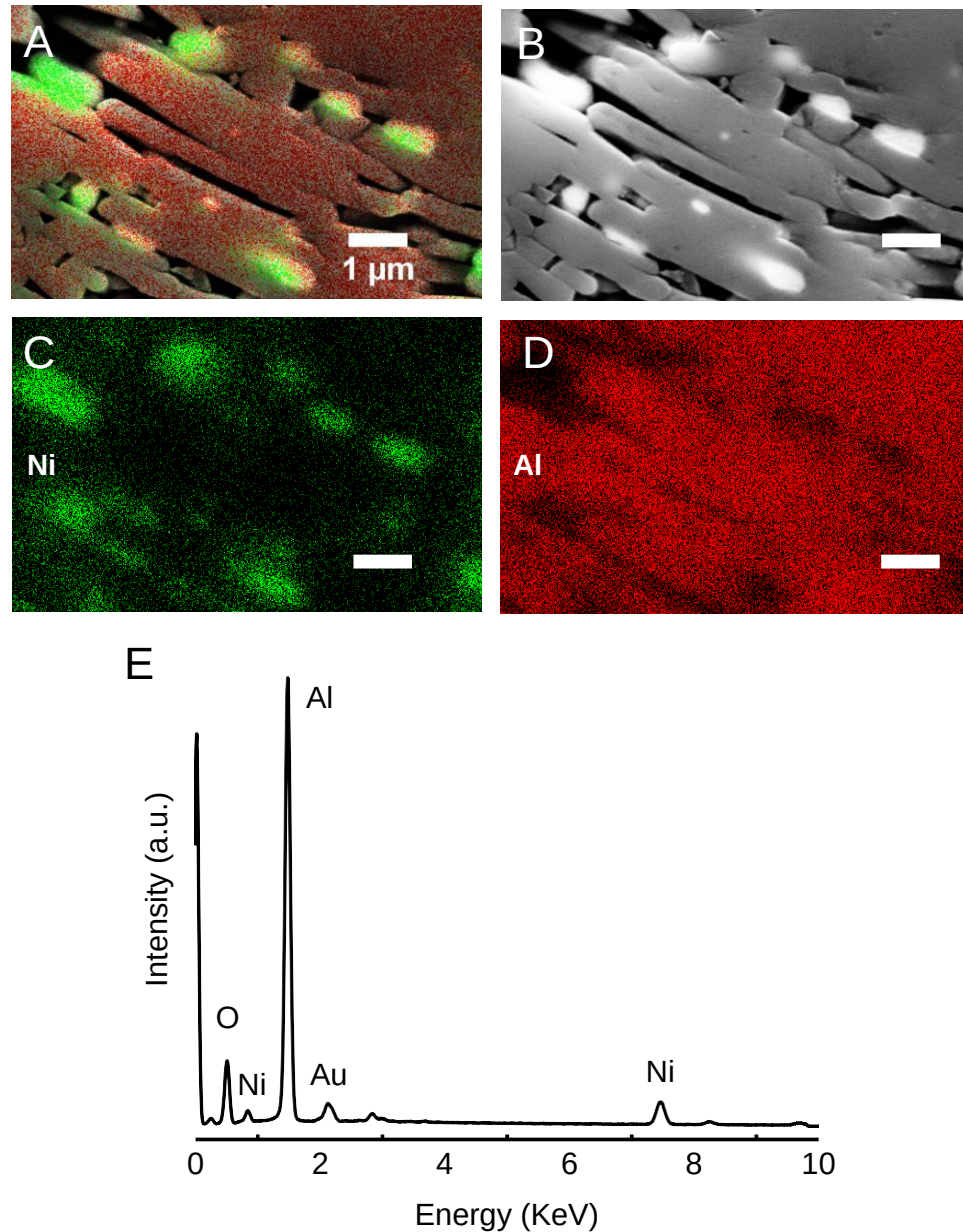


Figure 3.4. EDS map of the cross-section acquired from the composite processed in 1250°C. **(A)** Overlaid chemical elements map on SEM image. **(B)** The corresponding SEM image. The conductive Ni regions appear brighter. **(C)** and **(D)** Nickel map and aluminum map, respectively. Aluminum is from the alumina platelets. **(E)** The corresponding EDS spectrum.

Figure 3.5. shows mechanical properties of the composites for two processed temperatures obtained from 3-point flexure experiment. Both composites show a linear stress-strain relationship

up to failure point (Figure 3.5. A). Strengths of the composites were 161.3 ± 38.7 MPa and 96.7 ± 28.2 MPa for 1250 °C and 1050 °C, respectively. Corresponding elastic moduli obtained from the slope of the linear portion of stress-strain response were 75.7 ± 14.8 GPa and 54.5 ± 11.8 GPa, respectively. The composite sintered at 1250 °C shows both larger strength and elastic modulus. The results show that higher temperature results in better sintering of the ceramic platelets. Fracture toughness behavior of the composites was characterized using three-point bending single-edge notched beam (SENB) fracture test. Micro-notches with a root radius of ~ 20 μm were created on the beams such that the direction of the notch was perpendicular to the orientation of platelet layers. A sample crack is shown in Figure 3.6. A. The inset shows several of the beams used for these experiments. Figure 3.6. B shows typical load-displacement responses from three-point bending SENB fracture experiments. Both specimens show an initial linear response up to maximum load, which is followed by gradual decrease in load once the crack propagation initiates. The gradual decrease in load (in contrast to catastrophic failure) is an indication of operation of toughening mechanisms in the composite that result in stable crack growth. In order to quantify the fracture resistant behavior of the composites, R-curve response was calculated to evaluate fracture toughness in terms of the J-integral as a function of crack extension under an increasing uniaxial driving force. The R-curve calculation follows our previous work [48]. Changes in compliance (C) was used to indirectly determine the length of the crack of the SENB sample. The compliance C was determined from $C = u/f$, in which u is displacement, and f is the force at each point after crack initiation. Crack length was calculated from equation:

$$a_n = a_{n-1} + \frac{W - a_{n-1}}{2} \frac{C_n - C_{n-1}}{C_n} \quad (1)$$

in which W is the thickness of the specimen, a and c represent the crack length and compliance at n^{th} and $(n-1)^{\text{th}}$ steps. To assess the different mechanisms during the propagation of stable crack through the specimen, we calculated the J-integral as a function of crack extension [40]. The J-integral comprised of an elastic contribution J^{el} and a plastic contribution J^{pl} .

$$J^{el} = \frac{K^2(1-\nu^2)}{E} \quad (2)$$

$$J^{pl} = [J_{n-1}^{pl} + (\frac{1.9}{b_{n-1}}) (\frac{A_{n-1}^{pl}}{B} \frac{R_{n-1}^{pl}}{B})] [1 - \frac{1-a_n-a_{n-1}}{b_{n-1}}] \quad (3)$$

Here, K is the stress intensity factor, E and ν are the elastic modulus and Poisson's ratio of the sample respectively. K_{JC} accounts for toughening mechanisms during fracture propagation and was calculated from equation below,

$$K_{JC} = \sqrt{(J^{el} + J^{pl})E} \quad (4)$$

The initial K_{JC} (or K_{IC}) of composites sintered at 1250 °C and 1050 °C were obtained to be $1.9 \pm 0.31 \text{ MPa.m}^{1/2}$ and $0.69 \pm 0.21 \text{ MPa.m}^{1/2}$, respectively (Figure 3.6. C). Figure 3.6. D shows the R-curve behavior for samples. Both composites sintered at 1250 °C and 1050 °C show rising R-curve with increasing the driving force. The values of K_{JC} reach to $2.92 \pm 0.5 \text{ MPa.m}^{1/2}$ and $1.7 \pm 0.13 \text{ MPa.m}^{1/2}$ for composites sintered at 1250 °C and 1050 °C, respectively.

The fractured specimens were characterized by SEM in order to examine the failure modes and the toughening mechanisms during crack propagation. Figure 3.7. A shows the crack path in the entire beam. The cracks is deflected away from the straight line ahead of the crack tip. Figure 3.7. B shows the zoomed- in view of the boxed area in A, ahead of the crack, in which the main crack is split into several micro-cracks in different directions, shown by red arrows. Figures 3.7. C-E show several toughening mechanisms during crack growth, namely platelets pull-out mechanism,

crack deflection mechanism, and crack inhibition. Dashed lines in Figure 3.7. D and E show the crack path. All of these mechanisms work cooperatively ahead of the crack tip. In the acquired post-fracture SEM images, we did not observe any platelet failure, and all the cracks passed through the interfaces or the mortar layer. Overall, the most prominent toughening mechanism was crack deflection and platelet pull-out, where the aligned platelets effectively deflect the crack. On the other hand, the ductile-ligament bridging mechanism, which is common in polymer-ceramic composites, was not observed abundantly in this composite.

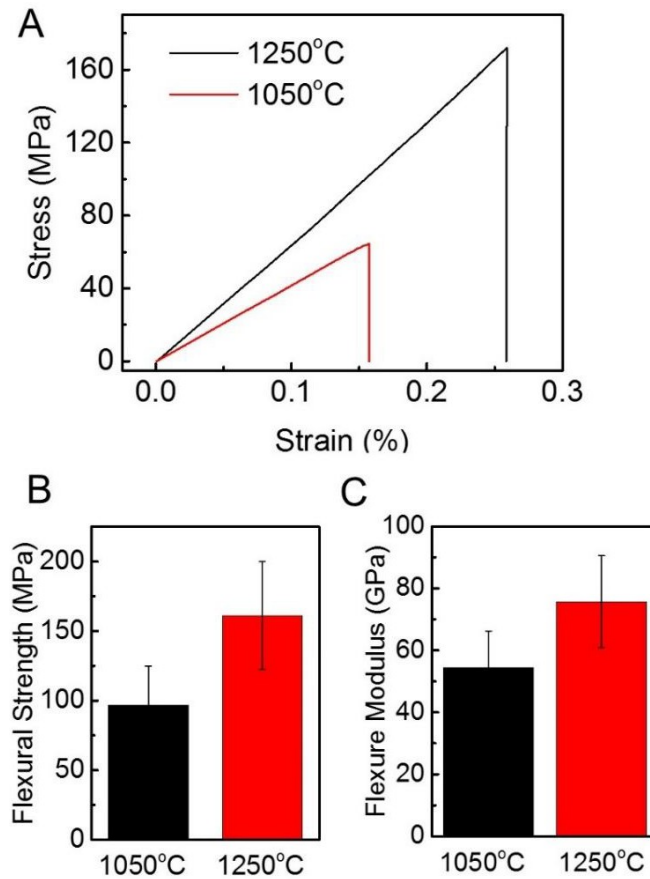


Figure 3.5. **(A)** Stress-strain responses from 3-point flexure experiment for two processed temperatures. **(B)** and **(C)** Comparison of flexure strength and flexure modulus for two processed temperatures (n=3).

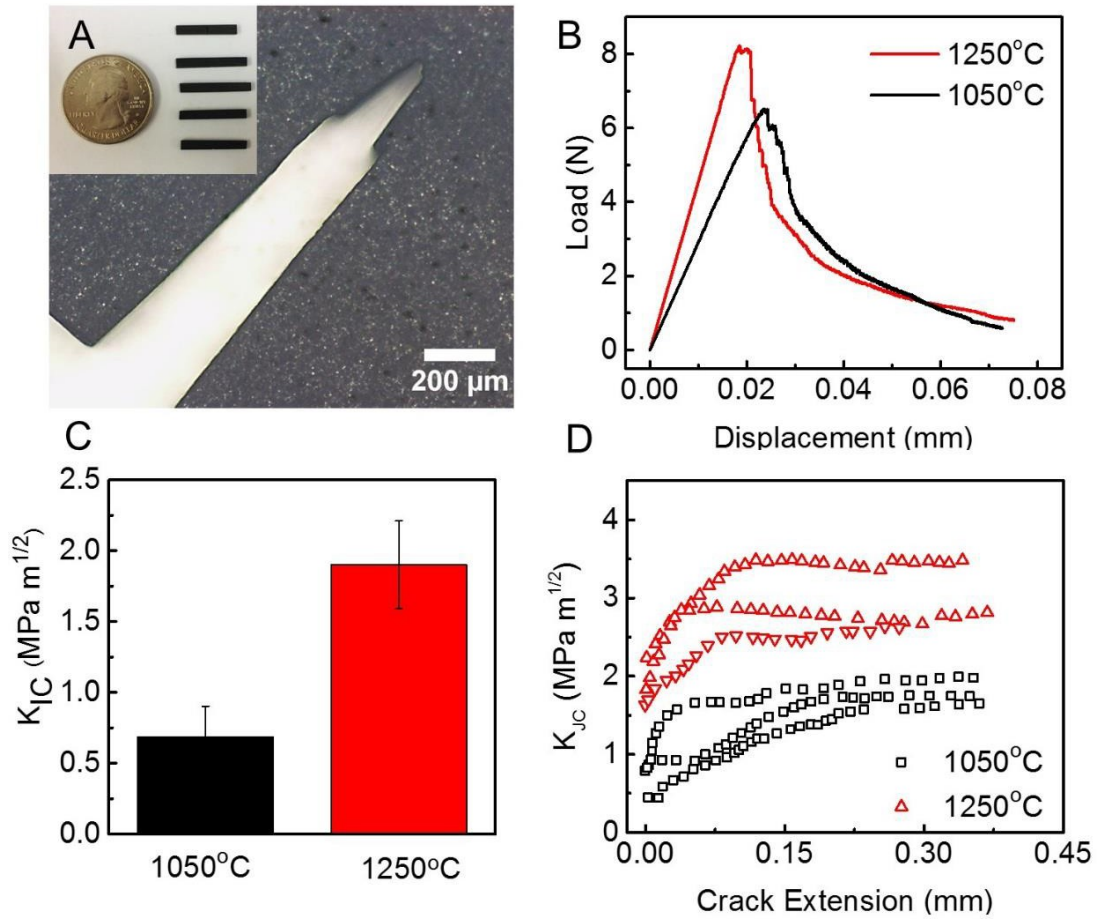


Figure 3.6. **(A)** An optical microscope image of a typical micro-notch prepared for fracture toughness measurement; the inset shows the image of the samples. **(B)** Typical load-displacement responses from single-edge notched beam fracture experiments. **(C)** K_{IC} fracture toughness of the samples for two processed temperatures. **(D)** R-curve response derived from fracture toughness experiment shows the fracture resistance vs. crack extension for two processed temperatures. (Number of tested samples for 1050°C and 1250°C is 3 and 5, respectively).

We envision several possibilities for the improvement of the properties of the composite. A thin coating of Ni on micro-platelets would be ideal for ceramic-metal composites. Such coating can be obtained on metal surfaces or polymer surfaces, or macro-scale alumina surfaces. However,

on micro-platelets the process resulted in formation of islands that covered the surface of the micro-platelets.

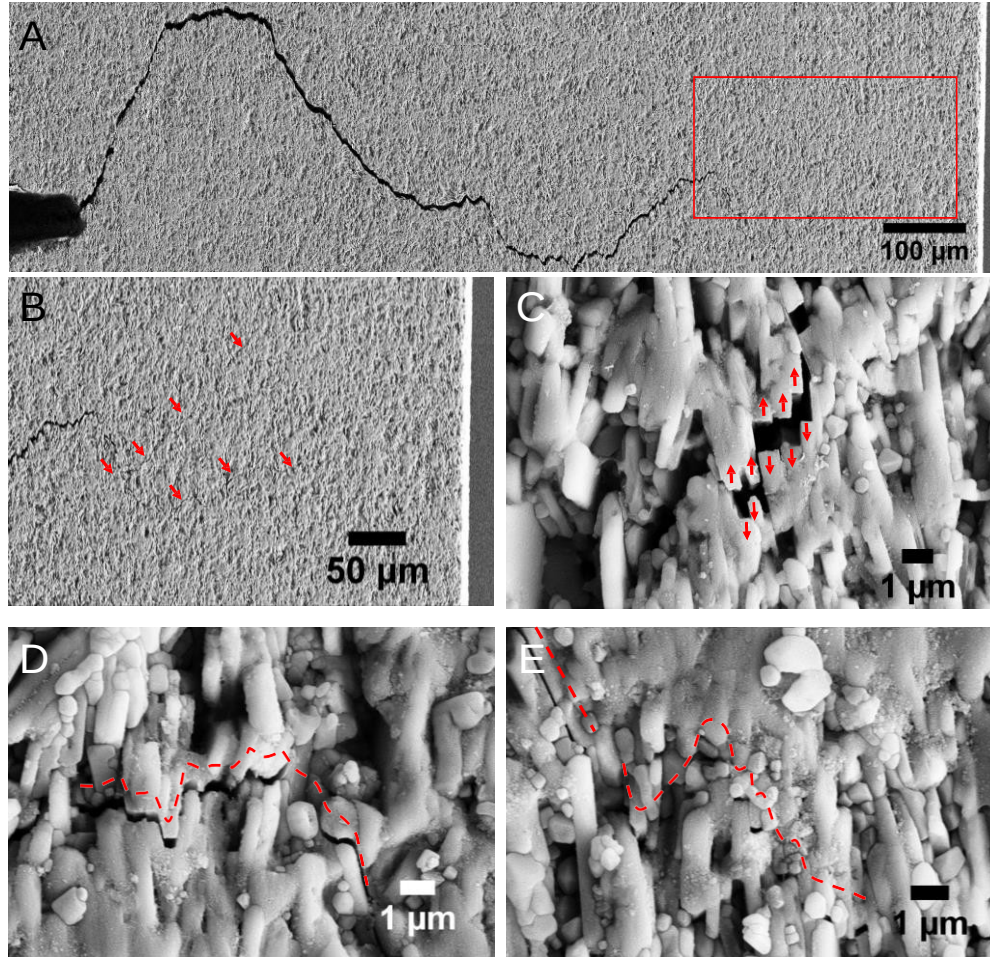


Figure 3.7. Visualization of the crack growth path in the composite using SEM images, for the composite sintered at 1250 °C. **(A)** The crack path in the entire beam, which shows the crack is largely deflected. **(B)** Zoom-in view of the area in rectangle in A, which shows the main crack ends in several branched micro-cracks. **(C)-(E)** Toughening mechanisms during crack growth: **(C)** platelets pull-out mechanism, **(D)** crack deflection mechanism, and **(E)** crack inhibition. The micro-crack path in D and E are shown by red-dashed lines that are intentionally shifted upward for better visualization.

Since nickel is heated to a temperature close to its melting temperature during the SPS process, most probably these islands merged together during processing. With further optimization of the

plating process, a thin coating of nickel should be obtainable. One possible route could be roughening the surface of the platelets by etching them with acid. This may also result in better adhesion between nickel and the alumina surface.

3.3 Conclusions

In this study, we report on fabrication and characterization of brick-and-mortar metal (Ni) - ceramic (alumina) composite. The electro-less plating was used to plate Ni on surfaces of micro-platelets of alumina. A home-built magnetic-assisted alignment system was used to effectively align the Ni-coated platelets, and the alignment of the platelets was well-preserved in the cured alginate block. Finally, the green body was processed via spark plasma sintering process. The final composite has a density of (~ 3.1 g/ml) and low metal content ($\sim 3.8\%$ wt.). In the fracture toughness measurement, this composite material exhibited various toughening mechanisms that contributes the toughness of the composite. For the two batches of composites that processed in 1250°C and 1050°C , the K_{JC} started from $1.9 \pm 0.31 \text{ MPa.m}^{1/2}$ and $0.69 \pm 0.21 \text{ MPa.m}^{1/2}$, respectively; then the values of K_{JC} elevated to $2.92 \pm 0.5 \text{ MPa.m}^{1/2}$ and $1.7 \pm 0.13 \text{ MPa.m}^{1/2}$. With further improvement, the metal-ceramic composite will have a wide range of applications, such as automobile and aerospace fields in high temperature.

CHAPTER 4

BIO-INSPIRED MULTIFUNCTIONAL CERAMIC PLATELET-REINFORCED PIEZOELECTRIC POLYMER COMPOSITE*

4.1 Introduction

Natural materials are often multifunctional [51]. The multifunctionality is often the result of hybrid nature of these materials combining complementary constituents. For instance, bone is tough and strong, and it is piezoelectric. Bone exhibits a fracture toughness $\sim 1.2 \text{ kJ/m}^2$ and strength of $\sim 100 \text{ MPa}$ by combining tough collagen protein phase with stiff and strong hydroxyapatite mineral phase [52-55]. The simultaneous toughness and strength of bone is attributed to its hierarchical structure [54], whereas its piezoelectric effect originates from individual collagen fibrils and has been related to bone's mechanical adaptivity [11, 56, 57]. Another example of multifunctional natural materials is “nacre” in seashells. With polymer and ceramic content of 5% and 95%, respectively, nacre achieves an elastic modulus of 60-70 GPa, a strength of 80-135 MPa, a fracture toughness $\sim 1.5 \text{ kJ/m}^2$, while it fails at a strain of $\sim 1\%$ [58, 59]. Interestingly, it has been shown that nacre also exhibits piezoelectric behavior, in which the piezoelectric effect originates from both the organic and mineral phases [60-62].

For quite practical purposes there has been much interest in making synthetic multifunctional materials [63]. Various functionalities of interest include simultaneous mechanical strength and

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toughness, electrical properties such as piezoresistivity and piezoelectricity, optical transparency, thermal conductivity, self-healing, fire retardancy, wear resistance, gas barrier properties, etc. [64-67]. Most strong engineering materials lack “flaw tolerance” that is found in natural materials [54, 64, 66, 68-80]. Development of synthetic hybrid materials combining strength and ductility (damage tolerance) is an area of active research [81-88]. In particular, hybrid materials of hard-soft constituents, similar to nacre and bone have shown the greatest promise in this regard.

Various materials such as graphene oxide (GO) sheets, silicate, carbon nanotubes, nano-clay, nano-cellulose and platelets (Al_2O_3 and CaCO_3) have been used for fabricating materials similar to nacre, by incorporating hydrogen bonding, covalent bonding or ionic bonding [3, 44, 58, 64, 89-103]. Excellent recent reviews summarize these studies [58, 104]. The polymer phase in these layered materials included chitosan, polyimide, dopamine, polypropylene, poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), sodium alginate, poly(allylamine) (PAA), polyurethane elastomer, among others. The most common methods for fabrication of these materials include layer-by-layer (LBL) assembly (spin-coating, immersive (dip-coating), vacuum filtration, spray coating, and electromagnetic and fluidic processes) and freeze-casting [105-107]. In particular, the LBL approach is a versatile technique that enables nanometer control of the film thickness, which allows engineering functional thin films for various applications in such fields as nano-composites, energy, optics, membranes, and biomedicine [106, 107].

One of the functionalities of interest in multifunctional materials is piezoelectricity, wherein electromechanical coupling enables sensing and actuation functionalities. The reported piezoelectric composites in the literature are often a combination of a piezoelectric ceramic and a soft polymer or carbon materials. The ceramic component can be in various forms including

nanoparticles, nanowires, etc. [108-110]. In this article, we use the LBL approach to fabricate a piezoelectric composite sheets incorporating P(VDF-TrFE) (poly(vinylidene fluoride-co-trifluoroethylene) piezoelectric copolymer and single crystal sapphire (Al_2O_3) micro-platelets. P(VDF-TrFE) is a piezoelectric polymer with the largest piezoelectric constant among piezoelectric polymers. P(VDF-TrFE) is a highly non-reactive, thermoplastic semi-crystalline fluoropolymer. Sapphire (Al_2O_3) was selected because of its outstanding strength (~ 2 GPa) and elastic modulus (300-400 GPa). Al_2O_3 platelet-reinforced composites have been reported in the literature [111-113]. Composite films fabricated using Al_2O_3 platelets and chitosan polymer achieved a strength of 350 MPa, and a toughness of 75 MJ/m³ [3]. Various methods such as magnetically controlled alignment of platelets have been also recently developed [112, 114]. Platelet geometry provides reinforcement in 2-dimension, which is an advantage over 1D materials such as carbon nanotubes and nanofibers for reinforcement [115]. We demonstrate fabrication of sheets of piezoelectric polymer reinforced by sapphire platelets and investigate their materials properties using DSC (differential scanning calorimetry), FTIR (Fourier transform infrared spectroscopy), XRD (X-ray diffraction), and UV-visible spectroscopy. In addition, we characterize piezoelectric and mechanical properties of the fabricated composite sheets as a function of thermal annealing. Given the semi-crystalline nature of P(VDF-TrFE), annealing can affect its crystalline nature, and hence it's mechanical and piezoelectric properties [36].

4.2 Results and Discussion

Figure 4.1. A schematically illustrates the layer-by-layer (LBL) process used for fabricating the piezoelectric polymer composite. The process repetitively involves a combination of spin-coating

of the polymer phase and subsequent dip-coating of the ceramic platelets. For the dip-coating step, the platelets were functionalized with (3-Aminopropyl) triethoxysilane to prevent their agglomeration in the solution. Figure 4.1. B shows a false-colored SEM (scanning electron microscope) image of the sapphire platelets. In Figure 4.1. C, an optical image shows sapphire platelets on the substrate after the dip-coating step. An AFM image of a single sapphire platelet is shown in the inset, Figure 4.1. C. The majority of the platelets are 4-8 μm in in-plane dimension and $\sim 450 \pm 100$ nm in thickness (Figure 4.2.). In the platelets, the (0 0 1) plane is parallel to the plan of the platelets. Figure 4.1. D shows atomistic model of the P(VDF-TrFE). The carbon backbone atoms are in zigzag orientation and the electric dipoles are generated as the result of large electronegativity of fluorine atoms, shown by the vertical arrow in the figure.

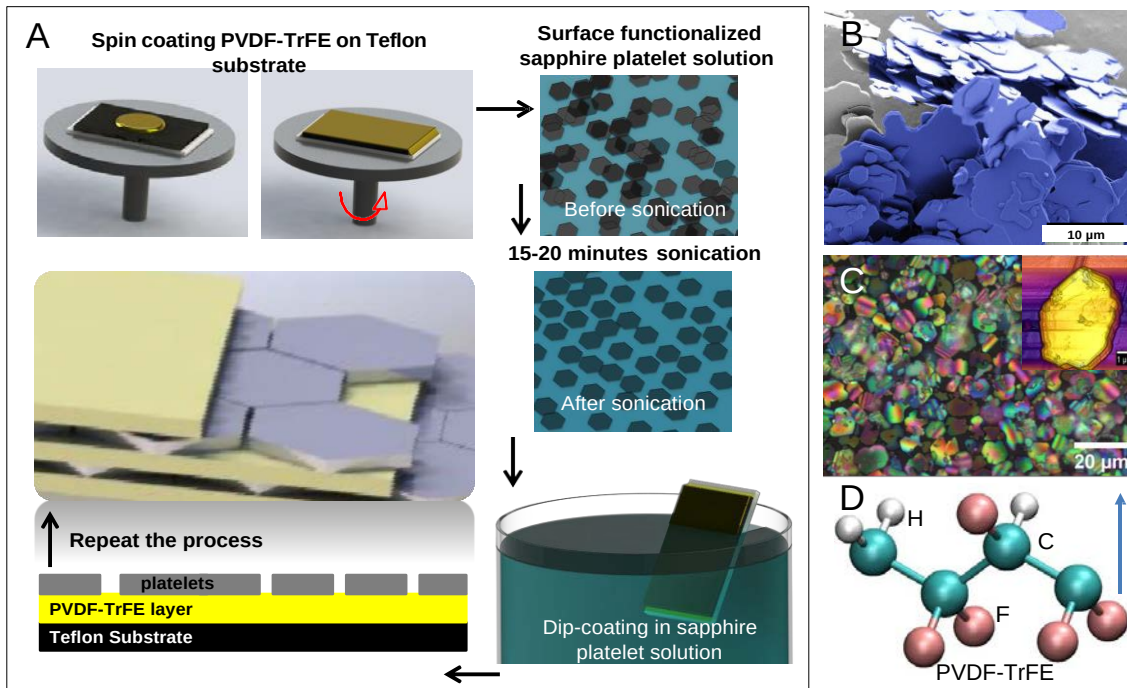


Figure 4.1. **(A)** Schematic shows the layer-by-layer process used for fabrication of the piezoelectric composite film through spin-coating and dip-coating processes. These processes are repeated to fabricate a multi-layer film. **(B)** False-colored SEM image of the sapphire platelets. **(C)** An optical

image shows sapphire platelets on the substrate after the dip-coating step. Uniform and nearly full coverage is obtained. The inset shows an AFM image of a single sapphire platelet. **(D)** Atomistic structure of P(VDF-TrFE) monomers, with the corresponding electric dipole direction shown by a vertical arrow.

The histogram in Figure 4.2. shows the distribution of the size of the sapphire platelets. Given the irregular shape of the platelets, we estimated the size of each platelet by using the circle estimation method. First, the contour of each sapphire platelet was drawn and the area of platelets that covered that contour was calculated using ImageJ software. This area was used to calculate the diameter of the corresponding circle with that area. This diameter was assigned to each platelet as the size reported in Figure 4.2. The thickness of the platelets was obtained from cross-section SEM images. The thickness of platelets was found to be 452.1 ± 98 nm ($n=15$).

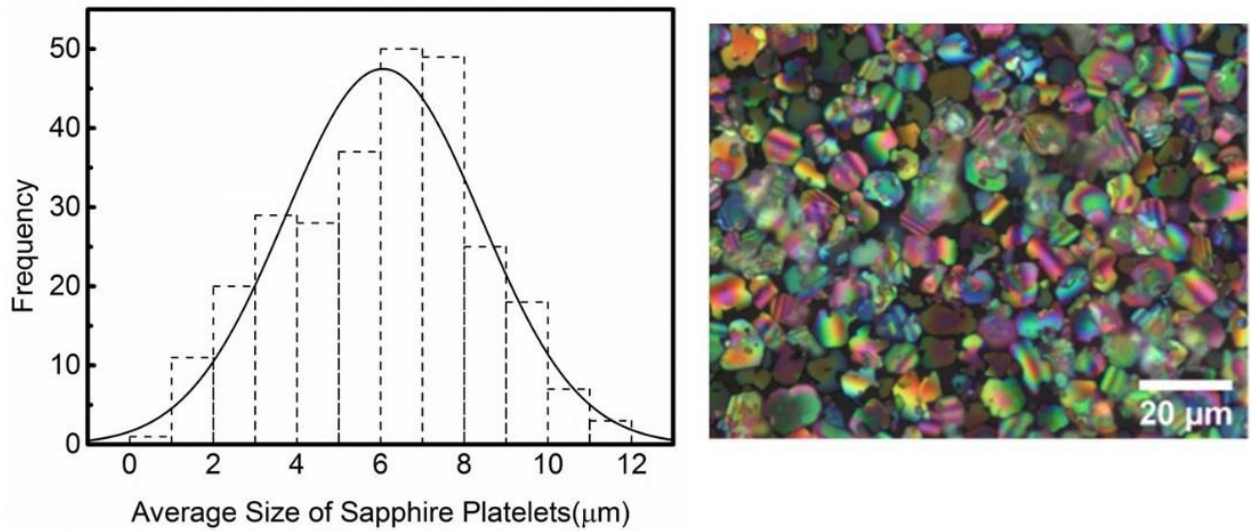


Figure 4.2. Distribution of the size of the sapphire platelets, which was obtained from the optical image shown on the right panel. The solid line is the fitted normal distribution on the left panel.

The spin-coating and dip-coating steps were repeated to fabricate composite films with desired number of layers. Samples from few bilayers to over fifteen-bilayers can be obtained (Figure 4.4. A-C). Here, we define a bilayer to include one layer of polymer and one layer of platelets. Thermogravimetric analysis shows that 10-bilayer and 15-bilayer sheets have polymer content of 55% and

77%, respectively (Figure 4.3.). Freeze-fractured SEM cross-sections show that the platelets maintain approximate alignment with respect to the sheets during the fabrication process. The final films are flexible and can be elastically bent, as shown in Figure 4.4. D. The AFM surface images show that the sample has a granular surface morphology, which originates from the polymer phase (Figure 4.4. E). Figure 4.4. F shows an optical image of a 10-bilayer sample against a background. UV-visible spectroscopy shows that the sample has an optical transparency of ~25 - 40% in the 200 - 600 nm wavelength (Figure 4.11. A). (The small drop in the UV-visible data originated from the equipment.) The transparency of the pure P(VDF-TrFE) film is ~60 - 80% in this range.

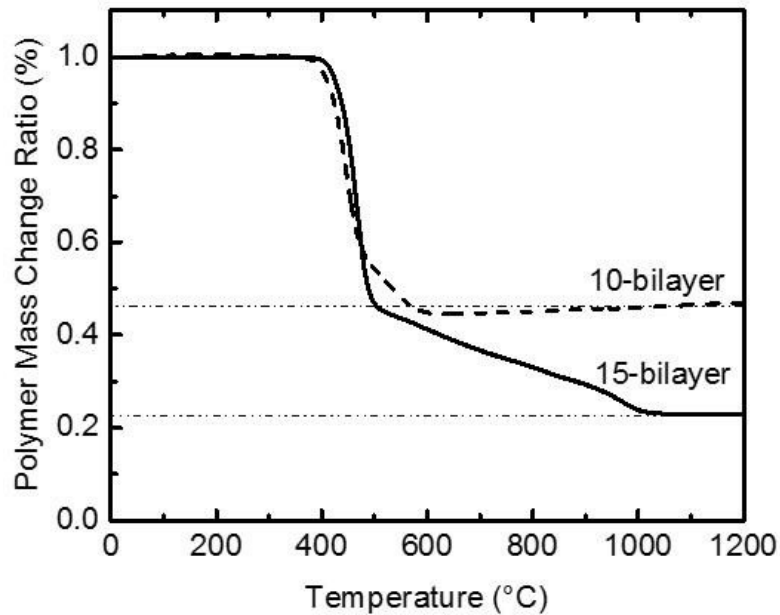


Figure 4.3. Thermo-gravimetric analysis (TGA) of composite sheets.

Thermo-gravimetric analysis (TGA) was performed using a SDT Q600 (TA instrument). The temperature was increased from ambient to 1200 °C at a heating rate of 10 °C/min. Nitrogen gas was purged into the furnace during the entire test at a rate of 100 ml/min.

To better visualize the alignment of the platelets in the films, focused ion beam (FIB) was used to obtain lateral cross-section cuts in the samples. Figure 4.5. A and B show two such cross-sections. Overall, the platelets were fairly well-aligned with the plane of the film. However, there were some variations in the distribution and angle of the platelets in different regions of the sheets. We used high magnification transmission electron microscopy (TEM) to observe the interface between the platelets and the polymer phase (Figure 4.6.). TEM images confirmed the single crystal structure of the platelets (Figure 4.6. A) and show that there is continuous, uniform interface between the polymer and platelets (Figure 4.6. C, D), which is critical for mechanical performance of the fabricated composite. For some samples, we noticed holes between the platelets and the polymer (Figure 4.7.). We believe that these holes were generated during the preparation of the ultra-thin TEM sample using FIB, since they were not visible in the original cross-section SEM images. This could be possibly the result of residual stresses in the sample during fabrication that were released during FIB preparation.

P(VDF-TrFE) is a semi-crystalline polymer in which the degree of crystallinity varies depending on the processing conditions and subsequent thermal annealing [36]. Changes in crystallinity will affect the mechanical properties of the composite film. It has been reported that annealing at temperatures between the Curie temperature (T_c) and melting temperature (T_m), i.e. at paraelectric phase of the polymer, results in maximum degree of crystallinity for P(VDF-TrFE) [36, 116, 117]. Therefore, we chose $T_A = 135$ °C for annealing process to obtain films with maximized crystallinity (Figure 4.8., $T_c \sim 111$ °C and $T_m \sim 149$ °C, for P(VDF-TrFE)).

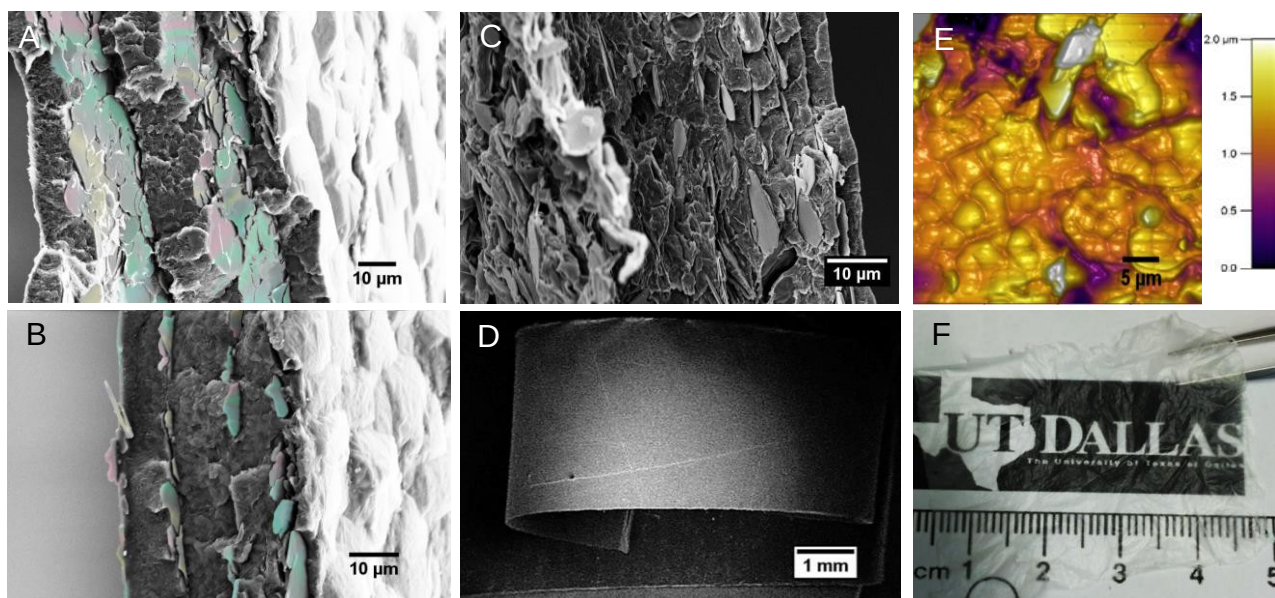


Figure 4.4. **(A)** and **(B)** SEM cross-section images of a 3-bilayer film and **(C)** a 15-bilayer film. The platelets in A and B are false-colored. **(D)** SEM image of a 10-bilayer film, bent to show its flexibility. **(E)** An AFM surface profile of the 10-bilayer film. **(F)** An optical image of the fabricated composite film with 10-bilayer shows its transparency.

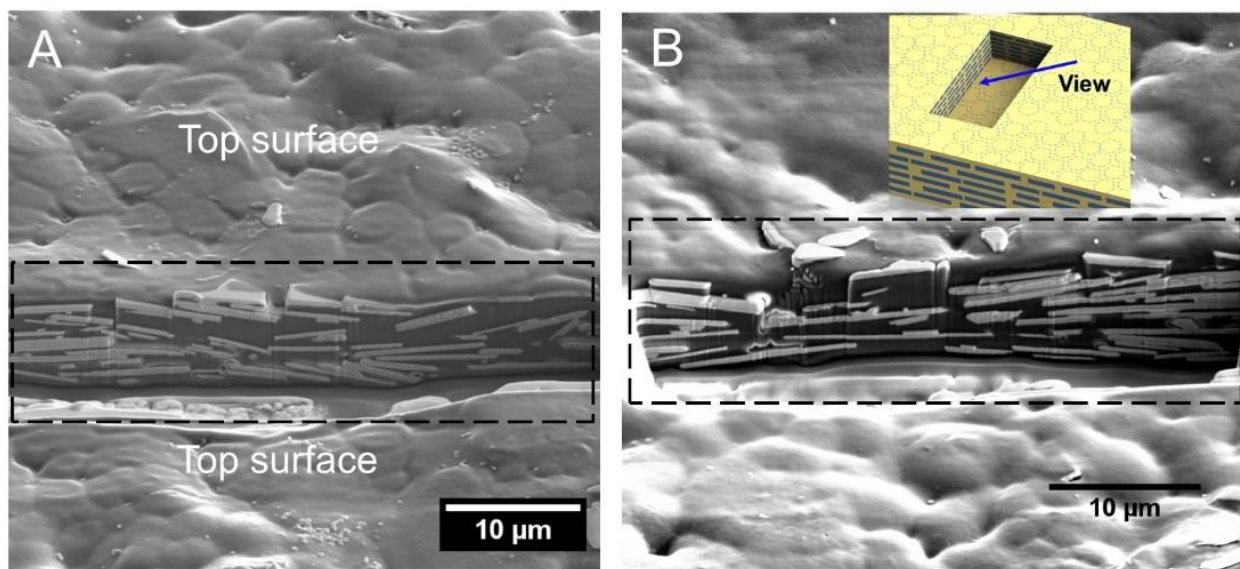


Figure 4.5. **(A)** and **(B)** FIB cross-section cuts in the sheets. The inset in B shows the view in the FIB-cross-section, where a cavity is cut in the sheet and the sample is tilted toward the ion beam for imaging.

Figure 4.11. B shows the DSC results obtained from the 10-bilayer composite film for as-made (as-fabricated) composite film and a 2-hour annealed sample. For the as-made composite, the Curie temperature during the heating process was $T_{c1} = 109\text{ }^{\circ}\text{C}$, the melting temperature and the solidification (crystallization) temperature were $T_m = 148.9\text{ }^{\circ}\text{C}$ and $T_s = 131.9\text{ }^{\circ}\text{C}$, respectively. These values are similar to the corresponding values for pure P(VDF-TrFE) film (Figure 4.8.).

Thermal annealing did not significantly change the melting temperature and the solidification temperature of the sample ($T_m = 149.4\text{ }^{\circ}\text{C}$ and $T_s = 131.4\text{ }^{\circ}\text{C}$). However, the Curie temperature slightly decreased to $T_{c1} = 106.2\text{ }^{\circ}\text{C}$ after annealing. The presence of clear Curie transition in the DSC response shows that the composite sheet is ferroelectric, since the Curie temperature marks the transition from ferroelectric phase to para-electric phase.

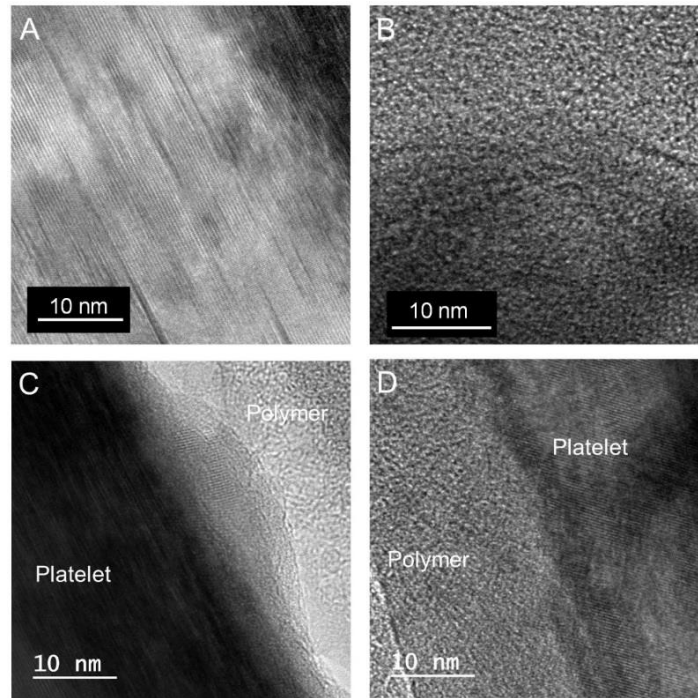


Figure 4.6. High resolution TEM images of the **(A)** Sapphire platelets and **(B)** P(VDF-TrFE) polymer. **(C)** and **(D)** High resolution TEM images show the interface between the polymer and platelets in the composite.

P(VDF-TrFE) can take several different phases, of which only the β -phase is piezoelectric. Hence, having this phase in the fabricated composite is an indication that the fabricated composite will exhibit piezoelectric effect. We confirmed that the β -phase forms in the P(VDF-TrFE) thin films fabricated by spin-coating under ordinary pressure without the need for electric poling and mechanical stretch.

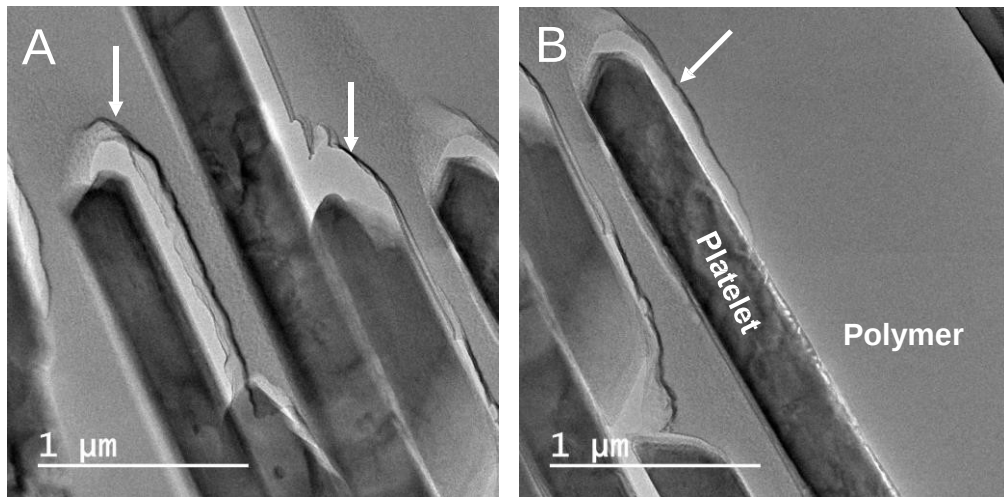


Figure 4.7. **(A)** and **(B)** show TEM images of platelet-polymer interface, in which holes were generated in the polymer at the interface during samples processing.

Figure 4.9. A shows the FTIR spectra of spin-coated P(VDF-TrFE) thin films with different annealing times (as-made, i.e., no annealing, and annealed for 1-hour, 2-hours and 3- hour). The four peaks associated with the β -phase are present, at 844 cm^{-1} , 1170 cm^{-1} , 1288 cm^{-1} , and 1430 cm^{-1} [118]. These main peaks associated with the β -phase in P(VDF-TrFE) are highlighted by the green ribbons in Figure 4.11. C. The FTIR spectra does not noticeably change as a result of annealing, as shown in the comparison of the FTIR spectra of Figure 4.12. C for as-made and 2-hour-annealed 10-bilayer films. The presence of the main β -phase peaks confirms that additional

processing and adding the platelets did not change the phase of the polymer film [118]. Figures 4.10. C and D show the relative FWHM (full width at half maximum) acquired from the pure film and the 10-bilayer composite film. The peak at 1400 cm^{-1} peak was used for calculation of the FWHM [119, 120]. Data shows that samples annealed for 2-hour show the sharpest peak, indicating that they contain largest β -phase content.

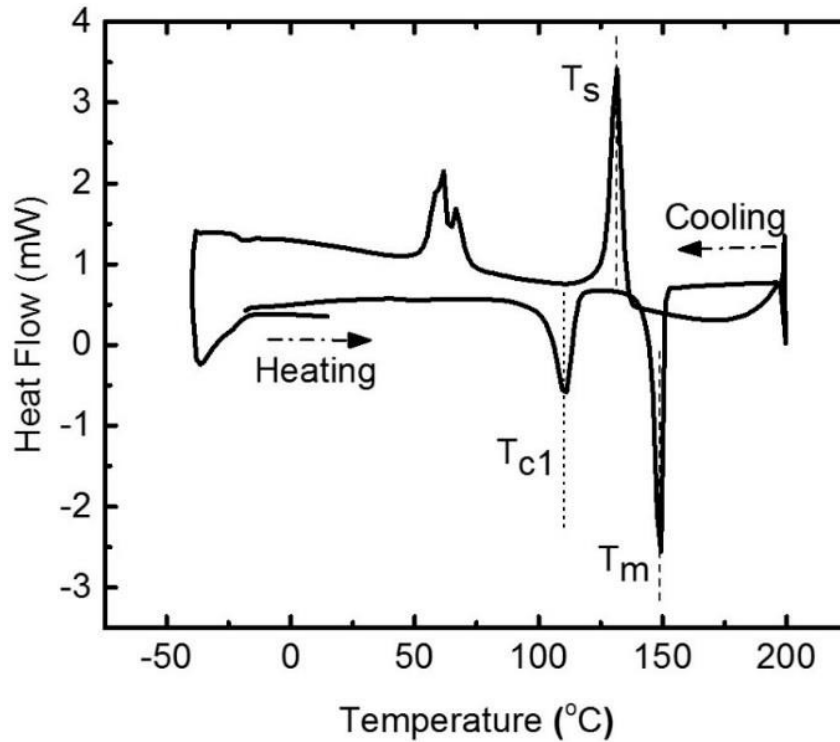


Figure 4.8. Differential scanning calorimetry (DSC) response of a P(VDF-TrFE) film. The Curie point (T_{c1}) is 111.2°C , the melting temperature (T_m) is 149°C and the solidification (crystallization) temperature (T_s) is 131.6°C .

Figure 4.11. D compares XRD data (Cu $K\alpha$ radiation at $\lambda = 0.15418\text{ nm}$) for as-made and 2-hour-annealed 10-bilayer composite films. The peak at $2\theta = 19.90^{\circ}$ is from the polymer phase [70, 118]. The other peaks at $2\theta = 35.06^{\circ}$ and $2\theta = 57.46^{\circ}$ are for the sapphire platelets. Similar to the case

for P(VDF-TrFE) film (Figure 4.10.), the intensity of the β -phase peak of the polymer phase in the composite for the 2-hour-annealed samples is higher than in the as-fabricated composite. Comparison of the degree of crystallinity for different annealing durations shows that for both the film and the composite, polymer phase achieves maximum crystallinity after a 2-hour annealing period [36], which is also consistent with the FTIR data. Therefore, we chose a 2-hour annealing time for further investigations in this article.

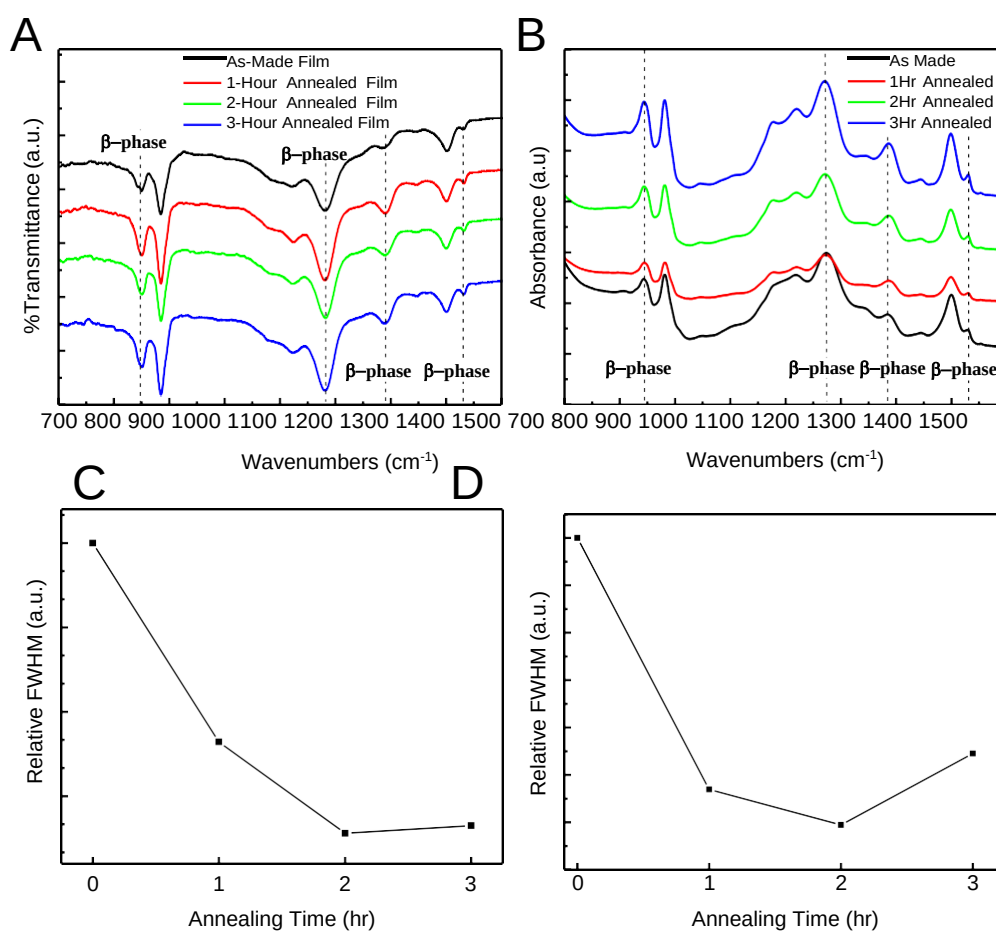


Figure 4.9. **(A)** FTIR spectra of P(VDF-TrFE) films that were annealed for different times at 135 °C. **(B)** FTIR spectra of 10-bilayer composite films that were annealed for different times at 135 °C. The dashed lines indicate wavenumbers 844 cm^{-1} , 1170 cm^{-1} , 1288 cm^{-1} and 1430 cm^{-1} , corresponding to the β -phase of P(VDF-TrFE). **(C)** and **(D)** The corresponding relative FWHM (full width at half maximum). The peak at 1400 cm^{-1} peak was used for calculation of the FWHM.

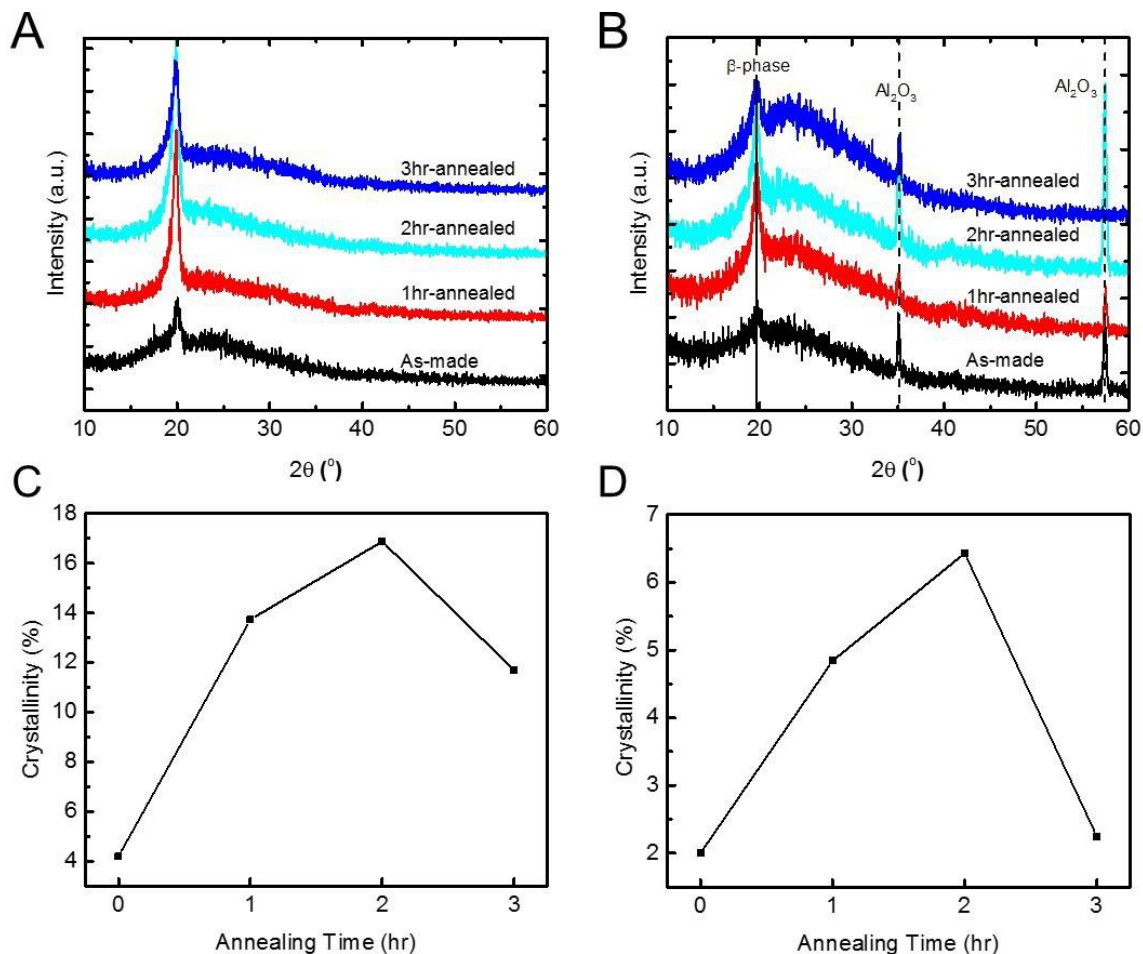


Figure 4.10. **(A)** XRD spectra of thin P(VDF-TrFE) sheets as a function of annealing times at 135°C. **(B)** XRD spectra of 10-bilayer composite sheets as a function of annealing times at 135°C. **(C)** and **(D)** The corresponding degree of crystallinity for the β -phase vs. annealing times for P(VDF-TrFE) film and composite film, respectively.

We established that the fabricated composite is piezoelectric. This was confirmed by piezoelectric mapping using piezo-response force microscopy (PFM), as well as experiments showing voltage generation during sheet flexing (Figure 4.12.). Figures 4.12. A-C show the PFM maps acquired from a 10-bilayer, 2-hour-annealed composite film, in which Figures 4.12. A, B and C are the topography, PFM amplitude and PFM phase images, respectively. Figure 4.12. D shows a piezo-

response amplitude vs. the applied voltage acquired from the composite film. The slope of this curve is used to extract the piezoelectric constant of the film.

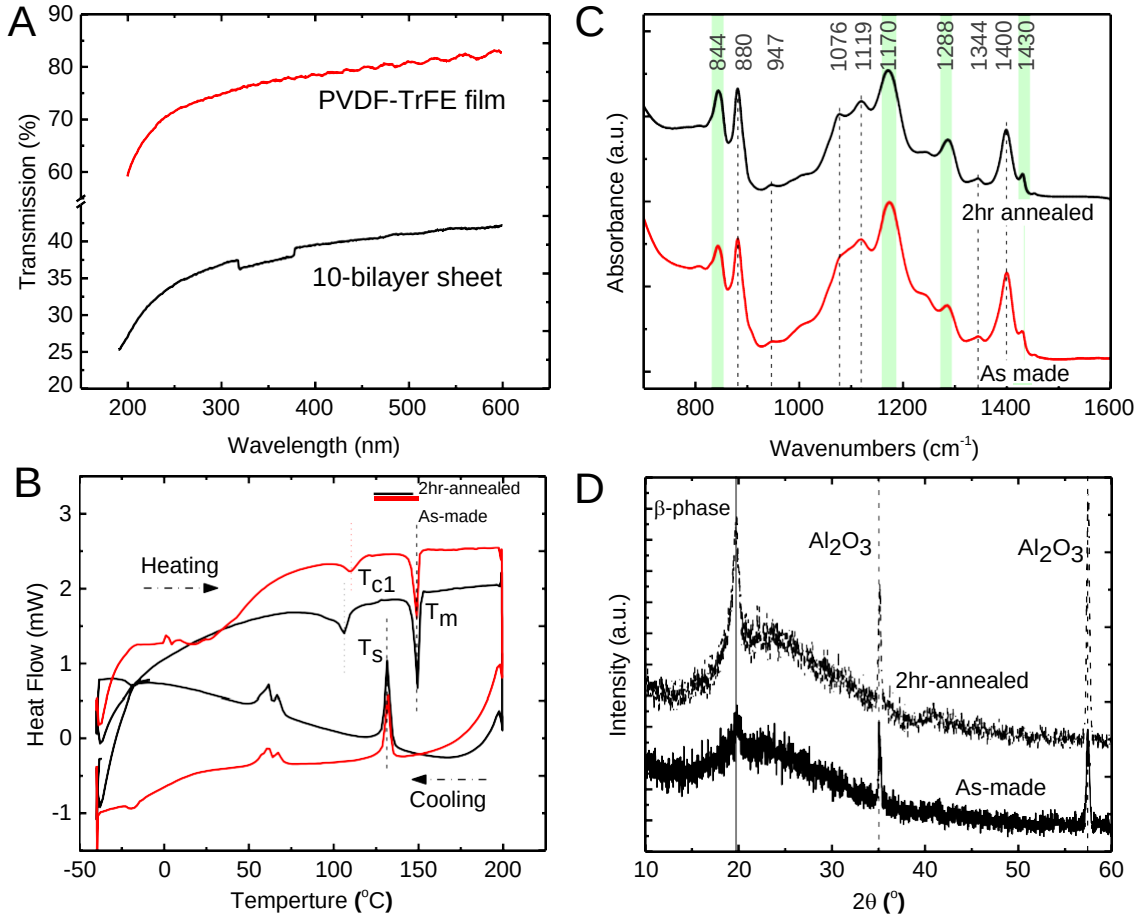


Figure 4.11. Properties of the as-fabricated and annealed composite films. **(A)** The UV-visible spectra; **(B)** DSC response; **(C)** FTIR spectrum, and **(D)** XRD data obtained for Cu K α radiation ($\lambda = 0.15418$ nm) .

The PFM data show that annealing and electric field poling enhances the piezoelectric response of the films. Figure 4.12. E compares the piezoelectric responses of the as-made, annealed and poled films. This data is the slope of the piezoelectric amplitude response vs. the voltage sweep obtained on several points on each sample. The piezoelectric amplitude of the as-made composite sample

is $\sim 14.4 \pm 6.2$ pm/V. This value increases to $\sim 24.6 \pm 10.4$ pm/V and $\sim 36.0 \pm 2.1$ pm/V for the 2-hour-annealed and the electrically poled samples, respectively.

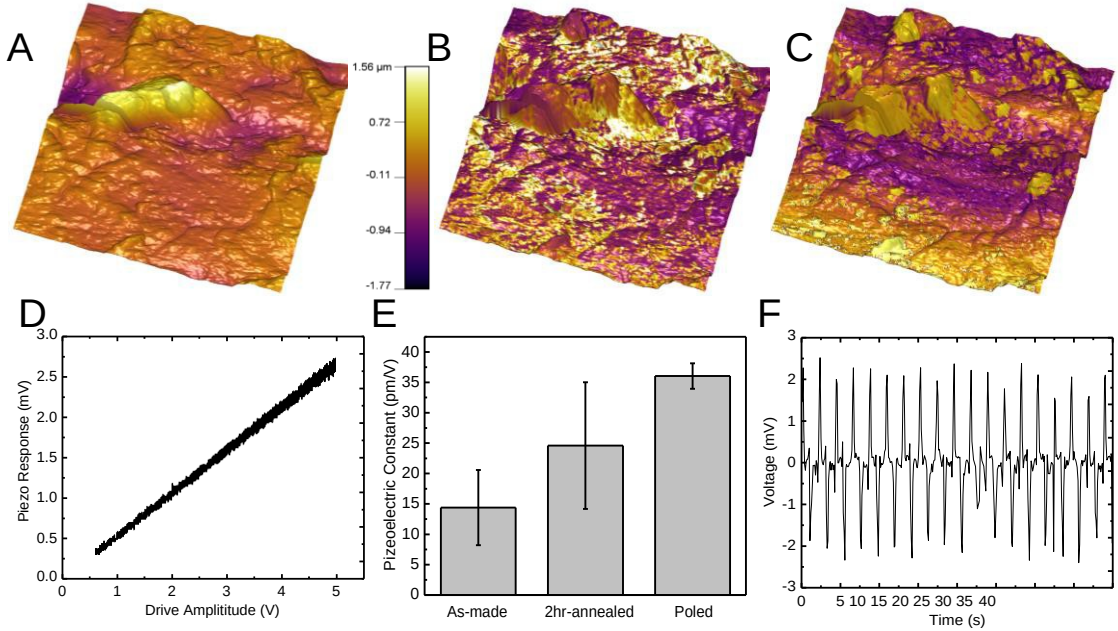


Figure 4.12. **(A)** The AFM topography image, **(B)** PFM amplitude and **(C)** PFM phase image of a 10-bilayer, 2-hour-annealed composite film. AFM images are $20 \mu\text{m} \times 20 \mu\text{m}$. **(D)** Piezo-response vs. drive voltage acquired from a composite film. **(E)** Piezo-response coefficient comparison for as-made vs. 2-hr annealed and poled films, $n = 7$. **(F)** Voltage generation under flexure mode from 2-hour-annealed composite film.

The piezoelectric effect in P(VDF-TrFE) is mainly from the crystalline domains of the polymer. The enhancement of the piezoelectric effect after annealing agrees with the XRD data (Figure 4.10. D), which show that the percentage of crystallinity of β -phase in the polymer increased after annealing. Moreover, the electric poling resulted in increase of the alignment of the dipoles, and hence enhanced piezoelectricity in the polymer. The standard deviation in piezoelectric responses (Figure 4.12. E) collected at various points on the sample are attributed to spatially varying crystal alignment (and hence dipole alignment) in the sample. This standard deviation substantially

decreased by electric field poling, since electric field poling results in more uniform alignment of the dipoles.

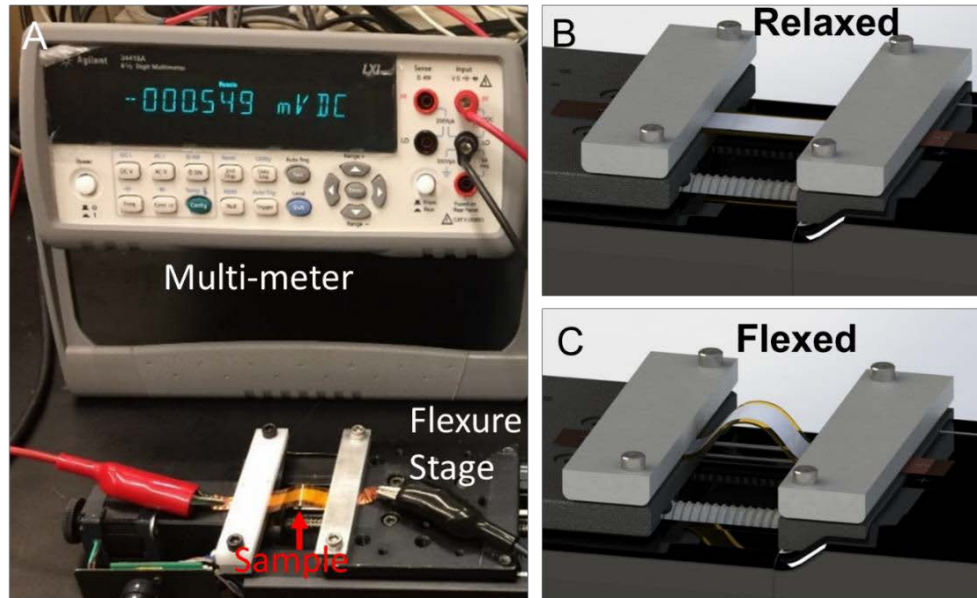


Figure 4.13. Voltage generation of annealed composite film by flexure test. **(A)** shows the experimental setup including the flexure stage that controlled by a step motor to flex a ribbon-shape sample and a digital multimeter to record the generated electric charges. **(B)** and **(C)** show the relaxed-flexed deformation in this test.

We used flexure experiment to observe voltage generated directly from piezoelectric effect in the piezoelectric sheets under mechanical flexure, in addition to PFM, which is based on converse piezoelectric effect. For the flexure experiment, a ribbon was cut from the composite film and fixed between two electrodes on a flexure stage. The electrodes were connected to a digital multimeter. Under repeated relaxed-flexed deformation, voltage is generated in the composite sample because of piezoelectric effect, which is registered in the digital multimeter (Figure 4.13.).

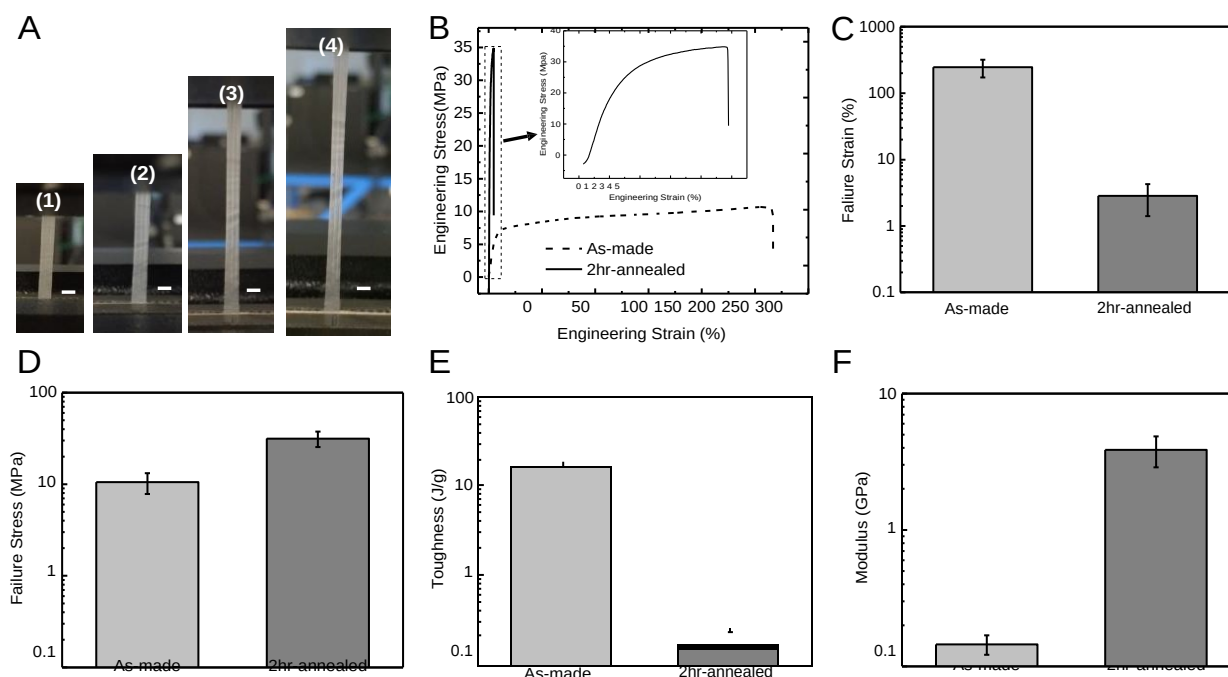


Figure 4.14. Mechanical properties of the fabricated composite films. **(A)** Series of optical micrographs taken during elongating of an as-made, 10-bilayer composite film by more than 200%. The scale bar in each image is 5 mm. **(B)** The engineering stress vs. engineering strain responses acquired from an as-made and a 2-hour-annealed 10-bilayer composite film. The inset is a magnified view of the stress-strain response for the annealed film. **(C)-(F)** The corresponding failure strain (ductility), failure stress (strength), tensile toughness and elastic modulus for the as-made and annealed samples. Error bars are standard deviation for $n = 5$ and $n = 4$ for as-made and annealed samples, respectively. Note that the data are on a log-scale.

Table 4.1. Summary of the tensile test data from as-made and 2-hour annealed 10-bilayer composite films.

Sample	Toughness (J/g)	Failure Strain (%)	Strength (MPa)	Modulus (GPa)
As-made-1	10.9	153	7.9	0.13
As-made-2	26.6	337.8	9.3	0.15
As-made-3	7.6	190.7	7.9	0.067
As-made-4	14.9	266.8	10.7	0.12
As-made-5	22.9	283.3	14.2	0.17
Average $\pm$ SD	16.6 $\pm$ 8	246 $\pm$ 74	10.0 $\pm$ 2.6	0.13 $\pm$ 0.04
2hr-annealed-1	0.037	2.12	24.3582	4.86

2hr-annealed-2	0.09	1.66	34.5955	4.55
2hr-annealed-3	0.14	2.69	28.9631	2.93
2hr-annealed-4	0.39	4.9	37.9679	3.11
Average $\pm$ SD	0.16 $\pm$ 0.15	2.84 $\pm$ 1.4	31.5 $\pm$ 6.0	3.87 $\pm$ 0.98

The mechanical properties of the samples were characterized by uniaxial tensile measurements in the sheet direction (Figure. 4.14.). Reported strength and modulus are engineering values, unless otherwise noted. Detailed results are presented in Table 1. Stress-strain measurements showed that as-made samples have two orders of magnitude larger ductility (failure strain) and toughness compared to the annealed samples, 246% as compared to 2.8% strain, and 16.6 J/g compared to 0.16 J/g energy to failure. Moreover, annealing significantly increased the elastic modulus of the samples. Elastic modulus increased to $\sim 3.9 \pm 1$ GPa for annealed samples from $\sim 0.13 \pm 0.04$ GPa for as-made samples. The engineering strength σ_e of the samples increased from $\sim 10 \pm 2$ MPa to $\sim 32 \pm 6$ MPa after annealing. Since the as-made samples undergo large deformation before rupture, true strength σ_t can be estimated as $\sigma_t = \sigma_e(1 + \varepsilon_e)$, in which ε_e is the engineering strain. For the as-made samples, true strength is estimated as ~ 35 MPa, which is close to the strength of the annealed samples. Therefore, it can be concluded that annealing process does not significantly change the true strength of the composite film. Recently, it was shown that annealing process does not affect the strength of P(VDF-TrFE) nanofibers, although annealing resulted in enhancement of elastic modulus of these nanofibers [36]. As-fabricated samples show elastic behavior, followed by large plasticity and strain hardening, whereas the annealed samples fail rather abruptly after small elastic strain. The significant changes in elastic behavior of the composite sheet after

annealing can be attributed to increased crystallinity of the polymer phase in the annealed sheets, as observed in the XRD data, Figure 4.10.

The sapphire platelets have an average aspect ratio of ~ 13 ($6 \mu\text{m}/450 \text{ nm}$), Figure 4.1.. The critical aspect ratio for transition from ductile failure (platelet pull-out) to brittle failure (platelet fracture)

is predicted for an aspect ratio of $s_c = \frac{\sigma_p}{\tau_y} \sim 510$ [121], in which $\sigma_p \sim 2 \text{ GPa}$ is the tensile strength

of the platelets. $\tau_y \sim 3.9 \text{ MPa}$ is the yield stress of P(VDF-TrFE) (obtained from separate experiments not shown here). For $s < s_c$, the matrix yields before the platelets break, and hence expected deformation mechanism are platelet pull-out or plastic flow of the polymer matrix. This trend is expected to hold even for the annealed samples, since a yield strength of $\tau_y \sim 150 \text{ MPa}$ is required for the critical aspect ratio to match the aspect ratio of the platelets, whereas $\tau_y \sim 10.2 \text{ MPa}$ for annealed P(VDF-TrFE). Hence, ductile failure is the deformation mechanism for the fabricated composites, regardless of the annealing conditions.

The theoretical strength of the platelet reinforced composite (σ_c) can be obtained from

$\sigma_c = \alpha V_p \sigma_p + (1-V_p) \sigma_m$ [121], where V_p is the volume fraction of the platelets and σ_m is the tensile strength of the matrix, in which $\alpha = \frac{\tau_y s}{2\sigma_p}$. The estimated theoretical strength for the 10-

bilayer sheet is $\sigma_c \sim 14.8 \text{ MPa}$ and $\sigma_c \sim 36.2 \text{ MPa}$ for the as-made and annealed sheets, which compares well with the $\sigma_c \sim 10 \pm 2.6 \text{ MPa}$ and $\sigma_c \sim 31.5 \pm 6 \text{ MPa}$ for the as-made and annealed

samples, respectively. Similarly, the elastic modulus of the fabricated composites can be estimated based on $E_c = \beta E_p V_p + (1 - V_p) E_m$, in which $\beta = [1 - \frac{\tanh(u)}{u}]$ is the modulus reduction factor, with u given as $u = s[\frac{G_m V_p}{E_p (1 - V_p)}]$, in which G_m and E_m are the shear modulus and elastic modulus of the polymer phase, and E_p is the elastic modulus of the platelets [122]. We calculated shear moduli based on uniaxial test experimental data. $G_m = 34.75$ MPa, and $G_m = 207$ MPa, for the as-made and annealed polymer films, respectively and a Poisson's ratio of 0.4. The calculated elastic modulus of the composite sheet was obtained to be $E_c \sim 0.88$ GPa and $E_c \sim 4.6$ GPa, for the as-made and annealed samples, respectively. Experimental values were $E_c \sim 0.13 \pm 0.04$ GPa and $E_c \sim 3.87 \pm 0.98$ GPa, for the as-made and annealed samples. While the theoretical estimation for elastic modulus of the annealed samples is close to the experimental values, however, there is a discrepancy between the theory and experiment for the modulus of the as-made samples. Such discrepancy was also observed in the literature for similar composite films, which was attributed to the limited control over the organic-inorganic interface or possible processing defects (voids) within the composite microstructure [3]. In addition, part of the difference between experimental values and theoretical prediction could be attributed to the misalignment of the platelets in the composite. Improvement in the processing conditions and better control of the interface could result in better agreement between the experiment and theory, and improvement in the overall mechanical properties of the fabricated sheets [122].

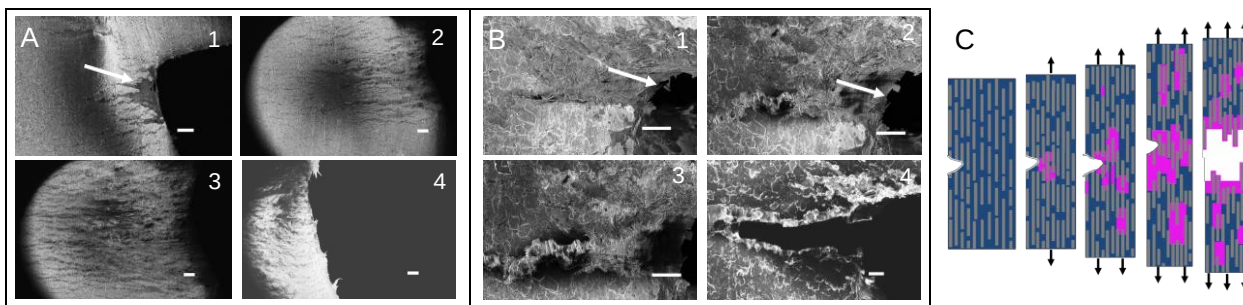


Figure 4.15. In situ SEM micro-tensile test. **(A)** and **(B)** Low magnification and high magnification snap-shots from in situ SEM tensile test, respectively. Scale bars are 100 μm in A and 20 μm in B. 1-4 are in the order of increasing deformation in the sheet. Arrows point to the notches created in the sheets. **(C)** Schematic of the failure propagation in the fabricated films. The overall deformation mechanism is governed by sliding of the platelets in the polymer phase. The polymer phase assists in propagation of failure to larger area in the sample.

Insights into deformation mechanism were obtained using *in situ* SEM tensile experiments, in which SEM images were acquired from the sample under tension (Figure 4.15.). Figures 4.15.A and B show low magnification and high magnification *in situ* SEM tensile tests from two different 10-bilayer films. For these experiments, the sample was mounted onto the micro-tensile stage, and a notch was created in the sample using a sharp scissor. Opening of this notch under tensile load was followed by capturing consecutive SEM images from the sample. The low magnification images in Figure 4.15. A 1-4 show that deformation is not localized in the vicinity of the notch and propagates to larger area through creation of many micro-cracks. This propagation facilitates dissipation of energy to a larger area, and hence results in large toughness and ductility. Higher magnification images in Figure 4.15. B 1-4 acquired from one of the micro-cracks show that the polymer matrix is stretched between the platelets and creates bridges that holds the platelets together before it totally fails and the notch grows forward. Figure 4.15. C schematically shows the overall deformation mechanism. As the tensile stress increases, the polymer matrix is continuously stretched, and platelets slide respect to each other with the polymer matrix in between

transferring the shear stress. The interaction at the interfaces between the platelets and the polymer is governed by van der Waals forces and possibly hydrogen bonds. The hydrogen bonds may form between the -NH₂ groups of the functionalized platelets and the fluorine atoms of the P(VDF-TrFE) polymer. These reversible interactions allow the break and reform of the bonds as the platelets slide.

4.3 Conclusions

We report the fabrication and characterization of ceramic platelet-reinforced piezoelectric polymer composite. Transparent ceramic micro-platelets of single crystal sapphire were embedded in a piezoelectric polymer P(VDF-TrFE) matrix via layer-by-layer assembly (LBL) process to fabricate flexible free-standing films. The LBL process included sequential spin-coating of the polymer phase and subsequent dip-coating of the ceramic platelets. The final composite had 55-77% polymer content. FIB cross-section and TEM analysis showed that the LBL process resulted in approximately aligned platelets in the film. UV-visible spectroscopy showed that the films exhibit 25~40% optical transmission between 200-600 nm wavelength. Piezoelectric characterization confirmed that the composite was piezoelectric with a piezoelectric constant of up to ~36 pm/V for electrically poled samples, which likely will be useful for applications in sensors and energy harvesting. The as-fabricated films showed extremely high ductility (strain-to-failure) in the range of 150-335% and an energy to failure (tensile toughness) in the range of 7.5-23 J/g. The elastic modulus of the samples was in the range of ~67-170 MPa. Moreover, we investigated effect of thermal annealing on the samples. Thermal annealing resulted in enhancement of piezoelectric constant by ~70%. The elastic modulus increased to ~3-4.9 GPa,

while the ductility dropped significantly to 1.6-4.9%. Theoretical models were used to estimate the strength and elastic modulus of the composite sheets. *In situ* SEM tensile experiments confirmed that the deformation mechanism of the samples was in the form of polymer stretch and platelet sliding respect to the polymer, which resulted in ductile failure under large strain.

CHAPTER 5

EVOLUTION OF ELECTROMECHANICAL AND MORPHOLOGICAL PROPERTIES OF PIEZOELECTRIC THIN FILMS WITH THERMOMECHANICAL PROCESSING*

5.1 Introduction

Piezoelectric polymers and ceramics, as an important class of multifunctional materials, have numerous applications for sensing, actuation and energy harvesting [123-130]. Although piezoelectric polymers, such as PVDF (polyvinylidene fluoride) and its co-polymer P(VDF-TrFE) (polyvinylidene fluoride trifluoroethylene), have smaller piezoelectric constants (d) compared to the piezoelectric ceramics, their flexibility, stretchability and processability makes them suitable for emerging applications requiring conformal and soft mechanics [128, 131-135]. In addition, piezoelectric polymers have much larger piezoelectric voltage constant $g = d/\epsilon r$ compared to most piezo ceramics, which makes them suitable for sensor applications.

PVDF is a semi-crystalline polymer, which exists in different crystalline phases with different characteristic properties. Among different crystalline phases, the β -phase and γ -phase are the polar phases, while β -phase has the highest dipole moment. The β -phase is known as all-trans conformation because of conformation of the backbone carbons chains. Various copolymers have been introduced for PVDF to enhance its properties. One of the most investigated co-polymers of PVDF is P(VDF-TrFE), which has higher β -phase ratio regardless of processing

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methods [97, 136]. Molar content ratio of VDF co-polymer to TrFE affects the Curie temperature and melting point of P(VDF-TrFE) copolymer. Curie temperature of PVDF is above melting point of PVDF[137], while by adding the TrFE to it, the Curie temperature drops to below melting point. Thus, P(VDF-TrFE) has the peculiar feature which can be annealed in the paraelectric phase (above the Curie temperature) without melting [138].

The electromechanical coupling factor, $k = \frac{d^2 Y}{\varepsilon}$, in which d , Y and ε are the piezoelectric constant, elastic modulus and dielectric constant, respectively, is an important performance metric for piezoelectric materials which determines the conversion efficiency between electrical and mechanical energy in piezoelectric materials [139, 140]. Therefore, both mechanical properties and electro-mechanical properties affect the performance of piezoelectric materials. Given the semi-crystalline nature of P(VDF-TrFE), these properties are highly dependent on the morphology of the polymer, i.e., crystallinity, orientation and size of the crystallites, alignment of the amorphous chains, etc [141]. High degree of crystallinity with the effective orientation of the crystallites are necessary to maximize the electromechanical coupling in this polymer. Post-processing treatments such as thermal annealing, and mechanical drawing are effective methods for altering the morphology, and as a result piezoelectric, mechanical and ferroelectric properties, of the piezoelectric polymers [142-146].

It has been reported that in as-cast and annealed (at 120 °C) thin films of P(VDF-TrFE) fabricated by spin-coating process, majority of the polymer chain were oriented along the substrate, predominantly forming “edge-on” lamellar crystals, whereas the melt-crystallized samples exhibited predominantly “face-on” lamellar crystals [142]. Elastic modulus of thin 30 nm-1 μ m spin-coated films of P(VDF-TrFE) was measured using buckling method, and it was shown that

elastic modulus of the films was strongly dependent on its microstructure, leading to more than five times difference for various annealing temperatures [143]. While heat treatment in the para-electric phase is the most effective in increasing crystallinity and improved piezoelectric behavior, heat treatment above the melting point nearly eliminates any piezoelectric or ferroelectric behavior [147].

The phase α -phase to β -phase transformation has been reported for uniaxially stretched PVDF at higher temperature ($>60\text{ }^{\circ}\text{C}$) [148]. Transformation from α -phase to β -phase as a result of stretching of PVDF fibers has been reported, while it was observed that the total crystallinity of the fibers did not change much by stretching [140]. For self-assembled PVDF fibers in the form of yarn structure, 17% and 41% increase in tensile modulus and strength, and $\sim 10\%$ improvement in β -phase content, respectively, was observed for 25% stretch at $100\text{ }^{\circ}\text{C}$ followed by annealing for 1 hr in the same temperature. This improvement in mechanical properties was attributed to improvement in crystallinity [149].

For P(VDF-TrFE), similar to other semi-crystalline polymers, a morphology of folded-chain lamellar crystal combined with amorphous chains is considered. “Single crystalline-like” films and nanofibers of P(VDF-TrFE) have been also reported [37, 150, 151]. It is suggested that in these polymers neither amorphous phase nor lamellar crystals exist, and the polymer is highly crystallized. These films and nanofiber mats were obtained by stretching, followed by annealing at the para-electric phase (at $138\text{ }^{\circ}\text{C}$ - $140\text{ }^{\circ}\text{C}$) for 2h. Specifically, the solution cast films of thickness $5\text{-}15\text{ }\mu\text{m}$ were stretched five times and the nanofiber mats were stretched to 150% of their original length, before annealing. However, quantitative piezoelectric properties, mechanical properties, molecular orientation and crystallinity and their evolution by annealing and drawing post-

processing conditions for P(VDF-TrFE) films is not yet fully understood. Understanding the evolution of the semi-crystalline morphology of P(VDF-TrFE) under these post-processing conditions is necessary for further improvement of the performance of this polymer for emerging applications.

In this article, spin-coated P(VDF-TrFE) (70/30) thin films were stretched up to 200% strain, then the stretched films were annealed at the paraelectric phase (135 °C) for 2 hours. Polarized FTIR and 2D XRD patterns were captured to reveal the effect of annealing and drawing on molecular conformation of polymer chain and the crystalline structure of the films. Mechanical properties and piezo-response of films were investigated by tensile test and PFM (piezoresponse force microscopy). Mechanical and piezoelectric properties confirm the results of the FTIR, and X-ray on the evolution of the morphology of the films.

5.2 Results and Discussion

P(VDF-TrFE) thin films were fabricated using spin-coating process. The thickness of the obtained films were in the range of 5-15 μm . Films with three different types of post-processing conditions were examined. As-fabricated films, films annealed at 135 °C for 2 hours, and films stretched to 200% strain using mechanical testing machine and subsequently annealed at the same conditions. These films are referred to as-fabricated, annealed, and drawn-and-annealed, respectively throughout the manuscript. The annealing temperature was chosen in the para-electric phase, which has been shown to results in maximum efficiency of annealing in terms of crystallization of the polymer chains [70, 152].

Figure 5.1. summarizes the mechanical properties of the films for different processing conditions.

Figure 5.1. A shows the engineering stress vs. engineering strain responses. The as-fabricated films, prior to any annealing, are highly ductile with a nearly elastic-perfectly plastic behavior, withstanding axial strains of $> 200\%$, at a flow stress of $\sim 6\text{-}8$ MPa. However, annealed samples regardless of the amount of drawing applied to them prior to annealing, demonstrate a drastically different behavior. To study the effect of annealing on mechanics of films, the as-fabricated polymer films were drawn to different strains (50%, 100% and 200%) using a tensile machine. After drawing process, the films were elastically unloaded. Tensile responses of the films during drawing process and elastic unloading were acquired. Each film was subsequently annealed, after the drawing step, and was then subjected to tensile test to the point of failure. In Figure 5.1., the responses during drawing process and after annealing to the point of failure are combined.

Figures 5.1. B and C show the strength (failure stress) and elastic moduli obtained from these tensile experiments. The dashed lines show the ultimate strength and modulus of the as-fabricated film. The results show that annealing and drawing resulted in increase of the strength of the films, compared to the as-fabricated films. In addition, by increasing the draw ratio, the strength increased, such that the strength of the films drawn to 200% (75.0 ± 9.9 MPa) was nearly 5-time larger than the films without any drawing (13.5 ± 3.0 MPa).

Elastic modulus vs. post-processing conditions shows similar behavior to the strength. The modulus of 200% drawn film (1.16 ± 0.07 GPa) was twice larger than the non-stretched-annealed film (0.54 ± 0.08 GPa), and almost 10-fold larger than the as-fabricated films (0.12 ± 0.02 GPa). As the stretch ratio increased, the modulus increased, correspondingly. No difference was observed for the elastic modulus between the annealed films and 50% drawn films, while the strength showed obvious difference for these films.

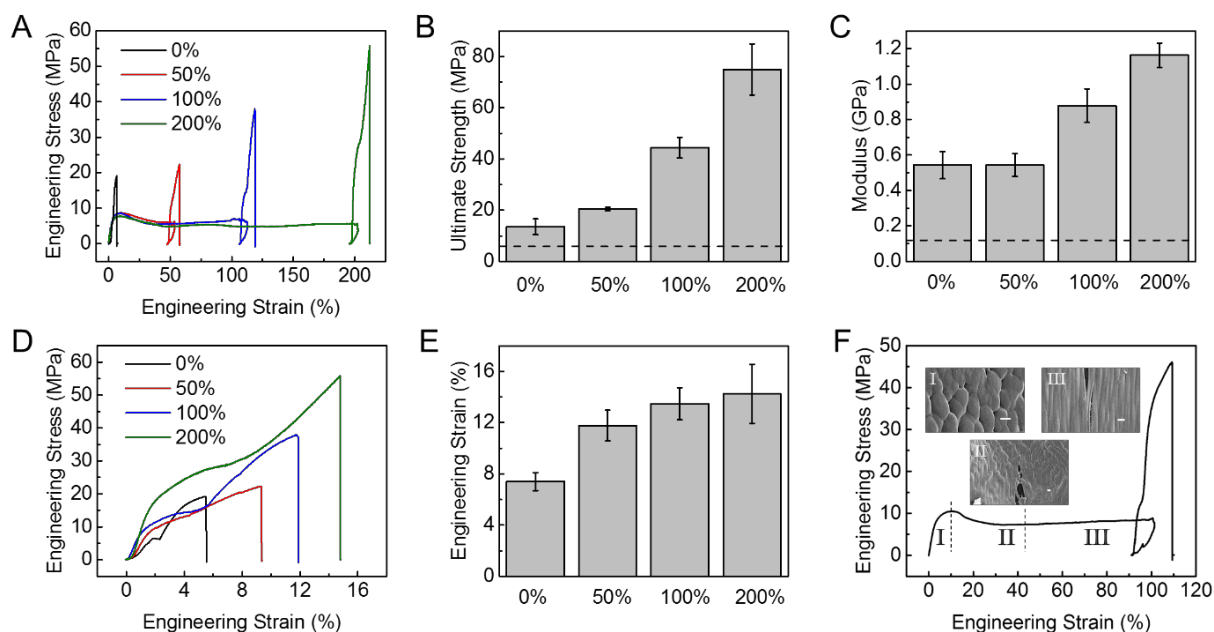


Figure 5.1. **(A)** The engineering stress vs engineering strain responses for films with different types of post-processing conditions. **(B)** Ultimate strength obtained from tensile tests. The dashed line shows the ultimate strength of the as-fabricated film ($n = 4$). **(C)** Elastic moduli calculated from tensile tests. The dashed line shows the modulus of the as-fabricated film. **(D)** Engineering strain and stress responses in A, without the initial drawing response. **(E)** Post-annealing engineering strain from Figure 5.1. D. **(F)** SEM images show the morphology changes correlated with the tensile test response. The scale bar in all three SEM images is 10 μm .

Often, in engineering materials enhancement of modulus and strength is accompanied by decrease in ductility (failure strain). An interesting observation from the tensile experiment was that drawing process not only resulted in enhanced modulus and strength, it also resulted in increase in the failure strain. These results are shown in Figure 5.1. D and E. Figure 5.1. D shows the stress – strain response from Figure 5.1. A, without the initial drawing response. As observed, the ductility increased by annealing and drawing process. Specifically, the ductility of the 200% drawn films ($14.2 \pm 2.3\%$) was 93% larger than the undrawn films.

Figure 5.1. F shows stress – strain response and three SEM images corresponding to different steps during the tensile test of a film drawn to 100%. Initially, the sample showed a granular structure

(stage I). After the yield point (stage II), the polymer film started to show the necking phenomena. The granular structure in stage II was stretched, which indicated that the chains started to get aligned under the applied mechanical stress. In final stage III, the entire granular structure was completely stretched, which means most of the molecular chains inside the film were aligned along the drawing direction. Stretch-induced crystallization, alignment of the crystallites and amorphous changes can be the reasons for enhancement in the elastic modulus and strength of the films. These changes can be confirmed by images from optical polarizer microscopy, FTIR and XRD spectra and DSC response of the polymer film, as shown in the following.

Figure 5.2. A shows polarized optical microscopy images taken from different areas of a film during drawing process. Image (i) is taken in the un-deformed area of the film. In this image, the granular structure with the maltese cross-patterns uniformly distributed on the film can be observed [153]. In the inset image of Figure 5.2. A, these cross-patterns can be observed more clearly [154-158]. During drawing process, crystallites change orientation toward the drawing axis. In addition, the chains in the amorphous phase stretch and orient toward the drawing axis. These processes initiate in the neck region of the film and extend to the entire film. Images (ii) show the color change observed using cross-polarizer in the transition region of the film from un-deformed region to the neck region. In the fully stretched region of the film, the color is uniform blue (iii), which may indicate more alignment of the crystallites and the amorphous chains in this region. These color changes correlated with the SEM images in inset of Figure 5.1. F, in which the quadrilateral-grain-shape morphology is transformed to the needle-grain-shape crystallites.

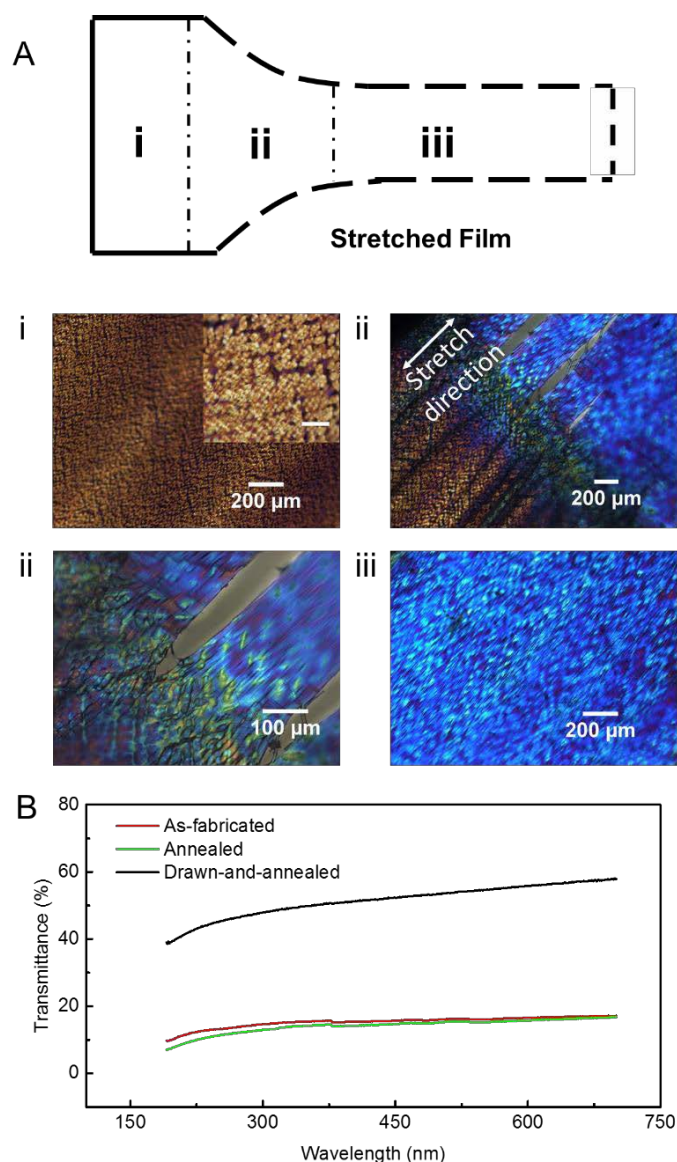


Figure 5.2. **(A)** The polarized optical microscopy images taken from different areas of a film during drawing process: (i) The un-deformed area of the polymer film. The inset is a zoomed-in image (scale bar 50 μm); (ii) Low magnification and zoomed-in images of the transition region between the un-deformed and deformed sections of the film; (iii) The fully stretched region of the film. **(B)** UV-Visible spectra acquired from the films.

The UV-Visible spectroscopy shows that the as-fabricated film and the annealed film have an optical transparency of $\sim 15\% - 20\%$ in the 200 – 600 nm wavelength. The transparency of the 200% drawn film increased to $\sim 40\% - 50\%$ in this range. Increase in transparency can be partially

attributed to the reduction in the thickness of the film after drawing process. Reorientation of the crystallites and amorphous chains is also responsible for part of the increase in UV-Visible transmittance.

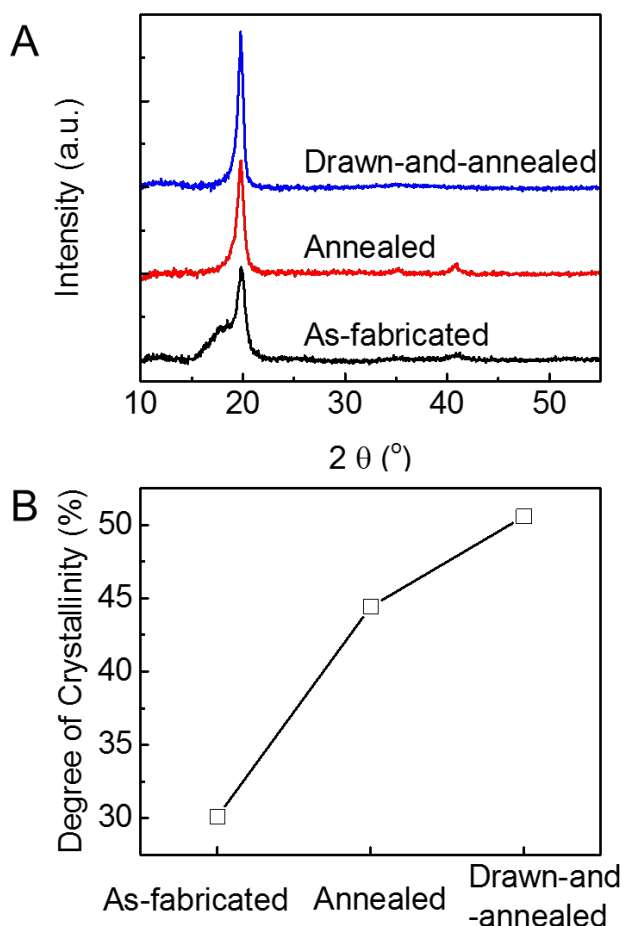


Figure 5.3. **(A)** XRD spectra, and **(B)** the degree of crystallinity of polymer films.

The X-ray powder diffraction (XRD) patterns of polymer films with different post-processing conditions are shown in Figure 5.3. A. In the diffraction spectrum of all samples, the peak at $2\theta \sim 19.8^{\circ}$ is attributed to the (110) and (200) planes of β -phase[152]. At the shoulder of this peak at slightly lower diffraction angles, a diffused peak is also present that corresponds to an amorphous

phase of the polymer. The degree of crystallinity was estimated from the XRD spectra [159]. The degree of crystallinity of the as-fabricated film was found to be ~30%, which increased to ~44% upon annealing, and was further increased to ~51% for samples drawn to 200% (Figure 5.3. B).

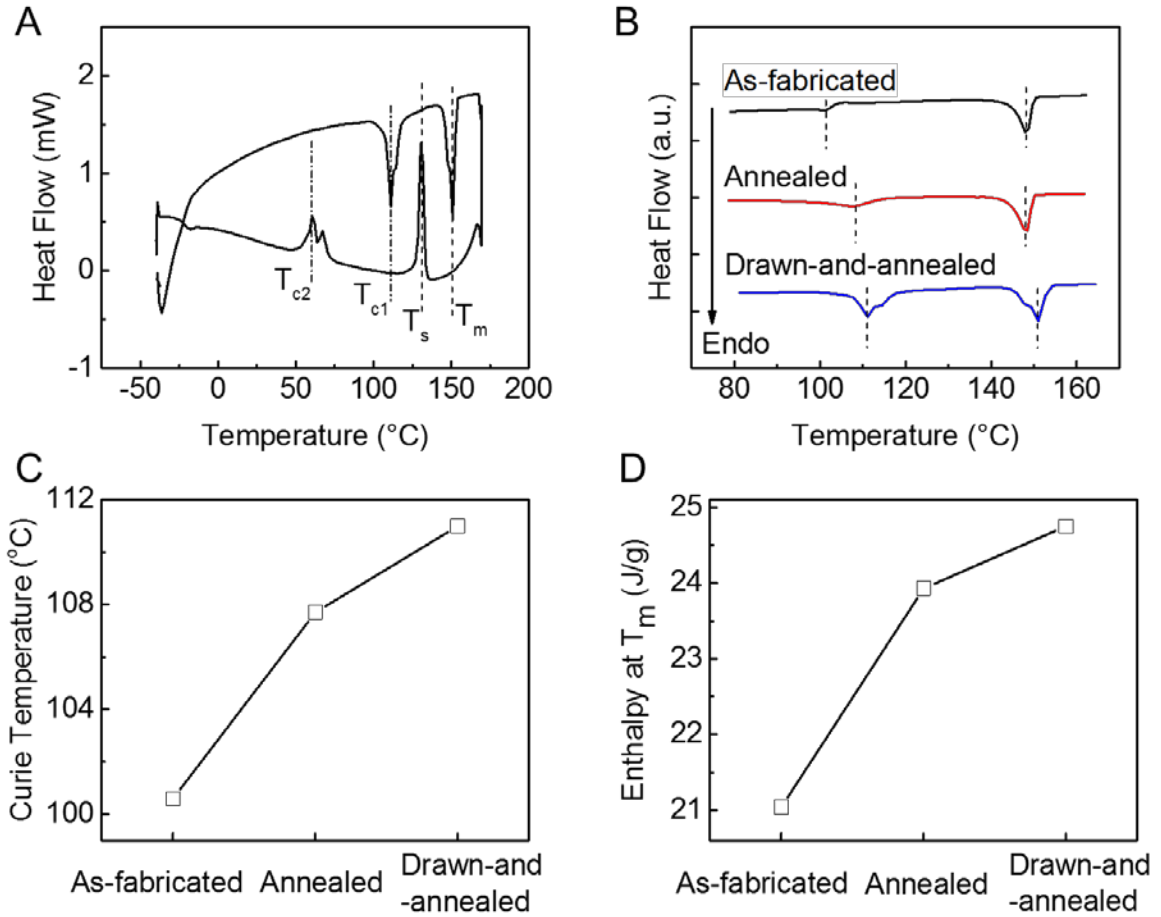


Figure 5.4. **(A)** DSC thermogram of the 200% drawn polymer film. **(B)** Curie and melting point temperature for different films. **(C)** and **(D)** Curie temperature and melting enthalpy vs. processing conditions.

Figure 5.4. A shows a differential scanning calorimetry (DSC) thermogram of a drawn-and-annealed polymer film. The DSC spectra of all films show similar overall pattern. T_s and T_m denote the crystallization and melting temperatures, respectively. T_{c1} and T_{c2} are the Curie transition

temperatures in heating and cooling cycles, respectively. Figure 5.4. B shows the portion of the DSC spectra for the Curie temperature (T_{c1}) and melting temperature for films with various post-processing conditions. The Curie temperature increased by annealing and drawing process (Figure 5.4. C). The Curie temperature was ~ 100.6 °C, ~ 107.7 °C and ~ 111.0 °C for as-fabricated, annealed, and drawn-and-annealed films, respectively. In addition, the endothermic heat absorption increased around the Curie temperature as a result of annealing and drawing, which indicates increase in the ferroelectric effect for annealed and drawn samples. Similarly, the melting temperature changes by post-processing, although to a less extend compared to the Curie temperature. The melting enthalpy shown in Figure 5.4. D was calculated by integrating each melting peak in DSC thermograms. The melting enthalpy for as-fabricated, annealed and 200% drawn films was obtained to be ~ 21 J/g, ~ 24 J/g and ~ 25 J/g, respectively. The increase in the melting enthalpy is an indication that the crystallinity in the polymer films increased by annealing and drawing process[160, 161].

In order to investigate the orientation of the crystallites or molecular chains in the P(VDF-TrFE) films, we used the polarized FTIR spectroscopy, WAXD (wide angle X-ray diffraction) and PFM (piezo-response force microscopy) experiments.

Figure 5.5. A shows FTIR-ATR spectra collected from as-fabricated, annealed and the 200% drawn-and-annealed films. For the drawn sample, the spectra was acquired from the fully stretched area (neck area) of the film. The peaks are associated with the β -phase and γ -phase.

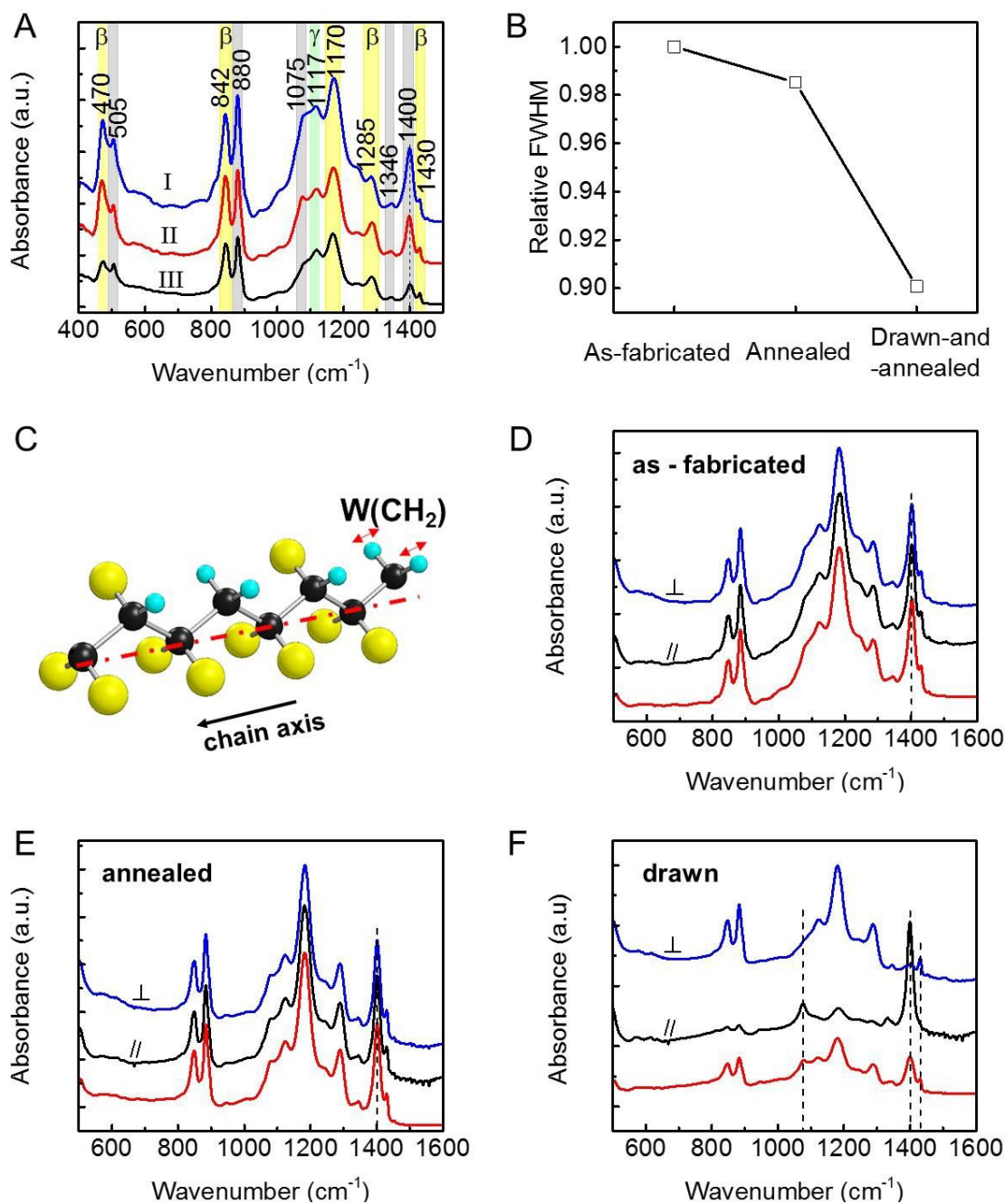


Figure 5.5. **(A)** FTIR-ATR spectra acquired from different films: I, II and III represent the as-fabricated, annealed and the 200% drawn-and-annealed films, respectively. **(B)** Full-width-half-maximum at 1400 cm^{-1} peak. **(C)** Schematic of molecular chain of P(VDF-TrFE) and wagging vibration of C-H bond. **(D)** - **(F)** FTIR spectra for as-fabricated, annealed, and 200% drawn films, respectively. The three responses for each films are for perpendicular polarizer, parallel polarizer and no polarizer, which are indicated in the figures.

The absorbance bands at 470 cm^{-1} , 842 cm^{-1} , 1170 cm^{-1} , 1285 cm^{-1} and 1430 cm^{-1} represent the β -phase of P(VDF-TrFE) [156, 162, 163]. The absorption band at 1117 cm^{-1} represents the γ -phase of P(VDF-TrFE). The absorption band at 1400 cm^{-1} is assigned to the wagging vibration of C-H bond, w (CH₂), parallel to the c-axis of the molecular chain of the polymer (Figure 5.5. C). This vibration mode depends on the chain orientation of the polymer [21, 162, 164]. Since the intensity at 1400 cm^{-1} band is reduced gradually from curve I to curve III, Figure 5.5. A, it reveals that the c-axis in the film is considerably parallel to the substrate, furthermore it shows that after mechanical stretching, the backbone of molecular chain is more aligned parallel to the stretch direction [164]. The 1400 cm^{-1} band is also related to the relative change of β -phase in P(VDF-TrFE) polymer[152]. The full width at half maximum (FWHM) for 1400 cm^{-1} band dropped $\sim 10\%$ from the as-fabricated films to the drawn films, which indicates that the content of β -phase increased by annealing and drawing process.

Figure 5.5. D - F shows the polarized FTIR spectra acquired from the polymer films. To acquire polarized FTIR spectra, the polymer films were placed vertically in the sample holder, with the sample perpendicular to the polarized IR source. For the as-fabricated and annealed films, there is no obvious difference among non-polarized, perpendicular-polarized and parallel-polarized FTIR spectra, Figure 5.5. D and E, which indicates that there is no preferential orientation of the crystallites in the polymer films. However, for the drawn polymer film, there is an obvious change in the polarized FTIR responses (Figure 5.5. F). For instance, the peak at 1075 cm^{-1} is absent in perpendicular-polarized response, and is present in parallel-polarized response; the peak at 1430 cm^{-1} is present in perpendicular-polarized response and is absent in parallel-polarized response. In

addition, intensities at several peaks changed between parallel and perpendicular polarized responses.

The peak in 1400 cm^{-1} for the drawn film appeared in parallel polarizer, and was absent in the perpendicular polarizer, which further indicates alignment of the molecular chain and crystallites by drawing process. More specifically, this indicates the “edge-on” orientation of the crystallites in the film, such that the backbone of the chains is parallel to the surface of the film [165]. In order to quantify the orientation of the molecular chains, we calculated the dichroic ratio (D.R.) on the basis of polarized FTIR spectra, for the peak at 1400 cm^{-1} . The D.R. equation is expressed as follows: [166],

$$D.R. = \frac{I_{\perp} - I_{\parallel}}{I_{\perp} + I_{\parallel}} \quad (1)$$

In Eqn. (1), $I_{\perp}$ and $I_{\parallel}$ are the intensity of the absorption in perpendicular and parallel directions, respectively. For a fully random chain ordination in the polymer, $D.R. = 0$; while for a perfect orientated chains, $D.R. = 1$. The D.R. for as-fabricated and annealed polymer films was calculated to be ~ 0.007 and 0.019 , respectively. D.R. increased to 0.84 for the drawn-and-annealed polymer films, which indicates significant alignment of the polymer chains as the result of drawing process. The piezoelectric effect in P(VDF-TrFE) polymer depends on the direction of the dipoles, which in turn depends on the crystallinity and orientation of the crystallites in the polymer. We measured piezoelectric constant of polymer films with various post-processing conditions. The results showed that after annealing at the para-electric phase, $135\text{ }^{\circ}\text{C}$ for 2 hours, the piezoelectric constant of the film increased by more than 17%, compared to the as-fabricated film ($23 \pm 1.4\text{ pm/V}$, and $27 \pm 2.4\text{ pm/V}$, for as-fabricated and annealed films, respectively). Drawing process, also increased the piezoelectric constant to $30 \pm 2.8\text{ pm/V}$. Improvement in piezoelectric constant can be partially

attributed to the increase in crystallinity as well as reorientation of the crystallites in the polymer film, such that crystallites not only orient more in the edge-on origination, but also their overall dipole orientation aligns with each other to provide stronger piezoelectric effect (Figure 5.6.).

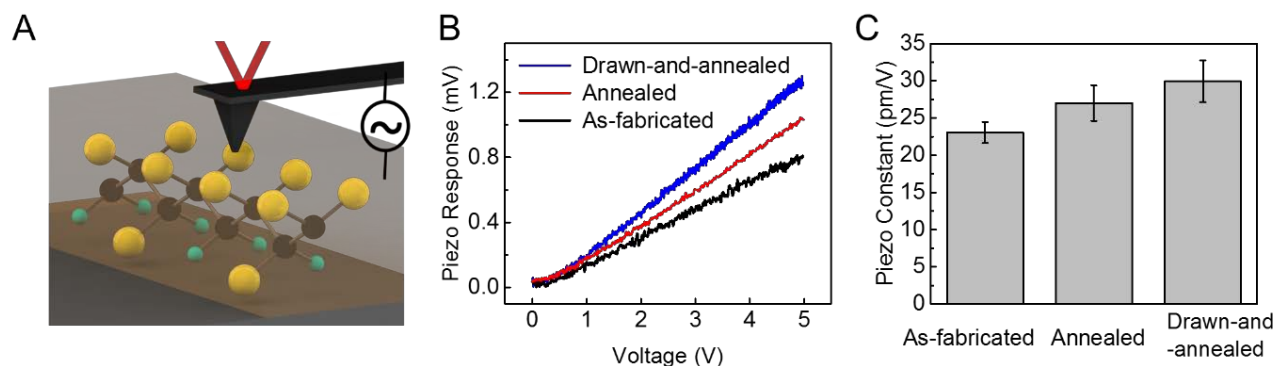


Figure 5.6. **(A)** Schematic of PFM (piezo-response force microscopy) on the P(VDF-TrFE) film. **(B)** Piezo-response vs. applied electric potential for polymer films. **(C)** Piezoelectric constant obtained from the slope of the piezo-response in B.

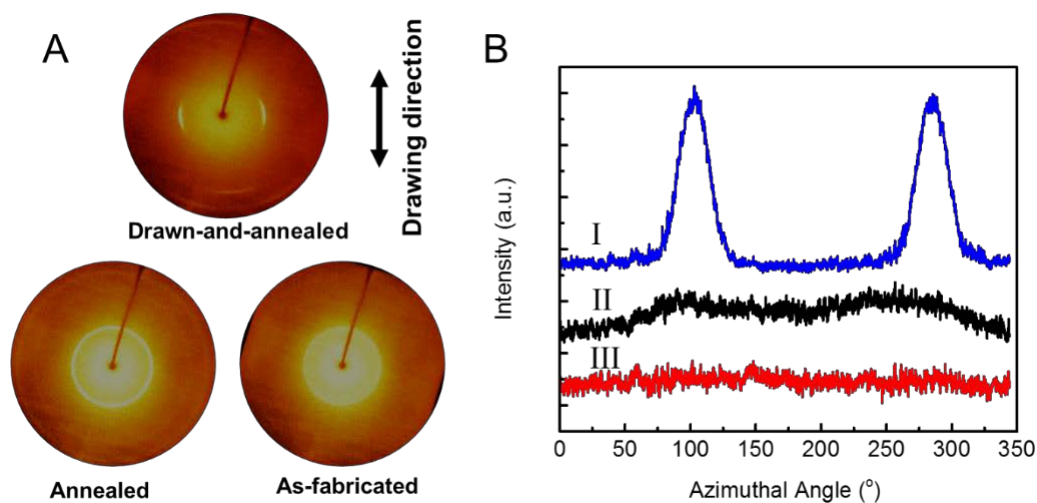


Figure 5.7. **(A)** WAXD patterns of P(VDF-TrFE) films. **(B)** The X-ray intensity as a function of the azimuthal angle. I – III correspond to 200% drawn, annealed, and as-fabricated films, respectively.

Further insight into the morphology of the polymer films was obtained from wide-angle X-ray diffraction (WAXD) patterns of the films (Figure 5.7.). In the as-fabricated film, a ring is clearly visible with nearly identical intensity at all azimuthal angles. This peak corresponds to diffraction angle $2\theta \sim 19.8^\circ$ in the powder diffraction pattern (β -phase). The axi-symmetric 2D diffraction pattern points to a random orientation distribution of the β -phase crystallites in the as-fabricated films. The 2D X-ray pattern of the annealed films are also nearly axisymmetric, although very broad and shallow peaks can be discerned at azimuthal angles which are 180° apart, pointing to a slightly preferential orientation of the crystalline phases attained after annealing. For the drawn-and-annealed film, strong peaks appear in the 2D X-ray pattern. These peaks are at azimuthal angles with 180° apart. The FWHM of these peaks were obtained to be $\sim 27^\circ$, Figure 5.7. B. It is also interesting to note that the increased intensity of the diffraction pattern at these two peaks is accompanied by a loss of intensity at other azimuthal angles, in particular at azimuthal angles of $\sim 0^\circ$ and $\sim 180^\circ$. Therefore, during drawing, the crystallites were reoriented such that their chain backbone was rotated towards the stretching direction. Overall, the WAXD data also confirm the PFM and FTIR results on the orientation of the crystallites in the films.

While the reorientation of the crystallites explains the emergence of the two peaks at azimuthal angles perpendicular to the fiber direction, and the disappearance of the peaks along the fiber axis, it does not explain the increased degree of crystallinity in the drawn-then-annealed samples compared to the annealed samples as observed in the powder diffraction patterns. The latter suggests a favorable arrangement of the chains in the amorphous phase of P(VDF-TrFE) films obtained as a result of stretching, which lowers the energy barrier for crystallization[167]. This is

similar to flow-induced crystallization in which the flow of the polymer chains can enhance chain alignment, thus accelerate crystalline nucleation process[168].

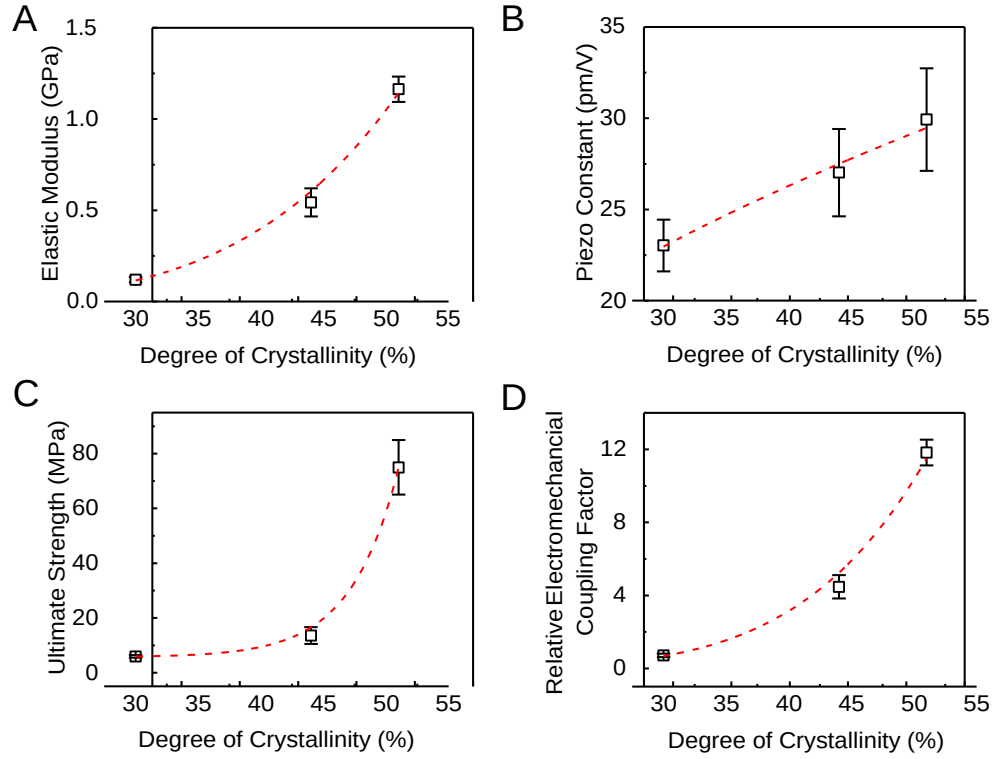


Figure 5.8. **(A)** Elastic modulus, **(B)** piezoelectric constant, **(C)** ultimate strength, and **(D)** relative electromechanical coupling factor of P(VDF-TrFE) films vs. degree of crystallinity.

Figure 5.8. summarizes the (A) elastic modulus, (B) piezoelectric constant, (C) ultimate strength, and (D) the relative electromechanical coupling factor of the polymer films vs. degree of crystallinity. These data were obtained from the as-fabricated, annealed, and 200% drawn-and-annealed films. Both the elastic modulus and the piezoelectric constant increased with increase of the degree of crystallinity, as well as the ultimate strength and relative electromechanical coupling factor. A ~65% increase in degree of crystallinity translated into ~nine-fold increases in the elastic modulus. The piezo constant of films increased by ~30% as a result of ~65% increase in degree of crystallinity. Similar to the elastic modulus, the ultimate strength increased 12 times by increase

in the degree of crystallinity of the polymer films from 30% to 51%. The results indicate that mechanical properties of the polymer are more sensitive to the degree of crystallization as compared to the piezoelectric constant. The relative electromechanical coupling efficiency was defined as:[169],

$$k^2\varepsilon = \frac{d^2}{\varepsilon_0} Y \quad (2)$$

where d is piezo constant, Y is the elastic modulus and ε_0 is the vacuum permittivity. The data were scaled to the values of as-fabricated films. The electromechanical coupling factor is an important metrics for performance of the piezoelectric films in sensors and energy harvesting applications. In this study, we did not attempt to measure the dielectric constant of the films. The relative electromechanical coupling factor increased nearly 17-fold by drawing process compared to the as-fabricated films.

5.3 Conclusions

On the basis of all the characterizations above, evolution of the morphology of the semi-crystalline piezoelectric film by processing is summarized in Figure 5.9. The as-fabricated films have nearly random orientation of crystallites with ~30% crystallinity. Annealing process results in an increase in crystallinity to ~45%, while the orientation of the crystallites or amorphous chains does not change significantly. The drawing process results in significant alignment of the amorphous chains, as well as reorientation of the available crystallites such as the backbone of the chains in crystallites are in the direction of the drawing. In addition, drawing process results in further increase in crystallinity to ~51%, which could be attributed to formation of crystallites as a result of alignment of the amorphous chains, which lowers the barrier to crystallization. Enhancement of

piezoelectric effect in the films is an indication that the dipole moments in the adjacent crystallites get oriented in the same direction.

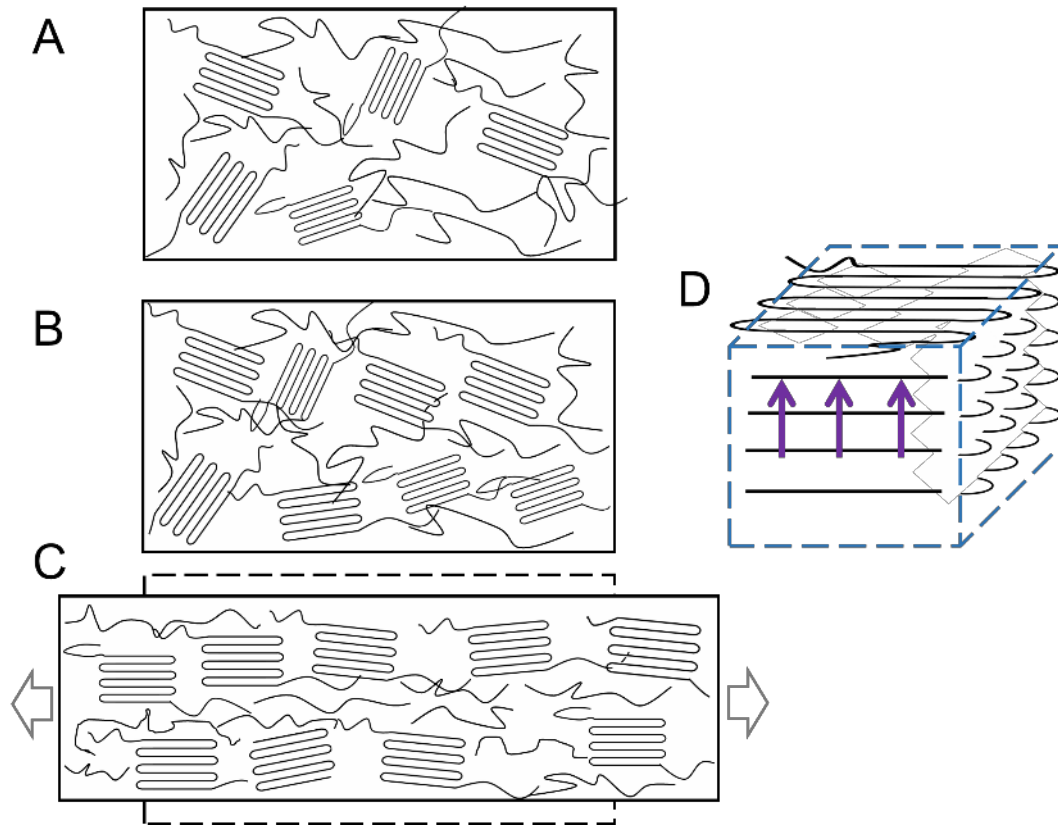


Figure 5.9. Schematic of the (top-view) morphology of the piezo polymer film, for **(A)** as-fabricated, **(B)** annealed, **(C)** drawn-and-annealed. Annealing results in increase in crystallinity with minor increase in the alignment of the crystallites. Drawing and annealing results in reorientation of the crystallites and amorphous chains toward the axial direction of the film as well as increase in crystallinity. **(D)** 3D structure of crystallite in the film. The arrows show the ordination of the overall dipole moment in the crystallites.

CHAPTER 6

OUTLOOK

6.1 Pulse Electro Deposition Application in Metal Ceramic Composite Material

Nacre, mother of pearl, widely existing in the shells of abalone and mussels, is known for its superior fracture toughness from a mechanical point of view. Nacre consists of 95% strong and brittle aragonite (calcium carbonate) and 5% soft organic (chitin) matrix can be ~3000 times more resistant to fracture than monolithic calcium carbonate in terms of energy because of its remarkable “brick-and-mortar” micro-structure. Numerous researches have been concentrated on fabricating and synthesizing composites with polymer and ceramic platelets having similar laminated architecture [3, 44]. Since soft polymer does not efficiently transfer the shear force between stiff ceramics, it is still a challenge to fabricate nacre-inspired composite that is robust, tough and also light-weight [4, 5].

Theoretically it is predicted that metallic mortar can be more effective than polymer for load transfer between stiff ceramic platelets [7]. The previous attempts have been to create the metallic matrix ceramic reinforcement composites [46, 170]. However, the inherent weaknesses constrain their mechanical performance, including the large weight percentage of metallic mortar content and the larger size of ceramic constituent from co-extrusion. In order to increase the efficiency of metal usage and reduce the requirement of energy that originates from melting metal and hot-extrusion, I proposed an approach based on micro sized (~6 μ m) ceramic platelets coated with a metal (nickel or copper) via electrochemical technique, fabricated by magnetic alignment, which does not involve the complicated freeze-casting apparatus.

The electrochemical-autocatalytic method, also named electro-less plating, is widely used in plating nonconductors such as plastics, printed circuit boards and microelectronics with various types of metals. There are several advantages, for example no limitations of the shape of coated surface, local deposition on the catalyzed surface, less consumed metal to render the surface conductive, etc [171]. Currently, I have created the recipe suitable for coating a thin layer of nickel on micro-size platelets. Based on the fact that nickel has the magnetic property, it inspires me to apply the rotating magnetic field to arrange the coated platelets in a viscous alginate solution [172]. The reason that alginate solution is used is because, first, its viscosity can be controlled by modifying the concentration of alginate and it can be cross-linked by adding calcium chloride solution, which it is good to remove the sample with intact microstructure from container, ready for further processing. The further process involves the hot-press process (spark plasma sintering process), so that the composite with ceramic platelets and the super thin metallic layer between them is assembled. The fracture toughness and the failure and toughening mechanism can be comprehensively studied in this first stage.

Metals containing homogeneous nanometer-size grains become brittle and show no ductility. It is critical to offer a mechanism of work-hardening and strain delocalization in nanostructure to enhance ductility. Twin boundaries with nanoscale spacing (λ) are effective for this purpose. The phenomenon has been proven in nanotwinned copper that maximum strength originating from a transition of the plastic deformation mechanism from dislocation slip transfer to nucleation and gliding of twinning partials [173]; in addition the reduction of twin thickness promotes dislocation-twin-boundary interactions resulting in a pronounced strain hardening [174]. Metallic mortars with twin boundaries are considered to be the best candidates to assemble “nacre-like” composite. In

the second stage, the research objective is focused on how to fill the scaffold with metal avoiding the hot-press step, and incorporating nanoscale structures in metals having twin boundaries and low-angle grain boundaries architectures. The basic methodology is to deposit the metal (copper) to fill the porous space via pulse-electro-plating technique[175, 176]. In order to fulfill this goal, the conductive scaffold made of nickel-rendered micro platelets will be utilized. Depending on the fact that the introduction of interfaces in nanostructured metals leads to improved strength, hardness and ductility, the properties of the composite can be improved correspondingly due to the enhanced mortar section [177]. In the future, the composite suitable for different applications can be designed by changing the angles between the orientation of ceramic platelets and the twin boundary (Figure 6.1.).

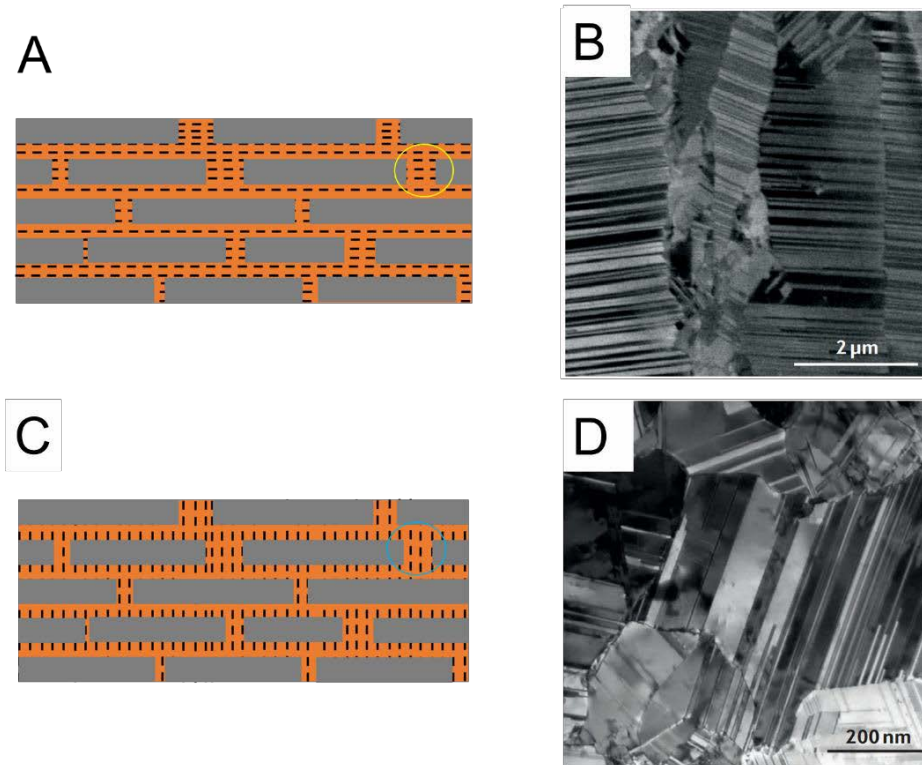


Figure 6.1. Copper matrix platelets reinforced composite. The black dash line indicates the twin-boundary in copper. **(A)** twin boundaries in horizontal direction, **(B)** SEM image of high density

of horizontal twin boundaries in columnar grains[178], **(C)** the direction of twin boundaries perpendicular to platelets, **(D)**TEM image of as-deposited sample with edge-on twin-boundaries which means the direction of TBs is normal to the substrate[179].

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BIOGRAPHICAL SKETCH

Zhe Xu was born in Jinan, China. Zhe entered the University of Jinan, China in 2007, he earned his bachelor's degree with a major in mechanical engineering and its automation in 2011. In August 2012, he left China and enrolled as a master student in The University of Dallas at Texas, Richardson, Texas. After studying two years at UTD, he received his master's degree with a major in mechanical engineering in May 2014. During the following three years, he was employed as a teaching/research assistant working for Dr. Majid Minary at Nano-bio lab at UTD.

CURRICULUM VITAE

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EDUCATION

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Thesis: *Nano/Micro Mechanical Characterization of Bacterial Biofilm*

B.S. in Mechanical Manufacturing and its Automation Sep 2007-May 2011

University of Jinan, Jinan, China

RESEARCH EXPERIENCE

Graduate Research Assistant Sep 2014-May 2017

Department of Mechanical Engineering, UTD Dallas, US

Bio-inspired Multifunctional Ceramic Platelet-Reinforced Piezoelectric Polymer Composite

- Fabricated polymer-matrix ceramic-reinforced composite by spin-coating
- Characterized the multifunctional composite using Instron test, AFM, PFM, FTIR, DSC, TGA, UV-Vis

- Composite interface (cross-section) study by Focus-ion beam and SEM

Evolution of Electromechanical and Morphological Properties of Piezoelectric Thin Films

- Fabricated thin film by spin-coating, conducted and analyzed all experimental data
- Characterized morphological properties using polarized FTIR, 2D WAXD
- Characterized electromechanical properties using piezo-response force microscopy

Assemble Nacre-Inspired Ceramic-Reinforced Metal (Nickel) Composite via Electro-less Deposition (on-going project)

- Designed the set-up, magnetic-assisted alignment device, to assemble the composite
- Created chemical recipes and procedures to coat micro ceramic platelets with Nickel
- Measured fracture toughness of composite with in situ SEM mechanical testing device
- Indentation-post analysis using in situ Nano-flip (Nano-indentation), FIB, TEM

Research Volunteer

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Sep 2012-May 2014

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RESEARCH SKILLS

Microstructural Characterization

- Scanning electron microscopy
- Atomic force microscopy
- Piezo-response force microscopy
- Focus ion beam
- X-ray diffraction
- Nano-indentation/ *in situ* Nano flip
- Fourier transform infrared spectroscopy
- Raman spectroscopy
- Differential scanning calorimetry
- Thermo-gravimetric analysis
- Instron/ *in situ* mechanical measurement
- Ultra-violet visible spectroscopy

Microfabrication

- Spin-coating
- E-beam evaporation
- Freeze casting
- Atomic layer deposition
- Electro-spinning
- Electro-less plating
- Electro plating
- Magnetic-assisted casting

Engineering and Programming Software

- Ansys
- Solidworks

- Abaqus
- Matlab
- AutoCAD

TEACHING EXPERIENCES

The University of Texas at Dallas, Dallas-TX

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|---|-------------|
| - Teaching assistant - Advanced Solid Mechanics | Fall 2016 |
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PROFESSIONAL MEMBERSHIP

- The American Society of Mechanical Engineers

CONFERENCE PRESENTATION

- **Zhe Xu**, Mahmoud Baniyadi, Majid Minary-Jolandan , “Bio-Inspired Ceramic-Platelet Reinforced Polymer Composite”, 2015 ASME IMECE conference, Houston, TX, November 17th, 2015.

PUBLICATIONS

1. **Zhe Xu**, Jiacheng Huang, Majid Minary-Jolandan. “Bioinspired Brick-and-Mortar Ceramic-Metal Composite Fabricated by Electro-less Plating and Spark Plasma Sintering”, in preparation
2. Enlong Yang, **Zhe Xu**, Lucas K Chur, Ali Behroozfar, Mahmoud Baniyadi, Salvador Moreno, Jiacheng Huang, Jules Gilligan, and Majid Minary-Jolandan. “Nanofibrous Smart Fabrics from Twisted Yarns of Electrospun Piezo Polymer”, *ACS Applied Materials & Interfaces*, submitted
3. Mahmoud Baniyadi, **Zhe Xu**, Jizhe Cai, Seyed Soheil Daryadel, Manuel Quevedo, Mohammad Naraghi, Majid Minary-Holandan. “Correlation of Annealing Temperature, Morphology, and Electro-Mechanical Properties of Electrospun Piezoelectric Nanofibers”, *Nanoscale*, submitted

4. Tingge Xu, Huiyang Luo, **Zhe Xu**, Zhenxing Hu, Majid Minary-Jolandan, Samit Roy, Hongbing Lu. "Evaluation of the effect of thermal oxidation and moisture on the interfacial shear strength of unidirectional IM7/BMI composite by fiber push-in nanoindentation", *Experimental Mechanics*, submitted
5. Jiacheng Huang, **Zhe Xu**, Moreno Salvador, Seyed Reza Morsali, Zhong Zhou, Mahmoud Baniyadi, Dong Qian, and Majid Minary-Jolandan. "Lamellar Ceramic-Semicrystalline Piezo Polymer Composite Fabricated by Freeze Casting", *Advanced Engineering Material*, in press
6. Mahmoud Baniyadi, **Zhe Xu**, Salvador Moreno, Seyed Soheil Daryadel, Sneha Chawla, Jizhe Cai, Mohammad Naraghi, and Majid Minary-Jolandan. "Effect of Thermomechanical Post-Processing on Chain Orientation and Crystallinity of P(VDF-TrFE) Electrospun Nanofiber", *Polymer*, in press
7. **Zhe Xu**, Julia Bykova, Mahmoud Baniyadi, Salvador Morenor, Zhong Zhou, Nandita Das, Sasaank Bandi, Yang Xi, Dong Qian, Ray H. Baughman and Majid Minary-Jolandan. "Bioinspired Multifunctional Ceramic Platelet-Reinforced Piezoelectric Polymer Composite", *Advanced Engineering Material* (2016) , doi:10.1002/adem.201600570
8. **Zhe Xu**, Mahmoud Baniyadi, Salvador Moreno, Jizhe Cai, Mohammad Naraghi and Majid Minary-Jolandan. " Evolution of Electromechanical and Morphological Properties of Piezoelectric Thin Films with Thermomechanical Processing ", *Polymer* (2016), doi:10.1016/j.polymer.2016.10.055
9. Mahmoud Baniyadi, Jiacheng Huang, **Zhe Xu**, Salvador Moreno, Xi Yang, Jason Chang, Manuel Angel Quevedo-Lopez, Mohammad Naraghi, and Majid Minary-Jolandan. "High-performance coils and yarns of polymeric piezoelectric nanofibers." *ACS applied materials & interfaces* 7, no. 9 (2015): 5358-5366.
10. Mahmoud Baniyadi, **Zhe Xu**, Seokjin Hong, Mohammad Naraghi, and Majid Minary-Jolandan. "Thermo-electromechanical Behavior of Piezoelectric Nanofibers." *ACS applied materials & interfaces* 8, no. 4 (2016): 2540-2551.
11. Yang Xi, Lidia El Bouanani, **Zhe Xu**, Manuel A. Quevedo-Lopez, and Majid Minary-Jolandan. "Solution-based Ag-doped ZnSe thin films with tunable electrical and optical properties." *Journal of Materials Chemistry C* 3, no. 38 (2015): 9781-9788.

12. Tingge Xu, Yingjie Du, Huiyang Luo, G-H. Kim, **Zhe Xu**, Majid Minary-Jolandan, Les Stark, Terry Baughn, and Hongbing Lu. "Measurement of Temperature-Dependent Young's Modulus at a Strain Rate for a Molding Compound by Nanoindentation." *Experimental Mechanics* (2016): 1-13.
13. Mahmoud Baniyadi, **Zhe Xu**, Leah Gandee, Yingjie Du, Hongbing Lu, Philippe Zimmern, and Majid Minary-Jolandan. "Nanoindentation of *Pseudomonas aeruginosa* bacterial biofilm using atomic force microscopy." *Materials Research Express* 1, no. 4 (2014): 045411.