Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry B

Materials for biology and medicine
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Journal of Materials Chemistry B

A conductive stretchable PEDOT-elastomer hybrid with versatile processing and properties

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Herein we describe the use of vapour phase polymerization (VPP) to form an elastomeric conducting hybrid, via the combination of poly(3,4-ethylene dioxythiophene) (PEDOT) and Poly(glycerol sabecate) (PGS). The extent of PGS curing inversly affected the degree of PEDOT penetration in the material. At longer cure times, samples exhibited a negligible strain-resistance relationship. However, by reducing cure times and allowing greater penetration of PEDOT into PGS, more stable properties were observed over repeated deformation. The isolation of the PEDOT towards the surface allowed the use of laser engraving to pattern conducting tracks with ease. Such a benefit points to its potential for uninvolved, rapid manufacture of electrode arrays for biomedical devices or to allow precision cell interaction in tissue engineering.

Electrodes for biomedical applications are constrained by conventional metallic materials, which may elicit high impedances and inflammatory responses. Additionally, the restricted reversible charge-injection capacity of these materials limits their further miniaturisation to improve resolution.[1,2] Advancements in material science now provide an opportunity to overcome this archetypal technology with more biologically suitable alternatives.[1,2]

One material class showing potential in this regard are conducting polymers (CPs), the foremost examples being polyanilines, polypyrroles and polythiophenes. CPs are suited for a number of biological applications, ranging from electrode interfaces to controlled drug delivery devices.[3,4] Furthermore, the ability of CPs to conduct ions allows them to interact directly with biological systems.[1] As such, CPs show great promise as the next generation of electrodes to interface with biological tissues.[5,6] However, the elastic moduli of CPs is still an order of magnitude greater than human tissue.[7,8]

Furthermore, the brittleness CP films severely limits their potential applications within flexible systems.[7]

Blending of polymers is the evident path to overcome such limitations, however modes to achieve this can require complicated procedures or result in wholly integrated materials, which then require expensive photolithography steps if patterning of the conductive regions is desired. Here we investigate vapour phase polymerisation as an uninvolved method for realizing a CP-elastomer hybrid, which contains an elastic, conductive surface region. The localisation of the conductive element towards the surface allows the effortless patterning of conductive tracks via laser engraving. This builds on previous work, using VPP to create CP-polymer blends,[9,10] and examines manipulating the substrate polymer to control the material properties. To demonstrate a proof of principle, the electrical performances of hybrids are measured as synthesised, as well as during and following deformation. For this investigation PGS was chosen as the elastomer substrate due to its promise as a cheap and versatile polymer suitable for a range of biomedical technologies, including tissue engineering and drug delivery.[11] As one of the quintessential CPs, PEDOT is selected as the conductive component within the hybrid material. As well as demonstrating good *in vivo* and *in vitro* biocompatibility,[12] PEDOT has improved long-term thermal and environmental stability compared to other notable CPs.[13,14]

Experimental

PGS pre-polymer was synthesised as previously reported (see ESI for details).[15] The produced pre-polymer was dissolved in tetrahydrofuran and then cast on glass slides. Following THF evaporation under ambient conditions, the PGS was cured under vacuum at 130 °C for either 48, 60 or 72 h. Hybrids fabricated will be designated according to their PGS cure time (i.e. 48h-PGS-PEDOT). The vacuum was released after cooling to room temperature and samples were soaked in water for 24 h and then peeled off the glass slides. PGS substrates were spincoated in oxidant solution and immediately transferred to

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J. Mater. Chem. B, 2015, **00**, 1-3 | **1**

the polymerisation chamber, containing 3,4-Ethylenedioxythiophene monomer, for 60 min at 70 °C.

The surfaces of samples were analysed by optical microscopy. Samples for scanning electron microscopy (SEM) analysis were frozen in liquid nitrogen and fractured to allow for cross-section analyses of PEDOT integration into PGS. SEM and energy-dispersive X-ray analysis (EDX) were performed on gold coated samples using a JOEL 7001F Field Emission Gun Scanning Electron Microscope at 5 and 15 kV, respectively. Resistance measurements were made using a four-point probe. In order to provide a proof of concept in this study, it was tested whether the samples retained conductivity, and if so to what degree, upon stretching. This was achieved by applying a uniaxial strain with a custom-built device (fig. S1) in conjunction with a VMP3 multichannel potentiostat.

Results & Discussion

VPP is typically used for the formation of discrete thin polymer films. The aim of this study was to use this same process to yield an integrative blend of materials. Swelling of the PGS with the butanol based oxidant solution allows the oxidant to penetrate into the elastomer. Subsequent VPP can then convert the absorbed oxidant into a PEDOT network. PEDOT uniquely contains Sulphur atoms as part of its backbone, providing a fingerprint with which to determine the relative depth of PEDOT ingress, via EDX (fig. 1a). While VPP of thin PEDOT films on rigid substrates yields layers of ~250 nm thickness,[16] here we observed PEDOT penetrating several microns into the surface. This disputes the possibility of a thin PEDOT film merely forming upon the surface and indicates that the VPP procedure successfully created the hybrid structure desired. Reducing the PGS cure time allows a deeper level of integration to be achieved with PEDOT. This is visible along the cross-section of the samples (fig. 1b-c), with the 72h-PGS-PEDOT showing a more distinct boundary between the PEDOT rich surface region and the unblended PGS elastomer matrix below. Reducing the cure time has the effect of lowering the crosslink density of the elastomer.[17] It appears that this lets the material to absorb the oxidant solution deeper into its structure, allowing the subsequent VPP to create a more extensive PEDOT network.

UV-vis absorption profiles indicate the formation of conductive
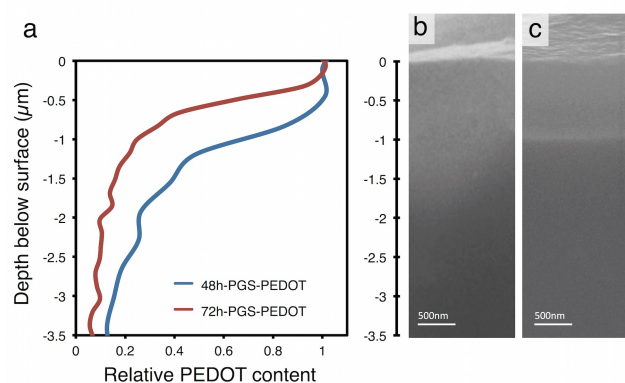

Figure 1. a) Relative PEDOT content (with respect to surface compositions) within PGS-PEDOT surfaces. SEMs of the cross-sections of b) 48-PGS-PEDOT-PGS and c) 72h-PGS-PEDOT-PGS. Lighter regions towards the surface correspond to richer PEDOT compositions Total thickness of films ~0.4 mm.
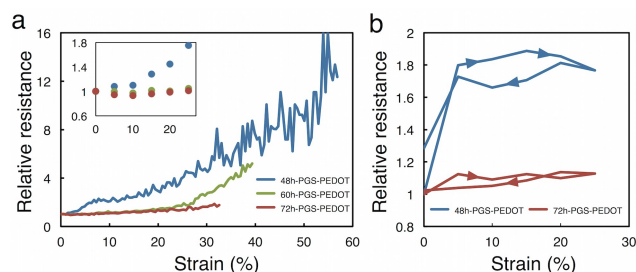

Figure 2. a) Relative change in electrical resistance for typical hybrids when strained continuously till failure. Relative changes upon incremental straining to 25% represented in the insert. b) Relative changes in electrical resistance upon incremental straining to 25% and relaxation to 0% after 50 cycles of deformation

PEDOT,[18,19] with this correlated to the PGS cure time (fig. S2). Here greater unreacted carboxylic acid groups in 48 & 60h-PGS likely hampered the oxidation of PEDOT.[11,15,20]. Surface resistances of the 48, 60 and 72h PGS-PEDOT hybrids are 700, 830, and 2900 Ω/sq, respectively, agreeing with the changes in absorption profiles between the samples.

When stretched to failure, a common trend of increasing resistance is noted across all samples (fig. 2a). However, this is becomes less notable as the PGS cure time is increased, with 72h-PGS-PEDOT only demonstrating marginal increase in resistance.

Differences in the electromechanical behaviour between hybrids is likely due to the respective PEDOT distribution within each sample. For 72h-PGS-PEDOT, PEDOT is concentrated into a smaller depth, increasing contact between PEDOT chains and increasing conductivity. While cracking during straining is more notable (fig. 3b), the neglible increase in resistance suggests current is easily bridged around and beneath these regions of local destruction. With a sparser PEDOT distribution, the composition of 48h-PGS-PEDOT would allow for a greater compromise in properties of the constituent materials. Naturally, the isolation of PEDOT chains lowers conductivity and exposes them to the motion of the surrounding elastomer network. Indeed, it is observed that resistance notably rises during stretching of 48h-PGS-PEDOT (fig. 2a), likely due to the imposed longitudinal strain breaking conduction paths. Due to the kinetics of the crosslinking step in PGS synthesis, the 60h-PGS has a crosslinking density more resembling 72h-PGS than 48h-PGS.[21] As such, one would expect only a modest increase in PEDOT ingress, supporting the marginal change in strain-resistance response observed (fig. 2a).

Following repeated straining to 25% the resistance of relaxed 48h-PGS-PEDOT and 72h-PGS-PEDOT increased 2 and 6-fold,
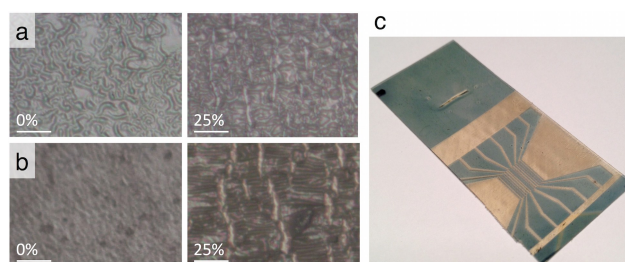

Figure 3. Optical microscope images of a) 48h-PGS-PEDOT and b) 72h-PGS –PEDOT before and during elongation to 25% strain. Scale bar represents 50 μm. c) Image of an electrode array patterned on the PGS-PEDOT composite

respectively (fig. S3). This is likely correlated to the more significant cracking observed for the 72h-PGS-PEDOT. The formation and successive deepening of cracks through repeated straining may eventually result in their penetration across the entire conduction region. Thus magnifying their resistive effects. After this repeated deformation, behaviour during straining also changed notably. At strains above 5%, both 48h-PGS-PEDOT and 72h-PGS-PEDOT showed a relatively constant response, with little hysteresis (Fig. 2b). One conjecture is that the repeated cycling provided a selective pressure of sorts, resulting in only the conductive networks able to accommodate such strain to remain intact. However, while the 72h-PGS exhibited quite a flat profile, the 48h-PGS still highlighted a strain-dependence upon the initial stages of elongation.

An inherent advantage of the proposed hybrid is that, due to the isolation of the conducting PEDOT region towards the surface, a simple laser engraving technique may be applied to create patterned conductive tracks (Fig. 3c). In this fast, non-contact technique, the specific wavelength of the laser is efficiently absorbed by PEDOT, creating rapid heating and ablation of the region.[22] Such a process is quick, cheap and allows a high degree of customisability. In contrast, for other processes used to develop elastic conductive materials, such patterning requires expensive or complicated processes (i.e. photolithography).[10,23] The electrode array demonstrated in this paper is a useful tool in neural or cardiac tissue engineering, allowing researchers to record and stimulate cells *in vitro*, which can strongly influence stem cell differentiation and growth.[24] However, it is difficult to create mediums which provide this functionality, yet are still viable for cell proliferation. It is our hope that the blend of properties in the presented material will resolve this issue, with future work aimed at confirming this hypothesis.

Conclusions

Here we have shown that a flexible, elastic and conducting polymer hybrid can be produced using the relatively straight-forward method of VPP. The distribution of PEDOT within the hybrids, as controlled via their cross-linking densities, was shown to greatly affect their properties. By reducing PGS cure times, deeper oxidant penetration and PEDOT polymerisation led to a stronger strain-resistance relationship. More stable behaviour was found following repeated deformation. The ease of synthesis and post-production of conductive tracks by laser patterning opens the possibility for rapid manufacture of biomedical electrode arrays to facilitate neural and cardiac tissue engineering.[12]

Acknowledgements

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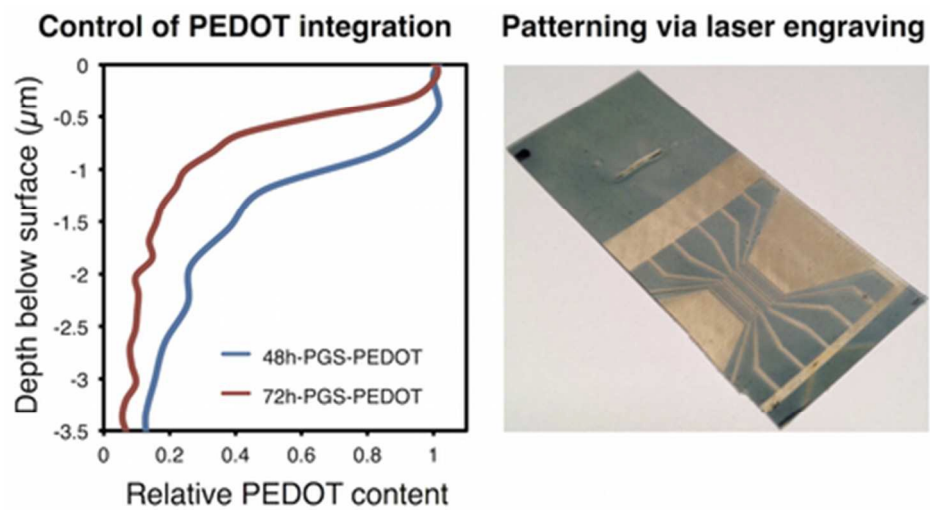
Generation of a hybrid PEDOT-elastomer material which retains conductivity upon stretching and is suitable for laser patterning techniques.
39x21mm (300 x 300 DPI)