# Conductive polymer yarns for electronic textiles

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# **Abbreviations**

AMPSA 2-acrylamido-2-methyl-1-propanesulfonic acid

**BPA** benzene phosphoric acid

CNT carbon nanotube

CPY conductive polymer yarn
CSA camphorsulfonic acid
DBSA dodecylbenzenesulfonic acid

DCAA dichloroacetic acid

**DEHS** di-(2-hylhexyl) sulfosuccinate

**DMF** dimethylformamide

**DMPU** N,N'-dimethylpropylene urea

DMSO dimethyl sulfoxide EB emeraldine base ES emeraldine salt

**ICP** intrinsically conductive polymer

LDPE low-density polyethylene
MWNT multiwalled nanotube
NMP N-methyl-2-pyrrolidone

PANI polyaniline PC polycarbonate

**PEDOT:PSS** poly(3,4-ethylenedioxythiophene):polystyrenesulfonate

**PEI** polyethylenimine

**PET** polyethylene terephthalate

**PLA** poly(lactic acid)

**PMMA** poly(methyl methacrylate)

PP polypropylene
PPy polypyrrole
PVA polyvinyl acetate

**SDBS** sodium dodecylbenzenesulfonate

**SWNT** single-walled nanotube

SS stainless steel

TEM transmission electron microscopy WAXD wide-angle X-ray diffraction

#### 2.1 Introduction

Over the past decade, tremendous effort has been put into the development of smart textiles (e-textiles), which generally are fabricated by integrating electrical circuits into traditional textiles to modify their functionalities. Generally speaking, these textiles are defined as "smart" because they have the functions that enable them to directly respond to environmental stimuli, such as mechanical, thermal, chemical, electrical, and magnetic. Potential applications of smart textiles and fabrics may include wearable computing fabrics (Berzowska, 2005; Kim et al., 2009; Marculescu et al., 2003), antistatic garments (Green, 2000; Banks, 2000), electromagnetic shielding garments (Zoran, 1992; Vladimir and Chirkov, 1999), data transfer within textiles (Tao, 2005), thermal or strain sensing for medical and athletic applications (Lorussi et al., 2003; Scilingo et al., 2003; Lorussi et al., 2005), tactile or touching textile sensors (Gorgutsa et al., 2012), and color-tunable textiles for illumination or decoration (Gauvreau et al., 2008; Sayed et al., 2010), to name a few. In order to realize the "smart" functions of a textile, conductive textile yarns or fibers are generally used to interface with other electronic devices integrated into the textile. Many of the conductive yarns used in the current generation of smart textiles are fabricated from metal yarns/fibers made from copper, stainless steel (SS), silver, brass nickel, and their alloys (swicofil, n.d.a). These metallic yarns, though featuring relatively high electrical conductivities, are generally heavier and stiffer than commercial textile yarns based on the polymer materials such as nylon, wool, and cotton. This would not only add weight to the textiles or garments fabricated thereof, but also make the garments physically uncomfortable or even unwearable, thus resulting in inconvenience for daily application. Therefore, a strong motivation has arisen for the development of polymer-based conductive yarns.

In this chapter, we provide an overview of recent progress in the development of conductive polymer yarns (CPYs). Generally, we classify CPYs into two categories: bulk CPYs and surface CPYs. The fabrication and processing techniques of each type of CPYs are reviewed. In addition, we briefly introduce the electrical and mechanical properties of these CPYs and summarize the corresponding advantages and limitations. The rest of this review chapter is organized as follows. In Section 2.2, we begin with a review of bulk CPYs. Particularly, we divide this type of polymer yarn into three subclasses: (1) intrinsically CPYs, (2) polymer yarns twisted/embedded with metallic filaments, and (3) polymer yarns filled with conductive additives such as carbon blacks (CBs), carbon nanotubes (CNTs), or conductive polymers. In Section 2.3, we provide a review of surface CPYs that are the polymer yarns coated with conductive layers. The conductive coatings may consist of metals, conductive polymers, or other conductive materials such as CNTs or CBs. Finally, in Section 2.4, the processing techniques of CPYs are briefly summarized.

#### 2.2 Bulk CPYs

#### 2.2.1 Intrinsically conductive polymer fibers/yarns

Intrinsically conductive polymers (ICPs), also known as conjugated polymers, are organic polymers that can conduct electricity. ICPs have been under intense investigation during the last 50 years; however, fibers or yarns based on the pure ICPs were not reported until the 1980s, because it was believed that ICPs were intractable from a conventional polymer-processing viewpoint (Skotheim and Reynolds, 2006). In fact, the majority of ICPs are nonthermoplastic materials that decompose at a temperature lower than their melting point, such that these ICPs cannot be melt-processed. One, therefore, has to resort to a solution-spinning method for fabrication of ICP fibers/yarns. In this section, we mainly focus on ICP fibers based on polyaniline (PANI) and polypyrrole (PPy), because these two ICPs are readily dissolved in a number of solvents (Skotheim, 1997).

#### 2.2.1.1 Intrinsically conductive PANI fibers/yarns

PANI, though discovered more than a century ago, did not receive intense attention until the mid-1980s, when MacDiarmid et al. found its three basic oxidation states and revealed its electrical conductivity using an acid doping method (Chiang and MacDiarmid, 1986; Huang et al., 1986; Angelopoulos et al., 1988). Particularly, PANI, prepared in the emeraldine oxidation state, is also called emeraldine base (EB), which is most valued among all the PANI oxidation states due to its environmental stability and relatively high conductivity by acidic doping. EB is soluble in a number of organic solvents, such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N'*-dimethylpropylene urea (DMPU), acetic acid, formic acid, and dimethyl sulfoxide, to name a few (Angelopoulos et al., 1988), which indicates the possibility of spinning PANI fibers based on the solution-spinning method.

Scherr et al. (1991) demonstrated that PANI fibers could be spun from 20 wt% EB solutions dissolved in NMP. An NMP/water solution was used as the coagulating agent. The tensile strength of the PANI fibers after stretching 3–4 times their original length was measured to be  $\sim$ 366 MPa, which is almost comparable to that of the commercial polymer fibers such as nylon-6 fibers with a similar diameter. The stretched fibers doped by 1 M HCl had a maximum conductivity of  $\sim$ 170 S/cm. A challenge in the solution-spinning process of EB fibers is that EBs in most of their solutions have a strong propensity to gel quickly when the concentration of the EB exceeds 6 wt% (Tzou and Gregory, 1993, 1995).

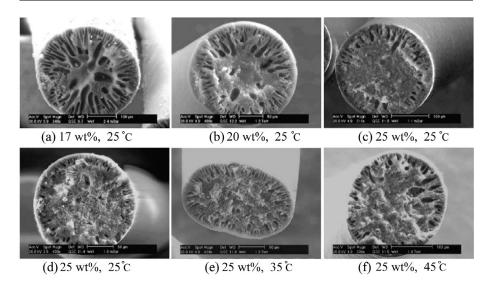
Cohen and Tietz (1992) and Hsu et al. (1993) found that adding certain amines (e.g., pyrrolidine) to the EB/NMP solution or using certain amines as solvents (e.g., 1,4-diaminocyclohexane) can delay the gelation time, thus allowing for the fiber

spinning in a meaningful scale. For example, they experimentally demonstrated that continuous fiber wet-spinning can be performed from an EB/1,4-diaminocyclohexane solution (10–20 wt% EB) (Hsu et al., 1993). The as-spun fibers showed an average tenacity of  $\sim$ 3.9 grams per denier (gpd). (The tensile strength in the yarn and textile industry is usually presented in the unit of gpd. Denier is a unit of linear mass density or fineness of a fiber or filament, which is defined as mass in grams per 9000 m. About 1 denier = 1 g per 9000 m). The conductivity of the as-spun fibers doped with 1 M HCl was up to  $\sim$ 157.8 S/cm.

In addition, Mattes et al. (1997) reported that more than 60 compounds potentially can be used as "gel inhibitors" to EB/NMP solutions. As an example, they added a small amount of a gel inhibitor, pyrrolidine, into EB/NMP solutions. Gelation times of the resultant EB solutions varied from a few hours to even several days, which allow continuous fiber spinning. The as-spun fibers were thermally stretched, with the stretching ratio up to 500%. Young's modulus, tenacity, and density of the as-spun fiber were 0.55 GPa, 0.32 gpd, and 0.52 g/cm³, respectively. The corresponding values of the four-times-stretched fibers were 2.21 GPa, 0.77 gpd, and 0.92 g/cm³, respectively. Apparently, the mechanical properties of fibers were enhanced by the thermal stretching, which led to a better alignment of polymer chains. The breaking elongation of the as-spun and stretched fibers were 9.1% and 6.04%, respectively. The stretched fibers were doped with a variety of organic or inorganic acids in order to increase the conductivity. The conductivity of the stretched fibers doped with benzene phosphoric acid (BPA) was up to ~50 S/cm.

Wang et al. (2000) reported another typical gel inhibitor of EB/NMP solutions, which is a secondary amine, 2-methylaziridine. By adding a small amount of 2-methylaziridine powder into EB/NMP solutions, the gelation time could be prolonged to several days. The as-spun EB fiber had Young's modulus of 0.54 GPa, tensile strength of 15 MPa, and breaking elongation of 9%, while the corresponding values of the four-times-stretched fibers were 1.85 GPa, 60 MPa, and 6%, respectively. Conductivity of the stretched fibers doped with BPA was measured to be 10.3 S/cm. Although 2-methylaziridine acts as an efficient gel inhibitor to EB/NMP solutions, it is a highly toxic material that is inconvenient for operation and maintenance (monographs, n.d.). Note that the concentration of the gel inhibitors in EB solutions should be carefully optimized. A deficient concentration leads to a short gelation time, while an excess concentration would dramatically reduce the mechanical and physical properties of the as-spun fibers (Mattes et al., 1997; Wang et al., 2000).

Moreover, Yang et al. (2001) reported that during the spinning process of the EB/NMP solution, many macrovoids are formed within the as-spun PANI fibers. They found that during the process of the coagulating bath, molecules of the coagulant (water in most cases) could penetrate the as-spun fibers. After a drying process, the water components gradually evaporate, leaving behind a number of macrovoids within the fibers. The presence of macrovoids would decrease the density of the fibers as well as reduce the fiber's mechanical strength (Young's modulus and tenacity) and thus should be minimized. It is suggested that increasing the EB concentration and reducing the temperature of the coagulating bath constitute two effective methods to reduce the volume concentration of microvoids (Yang et al., 2001), as these two



**Figure 2.1** Cross sections of PANI fibers spun with different PANI concentrations and temperatures. (a–c) PANI fibers are wet spun at 25 °C, and the concentrations of PANI in the spinning solutions are 17, 20, and 25 wt%, respectively. (d–f) PANI fibers are wet spun at 25, 35, and 45 °C, respectively, and the concentration of PANI in the spinning solutions is 25 wt%. Figures 4 and 7 from Yang et al. (2001).

methods would diminish the diffusivity of water into the fibers and thus limit the formation of macrovoids (see Figure 2.1).

Jain and Gregory (1995)) studied the solution viscometry of PANI/NMP and PANI/DMPU solutions, respectively, and they revealed that the gelation time of EB/DMPU solutions is much longer than that of EB/NMP solutions. Later, they (Tzou and Gregory, 1995) demonstrated the wet spinning of PANI fibers from 15 wt% EB solution dissolved in DMPU. The as-spun EB fibers had a tenacity of 0.6 gpd, Young's modulus of 27.9 gpd, and breaking elongation of 7.1%. With an acid-doping treatment, the as-spun fibers showed a conductivity of  $\sim$ 32 S/cm, and the four-timesstretched fibers showed a conductivity of  $\sim$ 350 S/cm.

In the previous paragraphs, we reviewed the method for the fabrication of PANI fiber from its "base" form. Thus, this method is generally referred to as the "base-processing method." Note that PANI fibers spun from this method generally require a post acid-doping treatment in order to increase the fiber conductivity. Normally, only acids with small molecules (e.g., HCl) can be used for doping, and, in most cases, the as-spun fibers are so dense that only doping near the fiber surface is achieved (Pomfret et al., 2000).

In addition to the base-processing method, PANI fibers can be spun using an acid-processing method, which potentially allows a uniform distribution of the dopant molecules in PANI fibers, thus resulting in a homogeneous electrical conductivity. The first demonstration of the spinning of PANI fibers based on the acid-processing

method was carried out by Andreatta et al. (1988). In their experiments, the PANI fibers were wet-spun using a solution of emeraldine salt (ES) dissolved in 98% sulfur acid at 60 °C, and cold water was used as the coagulating agent. The conductivity of the as-spun fibers was up to 60 S/cm.

Wang et al. (1995) used the wet-spinning method to fabricated PANI fibers from a PANI/camphorsulfonic-acid (CSA) solution that was prepared by dissolving the mixture of PANI and CSA in *m*-cresol. The as-spun PANI fibers had a tensile strength of 0.2 gpd, breaking elongation of 8.4%, and modulus of 7.3 gpd. The conductivity of the PANI fibers was measured to be ~200 S/cm. Pomfret et al. (2000) discovered a new combination of sulfonic-acid dopant and solvent for wet spinning of PANI, namely, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and dichloroacetic acid (DCAA). A number of coagulating agents were investigated for fiber spinning; three preferred agents were acetone, butyl acetate, and 4-methyl-2-pentanone, which lead to the formation of smoothly cylindrical PANI fibers. The modulus and tensile strength of the as-spun PANI fibers were 40–60 MPa and 20–60 MPa, respectively. The conductivity of the as-spun fibers was 130 S/cm, while the conductivity of the five-times-stretched fibers was up to ~1000 S/cm.

Several research groups (Mottaghitalab et al., 2006; Spinks et al., 2006; Liao et al., 2011) have recently demonstrated that the electrical and mechanical properties of PANI fibers could be reinforced by adding these fibers with CNTs. For example, Mottaghitalab et al. (2006) dispersed CNTs into the PANI/AMPSA/DCA spinning solutions and performed fiber wet spinning based on these composite solutions. Mechanical tests of the as-spun PANI fibers revealed that the addition of CNTs increased the fiber tensile strength from 170 to 255 MPa and the modulus from 3.4 to 7.3 GPa. The conductivity of the CNT-filled fibers was 716 S/cm, a 44% increment compared to the fibers without CNTs.

# 2.2.1.2 Intrinsically conductive PPy fibers/yarns

PPy is an ICP that features better environmental stability and biocompatibility compared to PANI (Skotheim, 1997). The first report (Li et al., 1993) for the production of continuous PPy fibers was given by Li et al. (1993). The fabrication process of PPy fibers was performed in an electrochemical flow cell where polymerization of pyrrole monomers occurred. A single piece of conductive PPy fiber could grow along the flow cell at rates of  $\sim$ 1 cm/h. This extremely low speed is impractical for the production of PPy fibers on a meaningful scale.

Recently, it has been found that PPy incorporated with di-(2-ehylhexyl) sulfosuccinate (DEHS) can be readily dissolved in a number of organic solvents, such as NMP, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and *m*-cresol, which indicates the possibility of the drawing of PPy fibers using the solution-spinning method (Foroughi et al., 2008). Foroughi et al. (2008) reported continuous PPy-fiber fabrication using the solution-spinning technique. In their research, the PPy–DEHS mixture was dissolved in DCAA as the spinning solution, and 40 wt% DMF aqueous solution was used as the coagulating agent. The ultimate tensile strength, modulus, and breaking elongation of the as-spun fibers were 25 MPa, 1.5GPa, and 2%, respectively.

The average conductivity of the as-spun fibers was measured to be  $\sim 3$  S/cm. Later, the same research group (Foroughi et al., 2009, 2010) reported that the electrical and mechanical properties of the as-spun fibers are dependent on the polymerization temperature of PPy. Experimentally, they decreased the polymerization temperature of PPy from 0 to -15 °C and used PPy synthesized thereby for fiber spinning. The tensile strength, Young's modulus, and breaking elongation of the as-spun fibers were increased to 136 MPa, 4.2 GPa, and 5%, respectively. A conductivity of  $\sim 30$  S/cm was obtained after the fiber was thermally stretched.

### 2.2.2 Polymer yarns twisted/embedded with metallic wires

# 2.2.2.1 Hybrid polymer–metal yarns fabricated by traditional spinning techniques

One of the simplest methods of fabricating polymer conductive yarns is to blend metal filaments or wires directly into traditional textile polymer yarns. Such conductive yarns can be readily fabricated by conventional yarn-spinning techniques such as the ring-spinning method or open-end spinning method. Generally speaking, the resistance of metal-wire-blended polymer yarns is relatively low  $(0.2-200~\Omega/m)$ , owing to the high conductivity of metal fibers in the yarns. As shown in Figure 2.2, Suh (textileworld, n.d.) categorized this type of conductive yarn into three subclasses: metal-core yarns, polymer-core yarns, and polymer-metal braided yarns. In Table 2.1, we summarize the hybrid polymer-metal yarns reported so far.

Metal-core yarns adopt a core-sheath structure in which one or more metal fibers constitutes the core wrapped by polymer fibers as the sheath (Figure 2.2a). Generally speaking, metallic wires (e.g., SS wires) are stiff, which makes them difficult to weave or knit directly on conventional weaving looms or knitting machines (Maier et al., 2005). Wrapping metallic wires with a polymer sheath could effectively reduce the friction between the yarn and a textile-weaving loom, which is favorable for textile fabrication. In addition, the polymer sheath could provide the metallic core with effective protection against mechanical abrasion (Byrnes and Haas, 1983; Toon, 1994), thus avoiding loss of yarn conductivity due to routine utilization. On the negative side, the yarns using this structure normally suffer from relatively low extensibility

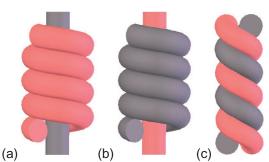


Figure 2.2 Three typical structures of hybrid polymer–metal yarns: (a) metal-core yarns, (b) polymer-core yarns, and (c) polymer–metal braided yarns. (Polymer fibers are shown in red, while metallic fibers are shown in gray.)

Electronic Textiles

Table 2.1 Summary of hybrid polymer-metal yarns

Metal-core yarns						
Core	Diameter	Sheath	Fineness	Twist density	Resistance	Reference
SS	0.08 mm	Cotton	44 tex	661 tpm	60 Ω/m	Patel et al. (2012)
SS	0.05-0.1 mm	KS + SS	50–100 tex	_	_	Cheng et al. (2003)
Copper	0.05 mm	KS + SS	50 tex	_	_	Cheng et al. (2003)
Copper + glass	0.12 mm	PP	930 denier	150 tpm	_	Cheng et al. (2000)
SS	0.1 mm	PP	863.5 denier	140 tpm	_	Cheng et al. (2002)
SS + PA	0.1 mm	PP	983.4 denier	140 tpm	_	Cheng et al. (2002)
Cu + PA	0.08 mm	SS	_	120–200 tpm	_	Chen et al. (2004, 2007)
Cu	0.09–0.1 mm	Cotton	_	_	$\sim$ 4 $\Omega$ /m	Perumalraj et al. (2009)
Cu + polyester	0.024 mm	Polyester	75 denier	400 tpm	_	Inoue et al. (1988)
Polymer-core yarns						
Core	Fineness	Sheath	Diameter	Twist density	Resistance	Reference
PP selvage	5651.1 denier	Cu	0.08 mm	280 tpm	_	Chen et al. (2004)
PP selvage	5651.1 denier	SS	0.08 mm	280 tpm	_	Chen et al. (2004)
Polyester or others	100–1500 denier	Nickel or others	0.002 inch	1–20 tpi	_	Rees (1988)
Polyester	600 denier	SS	35 μm	350 tpm	180 Ω/m	Watson (1999)

Spandex Spandex	44d tex 1880 dtex	Copper or others Copper + PA	20 μm ~50 μm	~1700 tpm 3600 tpm	_ _	Consoli et al. 2004) Maier et al. 2005)
Polymer-metal braided yarns						
Metal	Diameter	Polymer	Fineness	Twist density	Resistance	Reference
SS	8 μm	PP	2.2 dtex	_	$6 \times 10^5$ $\Omega/m$	Safarova and Militky (2012)
SS	_	Nylon	1200 denier	_	_	Gerald (1975)

Denier, dtex, and tex are units of linear mass density or fineness of yarns. 1 denier = 1 gram per 9000 m; 1 dtex = 1 gram per 10,000 m; 1 tex = 1 gram per 1000 m. tpm, twist per meter; tpi, twist per inch.

SS, stainless steel; KS, Kevlar; PA, polyamide; PP, polypropylene. Spandex is a synthetic fiber made of polyurethane-polyurea copolymer.

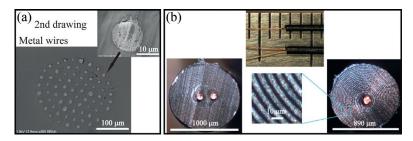
(typically less than 5%) and have virtually no elasticity due to the presence of the metallic core.

Polymer-core yarns have a structure of polymer core consisting of polymer fibers that are wrapped by metallic wires as the sheath (Figure 2.2b). The metallic wires used in the yarns are much longer than the core fiber, which potentially enables these yarns to have longer elongation compared to metal-core yarns. For example, Maier et al. (2005) reported a polymer-core conductive yarn spun by the ring-spinning technique. In the spinning process, a copper wire is first wrapped around a highly elastic polymer thread (Lycra spandex). Then, the yarn is further wrapped by a polyamide-66 multifilament thread to consolidate the whole structure. The resultant yarn showed a breaking elongation of 320%. In addition, following an elongation of 100%, this yarn recovered with a permanent elongation of  $\sim$ 2%, without loss of its electrical conductivity. The disadvantage of polymer-core yarns is that the metal fibers in a yarn are directly exposed to a working environment, thus being subject to rustiness or mechanical abrasion. To prevent this, the polymer-core yarn could use metal fibers that are precoated with a thin plastic layer, or the yarn could be further wrapped by polymer filaments for protection.

Polymer–metal braided yarns can be fabricated by simply twisting a polymer fiber and a metal fiber together (Figure 2.2c). However, only a limited number of yarns based on this structure have been reported, as these yarns generally suffer from poor mechanical extensibility, and the polymer components in these yarns could not provide effective protection to the metal wires. Some staple metal fibers (length: 1-10 cm) that cannot be spun into the other two structures are usually fabricated into braided yarns. For example, Safarova and Militky (2012) reported a polymer–metal braided yarn fabricated by twisting staple polypropylene fibers with staple SS fibers (average length: 5 cm) using the friction-spinning technique. The electrical conductivity of this yarn is dependent on the weight content of the staple SS fibers in the yarn. They experimentally found that the yarns containing 20 wt% of SS staple fibers have a resistance of  $6 \times 10^5 \,\Omega/m$ .

# 2.2.2.2 Hybrid polymer–metal fibers fabricated by fiber-drawing techniques

Another way to fabricate hybrid polymer–metal fibers/yarns is to embed metallic wires into a polymer fiber during a fiber-drawing process. The fibers drawn in this way are normally called metamaterial fibers (Mazhorova et al., 2010). The metal or alloy components in these fibers should generally have a melting temperature similar to those of the polymer materials. Our group (Mazhorova et al., 2010) has recently reported a polycarbonate (PC) fiber containing one or more bismuth–tin alloy (melting temperature  $\sim 140~^{\circ}\text{C}$ ) microwires. To fabricate the fiber, liquid melt of Bi $_{42}\text{Sn}_{58}$  is first filled into a PC tube to produce a fiber preform, which is subsequently drawn by a scientific polymer–fiber-drawing tower using a heating-and-drawing method. The resultant fiber has a cross section of metal core surrounded by a PC cladding. The electrical resistivity of the fiber depends on that of the alloy component. We experimentally measure the resistance of a fiber with a 200- $\mu$ m diameter core



**Figure 2.3** (a) A microstructured conductive fiber containing multiple bismuth–tin microwires. The inset is a magnified picture of a Bi–Sn wire. (b) Microstructured fiber capacitors with copper wires embedded.

Panel (a): Figure 1 from Mazhorova et al. (2010). Panel (b): Figure 2 from Gu et al. (2010).

to be  $\sim$ 12  $\Omega$ /m. Note that it is possible to stack these fibers within a PC tube as another preform and repeat the fiber drawing process (Mazhorova et al., 2010). Consequently, the drawn fibers would contain multiple metallic wires (Figure 2.3a). More recently, several research groups have demonstrated polymer fibers containing multiple indium (Tuniz et al., 2010, 2011), tin–zinc (Orf et al., 2011a,b), or tin–bismuth microwires (Ung and Skorobogatiy, 2013). While these conductive polymer fibers currently are mainly used in optical applications such as THz polarizers and filters, their potentialities in the smart textile industry need to be further explored.

Note that metal wires with relatively high melting temperatures could also be embedded in polymer fibers during a fiber-drawing process. For example, we have demonstrated a polymer fiber that integrates one or more copper wires during drawing (Gu et al., 2010). The fiber preform could be a cylindrical tube made of a thermoplastic (e.g., low-density polyethylene (LDPE) or PC). With a tension-adjustable reel installed on the top of a preform, copper wires can be passed through the preform core, pulled down, and embedded into the fiber center during drawing by collapsing the plastic cladding around them. The resultant fiber embedded with a 100-µm-diameter copper wire has a resistance of  $\sim 1 \Omega/m$ . Moreover, we may also co-roll alternating conductive and isolating films into a hollow-core structure (tube) and use it as the fiber preform. Thus, the fibers drawn subsequently would have copper cores surrounded by alternating conductive/isolating multilayer cladding, as shown in Figure 2.3b. We note that such a fiber constitutes a fiber-based capacitor. Experimentally, we choose carbon-black-filled LDPE and regular LDPE as conductive and isolating materials in the fiber cladding. The experimental capacitance of the fiber capacitor was measured to be 60–100 nF/m. An advantage of the metal-embedded polymer fiber is that the polymer cladding of the fiber could provide effective protection to the inner metal wires against chemical erosion and mechanical abrasion. In addition, metal-embedded polymer fibers produced by fiber-drawing techniques show great flexibility in the engineering of the fiber inner microstructure and may provide various electrical and optical functionalities to the textiles fabricated thereof (Gorgutsa et al., 2012; Gu et al., 2010).

#### 2.2.3 Polymer yarns with conductive fillers

## 2.2.3.1 Polymer yarns filled with CBs

CPYs can be fabricated by dispersing CB particles into traditional textile yarns. This technique was investigated intensively from the 1970s to 1990s (Ellis and Mieszkis, 1983; Bond, 1986; Hull, 1974, 1977; Howitt, 1986; Samuelson, 1993; Van and Weigand, 1984; Higuchi and Nagayasu, 1980; Takeda, 1988; Asher et al., 1999; Boe, 1976). The main advantage of CB-filled polymer yarns is low cost, commercial availability of CBs, and the ease of the synthesis process of the yarns. To synthesize CB-polymer composite yarns or fibers, a certain amount of CB particles (particle size: 20-100 nm) is directly added into melts of thermoplastic polymers, such as nylon, polyethylene, polyamide, and polyester, to name a few. Then, the polymer melts can be melt-spun into conductive polymer fibers or yarns. To achieve an effective conductive network of CBs within the polymer matrix, the concentration of CBs in the fiber (known as percolation threshold) is normally higher than 10 wt% (Ellis and Mieszkis, 1983; Bond, 1986; Hull, 1974, 1977; Howitt, 1986; Samuelson, 1993; Van and Weigand, 1984; Higuchi and Nagayasu, 1980; Takeda, 1988; Asher et al., 1999; Boe, 1976). Above this threshold, the conductivity of the as-spun fibers or yarns generally increases with increasing concentration of CBs. Note that addition of CBs tends to stiffen the as-spun yarns, which is unfavorable for weaving or knitting these yarns into textiles. Therefore, it is a trade-off between the conductivity and processability of the polymer yarns that renders an optimal concentration of CBs. Generally, the CB concentration in the yarns ranges from 10 to 40 wt%.

Many CB-filled fibers adopt a core-sheath structure. For example, Ellis and Mieszkis (1983) reported a polymer fiber that has a core derived from poly(hexamethylene adipamide) and a sheath derived from a CB-filled copolyamide containing 70% of hexamethylene adipamide units and 30% of caprolactam units. The resistance of the yarn with a fineness of 22 dtex was measured to be  $5\times10^6~\Omega/m$ . In addition, Bond (1986) reported another polymer fiber that had the nylon or polyester core and a CB-containing sheath made from the same polymer material of the core. The concentration of CBs varied from 20 to 30 wt%, and the resistance of the polyester yarn with a 50-µm diameter was  $0.2-2\times10^6~\Omega/in$ . Young's modulus and breaking strain of the fiber with a drawing ratio of 3.5 was up to 2.38 GPa and 68%, respectively.

Note that due to the black color of CBs, these yarns and the textiles made thereof would inevitably have a black or gray appearance, which is undesirable for many applications. Moreover, the conductivity of these yarns may be reduced if the sheath layer undergoes mechanical abrasion. Du Pont Inc (Hull, 1974, 1977; Howitt, 1986; Samuelson, 1993), therefore, has proposed several polymer fibers in which CBs (10–40 wt% of the fiber) are only added to the fiber core. The polymer sheath of these fibers, while providing mechanical protection to the conductive core, could be dyed as desired. However, the resistance of these fibers with a fineness of  $\sim$ 20 denier is normally as high as  $10^8$ – $10^{11}$   $\Omega$ /m due to the presence of the isolating sheath layer. The tenacity, Young's modulus, and breaking elongation of these fibers are 1.5–3.5 gpd, 15–25 gpd, and 20–30%, respectively (Hull, 1974, 1977; Howitt, 1986; Samuelson, 1993). Finally,

we note that the CB-filled polymer fibers or yarns, regardless of their structures, typically have a resistance larger than  $10^5 \,\Omega/m$  (Ellis and Mieszkis, 1983; Bond, 1986; Hull, 1974, 1977; Howitt, 1986; Samuelson, 1993; Van and Weigand, 1984; Higuchi and Nagayasu, 1980; Takeda, 1988; Asher et al., 1999; Boe, 1976). Therefore, these yarns are normally used for electrostatic-dissipation applications (e.g., antistatic garments) but not regular conductive-circuit applications. To date, a number of commercial carbon-black-filled polymer yarns are available (siri, n.d.).

#### 2.2.3.2 Polymer yarns filled with CNTs

CNTs, discovered by Iijima and coworkers in 1991 (Iijima, 1991), feature a unique one-dimensional structure and extraordinary physical properties, such as high aspect ratio, light weight, and good electrical and thermal conductivities (Min et al., 2009; Thostenson et al., 2001). Due to these appealing features, CNTs are considered a better conductive additive than CB for fabrication of CPYs. As mentioned in the previous section, the percolation threshold of CBs in polymer–CB composite yarns is normally higher than 10 wt% in order to achieve an effective conductive network. For polymer-CNT composite yarns, this percolation threshold could be as low as 0.0025 wt%, though in most previous investigations, the typical concentration of CNTs ranges from 0.1 to 5 wt% (Grunlan et al., 2004; Bryning et al., 2005; Sandler et al., 2003). Therefore, even though CNTs are more expensive than CBs, the fabrication cost of polymer-CNT composite yarns could be comparable or less than that of polymer-CB composite yarns. Moreover, it is well known that CNTs can work as a reinforcement component in polymer yarns. The mechanical properties (such as tenacity and breaking elongation) of CNT-filled composite yarns are generally improved compared to the original yarns (Min et al., 2009; Hou et al., 2005; Liu et al., 2007). This is in contrast with the CB-filled polymer yarns, which usually exhibit degraded mechanical strength. CNT-filled polymer yarns can be spun from a variety of polymer–CNT composites using solution-spinning, melt-spinning, or electrospinning techniques, which are reviewed in Section 2.4. The polymers used in the composites include PP, PET, PMMA, PVA, and PC, to name a few. These CNT-polymer composite fibers are summarized in Table 2.2.

### 2.2.3.3 Polymer yarns filled with ICPs

ICPs such as PANI or PPy could also be blended with other nonconductive polymers to form composites used for fiber spinning. The resultant fibers, while being electrically conductive, generally have better mechanical properties than pure ICP fibers. For example, Hsu et al. (1999) and Hsu (1998) reported high-tenacity, high-modulus, electrical-conductive composite fibers prepared by dry-jet wet spinning of PANI/poly(p-phenylene terephthalamide)/sulfuric acid solutions. The composite fibers had a conductivity approximately proportional to the weight concentration of PANI in the fiber, and experimental results suggested that the fiber containing 30 wt% PANI had a conductivity of 0.1–1.8 S/cm. The corresponding tenacity, modulus, and breaking elongation are  $\sim$ 15 gpd,  $\sim$ 300 gpd, and  $\sim$ 4%, respectively. Mirmohseni and

Table 2.2 Polymer fibers/yarns with CNT fillers

CNT type	Polymer	Spinning technique	Conductivity	Reference
MWNT	PP	Melt spinning	275 S/m	Deng et al. (2010)
MWNT	PC	Melt spinning	$\sim 2 \times 10^{-3} \text{ S/cm}$	Potschke et al. (2005)
CNT	PET	Melt spinning	$\sim 1 \times 10^{-8} \text{ S/cm}$	Li et al. (2006)
SWNT	PEI	Solution spinning	100–200 S/cm	Munoz et al. (2005)
SWNT	PVA	Solution spinning	0.1–2.5 S/cm	Munoz et al. (2005)
MWNT	PVA	Solution spinning	250 Ω/cm (linear resistivity)	Xue et al. (2007)
CNT	PLA	Solution spinning	$\sim$ 4 × 10 <sup>-2</sup> S/m	Alexandre et al. (2011)
MWNT	PVA	Electrospinning	~10 S/cm	Wang et al. (2006)
SWNT	PMMA	Electrospinning	0.1 S/m	Sundaray et al. (2008)

MWNT, multiwalled nanotube; SWNT, single-walled nanotube.

PP, polypropylene; PET, polyethylene terephthalate; PC, polycarbonate; PEI, polyethylenimine; PMMA, poly(methyl methacrylate); PLA, poly(lactic acid); PVA, polyvinyl acetate.

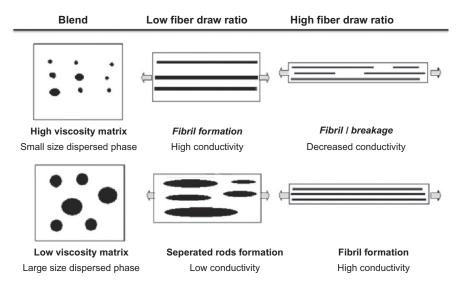
Salari (2006) demonstrated PANI/nylon-6 composite fibers using the wet-spinning technique. A 7.5 wt%  $\rm Li_2SO_4$  aqueous solution was used as coagulant. The electrical resistance of as-spun fibers containing 5–25 wt% PANI varies from 0.665 to 0.015 M $\Omega$ /cm after a doping treatment by formic acid. Jiang et al. (2005) reported wet spinning of PANI/polyacrylonitrile-methylacrylate (Co-PAN) composite fibers. The as-spun fibers with 7 wt% PANI had a conductivity of  $10^{-3}$  S/cm by a DBSA doping.

Zhang et al. (2002) demonstrated PANI/polyamide-11 (PA-11) composite fiber wet spun from concentrated PANI/PA-11/ $H_2SO_4$  solutions. Tap water was used as a coagulating agent. A morphological study of the as-spun fibers showed that PANI and PA-11 components are incompatible in the fiber. PANI components, forming fibrillar structures along the fiber's lengthwise direction, are responsible for the conductivity of the fiber. The composite fibers containing 20 wt% PANI with a draw ratio of 3.57 had a conductivity of  $10^{-1}$  S/cm and tensile strength of ~2 gdp. Later, they (Zhang et al., 2001) also studied the influence of wet-spinning conditions on electrical and mechanical properties of the as-spun fibers. They found that microvoids can always be found in the as-spun fibers, regardless of fiber-spinning conditions. However, increasing the concentration of sulfuric acid in the coagulating bath would lead to shrinkage of the void size, thus increasing mechanical properties of the as-spun

fibers. In addition, while increasing the concentration of PANI would increase the conductivity and reduce the microvoid size of the as-spun fibers, it actually has a negative influence on the mechanical properties of both the as-spun and drawn PANI fibers, due to the inherent fragility of PANI. Thus, the concentration of PANI in the fiber should be normally limited within 20 wt%.

As mentioned in Section 2.2.1, PANI is not a thermoplastic and thus is infusible. However, by adding certain plasticizers such as dodecylbenzenesulfonic acid (DBSA), PANI would transform into an electrically conductive salt-form complex that can be thermally processable with a temperature up to 200 °C (Fryczkowski et al., 2004). This indicates the possibility of fabricating PANI composite fibers/yarns using a melt-spinning technique. From the industrial point of view, melt spinning is more advantageous compared to the solution-spinning (wet-spinning) method, because the melt-spinning process is less complicated (no coagulation chemistry is involved), and a number of thermoplastic polymers potentially can be used (Laska et al., 1995). Note that the PANI complex is not a thermoplastic, and above 200 °C, cross-linking and degradation reactions occur in the PANI complex (Scherr et al., 1991). Therefore, the PANI complex is generally processed in a mixture with other thermoplastic polymers having low melting points (<200 °C), such that side reactions within PANI are suppressed. Particularly, polypropylene with a melting temperature of  $\sim 160$  °C is suitable for co-melt spinning with PANI (Kim et al., 2004; Passiniemi et al., 1997; Soroudi and Skrifvars, 2010, 2011, 2012; Soroudi et al., 2011). For instance, Kim et al. (2004) reported melt-spun fibers from a melt mixture of PANI-DBSA and PP. The electrical conductivity of the as-spun fibers was in the order of  $10^{-9}$  S/cm, while the PANI concentration in the mixture ranged from 1% to 40%. They attributed such low conductivity to the nonhomogenous distribution of PANI in the composite fiber. Scherr et al. (1991) achieved a more homogenous dispersion of PANI complex in PP matrix by prolonging the mixing time. They reported a conductivity of approximately  $10^{-6}$  S/cm, with a PANI concentration of 30 wt%. Passiniemi et al. (1997) used transmission electron microscopy (TEM) and the wide-angle X-ray diffraction (WAXD) technique to characterize the conductive fiber melt-spun from PP and PANIPOL (which is also a PANI-DBSA complex). They found that the as-spun fibers have a highly ordered PANI structure and exhibit a phase-separated morphology with continuous fibrils of PANI in the PP matrix. The continuous PANI fibril phase gives rise to an electrical conductivity up to  $10^{-3}$  S/cm, with the concentration of PANI ranging from 10 to 15 wt%.

Recently, Soroudi and Skrifvars (2011, 2012) and Soroudi et al. (2011) performed comprehensive studies on the morphological, electrical, and mechanical properties of PANIPOL-PP composite fibers. They confirmed that the PANI and PP in the fiber have a phase-separated morphology in which PANI forms fibrillar structures dispersed in the PP matrix. In addition, they found that (Soroudi and Skrifvars, 2011, 2012; Soroudi et al., 2011) two factors showed a substantial effect on the electrical resistance of fibers: size of the initial dispersed PANIPOL phase (droplet) in the fiber and the drawing ratio of the fiber. PANI in the as-spun fibers could be considered "droplets" dispersed in the PP matrix (Figure 2.4). The size of these droplets is dependent on the viscosity ratio between PANIPOL and PP. The lower the ratio, the smaller the size of droplets. Increasing the drawing ratio of the fiber would first lead to an



**Figure 2.4** Comparative scheme of morphology and conductivity changes during fiber drawing for PP/PANIPOL fibers prepared from blends made from high- and low-viscosity matrices. Figure 9 from Soroudi and Skrifvars (2011).

increase in the fiber conductivity, until it reaches a maximum value. During this process, the PANI droplets are stretched into fibrils. However, further increasing the drawing ratio would reduce the conductivity, which is a sign of breakage of the PANI fibrils. The optimal drawing ratio of the fiber to its initial length is experimentally found to be between 3 and 4. The maximum conductivity of the four-times-drawn fibers is  $10^{-4}$  S/cm. The corresponding tenacity, modulus, and breaking elongation are 1.53 cN/Tex, 3.05 cN/Tex, and 481.8%, respectively (Soroudi and Skrifvars, 2012). Moreover, the same research group also proposed that CNTs can be considered a coadditive to blend in the fibers in order to reinforce the mechanical strength of the fibers (Soroudi and Skrifvars, 2010).

### 2.3 Surface CPYs

# 2.3.1 Polymer yarns with metallic coatings

Polymer yarns with metallic coatings constitute one of the most popular products in the current "conductive yarn" market (swicofil, n.d.b; alibaba, n.d.; alibaba.com, n.d.), because these yarns can be conveniently fabricated by a simple metal-deposition treatment to a number of commercial textile yarns. To date, various types of metals, such as silver, copper, nickel, aluminum, and gold, have been successfully deposited on polymer yarns made of polyamide (nylon), polyester, PP, PET, and so on. A variety of coating techniques have been suggested and commercially used, including polymer–metal lamination, physical vapor deposition (e.g., sputter deposition), metallic-paint brushing, and

electroless plating (Alagirusamy and Das, 2010; Zhang et al., 2011). Among these techniques, we particularly focus on the electroless plating method due to its appealing advantages, such as low cost, uniformity of metallic coverage, excellent conductivity, and the possibility of mass production of industrial-strength yarns.

Electroless metal plating, also called autocatalytic plating, is a process in which reduction of metal ions and oxidation of a reducing agent take place simultaneously at a catalytic surface. The mechanism of electroless plating is systematically discussed in Mallory and Hajdu (1990) and Van De Meerakker and De Bakker (1990). Recently, Zhang et al. (2011) described the detailed procedures for electroless plating of Ag, Cu, Ni–P, and Cu–Ag on nylon yarns. The resistance of these yarns is generally from 1 to 10  $\Omega$ /cm. Jiang et al. (2004) reported coating a silver layer on cotton and polyester yarns and used them to fabricate antistatic garments. Gan et al. (2007) demonstrated the electroless plating of copper on polyethylene terephthalate (PET) yarn-based fabrics and used the fabrics for electromagnetic-shielding applications. Lee et al. (2013) demonstrated the electroless plating of aluminum on cotton threads, and the resistance of the conductive cotton threads was measured to be  $\sim\!\!0.2~\Omega/cm$ .

Note that a disadvantage of the metal-coated yarns is that the metal layer may be peeled off due to washing or other types of mechanical abrasion. This would compromise the yarn conductivity and may lead to a short-circuited connection for the yarns woven into a textile. To increase the metal-polymer bonding strength and thus enhance the abrasion resistance of the yarn, many attempts have been carried out to optimize the electroless plating process. Particularly, we note that coating an intermediate "buffer" polymer layer between the metal coating and the polymer substrate may constitute an effective method (Liu et al., 2010; Kim et al., 2013; Gasana et al., 2006; Schwarz et al., 2010). For example, Liu et al. (2010) demonstrated that by precoating a "polyelectrolyte brush" (a poly[2-(methacryloyloxy)ethyltrimethylammonium chloride] layer that covalently tethers one end on a surface) on a cotton-yarn substrate, the subsequent copper or nickel coating retained its excellent mechanical and electrical stabilities under extensive bending, stretching, and washing. The proposed yarn had a conductivity of  $\sim 1$  S/cm. In addition, several research groups (Kim et al., 2013; Gasana et al., 2006; Schwarz et al., 2010) have shown that precoating a buffer layer of PPy on the textile yarn substrate would enhance the bonding strength of the subsequent metal coating (e.g., Cu, Ni, or Cu-Au coating). A possible explanation for this is that the nitrogen center in a pyrrole molecule may act as a stable acceptor for growing metal layers on it (Gasana et al., 2006; Schwarz et al., 2010). Note that this PPy layer would also to some extent increase the yarn conductivity, because PPy is an ICP. The experimental resistance of the PPy-Cu-coated polyamide yarn (Schwarz et al., 2010) was measured to be as low as 0.037  $\Omega$ /cm.

# 2.3.2 Polymer yarns with ICP coatings

As noted in Section 2.2.1, ICP yarns, though featuring excellent electrical conductivity, usually suffer from poor mechanical strength. Therefore, fabrication of smart textiles or fabrics from these ICP yarns could be challenging. Coating traditional

textile yarns with an ICP layer could constitute a better alternative to pure ICP yarns, and good mechanical and electrical properties of the ICP-coated textile yarns are expected. To date, a number of polymer yarns coated by ICPs including PANI, PPy, and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) have been proposed and experimentally demonstrated. The substrate yarns could be made from natural polymers such cotton or silk, or synthetic polymers such as polyester, polypropylene, polyamide (nylon), polyacrylonitrile, and others. Two major techniques are commonly used to coat ICP layers onto textile yarns: the dipping-and-drying method and chemical solution/vapor polymerization. These two methods are introduced in Section 2.4. In Table 2.3, we summarize the textile yarns with ICP coatings reported so far.

The influence of ICP coatings on the mechanical properties of the textile yarn is complicated and is dependent on many factors, such as the material of ICPs and textile yarns, concentration of ICP and oxidative agent, coating uniformity and thickness, and twist density of textile yarn. By coating PPy on wool yarns, Kaynak et al. (2002, 2008) found that the tenacity and breaking elongation of the yarn increase up to 7% and 21%, respectively. They attributed the improved mechanical properties to the reduced fiberto-fiber friction due to the smooth ICP coating on the yarn surface. (Kim et al. (2006) reported improved modulus and tensile strength of PET yarns due to the PANI coating, and they attribute this to the interforce of PANI- conducting layers on the fiberfiber regions of the PET yarn. However, an early work reported by Nouri et al. (2000) suggested that the PANI coating showed an "insignificant" effect on the mechanical properties of nylon, wool, cotton, and polyester yarns. The electrical resistance of ICPcoated yarns generally increases due to bending, tensile stretching, and other mechanical abrasions of the yarns. In addition, ICP coatings generally oxidize in air, which leads to degradation of ICP coatings and reduction of yarn conductivity. Therefore, it is suggested that ICP-coated yarns should be restored in desiccators (Wu et al., 2005).

# 2.3.3 Polymer yarns coated with CNTs or CBs

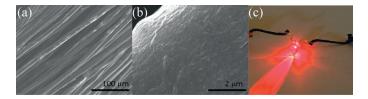
In this section, we focus on the review of polymer yarns with CNT or CB coatings. Unlike the metal coatings that involve multiple chemical-reaction processes or the ICP coatings that may require complicated chemical polymerization, coating of CNTs or CBs on polymer yarns is usually carried out by a simple dipping-and-drying technique. Using this method, Shim et al. (2008) prepared a CNT-coated cotton thread. CNTs were first dispersed in dilute Nafion–ethanol or PSS–water solutions. Then, cotton threads were dipped in the prepared CNT dispersions and dried (see Figure 2.5). After several repeated dips, the cotton threads had a resistance of  $\sim$ 25–120  $\Omega$ /cm. They also found that the tensile strength of the cotton yarn with CNT coatings was more than 2 times higher than that of the original cotton threads due to the reduction of yarn diameter, and stronger adhesion of the fibers in the yarn.

In addition, Guinovart et al. (2013) turned the commercial cotton yarns into electrical conductors through a simple dyeing process using a CNT ink (which is a CNT/sodium dodecylbenzenesulfonate (SDBS) aqueous solution). A resistance of  $\sim 500 \,\Omega/\text{cm}$  was reported with five dyeing cycles. Xue et al. (2007) prepared

**Table 2.3 Polymer yarns coated with intrinsically conductive polymers** 

ICP	Textile yarn	Coating technique	Linear resistivity (conductivity)	Reference
PANI	Wool, cotton, nylon, and polyester	Solution polymerization	23 kΩ/cm/ filament	Nouri et al. (2000)
PANI	PET	Dipping and drying	$\sim$ 70 $\Omega$ /cm	Kim et al. (2004)
PANI	PET	Dipping and drying	∼100 Ω/cm	Kim et al. (2006)
PPy	Wool	Solution polymerization	4.8 kΩ/cm	Varesano et al. (2005)
PPy	Wool	Solution polymerization	~50 Ω/cm	Kaynak et al. (2002)
PPy	Wool, cotton, and nylon	Vapor polymerization	0.37–3 kΩ/mm	Kaynak et al. (2008)
PPy	Wool	Vapor polymerization	0.43 kΩ/mm	Najar et al. (2007)
PPy	Nylon-6 and polyurethane	Vapor polymerization	_	Xue and Tao (2005)
PPy	Cotton and silk	Vapor polymerization and solution polymerization	$6.4 \times 10^{-4}$ S/cm (cotton) $3.2 \times 10^{-4}$ S/cm (silk)	Hosseini and Pairovi (2005)
PEDOT: PSS	Silk	Dipping and drying	8.5 S/cm	Irwin et al. (2011)
PEDOT: PSS	Silk	Dipping and drying	2 kΩ/mm	Tsukada et al. (2012)
PEDOT: PSS	Viscose	Vapor polymerization	_	Bashir et al. (2013)

CNTs/PVA mixed solutions and used them for coating five yarns including cotton, silk, wool-nylon, polyester, and PP yarns. Resistance of the fabricated yarns is in the order of  $\sim$ 1 k $\Omega$ /cm. Rui et al. (2012) demonstrated depositing a CNT–polyurethane composite coating on commercial spandex (polyurethane–polyurea copolymer) multifilament yarns. A resistance of  $10^5$   $\Omega$ /cm was obtained, with a concentration of CNT in



**Figure 2.5** (a and b) SEM photographs of a cotton thread coated with CNTs. (c) The coated cotton thread used in an electrical circuit to light up an LED. Figures 1 and 2 from Shim et al. (2008).

the yarn of  $\sim 0.02$  wt%. They also developed a strain sensor based on the fabricated yarns by characterizing the strain–resistivity relationship of the yarn. Recently, research performed by Vyver et al. (2013) revealed that by adding ultraviolet (UV) curable resin and photo-initiator to CNT dispersions, the resultant CNT coating on polymer yarns could be further consolidated by UV light, which potentially increases the fastness of the CNT coating.

Polymer yarns filled with CB particles could achieve an effective conductive network within the yarns. However, the mechanical properties of CB-filled yarns are degraded with increasing CB concentrations, which limits the CB concentrations in the yarn and thus the yarn conductivity. In contrast, coating a conductive thin layer of CB on textile yarns would preserve the flexibility and elasticity of the textile material to a great extent (Negru et al., 2012; Nauman et al., 2011).

Negru et al. (2012) recently used the dipping-and-drying technique to coat a fabric woven from cotton yarn with a CB layer. The minimum surface resistivity of the coated fabric was  $\sim 1.25 \text{ k}\Omega/\text{sq}$  when the CB concentration in the yarn was ~16 wt%. Nauman et al. (2011) demonstrated coating cotton, nylon, and PE yarns with a CB-Evoprene layer (Evoprene is a copolymer of styrene-butadienestyrene units). The experimental volume resistivity of the yarns or filaments was  $0.2-1 \text{ k}\Omega$  cm. They also used these conductive yarns to develop a smart fabric that can be used as a piezoresistive strain sensor. In order to reduce the loss of conductivity of CB-coated yarns, Jin et al. (2007a,b) modified this dipping-and-dryingcoating technique into a dissolving-coating technique. In this method, CB particles are dispersed into a solvent of the substrate yarns. Then, this CB dispersion is applied to the substrate yarns for an optimized period. The substrate yarns quickly become swollen due to etching of solvents, thus allowing CB particles to impregnate the yarn surface. Based on the modified method, conductive polyamide-6 (PA-6) yarns with CB coatings were fabricated. The volume resistivity of the PA-6 yarns fabricated by this technique was measured to be  $\sim$ 5  $\Omega$  cm, and after 50 washing cycles the volume resistivity increased to  $\sim$ 8  $\Omega$  m. For a comparison measurement, volume resistivity of the PA6 yarns produced by the traditional dipping-and-drying method increased by seven order in magnitude after 50 washing cycles.

# 2.4 Techniques for processing CPYs

#### 2.4.1 Wet-spinning technique

Wet spinning is a commonly used technique for fabrication of CPYs, especially when the yarns contain nonthermoplastic polymers (e.g., PANI, PPy) that are decomposed at a temperature lower than their melting point. In wet spinning (Pereira et al., 2000; Hoxie, 1951; East et al., 1984), the raw polymer materials are first dissolved or finely dispersed into a solvent, and then the polymer solution is pumped through a spinnerette placed above (or inside) a bath filled with a coagulating agent (Figure 2.6). A spinnerette is normally a metallic plate with a number of small holes. The polymer-solution streams extruded through the spinnerette would precipitate into filaments in the coagulation bath, as the solvent quickly diffuses into the coagulating agent (nonsolvent). The filaments are then drawn out of the bath, washed, and dried before being wound on the spools. Note that polymer fibers fabricated by this method may have voids within the fibers due to the diffusion of the coagulant molecules into the fiber structure, thus leading to a reduced density and tensile strength of the as-spun fibers (Yang et al., 2001). Therefore, as mentioned in Section 2.2.1, the spinning conditions need to be optimized in order to minimize the formation of the voids. The processing variables in wet spinning include concentration and temperature of the spinning solutions; composition, concentration, and temperature of the coagulating bath; and the stretching force applied during spinning.

## 2.4.2 Melt-spinning technique

Melt spinning is most applicable when polymer yarns are spun from thermoplastics such as nylon, polyethylene, polyester, cellulose triacetate, and PET, to name a few. Also, note that although some ICP complexes (e.g., PANI-DBSA composite) are not thermoplastics, they can still be used as conductive additives in melt spinning to produce conductive polymer composite yarns (see Section 2.2.3.3). In melt spinning (Figure 2.7), the raw polymer materials are heated to form a polymer melt with a viscosity suitable for extrusion through the spinnerette into an air chamber. Then, the extruded polymer streams cool

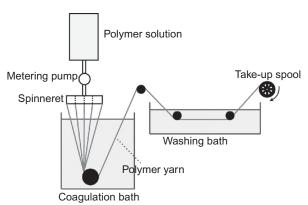


Figure 2.6 Schematic of a wetspinning setup. Shim et al. (2008).

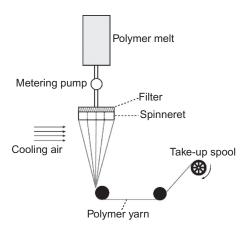
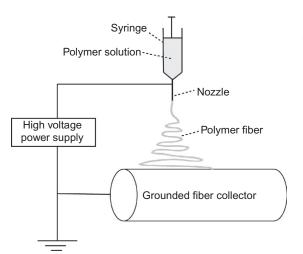


Figure 2.7 Schematic of a melt-spinning setup.

and solidify into continuous fibers that are drawn out of the air chamber and wound on fiber spools (Brackett-Rozinsky et al., 2011; Susumu and Matsuo, 1965). Unlike the wetspinning method, melt spinning, in principle, does not require the use of solvents, and no voids form within the as-spun fibers. Melt spinning is always used to produce polymer yarns containing conductive fillers such as ICPs, CBs, or CNTs.

### 2.4.3 Electrospinning technique

Another method used to produce CPYs from a polymer solution (or particulate suspension) is electrospinning (Hegde et al., 2005; Teo and Ramakrishna, 2006; Chronakis, 2005). Electrospinning allows the fabrication of fibers with diameters down to tens of nanometers. In electrospinning (Figure 2.8), a polymer solution is



**Figure 2.8** Schematic of an electrospinning setup.

pumped to the spinnerette (or nozzle) that is connected to a high-voltage (5–50 kV) power supply. The polymer solution charged by high voltage would eject out of the spinnerette and form a liquid jet. As the polymer jet evaporates, polymer microfibers or nanofibers are produced and collected by a fiber collector that is usually a grounded rotating drum (or a grounded metallic plate). The fibers collected could be further oriented and twisted into polymer yarns. Electrospinning is an efficient technique for fabrication of polymer nanofiber-based yarns, mats, and sheets without the use of coagulation chemistry or high temperature. Currently, many polymer–CNT composite fibers or yarns are fabricated based on this technique.

#### 2.4.4 Fiber-drawing technique

Conductive polymer fibers embedded with metallic wires could be fabricated by the fiber-drawing technique (Mazhorova et al., 2010; Tuniz et al., 2010, 2011; Orf et al., 2011a,b; Ung and Skorobogatiy, 2013; Gu et al., 2010). The metal components in these fibers normally have a melting temperature comparable to that of the polymer materials used in the fibers. To draw the fiber, a fiber preform is first fabricated by filling liquid melt of a metal or alloy inside a polymer cylinder (tube). Then, the preform is placed in the furnace of a fiber-drawing tower. Upon heating, the tip of the preform gets melted and forms a glob that falls down under the force of gravity, while shrinking in diameter to form a fiber strand. A clamp-tractor is used to control the fiber-drawing speed (Figure 2.9). The dimension of the drawn fiber is dependent on the parameters used in the drawing process, such as fiber-drawing speed, temperature distribution of furnace, preform-feeding speed, and pressurization of the preform (for hollow-core fibers). The resultant fiber would have a structure of one or more metal wires surrounded by the polymer cladding. Also, note that metals with a relatively high melting temperature could also be embedded in a polymer fiber during a fiber-drawing process (Gu et al., 2010). To do this, a metal wire is passed through a hollow-core polymer preform before fiber drawing. Once heated, the preform would

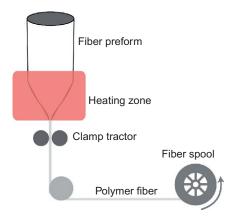


Figure 2.9 Schematic of fiber-drawing process.

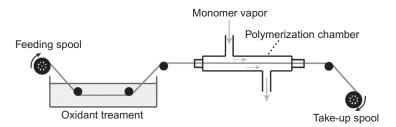
fall down along the metal wire and form the fiber cladding encapsulating the metal wire. Note that the structure of fiber cladding is mostly determined by that of the preform. Thus, it is possible to introduce a microstructure into the fiber cladding by engineering the corresponding structure of the preform. The fiber-drawing technique is, to some extent, similar to the abovementioned melt-spinning method. In both of the two methods, the raw polymer materials are heated into a viscous polymer melt, which is then drawn (or extruded) into fibers as the polymer melt cools and solidifies. However, the conductive fibers produced by the fiber-drawing technique show great flexibility in the engineering of the fibers' inner microstructure (Gu et al., 2010) and may provide various electrical and optical functionalities to the textiles fabricated thereof.

#### 2.4.5 Dipping-and-drying technique

CPYs can be produced by coating traditional textile yarns with a conductive layer. The dipping-and-drying method is probably the easiest method to produce such a conductive coating. In this method (Kim et al., 2004; Irwin et al., 2011; Tsukada et al., 2012), a solution is first prepared by dissolving or dispersing conductive materials into a solvent. Then, this solution is directly applied to the substrate textile yarns. As the solvent evaporates, a conductive layer is deposited on the yarn surface. To increase the conductivity, this dipping-and-drying process may be repeated several times. The conductive materials used for coating may include ICPs, metal particles, CBs, and CNTs, to name a few. Several alternative coating methods such as hand brushing and spray painting can be considered variants of the dipping-and-drying method. This technique is quite straightforward, and no expensive equipment or complicated operation is required. Note that conductivity of the coated yarns is dependent on uniformity of the distribution of the conductive materials in the solutions.

# 2.4.6 Chemical solution/vapor polymerization

In addition to the dipping-and-drying method, coating of ICPs on textile yarns could be carried out by chemical solution/vapor polymerization (Kaynak et al., 2008; Najar et al., 2007; Xue and Tao, 2005; Hosseini and Pairovi, 2005). Chemical polymerization is typically performed by the pretreatment of the substrate yarn with an oxidant (e.g., FeCl<sub>3</sub>), followed by the exposure of the substrate yarn to the monomers in the solution phase or vapor phase (Figure 2.10). The polymerization is initiated by the oxidation of monomers into radical cations, which then combine with each other to form insoluble oligomers and polymers depositing on the surface of substrate yarns. In general, chemical polymerization of ICPs on textile yarn would produce a denser and more homogenous coating that exhibits higher conductivity compared to that obtained by the dipping-and-drying method. However, in chemical polymerization, the substrate yarns are directly exposed to the corrosive-oxidizing agents used for the polymerization. In addition, for vapor polymerization, complicated ventilation equipment is normally required.



**Figure 2.10** Process of coating intrinsically conductive polymers (ICPs) on textile yarns using chemical vapor polymerization.

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