Special Issue Article

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Organic, Flexible, Polymer Composites for High-Temperature Piezoelectric Applications

Abstract: Industrial use of piezoelectric polymers is currently limited by low piezoelectric response and large performance losses at elevated operating temperatures. Leading polymers such as poly(vinylidene fluoride) and poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) possess piezoelectric d_{33} constants around -31 pC/N, and drop rapidly above 100°C operating temperatures. In this work, we fabricate a composite of P(VDF-TrFE) and carbon nanoparticles that possess a d_{33} piezoelectric constant of -40 pC/N at room temperature, 29% higher than pure P(VDF-TrFE). Additionally, the d_{33} value of the composite is 80% higher than the pure polymer at 140°C , with a value of -34 pC/N as compared to -19 pC/N. These materials, which are lead free, nontoxic and solution processable, are composed of Buckminsterfullerene (C_{60}) nanoparticles functionalized with diamine (N–R–N) crosslinking chains composited into a P(VDF-TrFE) polymer matrix. The blended thermoplastic was spin-coated into films and thermally cured to covalently attach the amine-functionalized C_{60} onto polymer backbones to form crosslinking “bridges.” X-ray diffraction spectra confirmed the presence of a crosslinked network, and differential scanning calorimetry thermographs show the

disappearance of the ferroelectric–paraelectric (F–P) transition peak at 106°C , indicating retention of ferroelectricity until the material melts at 152°C . The loss of this transition was confirmed through P–E hysteresis testing at 140°C , where the pure polymer showed paraelectric behavior and the composite remained ferroelectric. In addition, the crosslinked composites showed significant increases in remnant and maximum polarization above the pure polymer. Piezoresponse force microscopy (PFM) was used to measure local piezoelectric and hysteretic effects of crosslinked P(VDF-TrFE)/ C_{60} composites and demonstrated improvement over neat P(VDF-TrFE) samples. These materials show promise toward the design of sensors for extreme environments such as structural sensors, monitoring sensors in automobiles, vibrational sensors for machinery supporting oil, gas, mining and manufacturing operations, and for harvesting human-based or environmental energy.

Keywords: piezoelectric, ferroelectric, P(VDF-TrFE), flexible energy harvesting, high-temperature sensors, Buckminsterfullerene (C_{60})

DOI 10.1515/ehs-2013-0015

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Introduction

The ever-decreasing size and energy consumption of sensors and transmitters have driven recent efforts to enable “self-powered” devices that require no external power for operation. The ability to power small devices through ambient, harnessable energy is leading to a paradigm shift in modern wireless communication in which many objects around us can remain in constant communication. These wireless networks function collectively to both monitor and perform designated tasks without the need for battery replacement or recharging (Erturk and Inman 2011) and are essential to provide real-time feedback for oil, gas, mining and manufacturing operations and within automobiles. Thus, the ability to operate in a range of extreme temperature, pressure and electrical

environments is necessary (Atzori, Iera, and Morabito 2010). Vibrational energy harvesting, primarily driven through piezoelectric materials, is rapidly emerging as a leading technical approach to powering sensors and sensing systems to help bring about the “Internet of Things,” in which everyday devices can communicate among themselves to make society more efficient and more productive (Kortuem et al. 2010; Vermesan et al. 2011).

Piezoelectric materials have noncentrosymmetric point groups that develop net distortion from their equilibrium positions with the application of an electric field or mechanical stress, allowing for the conversion of mechanical stress into electrical charge, known as the “direct” effect, and conversion of electrical fields to mechanical strain, the “converse” effect (Ballato 1995; Jaffe, Cook, and Jaffe 1971; Cady 1964). Pressure sensors, devices for structural measurement and vibrational energy-scavenging devices utilize the direct piezoelectric effect, while the converse piezoelectric effect enables shape control, active vibrational dampening and actuation (Yu, Zhang, and Xie 2009; Auld 1990; Kim, Loh, and Lynch 2008; Anton and Sodano 2007).

While ceramic materials dominate the energy-harvesting market, they are limited in application by their brittleness, toxicity and requisite high driving voltages and forces. Piezoelectric polymers, on the other hand, provide flexibility and processability, allowing integration into small, lightweight devices for applications such as human-based or low-frequency environmental energy harvesting. The piezoelectric response of polymers, however, is generally at least an order of magnitude lower than that of ceramic materials, and polymers are limited to low operating temperatures (Deshmukh, Ounaies, and Krishnamoorti 2009; Janas and Safari 1995).

Since the discovery of piezoelectricity in poly(vinylidene fluoride) (PVDF) by Kawai in 1969 (Kawai 1969). Many new piezoelectric and ferroelectric polymers have been discovered and studied thoroughly (Brown 2000). However, PVDF still remains the most widely used piezoelectric polymer due to its relatively large piezoelectric response and wide commercial availability. PVDF exhibits both a nonpiezoelectric α -phase (trans) and a piezoelectric β -phase (cis), requiring processing such as drawing films $4\text{--}5\times$ in length at elevated temperatures to obtain large β -phase ratios to optimize piezoelectric performance up to -33 pC/N (Mirfakhrai, Madden, and Baughman 2007). While PVDF possesses higher piezoelectricity than most polymer systems, ceramics and single crystals are capable of producing charges an order of magnitude larger (Anton and Sodano 2007).

There have been many efforts to improve the piezoelectricity of polymer systems through the incorporation of fillers. Newnham et al. introduced composites which combined passive polymer matrices with piezoelectric ceramic particles, utilizing both the high piezoelectricity of ceramics and the flexibility of polymers (Newnham, Skinner, and Cross 1978; Ploss et al. 2000; Cui et al. 1997; Venkatragavaraj et al. 2001). Nonpiezoelectric host polymers such as thermosetting epoxies, rubbers and acrylics have been composited with piezoelectric ceramics such as lead titanate (PT), calcium-modified lead titanate (PTCa), lead titanium oxide (PbTiO_3) and lead zirconate titanate (PZT). A number of other groups have since researched the addition of piezoelectric ceramics into piezoelectrically active polymers. Some impressive results have been attained, with Yamada et al. reporting a 50% increase in d_{33} with the incorporation of PZT ceramics into PVDF (Yamada, Ueda, and Kitayama 1982). Recent work by Baur et al. has shown that the piezoelectricity of PVDF can be doubled from -33 to -67 pC/N through the incorporation of carbon nanomaterials (Baur et al. 2012).

Several copolymers of PVDF have been found to possess higher piezoelectric performance and remnant polarization compared to PVDF, along with other advantages such as higher energy conversion efficiency and no postprocessing requirements such as film stretching or annealing (Koga and Ohigashi 1986; Fukada 2000; Furukawa 1989; Yagi, Tatemoto, and Sako 1980; Martins, Lopes, and Lanceros-Mendez 2014). Generally, copolymers of PVDF are composed of alternating monomer structures with the general formula P(VDF-co-R) . Monomer units (R) that are copolymerized in prominent PVDF systems include trifluoroethylene P(VDF-TrFE) , tetrafluoroethylene P(VDF-TeFE) , hexafluoropropylene P(VDF-HFP) and chloride trifluoride ethylene P(VDF-CTFE) .

P(VDF-TrFE) is one of the most widely studied copolymers of PVDF, as it possesses several attractive advantages. The introduction of TrFE at roughly 30 mol% results in preferential crystallization into the piezoelectric β -phase, thus eliminating the drawing requirements of PVDF. The ordered crystallization of P(VDF-TrFE) also enables increased efficiency in converting mechanical to electrical energy, known as the electromechanical coupling factor (k) (Koga and Ohigashi 1986). P(VDF-HFP) exhibits low crystallinity (due to the bulky HPF group) while maintaining high ferroelectric and piezoelectric properties, making it very attractive for applications such as electrolytes for lithium ion batteries (Costa et al. 2012). P(VDF-CTFE) polymer shows extraordinary

electrostrictive properties, shrinking to nearly 5% with the application of an electrical field, making it of great interest for use as actuators such as artificial muscles (Cheng et al. 2008). Low mol% of CTFE in the copolymer backbone under 16% yields a semicrystalline structure while higher amounts produce an amorphous structure (Ameduri 2009).

Dias et al. fabricated composites of varying piezoelectric ceramics and polymers and found PTCa and P(VDF-TrFE) composites to possess d_{33} values of roughly -50 pC/N at optimal levels (Dias and Das-Gupta 1996). Many other groups have explored composites with P(VDF-TrFE) and P(VDF-TeFE) and have achieved elevated piezoelectric performance (Chan, Ng, and Choy 1999; Chan et al. 1998; Dietze and Es-Souni 2008). While there have been many significant advances in increasing the piezoelectricity of polymers to date, natural material limitations such as low operational temperatures still exist in polymeric systems. Specifically, PVDF and its composites begin to lose piezoelectric performance at temperatures around 100°C due to a loss of molecular polarization (Silva et al. 2011).

Polymer systems including amorphous polyimides and polyamides have been reported to withstand high temperatures before losing piezoelectricity (Park et al. 2004). Ounaies et al. extensively explored piezoelectricity in polyimides according to structure, including systems containing nitrile, ether and sulfone dipoles (Ounaies et al. 1999). They found that while polyimide systems can withstand temperatures as high as 250°C , the piezoelectricity is much lower (d_{31} 0.02–0.3 pC/N) than PVDF at room temperature (RT) (Ounaies et al. 1999). Amorphous polyamides such as Nylon 11 have also been reported to possess piezoelectricity stable until 150°C , with d_{31} piezoelectricity in the range of 3–6 pC/N (Mathur and Scheinbeim 1984). Others report cosystems of piezoelectric polymers such as PVDF/polyimide or PVDF/polyamide that are resistant to temperatures up to 150°C , also resulting in lowered piezoelectricity (Gutiérrez et al. 2012). While past research has yielded encouraging results toward increasing the temperature resistance of piezoelectric polymers, to our knowledge, all attempts have resulted in materials with lower piezoelectric responses than PVDF.

Table 1 presents the maximum operational temperatures of several well-studied piezoelectric polymer systems and their piezoelectric d_{31} coefficient. It is apparent that there is a general trade-off between the magnitude and the thermal stability of the piezoelectric coefficients.

In this work, we introduce a new method to increase both the temperature resistance and the piezoelectric

Table 1 Piezoelectric properties of prominent polymers

Polymer system	T_{max} ($^{\circ}\text{C}$)	d_{31} (pC/N)
PVDF (Silva et al. 2011)	100	20
P(VDF-TrFE) (Fukada 1998)	120	30
Vinylidene Cyanide-co-Vinyl Acetate (Fukada 1998)	170	7
Polyurea (Fukada 1998)	200	0.3
Polyimides (Ounaies et al. 1999)	250	10
Polyamides (Mathur and Scheinbeim 1984)	150	~6

coefficient of PVDF-TrFE polymer through the introduction of C_{60} -based, crosslinking particles. Building upon our previous work in which we increased the piezoelectricity of PVDF from -33 to -67 pC/N through the addition of carbon materials, we fabricate high-temperature composites of piezoelectric copolymer P(VDF-TrFE) and functionalized carbon nanoparticles. Specifically, amine-reactive groups are attached to Buckminsterfullerenes (C_{60}) and reacted with P(VDF-TrFE) to crosslink the polymer chains (Kuo, Hwu, and Chang 1997). Crosslinking is widely used for increasing the thermal resistance of polymers by creating a tightly bound three-dimensional network that restricts interchain movement (Jiazhen et al. 1993). Here, the effects of crosslinking on thermal transitions, crystalline structure and size, ferroelectric performance and piezoresponse of P(VDF-TrFE) are investigated. It is found that the crosslinked samples possess increased piezoelectricity at RT, and retain higher piezoelectricity when heated to elevated temperatures.

Experimental procedure

P(VDF-TrFE) (70:30) was purchased from PiezoTech, Héringue, France. C_{60} (99.5% pure) was purchased from NanoC, Westwood, MA. Dimethylacetamide, toluene, hydrochloric acid (HCl) and *N*-tert-butoxycarbonyl-1,6-hexanediamine were purchased from Sigma-Aldrich.

C_{60} functionalization was conducted in a 1 L round-bottom flask; 0.5 g of C_{60} was dissolved in 500 mL of toluene along with 8 g of *N*-tert-butoxycarbonyl-1,6-hexanediamine. The flask was purged with nitrogen and kept at positive pressure throughout the reaction. The solution was refluxed for 48 hours to carry out the reaction, and the remaining toluene was evaporated via rotary evaporator and washed with water, methanol, acetone and ether three times. The particles were then treated with a 1 M HCl/methanol solution for 1 hour. The precipitate was collected, washed and dried at 100°C in vacuo for 48 hours.

The particles were dispersed in dimethylacetamide via ultrasonication (Vertis 115V sonicator) in a vial for 30 minutes, followed by the gradual addition of P(VDF-TrFE) powder. Solutions were typically 5 wt% polymer particle/solvent, and were spin-coated at 300 rpm for 30 seconds using the static addition method to create 50 μm thick films. Films were cured at 80°C on a covered hot plate for 1 hour to remove solvent, and were transferred to an oven for crosslinking. Crosslinking was conducted by heating the spin-coated samples to 140°C and annealing for 1 hour, followed by a gradual cooling to RT. Conditions were chosen based on past results, where it was found that 1 hour of curing at 80°C, followed by 1 hour at 140°C optimized crystallinity and piezoelectricity (Van Son Nguyen et al.); 140°C is also the lowest temperature at which we saw crosslinking in our structures. Three sample compositions were used for this study: pure P(VDF-TrFE), P(VDF-TrFE)/6.5% C_{60} diamine and P(VDF-TrFE)/13% C_{60} diamine.

Differential scanning calorimetry (DSC) thermograms were obtained using a Mettler-Toledo DSC-1. Samples were heated from 25 to 200°C at a heating rate of 5°C/min. X-ray diffraction (XRD) spectra were obtained with a Rigaku Ultima III XRD at a scanning rate of 1 2θ /min from 10 to 40 2θ . Fourier transform infrared attenuated total reflection (FTIR-ATR) analyses of pure C_{60} and the diamine product were obtained via a thermo-Nicolet Magna 550 FTIR series II spectrophotometer with a high-endurance diamond ATR attachment. Polarization vs. Electric field (P-E) hysteresis curves were obtained using a Radiant Technologies' Precision Premier ferroelectric testing device based on the modified Sawyer-Tower technique. Voltages were swept continuously at a frequency of 1 Hz on the samples with a maximum electric field of ± 75 MV/m. Samples were preswept with a pause of 1 ms before measurement. For hysteresis measurements, samples were prepared by spin coating on chrome/gold-coated glass slides. After the crosslinking process, a gold layer of 300 nm was deposited on the surface using an Airco Temescal FC 3200 Cryogenic Evaporator.

An APC Products Inc. model YE2730A wide range d_{33} piezoelectric tester was used to make piezoelectric measurements. Five samples of each composite were tested to ensure statistical relevance, with all relative standard deviations under 5%. Measurements at elevated temperatures were taken by the use of a heated chamber in which a thermocouple and hot gun were used to precisely control temperature. A Bruker Dimension Icon with a conductive diamond-coated silicon cantilever tip (DDESP-FM-10, Bruker) was used to conduct piezoresponse force microscopy (PFM). High-speed PFM was used in

resonance-enhanced mode at an operating frequency of ~ 520 kHz. The deflection sensitivity of the tip was 97.47 nm/V and the AC drive amplitude was 90 V during the DC bias sweep. For the polarization switching test, samples were poled at selected locations on the film surface as a DC tip bias was applied during scanning.

Results and discussion

We present a new synthetic route to functionalize P(VDF-TrFE) with C_{60} structures which are chemically attached to the polymer backbones via diamine crosslinks, as confirmed by FTIR and XRD. The composite was dissolved in organic solvent, spin-coated and thermally annealed. Subsequent solubility tests, peak broadening observed in XRD and disappearance of the F-P transition and reduction in enthalpy of the melt transition in DSC confirmed crosslinking. We measured piezoelectric and ferroelectric performance as a function of C_{60} loading at RT and above the operating limitations of neat P(VDF-TrFE). PFM was used to measure local piezoelectric and hysteretic effects, which shows a strong piezoelectric performance of the C_{60} composites relative to neat P(VDF-TrFE). These results combine to validate a new C_{60} polymer composite as a thermally stable, high-performance piezoelectric material.

Figure 1 shows the synthetic route used to attach diamine functionalities to C_{60} structures and their subsequent reaction with P(VDF-TrFE) to form a crosslinked structure. The diamine attachment is a nucleophilic addition reaction that occurs directly between the fullerene cage structure and the amine end group. One side of the diamine was protected with a tert-butoxycarbonyl group to avoid both functional ends of the diamine attaching to the C_{60} . After the addition reaction, the protective group was removed, creating a primary amine to allow attachment to the P(VDF-TrFE) backbone.

FTIR-ATR spectra for the pure C_{60} and the diamine/ C_{60} adducts are shown in Figure 2 (top left). When comparing the two spectra, there is a clear emergence of a new peak at $1,043\text{ cm}^{-1}$ that can be attributed to a C-N amine stretch. The peak at $1,438\text{ cm}^{-1}$ that is seen in both spectra is a general C_{60} absorbance peak, and the series of peaks between $1,700$ and $2,500\text{ cm}^{-1}$ are due to the anharmonicity of the C_{60} molecule which is largely broken with diamine attachment. The $2,927\text{ cm}^{-1}$ (CH_2) peak is due to the hexanediamine carbons. Both the peak at $1,644\text{ cm}^{-1}$ (amide C=O) and $3,275\text{ cm}^{-1}$ (amide N-H) indicate the introduction of oxygen with the reaction. Elemental analysis via a LECO combustion analyzer revealed that the

Figure 1 Proposed mechanism of C_{60} diamine attachment and subsequent crosslinking reaction

pure C_{60} was above 99.5% carbon, containing less than 0.5% oxygen. After the reaction was carried out, nitrogen constituted 7.17% and oxygen constituted 8.80%. This ratio indicates that on average, each C_{60} molecule has 4.7 diamines attached to its periphery. The elevated oxygen content is presumably due to an incomplete

deprotection of the diamine. The oxygen does not appear to significantly interfere with the crosslinking reaction. Thermogravimetric analysis was used to determine the stability of the C_{60} diamine molecule compared to pure C_{60} (Figure 2 top right). While the pure C_{60} is stable to above 600°C, the diamine begins degradation at roughly

Figure 2 FTIR spectra (top left), thermogravimetric analysis (top right) and XRD (bottom) of pure C_{60} (black) vs. C_{60} /diamine (gray) molecules

175°C, with a 5% weight loss by 250°C. This earlier degradation is a further indication that the reaction occurred and that the diamine attachments are more susceptible to degradation than the fullerene cages. The large angle XRD spectral patterns of both pure C₆₀ and C₆₀ diamine are given in Figure 2 (bottom). The numbers above the peaks in the C₆₀ spectrum are the reflection indices in both the face-centered cubic and hexagonal close packed (in parenthesis) lattices. The pattern matches that reported in literature very well (Ginzburg et al. 2005). The C₆₀ diamine shows no peaks due to packing. The only peak that appears is a broad “halo” effect from 5 to 10 2θ that is indicative of an amorphous material. The amorphous nature of the C₆₀ diamine is due to the side chains preventing an efficient packing structure.

Composites were spin-coated and annealed at varying temperatures according to Table 2. The films were then submerged in dimethylacetamide for 1 hour to determine if crosslinking occurred.

C₆₀ diamine concentrations of 0, 3.25, 6.5 and 13 wt% were tested: above this concentration the solution is saturated and significant particle settling occurs. While the 3.25

wt% composite showed no ability to crosslink, 6.5 and 13 wt% crosslinked at a temperature of 140°C; 120°C was not sufficient to crosslink any sample, while 180°C appeared to only partially crosslink the 13 wt% composite.

Figure 3 shows the XRD patterns of the crosslinked P(VDF-TrFE)/C₆₀ diamine composites at 6.5 and 13 wt% vs. pure polymer fabricated under identical conditions. The dominant peak near 19.5 2θ is characteristic of the piezoelectric β-phase of the polymer (Ohigashi, Omote, and Gomyo 1995). The nonpiezoelectric α-phase would appear at 18 2θ if present. The absence of this peak shows that there is no disruption of the β-phase with the addition of particles (Choi et al. 2000). The relative intensity drops more than 20% between the pure and 6.5 wt% C₆₀ diamine samples, and more than 30% between the 6.5 and 13 wt% samples. This loss of intensity is characteristic of a lower crystallinity. In addition, the full-width half-maximum values of the curves narrow with an increasing concentration of C₆₀ diamine. According to Scherrer equation [1], crystallite size is inversely proportional to the width of the XRD peak; thus, the increasingly narrow peaks indicate a higher degree of crosslinking with increased loading level (Hilczner et al. 2002).

$$B(2\theta) = \frac{K\lambda}{L\cos\theta} \quad [1]$$

where B is the broadening of the peak, K is a Scherrer factor and L is the relative size of the crystallite (Patterson 1939).

The crosslinking trends in the XRD data are supported by DSC testing. Figure 4 shows the DSC curves of pure P(VDF-TrFE) vs. the P(VDF-TrFE)/C₆₀ diamine composites treated under identical crosslinking conditions. The cross-linked samples show a much smaller melting enthalpic peak than their pure polymer counterpart due to both a partial crosslinking. Crystallinity is also lowered from 37% (pure P(VDF-TrFE)) to 30% (P(VDF-TrFE)/C₆₀ diamine at 13 wt%) as calculated from the melting enthalpies and the

Table 2 Results of crosslinking procedure

P(VDF-TrFE)/C ₆₀ Diamine X wt%	Annealing temperature (°C)		
	120	150	180
X = 0	Soluble	Soluble	Soluble
X = 3.25	Soluble	Soluble	Soluble
X = 6.5	Soluble	Insoluble	Soluble
X = 13	Soluble	Insoluble	Semisoluble

Figure 3 XRD spectra of composites: pure P(VDF-TrFE) (solid line), P(VDF-TrFE)/6.5 wt% C₆₀ (dashed line) and P(VDF-TrFE)/13 wt% C₆₀ (dotted line)

Figure 4 DSC heating curves of composites: pure P(VDF-TrFE) (solid line), P(VDF-TrFE)/6.5 wt% C₆₀ (dashed line) and P(VDF-TrFE)/13 wt% C₆₀ (dotted line)

heat of fusion of 100% crystalline P(VDF-TrFE). The pure sample shows a well-defined peak at 106°C due to the transition between the ferroelectric and paraelectric crystalline phases, known as the F-P transition temperature. With the addition of C₆₀ diamine this peak nearly completely disappears, showing only a very small recession. This can be due to either the absence of ferroelectric β -phase in the samples or the stabilization of the β -phase due to internal crosslinking. Since XRD shows a completely β -phase structure, the disappearance of the Curie temperature can only be from crosslinked stabilization. The elimination of the F-P transition is significant because it indicates that the ferroelectric phase is retained until the material melts above 150°C, an increase of nearly 45°C from the neat P(VDF-TrFE) samples. As the loss of ferroelectricity is the limiting factor in regard to temperature, an increase in the F-P transition directly translates to an increase in the operational temperature.

Figure 5 displays a P-E hysteresis loop of the three materials at 0.1 Hz and RT. It is clear that the addition of the C₆₀ diamine facilitates both a higher remnant polarization (P_r) and a higher maximum polarization (P_{max}). This is consistent with past research reporting that C₆₀ extends and intensifies local electric fields while under an external field, and can enable a more complete polarization in ferroelectric polymer composites (Baur et al. 2012; Ullah et al. 2010).

It is interesting to note, however, that the coercive field (E_c) of the two crosslinked samples increases compared to the neat polymer. The coercive field is a measure of the resistance of the composites to being depolarized after saturation. This value is significant as it can be an

indication of the long-term ferroelectric stability of a material. One possible explanation for this is that a larger poling field is required to align the dipoles in the cross-linked structures because of the stability and immobility of an extended crosslinked network. The maximum P_r achieved (shown in Table 3) was in the P(VDF-TrFE)/13 wt% C₆₀ samples, and was 3.73 $\mu\text{C}/\text{cm}^2$.

In order to validate the ferroelectric stability of the crosslinked composites at elevated temperatures, hysteresis testing was performed at 140°C, well above the F-P transition temperature of 106°C for pure P(VDF-TrFE) (Bune et al. 1998). Shown in Figure 6, the pure and crosslinked samples exhibited drastically different hysteresis profiles. As expected, the pure P(VDF-TrFE) sample shows a P-E hysteresis characteristic of a paraelectric capacitor when characterized above the transition temperature. There is virtually no remnant polarization, and the polarization vs. electric field slope is linear until saturation begins to occur, when there is a slight reduction in the P-E slope, resulting in the well-known “s shape” (Su et al. 2012).

In contrast, the P-E hysteresis of the 13.5 wt% cross-linked sample remained largely unchanged at 140°C,

Table 3 P_r , P_{max} and E_c values of the composites

P(VDF-TrFE)/C ₆₀ Diamine X wt%	(μC/cm ²)		
	P_r	P_{max}	E_c
X = 0	2.64	3.55	3.77
X = 6.5	2.94	3.81	4.79
X = 13	3.73	4.48	4.46

Figure 5 P-E hysteresis loop of samples: pure P(VDF-TrFE) (solid line), P(VDF-TrFE)/6.5 wt% C₆₀ (dashed line) and P(VDF-TrFE)/13 wt% C₆₀ (dotted line)

Figure 6 P-E hysteresis loop at 140°C: pure P(VDF-TrFE) (dotted line), P(VDF-TrFE)/6.5 wt% C₆₀ (solid line)

indicating the retention of the ferroelectric phase. There was, however, a small reduction in maximum polarization (from 4.48 to under $4 \mu\text{C}/\text{cm}^2$) and remnant polarization (from 3.73 to roughly $3 \mu\text{C}/\text{cm}^2$), presumably due to an incomplete crosslinking. The retention of ferroelectric performance at elevated temperatures suggests that internal crosslinking provides significant thermal stability that increases the operational temperature of the composites.

The thermal stability of the piezoelectric composites was validated through the use of a wide range piezoelectric d_{33} tester (Table 4). Samples were first tested at RT, followed by four measurements at increasingly elevated temperatures. A piezoelectric thermal profile of pure P(VDF-TrFE) was first mapped. Consistent with the literature, at RT the polymer exhibited a d_{33} value of 31 pC/N, followed by significant loss, dropping to 19 pC/N when heated to 140°C for 30 minutes.

Table 4 Piezoelectric d_{33} values (pC/N) at increasing temperatures

($^\circ\text{C}$)	RT	50	80	110	140
Pure PVDF-TrFE	31	30	29	24	19
$X = 3.25$	35	34	30	28	25
$X = 6.5$	38	37	35	34	32
$X = 13$	40	39	38	36	34

Through the addition of a small amount (3.25%) of functionalized C_{60} and the introduction of crosslinking into the system, an improvement in d_{33} piezoelectric response to 35 pC/N is achieved. However, due to the lack of crosslinking in the system, piezoelectric performance drops largely at elevated temperatures. Likewise, the addition of 6.5% C_{60} results in a d_{33} value of 38 pC/N, with 13% C_{60} further increasing the value to 40 pC/N. Perhaps more significantly, the introduction of crosslinking into the samples above 3.25% C_{60} directly increases the piezoelectric stability at elevated temperatures. While the d_{33} constant of pure, noncrosslinked P(VDF-TrFE) polymer was reduced 39% when heated to 140°C for 30 minutes, crosslinked samples with 6.5% C_{60} experienced a 21% reduction and samples with 13% C_{60} lost only 15% performance when held at 140°C for 30 minutes.

In order to further understand the ferroelectric and piezoelectric properties of these composites on a microscale, PFM was conducted. PFM is a modification of scanning probe microscopy in which a conductive probing tip is used to scan a sample on a conductive substrate. When a biased alternating current is applied to the probing tip that is in contact with the sample surface, a piezoelectric sample will respond through

either expanding with a parallel field or contracting with an antiparallel field according to the converse piezoelectric effect (Kalinin and Bonnell 2002). This response can be used to map out the piezoelectric amplitude of the sample in millivolts (mV). Likewise this technique can be used to observe the polarization of the composite ferroelectric domains. PFM is a very powerful technique that provides information regarding the voltage required to pole a sample, the dynamics of poling ferroelectric domains and the piezoelectric response on a local level.

To observe the ability to reversibly polarize the ferroelectric phases in the composites, the field-induced polarization transition was explored. When the tip contacts the surface, the local piezoelectric effect appears as the first harmonic component of tip displacement, the phase φ . The φ phase of the piezoresponse provides information of the polarization direction under the tip. For domains normal to the surface pointing downward (c^-), applying a positive tip bias results in a local expansion, with surface oscillations in phase with the tip voltage ($\varphi = 0^\circ$). Likewise, if the domain is pointed upward (c^+) the response will be opposite ($\varphi = 180^\circ$), and the sample will contract.

Figure 7 shows the phase-switching behavior of the samples. When the phases contained in the unpoled

Figure 7 PFM phase testing where a-1, b-1 and c-1 are pure P(VDF-TrFE), P(VDF-TrFE) with 6.5 wt% C_{60} diamine and P(VDF-TrFE) 13 wt% diamine, respectively. The dashed yellow square is a $5 \times 5 \mu\text{m}^2$ region poled at $+180 \text{ V}$ for a-1 and b-2, and -180 V for c-1. Likewise a-2, b-2 and c-2 are the same corresponding samples in which the dashed blue square of $2.5 \times 2.5 \mu\text{m}^2$ has been poled at -180 V for a-1 and b-1 and $+180 \text{ V}$ for c-1. In order to show phase contrast, $\varphi = 0^\circ$ is shown in black and $\varphi = 180^\circ$ in white on a gradual scale

samples are mapped (a-1, b-1, c-1), there appears to be a marbled texture, with no real pattern or phase preference. In order to observe the ability to pole the composites, a square polarization pattern ($5\ \mu\text{m} \times 5\ \mu\text{m}$, yellow box) was generated in the center of the sample by scanning the surface with an applied $\pm 180\ \text{V}$ DC voltage (a-2, b-2, c-2). The enlarged bright/dark contrast of the phase image before and after the application of electric field confirms the polarization switching in these samples. The polarization appears to be widespread, with few areas that are not affected.

Subsequently, the ability to switch the polarization to the opposite phase was observed through poling a smaller $2.5\ \mu\text{m}$ by $2.5\ \mu\text{m}$ square in the center of the initial $5\ \mu\text{m}$ by $5\ \mu\text{m}$ square with an opposite $180\ \text{V}$ DC voltage (blue box) (a-3, b-3, c-3). In doing so, the maximum phase contrast between oppositely poled areas was obtained. The samples were tested at resonant frequency with an AC voltage of $90\ \text{V}$. For all samples there is a very clear domain switching between the two poled boxes. Additionally, all samples show a solid polarization in the effective area, showing few exclusions or broken polarization. The 13 wt % sample (c) was poled in the opposite direction as (a) and (b) because of the nature of the initial samples. While (a) and (b) show an initial polarization toward the $\varphi = 0^\circ$ phase, (c) is dominantly $\varphi = 180^\circ$.

Figure 8 shows the local hysteresis performance of each composite. There is a very clear variation of 180° in the samples with the application of a $\pm 180\ \text{V}$ tip bias. This suggests that the material is highly polarizable and the ferroelectric domains are easily switched completely.

Figure 9 shows the amplitude measurement of the samples. The first row shows the amplitude of the unpoled samples, which possess a very disperse, random

Figure 9 PFM amplitude: (a-1) pure P(VDF-TrFE), (b-1) P(VDF-TrFE) with 6.5 wt% C_{60} diamine and (c-1) P(VDF-TrFE) 13 wt% diamine. The dashed yellow square is a $5 \times 5\ \mu\text{m}^2$ region poled at $+180\ \text{V}$ for a-1 and b-2, and $-180\ \text{V}$ for c-1. Likewise a-2, b-2 and c-2 are the same corresponding samples in which the dashed yellow square of $2.5 \times 2.5\ \mu\text{m}^2$ has been poled at $-180\ \text{V}$ for a-1 and b-1 and $+180\ \text{V}$ for c-1

piezoelectric response with no dipole preference (a-1, b-1, c-1). When a $5 \times 5\ \mu\text{m}^2$ region is poled with $+180\ \text{V}$ (a-2, b-2, c-2), there is an increase in the amplitude. Further, poling a $2.5 \times 2.5\ \mu\text{m}^2$ square with a voltage of $-180\ \text{V}$ in the center of the larger, oppositely poled square results in a switching of the amplitude signal. The amplitude measurements yielded similar evidence of the ability to pole these composites. Both positive and negative poling voltages increased the local piezoelectric response amplitude.

Figure 8 PFM local hysteresis loops: (a) pure P(VDF-TrFE), (b) P(VDF-TrFE) with 6.5 wt% C_{60} diamine and (c) P(VDF-TrFE) 13 wt% diamine

Conclusion

Through the incorporation of diamine-functionalized C₆₀ fullerenes into P(VDF-TrFE) and crosslinking via thermal annealing, a new composite was created that exceeds the piezoelectric properties of pure P(VDF-TrFE) by up to 29% at RT and 79% at 140°C. XRD spectra indicate the enlargement of crystalline β -phase regions, but a slight decrease in crystallinity, indicating crosslinking in the system. The crosslinked material shows little to no F-P transition peak in DSC thermographs, indicating retention of polarization until the melt. P-E hysteresis testing at RT shows that the addition of functional C₆₀ increases both the remnant and maximum polarization, while increasing the coercive field. When hysteresis testing was conducted at 140°C (above the F-P transition of pure polymer), the pure P(VDF-TrFE) sample showed a closed “s shape” loop, while the crosslinked sample clearly retained its ferroelectric characteristics. These novel composites may find application in areas that require flexible and sensitive piezoelectric materials that can withstand elevated temperatures. Future work will involve the study of long-term piezoelectric performance of the composites under high temperature and pressure conditions, along with the ability to control stiffness and resonant frequency with variable crosslink density.

Acknowledgments: We would like to thank the NSF I/UCRC Center for Energy Harvesting Materials & Systems (Grant No. 37155043) and the Robert A. Welch Foundation (Grant AT-0041). Yuan Zhou and Shashank Priya would like to acknowledge funding from the NSF INAMM program. Walter Voit would like to acknowledge funding from the DARPA Young Faculty Award program.

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