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Twin screw extrusion of conductive citrate-based biomaterials

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Highlights

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- *Citric-acid based crosslinked elastomer processed by recirculated extrusion.*

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- *Solvent-free shear dispersion of MWCNT within elastomer matrix induces $K\Omega\text{ cm}^{-1}$ electrical conductivity to extruded composite.*

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- *Results are applicable to emerging 3D printing and electrically-conductive biomaterials.*

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Abstract

The range of processing methods for thermoset bioelastomers is limited due to the insolubility of their highly crosslinked nature. In-line extrusion of biodegradable polyester elastomers and their composites would open new possibilities for high-precision manufacturing (i.e. 3D printing), solvent-free additive dispersion, and adhesion development for future clinical needs. An effective method to extrude elastomeric, conductive composites is demonstrated for the first time with polyoctanediol citrate/sebacate (POCS) as the bioelastomer. The POCS pre-polymer in its liquid form was blended with untreated multiwall carbon nanotubes (MWCNTs) and partially cured to produce the feedstock for twin-screw hot-melt extrusion. MWCNTs were mechanically sheered within the POCS matrix at a processing temperature of 120 °C, which thermocured from a viscoelastic liquid into an extrudable crosslinked composite rubber. Furthermore, the composite was thermally and electrically conductive with swelling and hydrolytic degradation kinetic properties dependent on MWCNT concentration. Extruded composite strings are classified as conductive polymers, with lowest resistivity of 3.5 kΩ.cm measured for POCS-MWCNT-5% in comparison to POCS-MWCNT-1% at 22.7 kΩ.cm. Extruded strings (~2 mm in diameter) exhibit a tensile modulus of 5-7.5 MPa with an extensibility of 40-80%. The processing method lays the framework for rapid formulation development of citrate based biomaterial composites and scale-up production.

Key words: *polyoctanediol citrate/sebacate; carbon nanotubes; elastomer; conductive composite; extrusion.*

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1. Introduction

Tissue engineering employs resorbable, porous polymeric scaffolds that serve as a temporary extra-cellular matrix (ECM) for tissue regeneration. Ideally, tissue regeneration and polymer resorption are kinetically matched, requiring the scaffold to have a level of control over degradation kinetics. Another important design parameter is mechanical profile of the material that matches the target tissue: controllable mechanical moduli and strength are required for load bearing biocompatible materials. Of particular interest are semiconductive composite materials where the fillers (such as carbon nanotubes; CNTs) introduce electrical conductivity in otherwise insulating elastomers [1]. Conductive composites that include CNT fillers have demonstrated potential for nerve and cardiac tissue regeneration, where electric fields and potential transduction is an intrinsic property [2, 3]. Recently discovered voltage-activated adhesives require kohm bulk resistance properties, but these are limited to aqueous environments—hydrophobic biopolymers are insulators [4-7]. Apart from electrical conductivity, the filler concentration influences mechanical properties of biocompatible elastomers, such as citric acid (CA)-based polyesters.

Citric acid (3 -COOH groups molecule) reacts with alkane-diols in catalyst-free polycondensation, producing crosslinked polymer networks with a wide range of viscoelastic states and mechanical moduli (1-16 MPa) depending on the curing conditions [8-10]. CA-based polyesters are the materials of choice for soft tissue engineering, as they are amenable to viscous or elastic states where the melting temperature (T_m) can be tuned for the application [10]. The modulus of newly formed CA composites is strengthened with nanoparticle fillers, such as hydroxyapatite (HA) or zinc oxide (ZnO), which impart additional intrinsic material properties [11-13]. Nanoparticle fillers improve interfacial stress transfer/distribution, optimizing the fracture toughness and Young's modulus at the cost of elongation [14, 15]. As a conductive nanoparticle, single wall (SW) or multiwall (MW) carbon nanotubes (CNTs) [16] possess high flexibility, low mass density, large aspect ratio (>1000), high tensile strength (10's GPa) [17] and conductivity (100 S/m) making them ideal reinforcing fillers for biomaterials to transmit voltage or current [18]. CNT-polymer composites have been made into compliant electrodes for neural sensing/stimulation [19-22] or templates for cardiac and nerve tissue regeneration [23, 24].

Despite the advantages of conductive biopolymers, exploration is limited due to unreproducible and tedious production methods. Solvent casting allows mixing of carbon allotropes with dissolved polymers, but creates heterogenous phases as CNT fillers aggregate

at low shear rates (e.g. during thermoset curing) and has a limited choice of geometries [27-29]. Methods of CNT surface functionalization increase dispersion, but this may mitigate CNT conductivity [25-27] and increase CNT expense. Traces of organic solvents also present a risk of adverse responses [28, 29]. Thus, a method is required that maximizes shear dispersion during thermoset curing, allows a range of profiles, and removes traces of organic solvents—all without the need of additional surface functionalization or surfactants.

Melt blending via twin screw extrusion has the following advantage: solvent free methodology, in-line thermoset processing, fabrication time within minutes, melt recirculation, high shear rates for CNT dispersion, and numerous die geometries. For the first time, we present the one-pot synthesis and extrusion processing of elastomeric composite material based on copolyester polyoctanediol citrate/sebacate (POCS) with dispersed MWCNTs additives. The following hypothesis guides the results herein: POCS partial curing yields viscoelastic polymer precursors with thermoplastic and thermoset properties; the unique combination of material properties allows in situ thermocuring, application based profiling and homogenous CNT dispersion by twin screw extruders.

Figure 1. Schematic presentation of POCS-MWCNT nanocomposite fabrication method.

2. Materials and methods

2.1 Materials

High purity 1, 8-octanediol (OD) (molecular weight = 146.23 g/mol, T_m = 58-61 °C, citric acid (CA) (molecular weight = 192.13 g/mol, T_m = 153 °C), sebacic acid (SA) (molecular weight = 202.24 g/mol, T_m = 131-134.5 °C), 1, 4-dioxane reagents were purchased from Sigma (Singapore). Multi-walled carbon nanotubes (diameter 10-15 nm, length < 10 µm) were purchased from C-nano Technology Ltd.

2.2 Synthesis of POCS prepolymer and processing of POCS-MWCNT feedstock

POCS prepolymer was synthesized based on the previously published protocol [30]. Briefly, OD:CA:SA (2:1:1 molar ratio) were transferred into a 250 mL round bottom flask. The flask was stirred and heated till 160 °C; above CA melting point to obtain homogeneous mixture of three polymer melt. Gradually, the temperature was lowered to 140-150 °C and left for 1 h under constant stirring in nitrogen atmosphere. POCS pre-polymer (20 % (w/w) in 1,4-dioxane) were mixed with MWCNTs (1 %, 2.5 %, 5 % CNT/polymer (w/w)) and rapidly stirred at 50 °C for 2 h followed by sonication for 45 min to homogenise MWCNTs. The

viscous POCS-MWCNT suspension was casted in a Teflon dish and kept at 80 °C for 2 days for solvent evaporation and to be used as feedstock for twin-screw extrusion (Xplore MC5, Xplore Instruments BV, Netherlands). Extrusion feedstocks (neat POCS and POCS-MWNT) were removed from Teflon moulds and cut into 27-64 mm³ nurdles that had been vacuum dried for 24 h at < 10 Torr to remove excess VOC. Dried nurdles (3-5 cm³) were loaded into the hopper at an angular screw velocity of 50 rpm and barrel temperature of 120 °C. After loading, the partial polymer melt was recirculated for 5 min at 120 °C. Extrusion temperature was set to 150 °C for 2 min, before the extruder valve was opened to extrude composite string through 10 mm (L) x 1.5 mm round diameter die.

2.3 Surface morphology with field emission scanning electron microscope (FESEM)

The MWCNTs distribution and surface morphology was analysed with FESEM (JEOL FESEM 6340F). Neat POCS and POCS-MWCNT nanocomposite strings were immersed in liquid nitrogen (-196 °C) for 5 min, removed and snapped into discs (h ~ 2 mm) to obtain cross-section micrographs (pure MWCNTs were directly applied onto carbon tape). The sample disks were adhered onto carbon tape and coated with gold for 10 sec. Samples were analysed under accelerating voltage at 5 kV.

2.4 Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA)

The effect of MWCNTs filler on the thermal properties and thermal degradation profile was analysed with DSC (TA instruments Q10) and TGA (TA instruments Q500). Neat POCS was used as control. For DSC, the samples were first heated from -20 °C to 40 °C at 5°C min⁻¹ to remove thermal history of the processed samples. After initial cooling-heating the samples were scanned from -75 °C to 100 °C at the rate of 10 °C min⁻¹. For TGA, the samples were loaded into platinum pan and heated at the rate of 10 °C/min from room temperature to 500 °C. Glass transition temperatures (T_g), melting points (T_m), recrystallization temperatures (T_c), onsets of degradation (T_d) were calculated using TA Universal analysis software.

2.5 Mechanical tensile test of extruded strings

The mechanical behaviour when subjected to a constant strain rate in tensile direction was analyzed using universal testing machine (UTM; Instron 5567). The Samples with gauge length of 3.5 cm were loaded onto the UTM with 500 N load cell and strained at the rate of 10 mm/min. Elastic moduli were calculated by taking the slope of the curve between 0 – 10 % strain deformation. From the stress-strain curve, the yield point, ultimate tensile strength (stress maxima) and strain of failure were detected from the stress-strain curves.

2.6 Sheet resistance of POCS-MWCNT films

The electrical resistivity was measured through the surface of the flattened composites with a linear four-point-probe (Advanced Instrument Technology cmt-sr2000n). Conductivity of the composite surface was obtained by taking the inverse of resistivity.

2.7 Hydrolytic degradation and swelling of POCS-MWCNT

Extruded samples (1 g) were incubated in 10 mL phosphate buffer saline (PBS) at 37 °C and taken out in time intervals of: 1, 3, 7, 14 and 28 days. The PBS was changed on daily basis to ensure constant pH (7.4). After incubation the samples were dried in vacuum to the constant weight. The weight was recorded and the percentage degradation was calculated. Similarly, the swelling behaviour was assessed by incubating the samples for 0.25, 0.5, 1, 3, 5, 7 and 24 h for using the following equation:

$$\% \text{ Swelling/Degradation} = (M_d - M_0) / M_0 * 100 \quad (1)$$

M_0 is a sample mass prior to degradation and M_d is a sample mass after drying to a constant weight. The percentage swelling of the composite strings was measured by immersing in PBS at 37 °C.

2.8 Statistical Analysis

A one-way ANOVA with *ad-hoc* tuckey test was performed to ascertain significance. A $p < 0.05$ is considered to be statically significant (*).

3. Results

3.1 Twin screw extrusion of POCS-MWCNT composite

Herein, a modified fabrication method is presented where MWCNTs are dispersed in prepolymer and dried/cured for 2 days. Homogenization, thermoset activation, and profile extrusion takes in the final step of twin screw extrusion as displayed in **Fig. 1**. Thermoset activation is triggered through a 120 °C barrel temperature under high shear rates with twin screw extruder in recirculation mode. Rapid thermoset activation is achieved at a 150 °C barrel temperature, that is optimized against apparent viscosity low enough for extrusion out of a 1.5 mm round die. Temperature and time parameters are qualitatively determined through processing force—string are extruded when the processing force reached ~2500 N (the maximum processing force = 5000 N). Exceeding 2500 N created irreproducible extrusion conditions; e.g. vapors smelling of burnt plastic, extrusion spurting or congestion. Extruded string diameters are 2.4 ± 0.1 mm across all formulations with no drawdown forces

present (see **Fig. 2A**)—no significant differences are observed with MWCNT additives. Extrusion efficiency averaged 70 %; 5 g of loaded prepolymer yielded 3.5 g of composite string with losses attributed to coating of barrel and screw surfaces. Extruded composite strings are evaluated for surface morphology (SEM), thermoset curing (DSC), degradation temperature (TGA), Young's modulus/elongation (tensile stress/strain), electrical percolation (4-point probe), and aqueous stability (swelling/degradation in pH 7.4 buffer).

3.2 Surface morphology

MWCNTs are incorporated as received (no surface functionalization) prior to blending with POCS prepolymer. SEM displayed the entangled neat MWCNTs, inherent in high aspect ratio carbon nanotubes as seen in **Fig. 2B**. All the extruded samples result in irregular surfaces on the sidewalls (as seen in **Fig. 2C**). Die sheared strings display shark skin phenomena with micron-sized roughness [31, 32]. Surface irregularities are common for POCS (and similar polyesters) with wrinkled patterns and sub-micron voids after processing [30, 33-35]. The wrinkles at the cross-section (**Fig. 2D**) are expected from viscoelastic instability at high shears [36]. This phenomenon is evident from high-magnification FESEM images. Pure POCS is a semi-crystalline macromolecule that displays uniform surface morphology with sub-micron cracks (**Fig. 2E**), consistent with previously investigations [30]. MWCNT additive increases the surface roughness on the side walls (**Fig. 2C**), however we could not observe any changes in surface morphology over the multiple cross-sections taken from extruded samples. FESEM images showed consistent patterns and representative results are displayed in **Fig. 2F-H**, which is a notable exception from other methods of processing [12, 13, 37, 38].

Fig. 2. POCS-MWCNT nanocomposite samples - shape and morphology: (A) digital photograph of extruded samples (top: pure POCS; bottom: POCS-MWCNT-2.5 %); (B) pure MWCNTs; (B and C) FESEM images of side wall and string cross-section respectively of representative POCS-MWCNT-2.5 % (inset-magnified image of the sample sidewall; bar = 10 μ m). FESEM surface morphology analysis of POCS-MWCNT nanocomposite extruded string cross-sections: (E) pure POCS: (F) POCS-MWCNT-1%: (G) POCS-MWCNT-2.5 %; (H) POCS-MWCNT-5 %.

3.3 Thermal analysis

The influence of extrusion process and MWCNTs loading on the thermal properties of vacuum dried nurdles and extruded strings is assessed with DSC and TGA. Glass transition temperatures (T_g) were below 0 °C, (**Table 1**) confirming the elastomeric nature for all the extruded samples [11, 30]. DSC thermogram data in **Fig. 3A-B** display all composite melting points (T_m) at a few degrees above 37 °C. This is a consequence of higher thermal conductivity—the faster heat distribution requires lower thermal energy for dissociative processes. There was no significant difference in T_m values between raw and extruded samples (**Table 1**). Crystallization temperatures (T_c) increased significantly after extrusion, and is attributed to in-situ extruder crosslinking, shear induced crystallization within the die, or combination thereof. An increase in crosslinked polymer networks caused by melt recirculation requires higher thermal energy to deform into ordered, semi-crystalline morphology. This is consistent with our previously reported results where solvent-casted POCS film demonstrated $T_c = -18$ °C, however, solvent casting method resulted in significantly lower $T_m = 28$ °C of pure POCS [30]. TGA reveals the effects for high temperatures, beyond the T_m . Extruded strings are stable up to 200 °C and slowly began to lose mass, with onset of degradation (T_d) from 253 °C for pure polymer up to 257 °C for the highest concentration of filler (POCS-MWCNT-5 %; **Fig. 3C**). This is expected as MWCNTs raise thermal conductivity, that in turn results in higher thermal stability. Based on the TGA thermograms the material has mass loss in two stages: (1) a slow rate up to 330 °C (0.09 % wt / °C) and (2) rapid rate up to 500°C (0.41 % wt /°C) which is characteristic for all polymer composites produced with thermally stable fillers [39]. Note that the T_d values remained practically unchanged after the extrusion (**Table 1**).

Fig. 3. Thermal analysis of extruded POCS-MWCNT nanocomposites: (A) DSC analysis and detection of melting temperatures (T_m) shift from pure polymer due to the presence of filler (inset shows crystallisation temperatures (T_c)); (B) TGA analysis of pure POCS and POCS-MWCNT compositions (inset shows the shift of onset of degradation temperatures).

Table 1. Summary of thermal properties of neat POCS and POCS-MWCNTs nanocomposites

3.4 Electric conductivity and mechanical properties of extruded composites

Fig. 4A displays stress vs strain profile of composite strings in comparison to pure POCS. The tensile moduli are calculated at strains of less than 5 % and compared in **Fig. 4B**. Only POCS and POCS-MWCNT-5 % have a significant difference in elastic/Young's modulus. An increase in elastic modulus with the presence of nanoparticles is expected due to the higher crosslinking density [12, 13]. There was no significant increase in ultimate tensile strength, but yield stress increased with an observed lowered plastic elongation yield (compared in **Fig. 4C**). The resistivity values of the neat POCS string is outside the sensitivity range of the 4-point probe ($> 2 \text{ M}\Omega\cdot\text{cm}$). Upon addition on MWCNTs, sheet resistance ranged from (23 to 3.5 Kohm.cm, which puts in the range of conductive polymers or semi conductive materials electrostatic discharge polymers. Sheet conductivity displays an exponential curve (**Fig. 4D; inset**), suggesting sheet conductivity is at the brink of the 'S' percolation curve.

Fig. 4. Mechanical and conductive properties of the neat POCS and POCS-MWCNT extruded nanocomposite strings: (A) representative tensile stress-strain curves; (B) comparative Young's moduli (tensile); (C) ultimate tensile strength and elongation at break of nanocomposite strings in comparison to pure polymer; (D) surface resistivity of the nanocomposite strings (inset shows a conductivity increase due to the presence of MWCNT filler).

3.5 Water interaction: swelling and hydrolytic degradation

POCS-MWCNT composites displayed percentage swelling higher than neat POCS after 24 h (**Fig. 5A**). Similar to our previously reported results on elastomeric composites, there is an obvious hydrolytic cleavage of crosslinks between polymer matrix and the filler [40]. This in turn accelerated composite mass loss after 7 days (**Fig. 5B**) where between days 7 and 14, the weight loss is statistically higher for composite strings when compared to pure POCS. After 28 days, the weight loss of POCS string is 14 % while the composite strings have 20-30 % mass loss, displayed in **Fig. 5B**. Such behaviour is in contrast with increased crosslinking density induced by the presence of filler. Increased Young's modulus (**Fig. 4B**) indicates higher crosslinking density (according to a rubber elasticity theory) and is normally accompanied by slower degradation times and lower swelling ratios [8, 30]. This result could only be a consequence of weak interfacial forces between polymer matrix and the filler.

Fig. 5. Water interaction with POCS-MWCNT extruded nanocomposites over extended periods of time: (A) swelling-in-water behaviour; and (B) in vitro (hydrolytic) biodegradation kinetics.

4. Discussion

POCS was prepared by melt condensation that yields relatively low molecular weight prepolymer (1000-1400 Da, previously measured with MALDI-ToF-MS) with glue-like liquid consistency soluble in dioxane [30]. Upon thermal curing, the prepolymer turns into highly elastic rubber. The prepolymer solution is normally crosslinked at mild temperatures (80 °C) for 7 days to produce elastomeric materials in various forms (coatings, films, porous scaffolds etc.) [8, 34]. Once crosslinked, citrate based elastomers are not soluble in any solvent and therefore the biomaterial processing is limited to simplified methods of solvent casting [10]. In order to make the extrusion of such material possible, we have only partially crosslinked POCS (prepolymer cured for 2 instead of 7 days) that was mixed with MWCNTs and further crosslinked during the extrusion process. Novel method of extrusion of citrate based elastomers (and their composites) presents an alternative that minimizes VOCs, offers production scale-up, and simplifies methods of additive incorporation. The synthesis and processing steps described herein demonstrate an advance that is applicable to the emerging fields of 3D biopolymer printing, electroceutical biomaterials, and high-throughput processing of bioelastomer thermosets [41, 42]. Further engineering optimization of this novel approach (i.e. reduction of processing steps) is recommended for future inline large-scale production.

Our processing method was demonstrated with one of the most difficult additives to disperse; multiwall carbon nanotubes (MWCNTs)—an additive that often requires surfactants or surface functionalization for complete dispersion. These processing aids add expense and erratically alter material properties. The simplified method herein avoids these processing aids by incorporating entangled MWCNTs into the citrate prepolymer, disrupt entangled MWCNTs with sonication, followed by high shearing with simultaneously thermocuring the prepolymer thermoplastic. Continuously rising viscosity and shear rates should break aggregates and prevent further MWCNT flocculation in the polymer melt.

Twin screw extrusion is uniquely suitable for this purpose—twin screw designs have ca. 3 times the output of single screw extruders and more adept for polymers with poor flow properties (e.g. entangled branched polymers) that degrade quickly (e.g. polyesters). The

conjugated, co-rotating screws employed offer superior mixing dynamics vs. single screw extruders or counter-rotating screws. The combination of twin screw, co-rotating dynamics further shear the MWCNTs and allow the prepolymer chains to intercalate under high shear rate ($> 1000 \text{ s}^{-1}$ assuming polymer melts have $\eta_{\text{app}} > 5000 \text{ Pa.s}$) conditions. Recirculation within the twin screw extruder allows parameter optimization between thermocuring and MWCNT dispersion thus influencing extruded material properties. Reversal of MWCNT aggregation is prevented by closing the recirculation loop and rapid extrusion through a die profile. Once extruded, the crosslinking process produces bioelastomers not soluble in ordinary organic solvents, but may be further processed; e.g. 3D printing ribbons, calendaring into thin films, additive nurdle masterbatches, or drawdown orientation.

MWCNTs in the matrix do not appear to influence crystallite growth within POCS, as T_c 's are constant across all formulations after extrusion—thus material properties weren't significantly affected. The limited surface interactions between POCS and MWCNT prevented intrinsic impact modifier attributes which are typically seen in thermoplastics. When polymer melt is pushed through the 1.5 mm round die profile, a large die swell is observed in the final diameter of 2.4 mm. Die swell is characteristic of non-Newtonian shear thinning polymers; polymer chains align in the die, and then relax into random configuration after die exit. Die swell in the composite is attributed solely to the POCS alignment and recovery (vs. MWCNT alignment), as no differences in die swell diameter were observed between neat POCS or MWCNT composites. The temperature drop within the round die is speculated not to transition through the gelation point, which would account for the relatively large die swell observed. Drawdown orientation, optimal die temperature, gradient cooling baths, or combination thereof can tune die swell and allow specific diameters to be achieved from 1.5 - 2.4 mm, which is in the range required for 3D printing ribbons and conductive conduits.

The considerable die swell is speculated to impair the electrical conductivity—the laminar die flow would align the $10 \text{ }\mu\text{m}$ long MWCNTs (lower transverse resistance), but would be disrupted by the orthogonal volume expansion on die exit. Regardless, the surface resistance of $10^3 \text{ }\Omega\text{.cm}$ measured is classified as a semiconductor material or conductive polymer, in regards to electrostatic discharge materials for composites extruded by melt blending processes [43, 44]. Similar resistivity/conductivity trend is observed when different carbon allotropes are used as conductive fillers [45]. To our knowledge, this is the first demonstration of a MWCNT conductive composite of citrate-based biomaterials, although

others have recently made similar composites with MWCNT (no conductivity reported) or reduced graphene oxide under typical solvent processing and in-situ polymerisation methods[46-48]. Zhang et. al demonstrated a maximum conductivity of 10 Ω .cm with MWCNTs in polyester thermoplastics, but it required relatively high loadings of 14 wt % [49]. At similar MWCNT wt %, our results are ca. 5x higher than PLLA thermoplastics, and this is attributed to the POCS extrusion processing. Jang et. al achieved a remarkable 1 Ω .cm with 5 wt % additive, but this required direct surface functionalization of monomer on MWCNT. [50]

There are drawbacks to this method that prevented extrusion only preparation and further optimization is warranted. Attempts to prepare the prepolymer directly in the twin screw extruder chamber didn't yield reproducible results, which was attributed to insufficient recirculation of the low viscosity melt and reagent coatings on the metal surfaces. Removing solvent entirely wasn't achievable, as the MWCNTs don't disperse in prepolymer unless solvent and sonication are present—shear induced twin screw extrusion couldn't disperse the MWCNTs from a dry state. Furthermore, there were some inconsistencies associated with thermal properties (**Fig. 3B**), elastic moduli (**Fig. 4B**) and hydrolytic degradation kinetics (**Fig. 5B**); it was anticipated that the change in measured values will follow the trend of increased MWCNT concentration (1-5 %). This was the most obvious in degradation experiment where the concentration of MWCNT 2.5 % degrades faster than 5 %. At this stage, those inconsistencies could only be speculated to stem from unpredictable interaction between MWCNTs and POCS polymer. Carbon allotropes with oxygen defects may be more suitable, as they offer thermoset crosslinking anchors and might show better consistency in terms of mechanical behaviour and hydrolytic degradation as a function of filler concentration [51]. Better wetting of functionalized carbon fillers with polymer matrix would enable MWCNTs to impart impact modifier properties towards controlled fracture strength and increased elongation. Die geometry and die swell needs further optimization to align MWCNTs, improve electrical conductivity, and tune the output diameter. This will be the focus of our future work.

5. Conclusion

For the first time, citrate based biomaterial is made conductive with MWCNTs via an extrusion based process. The biodegradable and electrically conductive elastomeric composite strings prepared in two step process: 1) mixing MWCNTs with POCS prepolymer and removing solvent; 2) melt blending and thermocuring followed by extrusion into 2.4 mm-

diameter strings. The method described herein introduces a new possibility to manufacture composite bioelastomer in a scalable method with dispersion of difficult carbon allotropes without surfactants or surface functionalization. The straight-forward twin-screw processing method allows extrusion die geometries for translational approaches in the fields of nerve, cardiac, or bone tissue engineering. The electrically conductive materials are suitable for electroceutical implants, production of 3D ribbons, and solvent-free in situ drug depots with their inherent low melting temperatures.

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Fig 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1

	Thermal Properties							
MWCNTs loading (%)	Glass transition temperature (°C)		Melting point (°C)		Crystallization temperature (°C)		Onset of rapid degradation (°C)	
	Before	After	Before	After	Before	After	Before	After
0.0	-32 ± 4	-33 ± 3	42 ± 1	42 ± 1	-6 ± 3	14 ± 2	255 ± 4	254 ± 4
1.0	-31 ± 2	-32 ± 2	40 ± 1	40 ± 1	3 ± 3	13 ± 1	253 ± 5	253 ± 6
2.5	-30 ± 1	-30 ± 1	40 ± 1	41 ± 1	2 ± 4	13 ± 1	257 ± 6	255 ± 7
5.0	-30 ± 2	-20 ± 1	39 ± 1	40 ± 1	5 ± 1	15 ± 1	258 ± 11	258 ± 12