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Electrically conducting fibres for e-textiles: An open playground for conjugated polymers and carbon nanomaterials

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ABSTRACT

Conducting fibres and yarns promise to become an essential part of the next generation of wearable electronics that seamlessly integrate electronic function into one of the most versatile and most widely used form of materials: textiles. This review explores the many types of conducting fibres and yarns that can be realised with conjugated polymers and carbon materials, including carbon black, carbon nanotubes and graphene. We discuss how the interplay of materials properties and the chosen processing technique lead to fibres with a wide range of electrical and mechanical properties. Depending on the choice of conjugated polymer, carbon nanotube, graphene, polymer blend, or nanocomposite the electrical conductivity can vary from less than 10^{-3} to more than $10^{3}\ \mathrm{S\,cm^{-1}}$, accompanied by an increase in Young's modulus from 10 s of MPa to 100 s of GPa. Further, we discuss how conducting fibres can be integrated into electronic textiles (e-textiles) through e.g. weaving and knitting. Then, we provide an overview of some of the envisaged functionalities, such as sensing, data processing and storage, as well as energy harvesting e.g. by using the piezoelectric, thermoelectric, triboelectric or photovoltaic effect. Finally, we critically discuss sustainability aspects such as the supply of materials, their toxicity, the embodied energy of fibre and textile production and recyclability, which currently are not adequately considered but must be taken into account to ready carbon based conducting fibres for truly practical e-textile applications.

1. Introduction

Textiles are ubiquitous; we continuously interact with textiles in some form such as garments, bed linen, towels, furniture upholstery. Moreover, medical textiles – including wipes, bandages, wound dressings – as well as textiles used in construction and the automobile industry are an integral part of our everyday lives. One intriguing avenue that promises to greatly expand the ways in which we use and interact with textiles is the integration of electronic functionalities. Such electronic textiles (e-textiles) will be able to connect to the *Internet*

Abbreviations: APS, ammonium peroxydisulfate; AQSA, anthraquinone-2-sulfonic acid sodium salt; BSA, bovine serum albumin; CNT, carbon nanotube; CSA, camphorsulfonic acid; CTAB, hexadecyltrimethylammonium bromide; DBSA, dodecylbenzenesulfonic acid; DCSS, dicyclohexyl sulfosuccinate sodium salt; DWNT, double-walled carbon nanotubes; ECG, electrocardiography; e-textile, electronic textile; FeTos, Iron (III) tosylate; FWNT, few-walled carbon nanotubes; GO, graphene oxide; HBF_4, tetrafluoroboric acid; HI, hydroiodic acid; IL, ionic liquid; LC, liquid crystalline; LCA, life cycle assessment; LED, light emitting diode; MEMS, microelectromechanical systems; MWNT, multi-walled carbon nanotubes; NDS, sodium naphtalene disulfonate; NDSA, 1,5-naphthalenedisulfonic acid tetrahydrate; NSDA, 1,5 Naphthalenedisulfonic acid sodium salt; NW, nano-wires; oCVD, oxidative chemical vapour deposition; OECT, organic electrochemical transistors; OFET, organic field-effect transistor; PA, polyamide; PA 6, polyamide 6; PAc, polyacetylene; PAN, polyacrylonitrile; PANI, polyaniline; PC, polycarbonate; PDMPV, poly(2,5-dimethoxy-*p*-phenylenevinylene); PDMS, polydimethylsiloxane; PE, polyethylene; PEDOT, poly(3,4-ethylenedioxythiophene); PEDOT-S, poly(4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-ylmethoxy)-1-butanesulfonic acid, sodium salt); pEGDMA, poly(ethylene glycol dimethacrylate); PEI, poly(ether imide); PEK, poly (ether ketone); PET, poly(ethylene terephthalate); PLGA, poly(lactic-co-glycolic acid); MEH-PPV, poly(metoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene); PMMA, poly(methyl methacrylate); PP, polypropylene; PPTA, poly(*p*-phenylene terephthalamide); PPV, poly(*p*-phenylenevinylene); PPy, polypyrrole; PSS, poly(styrenesulfonate); PTT, poly(trimethylene terephthalate); PTV, poly(2,5-Thienylene vinylene); PU, polyurethane; PVA, poly(vinyl alcohol); PVDF, poly(vinylidene fluoride); P3AT, poly(3-alkylthiophene); P3DDT, poly(3-dodecylthiophene-2,5-diyl); P3HT, poly(3-hexylthiophene-2,5-diyl); P3OT, poly(3-octylthiophene-2,5-diyl); rGO, reduced graphene oxide; SA, sulfonic acid; SEM, scanning electron microscopy; SIBS, styrene-isobutylene-styrene block copolymer; SWNT, single-walled carbon nanotubes; TEM, transmission electron microscopy; T_g, glass transition temperature; T_m, crystal melting temperature; UHMWPE, ultra-high molecular weight polyethylene

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of Things, i.e. the rapidly growing network of countless tiny devices that surround us. E-textiles will be able to collect, process, store and display information and as such enrich a wide range of application areas from fashion and functional clothing to healthcare and interior design. Textile-based devices have been demonstrated that provide the necessary functionalities: sensors and keyboards collect data [1–6], that are processed by logic circuits [7,8], stored by memory devices [9], and finally relayed by antennas [10] or displays [11]. In addition, to power these devices, energy harvesting textiles are widely explored that utilise the triboelectric [12,13], piezoelectric [14–17], thermoelectric [18–20] or photovoltaic effect [21,22] to turn motion, heat or light into electricity. Moreover, energy storage in the form of textile-based batteries and supercapacitors receives considerable attention [23–26].

One component that is critical as both, a basic building block of many textile-based electronic devices, as well as for interconnections between discrete devices, are fibres and yarns that can conduct electricity (see Sections 2.1 and 2.5 for definitions of fibres and yarns). For instance, a conducting fibre can be used as a *resistor*, two conducting fibres separated by a dielectric medium form a *capacitor*, and two conducting fibres separated by an electrolyte can be used as an electrochemical *transistor* [7,8] (cf. section 4.8). This review will focus on conducting fibres produced from conjugated polymers and/or carbon nanomaterials, and discuss their particular advantages and disadvantages, highlighting areas where further development is necessary. Conducting fibres may consist only of the charge conducting material: (1) conjugated polymers, (2) carbon nanotubes (CNTs), and (3) graphene or graphene oxide (GO). Further, an insulating polymer can be added, leading to fibres made from (4) blends of a conjugated and a matrix polymer, and (5) nanocomposites that comprise a carbon nanomaterial (or carbon black) embedded in a polymer matrix. Alternatively, the conducting material can be applied as (6) a coating to an already existing textile fibre or fabric that acts as a template.

The electrical and mechanical properties of a conducting fibre are dictated by the materials used to produce them, as well as by the method by which they are processed. We have constructed an Ashby plot comparing the electrical conductivity and Young's modulus of different types of fibres and yarns (Fig. 1), and find that across the different types of fibres, the modulus can vary by more than four orders of magnitude, ranging from only 10 s of MPa in case of elastic and therefore pliable fibres, to 100 s of GPa in case of stiff high-modulus fibres. Likewise, the electrical conductivity can vary from poorly conducting fibres with a value of only about 10^{-3} S cm^{-1} (or less if the amount of conducting material is reduced further) to highly conducting fibres that offer more than 10^3 S cm^{-1}. We note that, overall, more conducting fibres also tend to display a higher modulus. This trend arises because both charge transport and the transmission of mechanical force along the long axis of the fibre benefit from alignment of the fibre-forming material (cf. Sections 2 & 3). The most conducting and at the same time stiffest fibres are situated in the top right corner of the Ashby plot shown in Fig. 1: carbon fibres can display values of almost 10^4 S cm^{-1} and 10^3 GPa [27]. Fibres fabricated exclusively of a charge conducting material, i.e. conducting polymers, graphene and in particular CNTs, can offer properties that approach those of carbon fibres, with a conductivity and modulus of more than 10^3 S cm^{-1} and 100 GPa, respectively.

Polymer blends, coated fibres and nanocomposites make up the lower left corner of the conductivity/modulus Ashby plot and appear to be limited by a maximum conductivity of about 10 S cm^{-1}. This is because a large fraction of the fibre is composed of an insulating polymer, either in the form of a matrix or inner core of the fibre, which reduces the amount of charge conducting material. On the other hand, polymer blends allow to disentangle the mechanical and electrical properties of the fibre: the amount and connectivity of the conjugated polymer determines the electrical conductivity. Instead, the mechanical properties depend on the properties of the matrix polymer and can range from about 20 MPa in case of an elastic polyurethane (PU) matrix

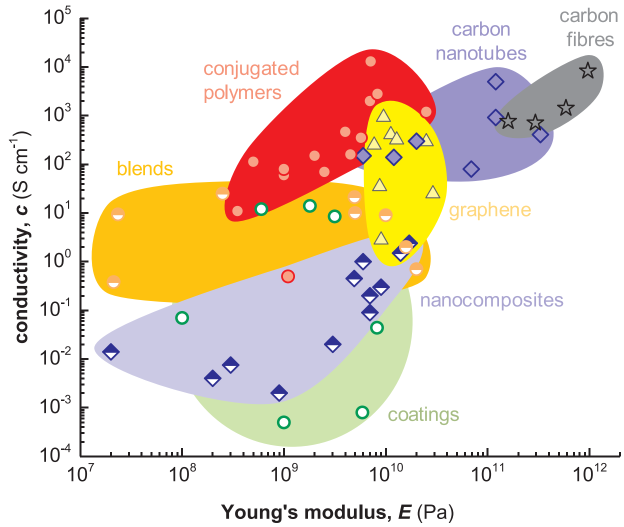

Fig. 1. Ashby plot of the electrical conductivity vs. Young's modulus of fibres based on (grey stars) carbon fibres, (blue diamonds) carbon nanotubes, (yellow triangles) graphene, (red circles) conjugated polymers, (orange/white circles) blends of conjugated and insulating polymers, (blue/white diamonds) nanocomposites of carbon black, carbon nanotubes or graphene embedded in an insulating polymer matrix and (green/white circles) coatings of textile fibres with conjugated polymers, carbon nanotubes or graphene. Data were extracted from the references as indicated in Tables 2–6. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[4], to 20 GPa if ultra-high molecular weight polyethylene (UHMWPE) is used as the matrix [28] (cf. Section 3.2). Fibres that are coated with either conjugated polymers or carbon nanomaterials display a similar behaviour, i.e. the modulus depends on the properties of the fibre core, which carries the mechanical load. In case of nanocomposite fibres where the carbon nanomaterial is instead embedded in a polymer matrix, there exists a trade-off between draw ratio and conductivity (cf. Section 3.4) limiting the effective degree of alignment that can be imparted in the fibre. Still, the reinforcing effect of the nanofillers results in mechanical properties comparable to that of fibres with higher draw ratios.

In addition to suitable electrical and mechanical properties, which can be adjusted with regard to the intended application, fibres need to fulfil a number of other criteria. For instance, fibres must be able to handle the different types of mechanical stresses that arise during both textile production and later during use (cf. Sections 2 and 5). Further, fibres must be able to maintain their functionality in different types of environments, including (1) exposure to ambient atmosphere, which is a challenge if volatile dopants are used to adjust the electrical conductivity, (2) exposure to water during washing and use (sweat, rain, etc.), as well as (3) exposure to other chemical agents (e.g. washing powder). These additional requirements may necessitate compromises with regard to the electrical and mechanical performance, as discussed in more detail in Section 3.

In the next chapter of this review we will first introduce the reader to the most important fundamental aspects of fibre technology covering both structure and function. We recommend that readers skilled in the field skip Section 2 and immediately move on to Section 3, where we introduce the main types of conjugated polymer and/or carbon nanomaterial-based fibres. In Section 4 we then discuss the integration of conducting fibres into e-textiles, as well as some of the envisaged applications. Finally, in Section 5, we provide a critical perspective on the – often neglected – sustainability aspects of conducting fibres and e-textiles.