

THE EFFECTS OF SINGLE-WALL CARBON NANOTUBES ON THE SHEAR PIEZOELECTRICITY OF BIOPOLYMERS

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ABSTRACT

Shear piezoelectricity was investigated in a series of composites consisting of increased loadings of single-wall carbon nanotubes (SWCNTs) in poly (γ -benzyl-L-glutamate), or PBLG. The effects of the SWCNTs on this material property in PBLG will be discussed. Their influence on the morphology of the polymer (degree of orientation and crystallinity), and electrical and dielectric properties of the composite will be reported.

KEY WORDS: Materials – Piezoelectric, Nanocomposites, Biomaterials

1. INTRODUCTION

Prior to the discovery of piezoelectricity in poly (vinylidene fluoride), or PVDF (1), Eiichi Fukada noticed this electrical phenomenon in certain types of naturally occurring polymers. These materials, such as wood (2), collagen (3), and cellulose (4), are usually chiral, α -helical molecules and exhibit piezoelectricity unlike that observed in PVDF, which requires a high electric field poling treatment to become piezoelectric (1). It has been shown that this biopolymer phenomenon results from the shear-induced internal rotation of the CO-NH bond associated with the asymmetric carbon atoms in the molecule's backbone, giving these polymers intrinsic shear piezoelectricity (5,6). Although chain alignment in these polymers yields a relatively weak piezoelectric response compared to poled polymers and ceramics, this class of biopolymers has the distinct advantage of not requiring poling to become piezoelectric.

While piezoelectric polymers may provide a lightweight and flexible alternative to piezoelectric ceramics, few natural biopolymers are sufficiently robust to endure practical exploitation of their sensing and actuating capabilities (7). In addition to increasing the molecular weight of polymers to enhance their strength and toughness, recent efforts have also been made to incorporate carbon nanotubes into polymers to improve strength and increase electrical conductivity (8,9). However, the impact of carbon nanotubes on polymer piezoelectricity is not well understood at this time. There have been several reports in the literature regarding the

doping of ferroelectric polymers with carbon nanotubes and their impact on piezoelectricity (10-12). One study claimed that a slight increase in the piezoelectric activity of nanotube/PVDF composites resulted from a higher piezoelectric β -phase volume fraction which was facilitated by the presence of the nanotubes (10). Another study which combined nanotubes with a copolymer of PVDF found no change in the piezoelectric coefficient (11). The authors suggested that the increase in Young's Modulus of the composite films due to the addition of carbon nanotubes does improve the inverse piezoelectric, or actuation, effect. Lastly, Kang *et. al.* investigated the consequences of doping a piezoelectric-like polyimide, (β -CN)APB/ODPA, with SWCNTs (12). In their findings, they concluded that interfacial polarization, or the build-up of charge at the nanotube/matrix interface, created dipole moments which enhanced the dipole orientation of the polyimide during the poling treatment. This interfacial effect led to greater polymer dipole alignment, and thus a larger tensile piezoelectric constant.

While effects of nanotube doping on properties of piezoelectric polymers requiring poling have been explored, the effect of these fillers on biopolymer shear piezoelectricity has not been determined. Variables associated with SWCNTs that may influence the shear piezoelectric output from composite films include dispersion level, impediment of dipole rotations, influence on polymer crystallinity, and disruption of the shear-induced internal electric field. This study aims to investigate the piezoelectric behavior of a high molecular weight, nanotube-doped biopolymer (PBLG) and to understand how the interactions of the SWCNTs and biopolymer chains affect the underlying mechanisms of its shear piezoelectricity.

2. MATERIALS

Poly (γ -benzyl-L-glutamate), or PBLG, is a well-known, shear piezoelectric biopolymer that has been studied extensively in the literature (13-17). Its biocompatibility, commercial availability (Sigma Aldrich, 216 kDa), and similarity to many other α -helical biopolymers and polypeptides (18) make it an excellent initial selection for this study. Furthermore, it has been shown that aromatic species which are present on the side chains of PBLG aid in the dispersion of SWCNTs due to dispersion interactions (19,20). The similarity in size and shape of a PBLG helical rod and SWCNT increase the entropy of mixing (21) and lower the Gibbs free energy of mixing. Enhanced compatibility between matrix and filler creates thorough dispersion, enabling the fabrication of high quality polymer/nanotube thin films. Purified SWCNTs made by the High Pressure Carbon Monoxide (HiPCO) synthesis method were purchased from Carbon Nanotechnologies, Inc., and chloroform, used as the solvent, was purchased from Fisher Scientific.

3. EXPERIMENTAL

3.1 Sample Preparation. To fabricate the composite samples, a SWCNT/chloroform blend was pulse-sonicated (5 seconds on, 5 seconds off) for 18 minutes at 12 W and 20 kHz. A low wattage was used for the nanotube solutions to avoid potential SWCNT damage (22). Aliquots of SWCNT/chloroform solutions were added to dry PBLG, and then diluted to 3.5 wt % with the addition to more chloroform. After mechanical stirring overnight to ensure complete dissolution of the polymer, the mixtures underwent a series of sonication treatments. Each sample was pulse-sonicated (5 seconds on, 5 seconds off) for 18 minutes (27 W, 20 kHz), followed by an

hour long bath sonication (70 W, 42 kHz). Six composite samples were made with increased loadings of SWCNTs: 0.005, 0.01, 0.05, 0.075 and 0.15 wt %. While the pristine PBLG solutions did not require sonication to dissolve, they were sonicated by the same procedure as the SWNT/PBLG solutions.

The solutions were cast in film form on a Teflon® substrate in a dry box using a film applicator. Due to the relatively low boiling point of chloroform (61 °C), dry ice was placed inside the dry box to lower the temperature to approximately 10 °C, and a coverglass was placed over the cast solution. Films cast at room temperature and without a coverglass were found to evaporate at a rate sufficient to produce cracks and surface irregularities. After three hours of evaporation in the dry box, the films on the Teflon substrate were placed in a vacuum oven at room temperature for another three hours. The temperature was then increased to 50 °C and vacuum conditions were maintained overnight to ensure complete removal of the solvent. Following the process outlined above, the films were removed from the substrate using a razorblade.

In order to achieve shear piezoelectricity in the PBLG films, post processing was required. When an isotropic polymer film containing chiral α -helical chains is elongated, the symmetry of the system changes from a non-piezoelectric $D_{\infty v}$ to the piezoelectric D_{∞} due to the disappearance of a vertical mirror plane (23). The piezoelectric tensor then mathematically reduces to only two non-zero terms, d_{14} and d_{25} , both of which represent shear piezoelectricity (4,24). In order to achieve localized shear on the polymer backbones, and thus rotate the CO-NH dipole and induce a surface charge, the PBLG composite films were first drawn at 70 °C to 30 % strain, held for 10 minutes, and then cooled to room temperature at constant strain. A gauge length of 25.4 mm and strain rate of 2.54 mm/min were used for all samples. After cutting a rectangular sample at a 45° orientation with respect to the drawing axis, shear was then imposed on the molecules in the sample by a tensile strain in the long axis of the rectangle. The 45°-angled polymer chains try rotating to align their backbone with the tensile direction, and they “slide” against one another causing a shear force to develop between the molecules, which rotates the CO-NH group around the C-N bond. Although the aligned polymer chains do have a random sense of polarity, the shear-induced polarization of each dipole actually creates a charge separation of the same sign regardless of molecular polarity (25).

3.2 Characterization. Since the piezoelectric potential of a material depends to a large degree on its electric and dielectric properties, initial studies were conducted using a Novocontrol Broadband Dielectric Converter and a Solartron Impedance Gain/Phase Analyzer. A silver electrode (~50 to 80 nanometers) was evaporated on both sides of the film for the measurement. A modified Rheovibron was used to evaluate the shear piezoelectric constants. Since PBLG is viscoelastic, the piezoelectric constant is a frequency dependent quantity with real and imaginary components. For this reason, the modified Rheovibron was run over a frequency range of 0.1 to 100 Hz and a temperature range of 25 to 77°C. X-ray Diffraction (θ - θ Bruker XRD system configured with a scintillation detector) was performed to study the degree of crystallinity as a function of nanotube concentration and mechanical alignment.

4. RESULTS AND DISCUSSION

4.1 Electrical properties. Figure 1 shows the real conductivity data as a function of frequency for undrawn PBLG, where the percolation threshold appears to be between 0.075 and 0.15 wt % carbon nanotubes. The samples at or below 0.075 wt % are insulating, with the conductivity exhibiting an approximate power law behavior. Above this doping level, the conductivity is constant at lower frequencies where the DC component of the conductivity dominates the AC component. The SWCNT/PBLG nanocomposite dielectric constants are shown in Figure 2. These results follow a similar percolation trend, with the samples containing lower levels of carbon nanotubes showing a less frequency dependent dielectric constant. For the 0.15 wt % samples, the presence of the carbon nanotubes results in a dramatic increase in the dielectric constant as a function of frequency.

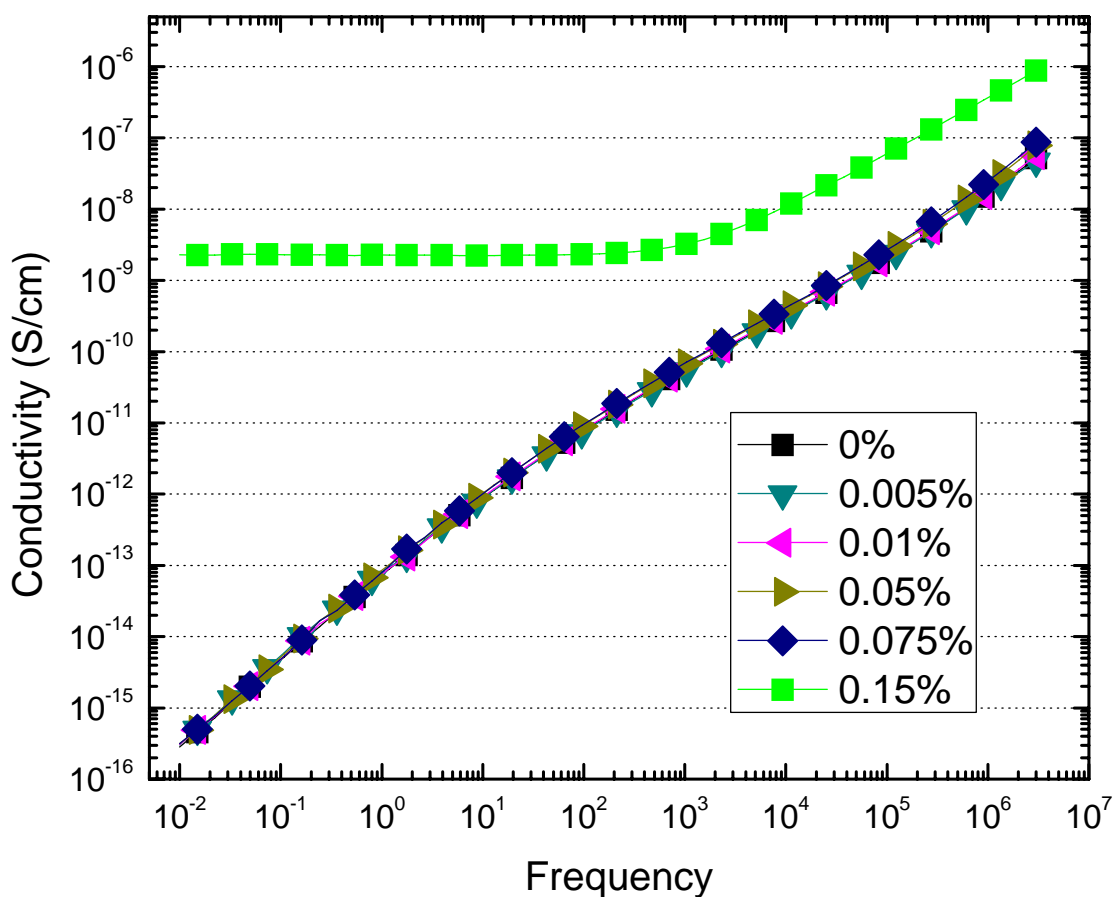


Figure 1. Conductivity of the single-wall carbon nanotube/poly (γ -benzyl-L-glutamate) composites. A clear percolation threshold occurs between 0.075 wt % and 0.15 wt % SWCNT.

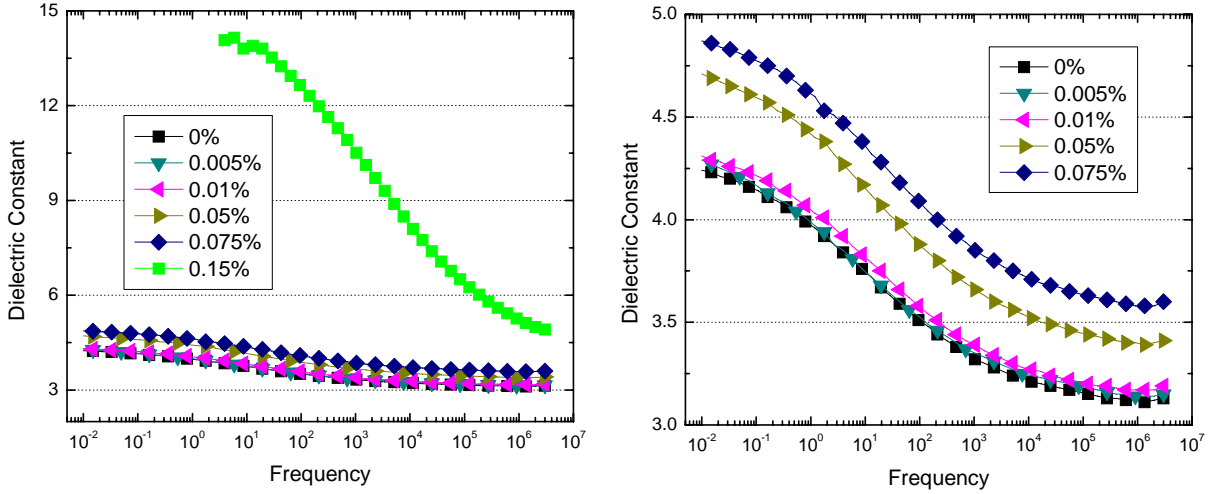


Figure 2. Dielectric constants of the SWCNT/PBLG composites, showing a similar percolation threshold as the conductivity data.

4.2 Shear Piezoelectricity. To verify the shear piezoelectric characteristics of PBLG, four pristine samples were drawn to 30% strain (10% strain/min) at 70°C, held for 10 minutes, and then cooled to room temperature while maintaining a constant strain. Rectangular samples, approximately 7 by 37 millimeters, were cut from each film oriented to the elongation axis at 0°, 45°, 90°, and 135°. The samples were then electroded on both sides, and tested in a modified Rheovibron. Figure 3 shows the orientation dependence of PBLG piezoelectricity, with comparison to an undrawn sample (red line) prepared in a similar fashion. The strain shear piezoelectric constant is expressed as the letter “d”, with the first and second subscripts denoting the polarization and loading directions respectively.

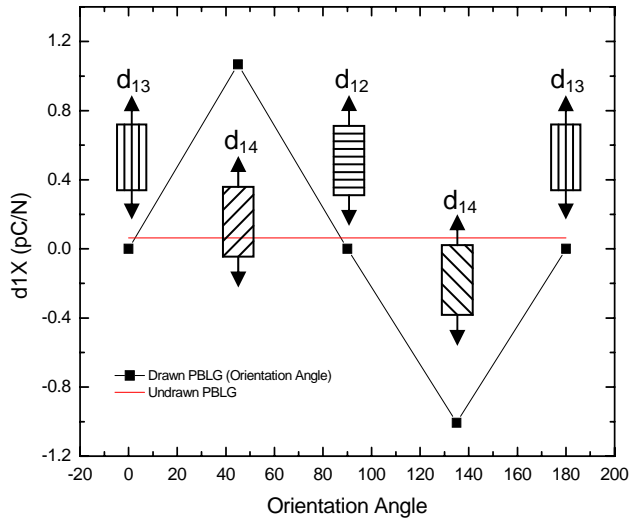


Figure 3. Orientation dependence of the piezoelectric constant of pristine PBLG. Data taken at 77°C and a loading frequency of 20 Hz.

The data suggest that shear piezoelectric behavior is active in these films, with the 45° and 135° samples exhibiting increased piezoelectric constants, in agreement with the literature (15).

The SWCNT/PBLG samples were then drawn in a similar manner (30% strain at 70 °C). The samples were cut out at a 45° angle to the drawing axis, and the full spectrum of samples was analyzed to investigate the effects of carbon nanotubes on the PBLG shear piezoelectric constant. Two samples from each doping level were drawn and tested for shear piezoelectricity. Figure 4 shows the

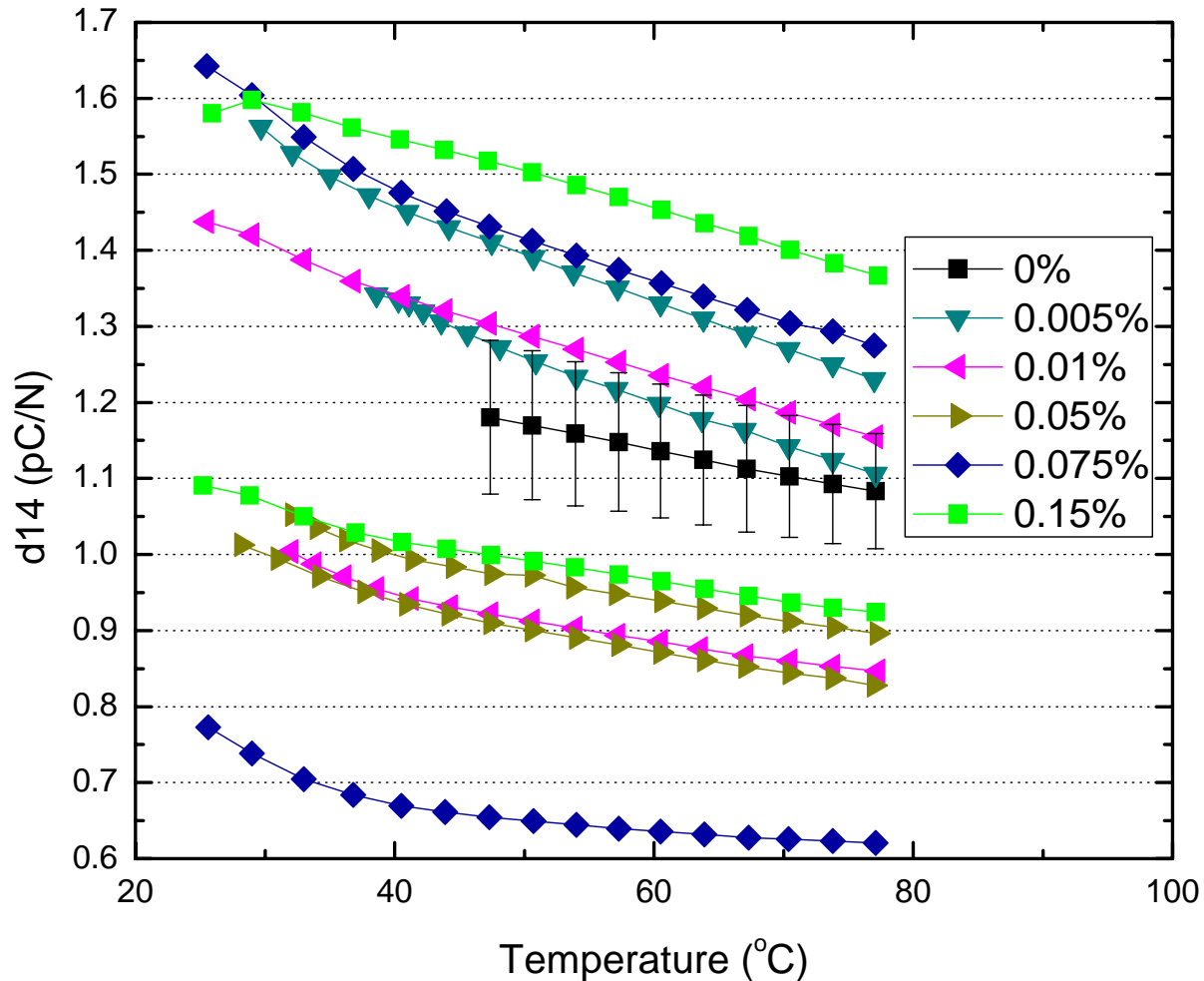


Figure 4. The temperature and SWCNT concentration dependence of the shear piezoelectric constant, d_{14} , of PBLG.

d_{14} values for each sample in the SWCNT/PBLG series as a function of temperature, with the values shown being the second runs and taken at a frequency of 20 Hz. The 0% (black squares) values are the average of six different samples from four different films, and the error bars represent one standard deviation. Shear piezoelectric constants were measured for two samples from each nanotube doping level. The incorporation of carbon nanotubes influences the d_{14} constants, but a clear trend is not evident yet.

4.3 X-ray Diffraction. It has been reported in the literature that the shear piezoelectric constant is proportional to the product of the degree of crystallinity and degree of orientation of the polymer chains (15). Therefore, in order to understand the absence of a trend in shear piezoelectric constants (Figure 4), X-ray diffraction (Cu $K\alpha$ radiation) was performed on the pristine polymer and the 0.075 wt % SWCNT/PBLG samples (drawn and undrawn), as shown in Figure 5. This specific nanotube loading level was chosen due to the wide variation in the shear piezoelectric output for the two samples tested from this film (see Figure 4) to evaluate the piezoelectric response as a function of crystallinity. The % crystallinity can be found by

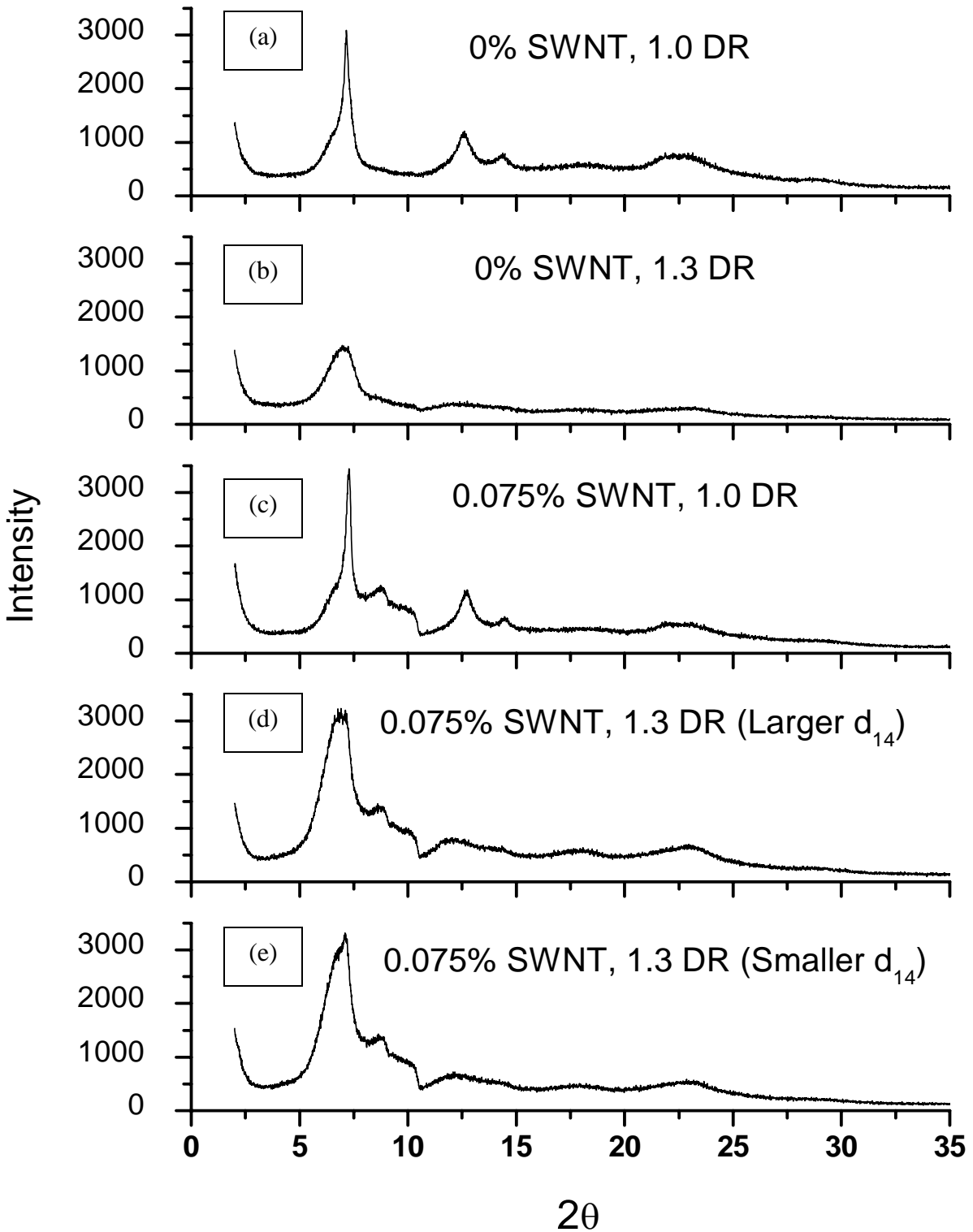


Figure 5. X-ray diffraction patterns (Cu $K\alpha$ radiation) of the drawn and undrawn 0 and 0.075 wt % SWCNT/PBLG films (DR = Draw Ratio). There is a clear reduction in crystallinity with drawing, while the SWCNTs appear to enhance the crystalline characteristics. This is shown by the peak appearing around $2\theta = 8^\circ$ in the composite samples.

examining the ratio of the crystalline peak areas to the total area under the XRD plot (15). The 0.075 wt % sample with the larger shear piezoelectric constant (Figure 5d) exhibits a higher degree of crystallinity based on this method. However, the overall variation in crystallinity does not appear to be significant enough to account for the substantial increase in shear piezoelectricity. Therefore, the degree of orientation, which has not yet been measured and is also proportional to the shear piezoelectricity, should be probed to see if this material property can account for the high standard deviation. Other worthwhile observations from this XRD data include the reduction in crystalline peaks around $2\theta = 12.6^\circ$ and 14.4° for the drawn samples (Figures 5b, d and e), implying a decrease in the % crystallinity and a disruption of the hexagonal packing of the polymer chains (26). The broadening of the main peak around $2\theta = 7.2^\circ$ (d spacing of ~ 1.23 nm) in the drawn composite samples (Figures 5d and e) implies a reduction in crystallite size (27), suggesting the carbon nanotubes act as nucleation sites, creating smaller, but greater number of crystalline zones.

5. CONCLUSIONS AND FUTURE WORK

Single-wall carbon nanotube doped poly (γ -benzyl-L-glutamate) films were made, and their electrical properties and shear piezoelectric behavior were measured. While shear piezoelectric effects have clearly been confirmed in this polymer, the effect of carbon nanotubes on this property has not been fully quantified, owing to large standard deviations for the composite systems. Nevertheless, the data suggests that the SWCNT fillers have an impact on shear piezoelectricity. Additional analysis, including high-resolution XRD, thermally stimulating current (TSC), Fourier transform infrared spectroscopy (FTIR) and polarized Raman spectroscopy, will be performed to probe the SWCNT's effects on polymer morphology and dipole rotations in the α -helical molecule. Acid-treated SWCNTs, with various degrees of electrical conductivity, will be incorporated into several PBLG films at a constant doping level, and the composite films will be tested for shear piezoelectricity. This will determine if the physical presence of the nanotubes, or merely the electrical field that they produce, is the main influence on the shear piezoelectricity.

6. REFERENCES

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