



# Enhancement of the ferroelectricity of poly(vinylidene fluoride)/multiwalled carbon nanotube composite scaffolds and its effect on the cellular metabolic activity



Jun Young Lim <sup>a,1</sup>, Sook Young Park <sup>b,1</sup>, Soonjong Kwak <sup>c</sup>, Hyun Jeong Kim <sup>b,\*\*</sup>,  
Yongsok Seo <sup>a,\*</sup>

<sup>a</sup> RIAM, Department of Materials Science and Engineering, College of Engineering, Seoul National University, Kwanakro 1, Kwanakgu, Seoul, 151-744, Republic of Korea

<sup>b</sup> Department of Dental Anesthesiology and Dental Research Institute, School of Dentistry, Seoul National University, Daehakro 101, Jongrogu, Seoul, 110-768, Republic of Korea

<sup>c</sup> Polymer Hybrid Research Center, Korea Institute of Science & Technology, P.O.Box 131, Cheongryang, Seoul, 136-791, Republic of Korea

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## ABSTRACT

The highly polar surfaces having a strong effect on the cellular growth are desirable for the preparation of effective scaffolds. Here, we demonstrate that poly(vinylidene fluoride) (PVDF)/multiwalled carbon nanotube (MWCNT) composite films having a very high  $\beta$ -phase that shows the ferroelectric properties are quite effective for cell growth of RT4-D6P2T cells (Schwannoma cell line of rats), U87-MG (glioblastoma cell line of human) and SH-SY5Y (neuroblastoma cell line of human) cells. The contents of polar  $\beta$ -phase in the nanocomposite films could be finely tuned by the variation of MWCNT amount. The cell growth behavior of the three types of cells was congruent with the amount of the polar  $\beta$ -phase. Addition of 0.5 wt% MWCNT could generate 10% more  $\beta$ -phase in the composite, but show 250% more cell proliferation rates for all three cells than neat PVDF film after 7 days of incubation. *In vitro* tests revealed synergy effects of scaffold's stiffness and ferroelectricity on the cellular activity with the amount of MWCNT in the composite film.

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## 1. Introduction

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer with typical crystallinity of 50% which has molecular structure of  $(-\text{CH}_2\text{CF}_2-)_n$ . It has various unique properties such as piezo-, pyro-, and ferroelectric properties besides its other useful properties [1]. Those unique properties come from distinct crystallite polymorphs of PVDF. The most common crystalline form of PVDF is the  $\alpha$ -phase, which has a monoclinic unit cell of TGT $\bar{G}$  conformation (T = trans, G = gauche +,  $\bar{G}$  = gauche -) [2,3]. It is known that the unit cell of the  $\alpha$ -PVDF lattice consists of two chains in a TGT $\bar{G}$  conformation, whose dipole components normal to the chain axis are antiparallel, thus neutralizing each other [4,5]. Hence, the  $\alpha$ -phase is non-polar,

non-piezoelectric, non-pyroelectric. The polymorph of the piezoelectric property is the  $\beta$ -phase having all-trans (TTTT) conformation, with an orthorhombic unit cell. Its unit cell consists of two all-trans chains packed with their dipoles pointing in the same direction [5]. The  $\gamma$ -phase has a TTTGTT $\bar{G}$  chain conformation with orthorhombic unit cell, also showing piezoelectric properties. The other two polymorphs ( $\delta$  and  $\epsilon$ ) are known to be the polar and antipolar analogues of the  $\alpha$  and  $\gamma$  forms, respectively [3]. The  $\alpha$ -phase and the  $\beta$ -phase are the most general and important ones among those polymorphs. Since the fluorine atom diameter (0.270 nm) is slightly larger than the space provided by an all-trans carbon chain (0.256 nm), neighboring fluorine atoms have to be overlapped once in all trans conformation [6]. In order to diminish this overlap,  $\text{CF}_2$  groups are tilted to the right and left, relative to their original conformation, of which  $\text{CF}_2$  groups deflection converts the all-trans form ( $\beta$  form) into TGT $\bar{G}$  ( $\alpha$  form) or TTTGTT $\bar{G}$  ( $\gamma$  form). The  $\alpha$ -phase is thus more commonly obtainable than the  $\beta$ -phase from the PVDF melt crystallization. On the other hand, the molecular dipoles in the  $\beta$ -phase are entirely aligned in one

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [dentane@snu.ac.kr](mailto:dentane@snu.ac.kr) (H.J. Kim), [ysseo@snu.ac.kr](mailto:ysseo@snu.ac.kr) (Y. Seo).

<sup>1</sup> These authors contributed equally.

direction, which can generate the largest spontaneous polarization to exhibit strong ferroelectric and piezoelectric properties [1–6].

Because of its ferroelectric and piezoelectric properties and hydrophobic surface property, the PVDF film has been exploited as a biomaterial which can enhance the cellular adhesion and proliferation [7–11]. Rodrigues et al. reported enhanced proliferation, attachment and alkaline phosphatase activity of goat bone marrow cells when they were seeded on  $\beta$ -phase PVDF membranes [7]. Klee et al. studied the effect of PVDF surface modification on the cell attachment and its proliferation [8]. Hydrophobicity of PVDF surface induced better cell attachment and more fibronectin binding to surfaces. Lanceros-Mendez et al. observed that  $\beta$ -phase PVDF was more hydrophobic to enhance cell adhesion and cell numbers [9]. Their results open the variability of cell culture stimulation by the polymer crystalline phase (piezocrystalline  $\beta$ -phase). Young et al. also observed that hydrophobic PVDF with a porous structure was the best substrate for culturing acinar cells among several polymers such as polyvinyl alcohol, chitosan, poly(ethylene-co-vinyl alcohol) [10]. Very recently, Ng et al. investigated the influence of the piezoelectric property of PVDF on the cellular adhesion and proliferation [11]. Their results indicated that  $\beta$ -phase PVDF induced more homogeneous distribution of murine fibroblasts and more significant deposition of fibronectin towards the cell-material interface.

Although previous studies agreed that piezoelectricity plays an important role for cellular activities, it is still poorly understood since the behavior of cells cultured on substrates is highly dependent on other factors too, such as surface chemical composition, wettability, topography, stiffness, viscoelastic properties, electric charge distribution, etc. [12]. More importantly, most previous studies reported that piezoelectricity of the scaffolds helped the cell growth. However, the piezoelectricity of PVDF or PVDF composites does not play any role for the cell growth unless there is an external stimulus of the electric field. In the quiescent condition without a motion, charge generation does not occur at all [1,2]. Ferroelectric materials are piezoelectric, but not necessarily vice versa. Ferroelectricity means a spontaneous polarization of a material that can be reversed by the application of an external electric field [13]. Even when the applied electric field is off, ferroelectric materials demonstrate a nonzero spontaneous polarization. Polarized PVDF is a ferroelectric and thus a piezoelectric material. Since the cell growth is directly affected by the surface polarity of the scaffolds, the correct term in this case should be the surface polarity or ferroelectricity of the composites, but not necessarily piezoelectricity. The main issue to be clarified is the effect of PVDF polymorphism on the cell adhesion and proliferation.

Recently, we demonstrated that the contents of polar  $\beta$ -phase in the PVDF thin film could be precisely controlled by adding a proper amount of carbon nanotubes and applying appropriate processing conditions [1–3]. The most common technique for obtaining polar  $\beta$ -phase of PVDF involves mechanical extension (drawing) and electrical poling because mechanical drawing enables the transition of the original spherulitic structure into a crystal array, in which the molecules are forced into their most extended conformation (polar  $\beta$ -phase) while application of an electric field on both sides of the PVDF electrets (poling) also results in the orientation of the crystallite polar axis along the field direction to make the  $\beta$ -phase [1,2]. Recent additions to techniques for the conversion of  $\alpha$ -phase into the  $\beta$ -phase are the use of blending with nanofillers. One of them tried very recently is the carbon nanotubes (CNTs) [12]. In this study, they have shown that the  $\beta$ -phase content in the PVDF/MWCNT composite could be controlled and the PVDF/MWCNT composites displayed remarkably enhanced piezoelectric properties. In order to elucidate the effect of polymorphism of PVDF on the cell growth and proliferation, several PVDF/MWCNT nanocomposite films were

prepared and used as scaffold materials to regulate a few cells behaviors. The cellular growth activity of PVDF/MWCNT nanocomposite scaffolds show a correlation with the amount of ferroelectricity variation. Difference between the CNT concentrations for the ferroelectricity peak and the proliferation rate peak was ascribed to the additive effects of the scaffolds ferroelectricity and the stiffness.

## 2. Experimental section

### 2.1. Materials

The polymer used in our study was semicrystalline poly(vinylidene fluoride) (Atofina, Kynar761), having a number average molecular weight of  $5.2 \times 10^5$  Da. Multiwalled carbon nanotubes (MWCNTs) (purity, >95%; average diameter, 10–15 nm) was purchased from Hanwha nanotech corp.

### 2.2. Preparation of melt film

We use the same preparation method as we applied before [1,2]. Heat treatment at 400 °C was done for MWCNTs in an oven for 3 h to remove impurities such as amorphous carbon, catalyst metals, and graphite particles. MWCNTs were then put in a concentrated  $H_2SO_4/HNO_3$  (1:3 vol %) solution, and stirred for 48 h. Ultrasonication was applied for 2 h to remove further impurities, and to maximize the number of carboxylic acid groups on the surface of MWCNT with little destruction of the tube walls. Extra acid was removed by filtration through a 0.4  $\mu$ m PVDF porous membrane. The MWCNT slurry was rinsed by distilled water several times, until the pH value of the solution reached 7. The functionalized MWCNT was dispersed in dimethylformamide (DMF) (0.1% w/v) by sonicator for 30 min in an ultrasonic bath. The solution was very stable for a few weeks. PVDF was dissolved in DMF to make a 2% (w/v) solution [2]. The PVDF solution was mixed with the functionalized MWCNT solution in the required proportion to produce different compositions of functionalized MWCNT in PVDF. They were homogenized by sonicator for 30 min, and poured into the distilled water. The precipitate was dried in a vacuum oven at 80 °C for 24 h to remove the residual solvent and water. After drying, it was molded as a film under a hot press at the temperature of 230 °C under nitrogen atmosphere with predetermined dimensions. The films of PVDF with a thickness of 0.15 mm, a length of 50 mm and a width of 35 mm were then mounted in the automatic laboratory stretching device at 80–100 °C and stretched at 1 mm/s strain rate. Poling was done by applying high voltage between both sides of electrodes in a silicon oil bath equipped with a high DC voltage supplies and high voltage amplifier. The films were poled at electric fields of 1.5 MV/cm at 100 °C. The poling time was 30 min.

### 2.3. Analysis of the crystalline structure

Infrared spectra were obtained using ATR-Fourier Transform infrared spectroscopy (FTIR spectrum 65, Perkin Elmer) with an average of 1000 scan in 500–1600  $cm^{-1}$  range. The crystal structures of these samples were also determined using a wide-angle X-ray diffractometer (WAXD, HTK 1200 N High-Temperature XRD, PANalytical) with 40 kV and 100 mA.

### 2.4. Measurement of ferro- and piezoelectric properties

Aluminum electrodes were thermally evaporated onto both surfaces of samples in 10  $\times$  15 mm rectangular area by a vacuum thermal evaporator (MEP5000, SNTec). The metal deposition was

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