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Additive manufacturing electrochemistry: An overview of producing bespoke conductive additive manufacturing filaments

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Additive manufacturing represents a state-of-the-art technology that has been extensively disseminated in both the academic and industrial sectors. This technology enables the cost-effective, simple, and automated production of objects with diverse designs. Moreover, within the academic community, additive manufacturing has provided genuine scientific revolutions, particularly in the field of electrochemistry, due to the accessibility of the Fused Filament Fabrication printing methodology, which utilizes thermoplastic filaments for electrochemical platforms. Additive manufacturing has facilitated the production of conductive components for various applications, including electrochemical sensors, batteries, supercapacitors, and electrical circuits. Within recent years, the scientific community has taken an interest in bespoke filaments that are doped with highly conductive particles, which can be optimized and tailored enabling groups to produce a wide range of filaments with uncountable applications. Thus, the present review article explores the distinct methods of bespoke filament manufacturing, emphasizing its significance in the scientific landscape, and investigating the principal materials utilised in its production, such as thermoplastics, plasticizers, and conductive substances, focusing on electrochemistry applications. Furthermore, all reported additive manufacturing methods will be thoroughly discussed, along with their main advantages and disadvantages. Last, future perspectives will be addressed to guide novel advancements and applications of bespoke filaments for use within electrochemistry.

Keywords: Additive manufacturing; Filament production; Circular Economy Electrochemistry; Electrochemistry; Polymers; Nanomaterials; Recycling

Introduction

Additive manufacturing, commonly referred to as 3D-printing, is a group of manufacturing processes in which computer-aided design (CAD) files are processed into physical objects through the deposition of material in consecutive, thin-layered cross-sections [1]. One of the most widespread and inexpensive method of additive manufacturing is Fused Filament Fabrication (FFF), commonly referred to as Fused Deposition Modelling (FDM) which has a low-cost of entry, with printers being available for hundreds of pounds rather than the thousands,

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tens-of-thousands, or hundreds-of-thousands some other printers can cost [2–4].

FFF as an additive manufacturing technology is attractive to various demographics because of several advantages, in addition to low cost of entry since printers and printing materials are relatively cheap, they have: low-waste compared to traditional subtractive manufacturing methods; short lead times and lower cost production runs; ability to produce complex part geometries with a high degree of customisability, as the CAD file can quickly be altered; on-site manufacturing and global connectivity, as designs and print files can be sent globally and printed anywhere a printer can be powered [5]. Such advantages have led to a rapid increase in the adoption of additive manufacturing technologies throughout both industry and academia [6,7]. They are particularly useful for laboratory environments, as they can be used to produce bespoke sample holders, fixtures, and complete devices, that otherwise can be prohibitively expensive, especially to less well-funded research groups [8–12].

Electrochemical research is one academic area that has seen increasing adoption of FFF because of its aforementioned advantages, and because electrically conductive filaments, which can be used effectively as electrode materials have been on the commercial market for some time [13–18]. While a slightly more diverse range of options has become available as the popularity of these filaments has increased, the most used filament is Protopasta®, which was one of the earliest available commercial conductive printing materials. This filament is comprised of poly (lactic acid) (PLA, >65 wt%), acting as the bulk material, an unidentified polymer (<12.7 wt%) acting as some form of plasticiser, and carbon black (CB, <21.43 wt%) acting as the conductive filler [19,20]. Another filament seen throughout the literature is the graphene-based Black Magic®, although this has become less common due to commercial supply issues. Some of the most basic electrodes can be printed using less than 1 g of material, and when the cost of Protopasta® (at the time of writing, autumn 2023) ranges from £50–75 depending on the supplier for 500 g of material, which serves to highlight why the additive manufacturing approach is attractive to electrochemists considering the relatively high cost of traditional electrodes (typically on the order of £100's per electrode).

The development of additively manufactured electrodes from electrically conductive filaments began with additive manufacturing of just the working electrode, and indeed the most used designs in literature continue to be disc or lollipop shapes due to their design simplicity [10], although recent work by Ferrari *et al.* [21] has explored alternative shapes, namely, discs, squares, equilateral triangles and six-point stars with varying working electrode (WE) widths from 2 to 10 mm evaluated towards the near-ideal outer-sphere redox probe hexaamineruthenium(III) chloride. This work highlights the ability of additive manufacturing to print more complex shapes of working electrodes.

Subsequent advances in the design of electrochemical platforms were made through additive manufacturing of the entire cell, including all three electrodes, where a *pseudo*-reference was used for electroanalysis, and the cell was put together post-print [22]). This idea was taken further through the use of an independent dual-extruder additive manufacturing printer [23], where the three electrodes were printed directly into the base of the electrochemical cell, managing to produce a full electrochemical platform in a single print, with no post-assembly required. Further examples of bespoke platforms can be seen throughout the literature, with FFF being utilised alongside commercial electrically conductive filament for all areas of electrochemical research, including the production of equipment for fundamental electrochemical experiments [9]; supercapacitor production [24–27]; substrates for the electrodeposition of catalysts for the hydrogen evolution reaction [28,29]; electroanalysis of various environmental [30,31] or forensic [32–37] analytes, and the production of biosensing devices [38–42]. These devices, when activated and/or modified, produce acceptable results and the inherent flexibility that the additive manufacturing technique affords can often outweigh any further performance gains that could be achieved by traditional devices. In fact, a large proportion of published works now, do not report different electrode platforms or modifications, but rather just different print designs for a new known analyte, yet to be explored using additive manufacturing electrochemistry.

For the researchers combining electrochemistry and FFF, the next frontier is in the production of bespoke filaments for their specific applications and understanding how the fundamental materials work. There have been some reports in the literature of research groups taking this step, which we will discuss in detail later in this review. First, we aim to explore the parts of FFF filament, discussing their physiochemical properties and highlighting potential advantages and disadvantages when used to produce electrically conductive filament. We then move to discuss different filament manufacturing methods, followed by an overview of the reported bespoke filaments in the literature and their applications, before discussing where we think the field can go to maximise its impact.We first look towards the thermoplastic polymer used as the base to create the FFF filament.

Thermoplastics

As explained earlier, FFF printing functions through the extrusion of a millimetre scale thermoplastic polymer filament through a heated nozzle. Thermoplastic polymers are made from long chain molecules that can slide past each other under shear forces when above a certain temperature, such that the molecules have enough energy to overcome the intermolecular attractions [43]. Fig. 1 provides an overview of the repeat units for some of the thermoplastics commonly used to make filament suitable for FFF printing, and Table 1 provides some key information on the polymer properties and common printing parameters.

Poly(lactic acid) (PLA) is the most utilised thermoplastic for FFF printing in general due to its low printing temperature, as well as being the most commonly found in additive manufacturing electrochemical devices, giving rise to excellent printability and a decent end products. Significant attention is brought to the biodegradability of PLA, which is an additional advantage over other polymers for additive manufacturing. However, it must be noted that the biodegradation of PLA must be done industrially through composting/anaerobic digestion making the process significantly harder and less environmentally friendly than many publications would lead you to believe

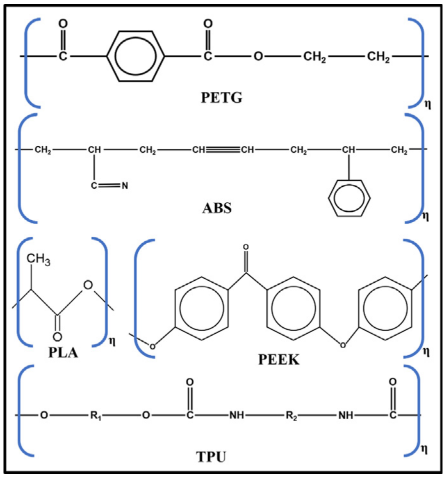


FIG. 1

Chemical structure of common thermoplastics used in additive manufacturing.

[44]. There is no data supporting its biodegradability in home compost, soil or landfill. The most popular commercially available conductive filament (Protopasta®), is a blend of PLA, carbon black and a polymeric plasticiser [19,45] and this has been used in a significant amount of publications throughout the literature. To improve the performance of the electrochemical devices made through additive manufacturing, there have now been numerous publications on the production of bespoke conductive filaments based on PLA [3]. On the other hand, the majority of the electrodes printed from these are single-use due to issues with memory-effects, poor chemical stability and solution ingress into the PLA matrix [46,47].

As such, there have been reports using other polymeric materials for the production of conductive filament, such as acrylonitrile butadiene styrene (ABS) [48]. ABS is one of the most commonly used plastics worldwide, with it being famous for its use within Lego® bricks. It has widespread acceptance for various applications such as within car bodies and household appliances due to its high impact resistance, good stiffness, excellent surface quality, high dimensional stability at elevated temperatures, good chemical resistance, and good stress cracking [43]. Polyethylene terephthalate glycol (PETg) is a glycolised form of polyethylene terephthalate, which is commonly used within food packaging and has seen widespread use within general additive manufacturing due to the ease of printing but high chemical and thermal resistance and strength compared to PLA [46]. As yet to our knowledge, no bespoke conductive PETg filaments have been reported in the literature.

The number of polymers capable of being used in FFF additive manufacturing is ever increasing with the use of poly(propylene) (PP), thermoplastic polyurethane (TPU), and high-end performance plastics such as polyaryletherketones and polyetherimides now being commercially available as filament. This gives a glimpse into the expansion that will be seen over the coming years into the production of conductive filament from an ever-expanding range of polymers, where the filament can be tailored to the application requirements. We note the ethos stated by Weyhrich and Long [49] which they state as "*... the additive manufacturing materials toolbox only contains a fraction of commercially available high-performance polymers due to unique processing constraints.*", which we totally agree with; there are many more polymers that can, and need to be used, and can be applied using additive manufacturing for highly demanding applications.

Plasticisers

Low-temperature flexibility is a vital property of the thermoplastic filament for FFF due to the rapid motion of the print head whilst the filament is being pulled through the extruder, hot end, and nozzle. For standard filaments this movement is not typically a problem, but when the thermoplastic polymer matrix is embedded with the high loadings of filler required to induce electrical conductivity, the filament becomes increasingly brittle. The fragility of the filament can lead to breaking in numerous places during a print and ruining the final product. This includes between the spool and print head, meaning there will not be enough filament to complete a print or be crushed in the extruder gear causing a blockage or hindering the extruder function. To help improve the quality of the filament, when high levels of filler are used, plasticisers can be blended with the polymer at elevated temperatures or in the presence of volatile solvents, which can be removed at a later stage. The Council of the International Union of Pure and Applied Chemistry (IUPAC) has adopted the following definition: "*A plasticiser is a substance or material incorporated in a material (usually plastic or elastomer) to increase its flexibility, workability, or distensibility*" [50]. Plasticisers are non-volatile liquids, or in rare cases solids, that must conform to the following requirements: have a molecular weight above 300 g mol^{-1}; possess a similar solubility parameter to the polymer; be capable of specific interactions with the polymer if it has any tendencies to crystallise; and not be a crystalline solid at ambient temperature unless it is capable of a specific interac-

TABLE 1

Properties of the polymers that are used within additive manufacturing filament production.

Filament	Density g/cm^3	Printing temperature (°C)	Bed temperature (°C)	Mechanical resistance	Chemical resistance
PLA	1.24	180–220	45–60	High	Salt and acid [a]
ABS	1.06	225–260	90–110	Low	Salt, acid, and alkali [b]
PETg	1.27	225–255	80–90	High	Salt, acid, alkali and alcohol [c]
TPU	1.25	220 – 250	45–60	High	Salt and acid [d]
PEEK	1.30	390–420	155–165	Ultra-high	Salt, acid, alkali and alcohol [e]

Key: All information was obtained from the manufacturers' specifications[a] moderate resistance to some acids and salts; [b] high resistance to acids, alkalis and bases, with moderate resistance to salts; [c] high resistance to most acids, alkalis, alcohols and salts; [d] high resistance to some acids and salts; [e] high resistance to acids, alkalis, alcohols and salts.

tion with the polymer [43]. An example of a plasticiser in action outside of the world of additive manufacturing, is in the addition of 70 parts di-*iso*-octyl phthalate to 100 parts poly(vinyl chloride), which converts the polymer from a hard rigid solid at room temperature to a rubber-like material [43]. For a plasticiser to properly modify the fundamental properties of the base polymer it is mixed with, it must be thoroughly incorporated into the matrix, but importantly it does not create chemical bonds [50] as attachment of the plasticiser to the polymer would hinder its ability to move effectively. A well plasticised material gains low-temperature flexibility compared to a standard non-flexible, rigid, and brittle plastic at room temperature. Daniels *et al.* [51] provide a review of the different mechanistic theories on plasticisation in poly(vinyl chloride), which can be adapted for various polymeric matrices.

Various approaches can be taken to classify different plasticisers, such as: through molecular weight boundaries (monomeric or polymeric plasticisers); through plasticiser properties like general purpose, low volatility, low temperature, fast fusing, and specialty; or chemical type, including phthalate esters, terephthalates, dibasic acid esters, trimellitate esters, etc. [50]. It is important to note that all plasticisers will have different solubility parameters, which can be used to give a good indication of whether a plasticiser and polymer will be compatible. Two common solubility parameter models used are the Hildebrand and Hansen models which have both been shown to have their place within the field. The Hildebrand model has available data for a wide range of polymer materials but has been seen to have lower predictive accuracy than the Hansen model, especially when using polar polymers [52]. However, the use of these tools can give a good indication of what plasticisers could be useful to a particular application and narrow the field.

To produce bespoke conductive FFF filaments, polyethylene glycol (PEG) is a well-reported plasticiser. For example, Ghosh *et al.* [53] used PEG in high loadings over the range of 16.6 – 21 wt% for the production of PLA-based filaments incorporating very high loadings of conductive filler (>35 wt%) of graphite, MWCNT, activated carbon, and MoS_2. Even with these high loadings of plasticiser, many of the filaments were reported to be either very brittle or possessed poor conductivities. The optimum filament was then used for energy conversion and storage applications. Wuamprakhon *et al.* [54] utilised a loading of 10 wt% PEG to stabilise a 26 wt% loading of carbon black incorporated with PLA (67.5 wt%). The inclusion of PEG also greatly increased the charge-storing capabilities of the electrode. Other approaches to produce electroanalytical platforms, for example, Sigley and co-workers [55] produced a filament using 10 wt% polyethylene succinate (PES) to stabilise 28 wt% of carbon black within a recycled PLA filament. This produced a filament with very low background currents and a wide working potential range for the detection of caffeine electroanalytically. To further improve the sustainability of filament production, Crapnell *et al.* [56] have recently reported the use of the bio-based material castor oil as a plasticiser in 10 wt% to stabilise a 25 wt% carbon black in PLA filament. They report a filament with excellent low-temperature flexibility and high conductivities, with the filament applied to the detection of bisphenol A in water samples.

Conductive fillers

The production of conductive filaments is normally performed by mixing a polymeric matrix with electrically conductive particles, such as carbon-based materials, metals, or conductive polymers, thereby forming a conductive composite material. As well as electrical conductivity, the intrinsic properties of the component materials directly affect the filament's other material properties, including mechanical and thermal properties, as well as physical properties such as density. [57,58] All of these filament properties also depend on the relative volume fractions and the extent of mixing of the components. For the successful design and manufacture of high-quality conductive filaments, a good understanding of all these factors is crucial.

The density of the filament can be an important factor where weight or buoyancy are concerns for the final application, for example in vehicles or aquatic environments, respectively. Filament density will depend on the densities of the fillers being used as well as the relative volume fractions of filler and bulk polymer. However, the density of the composite material may not simply be calculable from these because it is well known that the presence of filler particles in a semi-crystalline polymer can affect the extent of crystallinity and, hence, the density of the material [59]. The relationship between crystallinity and the properties of additively manufactured electrodes has not been well explored, and while it is not dealt with further in this review, it is noted as an important area for future research.

The mechanical properties of a filament (*i.e.*, strength, Young’s modulus, and hardness) are dependent on the mechanical properties of the bulk polymer and filler and the volume fractions of each [60]. More specifically, most filler materials are more mechanically robust than the polymer matrix and hence can reinforce part of a composite material. However, this is highly dependent on the quality of mixing of the bulk and filler, with poor mixing (*i.e.*, high degrees of filler particle agglomeration) causing at best, no change in mechanical properties, and at worst, significantly increasing the brittleness of the material as large agglomerates can act as stress-concentrating inclusions which promote material failure under load. Similarly, the addition of too much filler will cause a reduction in strength and ductility regardless of mixing quality; once the filler is present above a critical volume fraction, the particles can form a percolating network throughout the material which significantly enhances the ease of crack propagation. While additive manufactured electrochemical platforms or other conductive components may not bear significant load in their final application, filler-induced changes in mechanical properties are nonetheless an especially important concern for filament production, where materials must be flexible enough to be able to be spooled and fed into the printer nozzle without breaking [61]. Note that the maximum limit of filler concentrations are dependent on various factors (filter type, polymer used, conductive phases and its end use) but most important, it needs to be able to be fully printable.

Perhaps the most obviously important property of a filament for use in additive manufacturing electrode production is electrical conductivity. The conductivity of the polymer composite material depends on the conductivity of the filler particles themselves but is also directly related to percolation, in that a minimum volume fraction of conductive filler is required to form continuous electrically conducting pathways and turn the insulating polymer matrix into a conductive composite material [62]. The percolation threshold depends on: the shape and size distribution of the conductive particles; the production method, *i.e.* the level to which the particles are distributed individually and homogenously within the composite; and the attractive interaction between the conductive particles and the polymer matrices [63,64]. A significant challenge in the production of conductive composite filaments is therefore identifying a mixing method and volume fraction of filler sufficient to produce an electrically conductive material, without causing a decrease in mechanical properties to an extent that decreases printability.

Good mechanical and electrical properties can be achieved but it also depends on the nature of the filler particles themselves, including their surface chemistry and its indeed application. In terms of mixing, dispersion of the particles will occur more readily the more compatible the particle surface is within the bulk polymer, and hence the more favourable the thermodynamic driving force towards mixing. Some filler/polymer combinations have intrinsically favourable energetic reactions, but the filler surface can also be modified to increase its compatibility with the bulk. This will also improve the composite's mechanical properties, since a stronger adhesion force will lead to more effective stress transfer from the bulk matrix to the filler, especially if the surface functional groups can covalently bond to both the filler and the bulk polymer. However, the benefits of surface modification must be weighed against any changes in properties that might also arise at the surface. For example, electron transfer at the surface of a conductive particle will be affected by any surface modifications, which is of obvious concern to electrochemists. The specific surface area (SSA) of the particles is also an important factor to be aware of, as this informs the amount of filler likely to be needed to achieve the desired composite properties; in cases where the filler material is dense or expensive, high SSA, and, in particular, anisotropic particles are typically preferable, as these have a higher surface area per mass for interaction with the bulk, and hence should be required at a lower volume fraction to achieve the same effects in the composite materials. Table 2 shows the main physical and electrical properties of common conductive fillers, according to reports in the literature.

Carbon-based materials *i.e.*, graphite, carbon black, graphene, carbon nanotubes, and nanofibers have been widely used for this purpose [55,92–100]. This is attributed to their high SSA, excellent thermal and electrical conductivity, and robust mechanical properties [16,101]. Carbon materials have been the most used for the production of bespoke filaments, which may be related to their advantages over metals, such as corrosion resistance, lower density, good processability, longer shelf life, and relatively low-cost [94,95]. Furthermore, carbon-based composites can be easily manufactured into filaments for additive manufacturing on desktop-sized low-cost FFF printers [94]. In addition, carbon-based materials can be easily surface modified to improve their physical–chemical characteristics. This includes the introduction to their surfaces of functional groups containing hydrogen and oxygen, for example, by activation treatment of the material's surface using acidic, basic, or solvent solutions [102,103], which can change the nature of electron transfer at the surface affect the conductivity of the material [104]. These functional groups can also be used to attach other species to the surface, such as nanoparticles or biomolecules. Thus, the modification of surface functional groups may provide interesting applications for bespoke filaments.

One of the advantages of producing bespoke filaments is the versatility of changing their components, aiming to improve them in comparison with the available commercial filaments, which normally show relatively poor conductivity and performance. The addition of increasing amounts of nanographite as filler has been demonstrated to change electrical resistivity, with the conductivity increasing with the addition of up to approximately 20–30 wt% filler loading [92]. Above 25 wt%, however, the filament becomes brittle enough to affect printability; a plasticizer is needed. Another problem to be overcome with commercial filaments concerns the need for surface activation, *i.e.,* removal of surface polymer, to improve the performance of additive manufacturing devices. However, it has been shown that bespoke filaments based on graphite can be produced with good electrochemical performance even without any surface treatment, thereby facilitating the additive manufacturing of a ready-to-use biosensor [105]. The need for activation was probably avoided due to the use of a larger volume fraction of conductive material. On the other hand, the proposed filament was more brittle when compared to the commercial one, which in general is made of graphene or carbon black with plasticizers.

Nanostructured carbon-based materials, such as graphene, carbon black, and carbon nanotubes, have shown significantly improved properties compared to 3D macro-materials (*i.e.*, graphite) [106]. For example, graphene and graphene oxide (GO) have been effectively used as fillers, improving mechanical reinforcement, flame retardancy, and electrical conductivity in filaments [74]. Graphene oxide has shown better dispersion in the polymer matrix compared to graphene sheets, which is due to the presence of oxygenated functional groups on basal planes [107]. However, functional groups can affect the conductivity of the material, which can be mitigated by chemically reducing them to restore the sp^2 bonds in graphitic domains. This has been done by using reducing agents such as hydrazine, or thermal, or electrochemical methods [16,40]. The reduction of graphene oxide can improve the electrical conductivity of the composite material. As an example, graphene-based filaments based on PLA showed better additive manufacturing and conductivity for electrochemical battery applications after chemical treatments, increasing the porosity and the specific capacity [100]. Thus, graphene-based bespoke filaments have been applied for the development of additive manufacturing devices for sensing and biosensing [101], and energy applications *i.e.,* supercapacitors, batteries, and fuel cells, among others [107,108].

Carbon nanotubes have been considered promising materials as fillers in polymers due to their excellent thermal and electrical properties [80]). Carbon nanotubes have been reported to produce bespoke filaments at proportions of 0.25–10 wt%, which provided improvement in the electrical and thermal conductivity, and mechanical properties [98,109,110]. Depending on the preparation conditions, single- or multi-walled carbon nanotubes (SWCNT or MWCNT) can be obtained. MWCNTs show better thermal properties than SWCNTs, offering some addi-

TABLE 2

Physical and electrical properties of common conductive fillers.

Conductive filler	Particle size order (Smallest Dimension)	Electrical conductivity (S cm^{-1})	Thermal conductivity (W/mK)	Specific surface area (m^2/g)	True Density (g cm^{-3})
Graphite	Micrometres [a](3D)	Moderate ($\sim 10^5$) [b]	Low (100–400) [c]	Low (60–150) [d]	Low (1.9–2.3) [e]
Carbon black	Nanometres [f](0D)	Moderate ($\sim 10^3$) [g]	Low ($\sim$90) [h]	Low (40–250) [i]	Low (1.7–1.9) [h]
Graphene	Nanometres [j](2D)	Very high (10^6 10^8) [k]	High (3000–5000) [l]	Very high ($\sim$2600) [m]	Low ($\sim$2.3) [n]
Carbon nanotubes	Variable [o](1D)	High (10^5 10^7) [p]	Variable [q] (2000–6000)	Variable [r] (50–1300)	Low (1.3–1.8) [h]
Carbon nanofibers	Variable [s](1D)	Moderate ($\sim$1.0) [t]	Variable [u] (10–2000)	High(300–700) [v]	Low (1.3–2.0) [h]
$MoSe_2$	Variable [x](2D)	Moderate (<1.0) [y]	Low (10–45) [w]	Low (30–130) [z]	Moderate ($\sim$6.9) [zz]

Key: [a] $\sim$ 30–150 μm [58,65]. [b] Variable depending on the source [65]. [c] [66]. [d] Depends on the adsorbed vapor [58]. [e] [58,67]. [f] 20–50 nm [68,69]. [g] [65]. [h] [58]. [i] [69]. [j] Depends on the graphene structure. > 100 nm in both dimensions for graphene sheets and flakes. 1.0–100 nm for nanographene [70]. [k] Variable for pristine graphene (10^4 10^6 S m^{-1}) or reduced graphene oxide monolayers ($\sim 10^2$ S m^{-1}) [65,71,72]. [l] [66,73]. [m] [74,75]. [n] [67]· [o] Depends on the length of nanotubes. Average: 6.0–50 nm in diameter and 1.0–30 μm in length [76–78]. [p] [65,79]. [q] Depends on the length and the single or multi-walled nanotubes [66,80,81]. [r] Depends on the length of nanotubes [82]. [s] Depends on the length of nanofibers. Average: 5.0–100 nm in diameter and 5.0–100 μm in length [83]. [t] [84]. [u] $\sim$ 2000 W/mK or 10–100 W/mK for axial or transverse direction [66]. [v] Depends on the length of nanofibers [83]. [x] Depends on the synthesis method. Nanosheets: $\sim$200 nm; Single crystals: μm – mm [85,86]. [y] [87]· [w] [88]. [z] [89,90]. [zz] [91].

tional benefits [80]. MWCNTs have also shown more biocompatible characteristics, for example enhancing protein adsorption, mechanical properties, and other biological properties necessary for the development of additive manufacturing porous scaffolds for bone tissue regeneration [110]. In addition, the length of nanotubes has been shown to influence the properties of conductive polymeric composites; recent work have concluded that using longer MWCNTs leads to increased electrical and thermal conductivities in composite materials, as they are more effective in forming the electrical path, regardless of the filler proportion added to the polymeric matrix (1.0–10 wt%) [80]. Similarly, long carboxylated MWCNTs-based conductive filaments showed enhanced conductivity and electrochemical performance compared to short ones [98]. These characteristics were essential for the conductive filament's application as an additive manufacturing device for yellow fever virus biosensing. This demonstrates that long MWCNTs can be more advantageous for making bespoke filaments, specifically because less filler content is required to achieve electrical percolation.

In addition to carbon-based materials, the use of metal particles in conductive FFF filaments has also been reported [53,111–113]. As an example, $MoSe_2$ is a 2D transition metal dichalcogenide that has shown effective results as an electrocatalyst, in which its catalytic activity is associated with its morphology and edge sites [114]. $MoSe_2$ incorporated into a conductive carbon-based filament was responsible for the reduction in the electronegativity of the hydrogen evolution reaction onset potentials of additive manufacturing electrodes applied for water splitting [111]. As another example of metal-based fillers, nickel particles and a low melting point metal alloy ($Sn_{95}Ag_4Cu_1$) were described for the fabrication of a highly conductive filament based on nylon – 6 or polyethylene (PE) polymer matrixes [112]. In this case, metal volume above 25 vol% allowed to achieve the percolation, increasing the conductivity of the material, as well as showed lower melt viscosity, and resistance $\leq 1\ \Omega$.

Conductive polymers, such as PEDOT and polyaniline, are also interesting alternatives to produce bespoke filaments since they show excellent mechanical and conductivity properties [115–117]. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and poly(ethylene oxide) mixture showed high conductivity with low loadings, demonstrating that they are efficient candidates for the fabrication of conductive filaments aiming the manufacturing of electrodes [118]. PEDOT:PSS shows thermal stability and high conductivity, while poly(ethylene oxide) performs good melt-state processability by extrusion, behaving like rubber at room temperature [66,119]. Based on this, the use of conducting polymers for additive manufacturing has been reported for several electronic applications, such as for (bio)sensing, energy storage, wearable devices, bones, and tissue engineering, among others [116].

The mixture of two or more conductive filler materials can be advantageous since the physicochemical properties of both materials can combine synergistically in the filament, especially for improvement in conductivity. Regarding carbon-based materials, this combination can be seen with carbon nanofibers and graphite [120,121], or carbon black and carbon nanotubes [98]. For example, a filament based on carbon nanofibers and graphite fillers at the same proportion of 20 wt% each showed better electrical conductivity, mechanical and additive manufacturing properties when compared to their constituents [120]. Below 10 wt% loading of conductive fillers, the material showed dielectric behaviour, suggesting that the percolation threshold has not been achieved. Recently, the influence of mixing carbon black with or without MWCNTs (25 wt% loading) has been investigated to produce a conductive filament. The addition of 10 wt % MWCNTs showed improved electrochemical performance and surface area, allowing its application in biosensing [98].

Catalytic materials have also been used as fillers, for example aiming for the development of electrochemical devices for water splitting, and energy conversion and storage [53]. As an example, a PLA conductive filament was produced by mixing metals and carbon materials [111]. The filament was composed of $MoSe_2$, carbon black, and Pt on carbon (Pt/C), and showed electrocatalytic behaviour for water-splitting applications. The electrochemical performance for hydrogen and oxygen evolution reactions showed improvement compared to carbon-based electrodes. Another example was the production of a graphene-based filament containing $Ni(OH)_2$ microparticles for the electrocatalytic oxidation of glucose [40]. This is a good demonstration of how bespoke conductive filaments can be designed for use in specialised applications by experimenting with changing the composition of the filler.

Filament production

The practice of producing conductive filaments for use in conjunction with FFF additive manufacturing technology has gained significant attention in recent years. By producing bespoke conductive filaments, research groups have explored a wide range of materials in various proportions for application in additive manufacturing, with a particular emphasis on the manufacture of electronic devices. However, since the emergence of the first bespoke conductive filament, new methods based on the limitations and laboratory structures of research groups have been reported. Two approaches to filament production have emerged: one that produces conductive composites using solvent-based methods, and another that employs thermal procedures. It is important to note that most production routes used to obtain conductive composites require a final extrusion step. The extrusion of the material, whether initially produced using solvent-based methods or thermal procedures, is necessary to create filaments capable of being used in conjunction with additive manufacturing. An overview of how these methods are generally performed can be seen within Fig. 2. Importantly, the production methods consist of highly reproducible basic systems as will be further presented.

Regarding solvent-based methods, it is possible to employ a variety of different solvents, such as acetone, chloroform, xylene, *N*-methylpyrrolidone, and dichloromethane, among others. In solvent-based methods, the bulk polymer is dissolved to make a relatively dilute solution, into which the conductive filler can easily be dispersed. Upon removal of the solvent by evaporation and drying, a conductive composite material is formed as the polymer encapsulates the particles. In general, dissolution of the polymer is slow and tedious, although heating can be employed to accelerate this process (provided this can be performed without causing too much solvent evaporation or a build-up of pressure in a sealed vessel). Stirring of the solutions is typically necessary to effectively dissolve the polymer and provide a homogeneous mixture and reduce agglomeration of the particles. Ideally, high-shear mixing processes, *e.g.,* high-power ultrasonication, would be employed to break up agglomerates of particles and finely disperse them into solution, although care must be taken not to damage the polymer or overheat the solution. Indeed, most reports where filaments are produced by solvent mixing use standard, low-shear techniques like magnetic stirring. Overall, while simple and easily accessible, solvent-based methods suffer from long preparation times as a consequence of the long dissolution and evaporation/drying steps. With the low-shear techniques typically used, it is also difficult to disperse the filler particles to a level smaller than those already present in the powder unless the filler and solvent are especially energetically compatible (which is unlikely in the case of commonly used carbon fillers and solvents).

By contrast, thermal methods typically heat and melt the polymeric matrix in a sealed chamber, while simultaneously incorporating the conductive filler with a mixing element. Because of the high viscosity of polymer melts, and the design of the chamber/mixing elements, high shears can be generated in the mixtures which readily disperses the filler particles. This process is both considerably faster than solvent dissolution and able to disperse the particles to a much finer level. In addition, the thermal method does not require the use of hazardous solvents, making it more environmentally friendly. However, it requires sophisticated and costly equipment and infrastructure, which may not be feasible for all research laboratories, especially those specialising in analytical chemistry. Thus, despite its disadvantages, the solvent-based method remains one of the most viable and practical options to be employed by such laboratories.

To ensure the obtention of more uniform filaments, the extrusion step is an important part of filament fabrication. The choice of extrusion equipment is important for providing smooth filaments with only small variations in diameter and therefore consistent printing behaviour. In the extrusion step, the process begins with feeding the conductive polymer composite, which has typically been made by solvent or thermal processing and then pelletised, into the equipment. One of the main components of the extruder is called the “screw,” which is essential for the filament formation process. The screw is responsible for transporting, heating, and pressurizing the material throughout the process. The screw has a helical shape, and as it rotates, it transports the composite through the heat zones in a pressurized manner to be expelled as filament at a constant rate. Thus, the screw is the central point that guides the material in the formation of filaments to be used in additive manufacturing.

One of the first works to demonstrate the production and applicability of a conductive filament using solvent-based methods was by Leigh *et al.* who produced filaments based on polymorph thermoplastic and carbon black for electrical sensor fabrication [96]. In the composite production process, the polymer and carbon black were added to dichloromethane under continuous stirring for 1 h. Subsequently, solvent evaporation and heating steps were performed to obtain the desired composite. This enabled the production of conductive filaments ready for use in the fabrication of desired sensors. Wei *et al*. fabricated a graphene composite for additive manufacturing printing applications. The filament production method involved the use of a solvent (*N*-methylpyrrolidone) to produce graphene-based composites with the polymer (ABS or PLA) [74]. Once the composites were obtained, they were extruded to form filaments, which were then used in conjunction with an additive manufacturing printer to produce desired parts. Highlighting the practicality offered by solvent-based methods in the manufacturing of conductive filaments, Foster *et al.,* presented a new conductive filaments for anode production in batteries [100] where the filament were composed of PLA and conductive material (graphene). In their

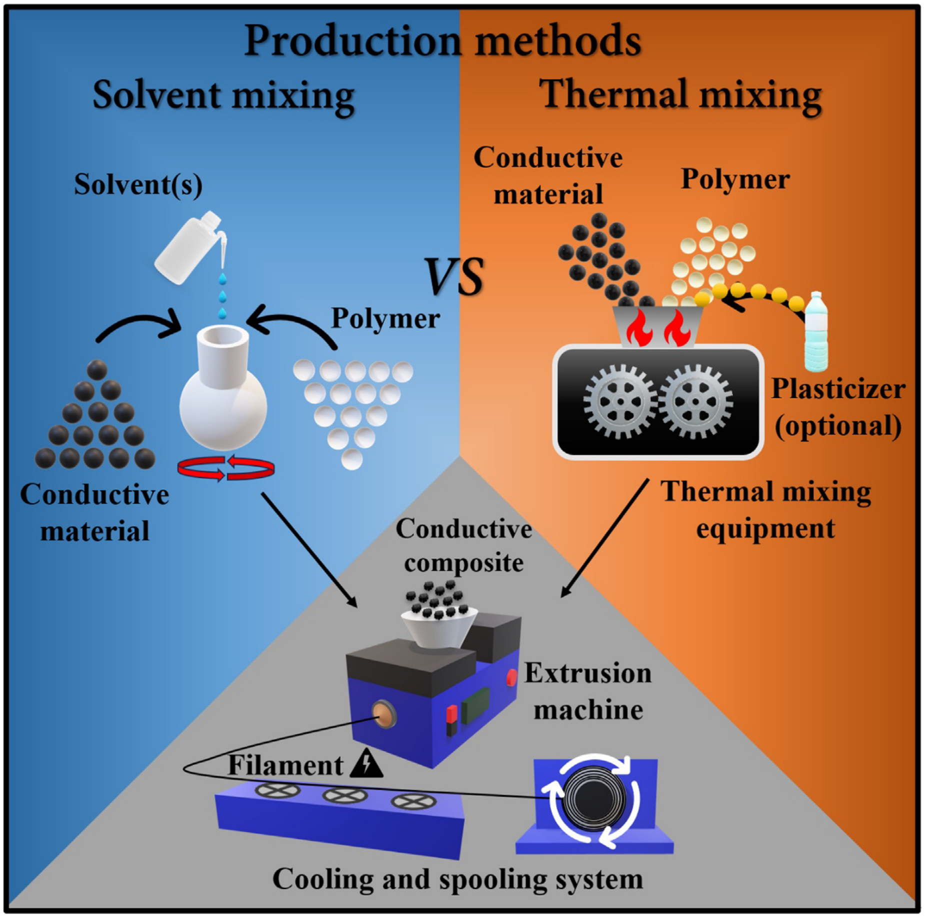


FIG. 2

General scheme of the main methods involved in the production of conductive composites involving thermal and solvent approaches and standard method for extrusion and manufacture of conductive filaments. Note that the size and proportions of conductive material and polymer are illustrative only, and not shown to scale.

approach, the filament produced employed the same solvent-based method, which involved dispersing the conductive material in xylene under constant heating and stirring for 3 h, followed by the addition of the polymer (PLA) for an additional 3 h to achieve a homogeneous composite [100]. The composite was then precipitated and washed using methanol, dried, and extruded to form the conductive filaments.

The development of thermal procedures for the production of conductive filaments has garnered significant attention in the realm of additive manufacturing. In a pioneering study, Zhang *et al.* successfully manufactured conductive filaments using PLA and rGO for fabricating flexible additive manufactured circuits [122]. The thermal fabrication method employed involved two distinct steps. Firstly, pulverized rGO and PLA were added to a twin-screw melt mixer to form a composite. Subsequently, the composite underwent another round of pulverization before being fed into an extruder to produce conductive filaments based on PLA and rGO. In a similar vein, Kowk *et al.* demonstrated the production of an elegant conductive composite by simply mixing homo-poly(propylene) and carbon black in a single-screw extruder [94]. The resulting conductive filaments were then utilized for manufacturing of 3D-printed electrical circuits. Continuing the quest for new applications of additive manufacturing in the field of electrochemistry, Wuamprakhon *et al.* successfully produced a bespoke conductive filament using carbon black and recycled PLA for fabricating supercapacitors [54]. The production process involved utilizing a thermal rheomixer to create the desired conductive composite, which was subsequently fed into an extruder to fabricate the conductive filaments.

The production of conductive filaments has led to fascinating and versatile outcomes, opening up a world of possibilities for electrical device fabrication. In recent years, its prominence has increased, especially when referring to the use in the fabrication of additive manufacturing electrochemical sensors, captivating the attention of analytical chemists worldwide. This field continues to expand exponentially since the ground-breaking introduction of the first electrochemical sensor proposed using bespoke conductive filaments by Foster *et al.* who delivered a nanographite loaded filament (25 wt%) within PLA who shows that the simultaneous detection of lead (II) and cadmium (II) is possible. [92]. Other work has reported on the development of two optimized filaments the combination of PLA and high loading of graphite (40 wt%), while the other employed carbon black (28.5 wt %) as a conductive filler [20,105]. The authors employed solvent-based preparation methods, aiming at the use of less toxic solvents. The production process involves a meticulous preparation step, where the conductive composite is obtained in the presence of acetone and chloroform using a reflux system to avoid the escape of solvents. Subsequently, the precipitation process was performed using ethanol, culminating in the extrusion of the dried conductive composites, reaching the final filaments. Remarkably, the use of the filament based on graphite-PLA provided excellent results as electrochemical sensors, eliminating the need for surface treatments previous to use, a procedure frequently demanded when using additive manufacturing electrochemical sensors [105]. The procedure developed by the authors is summarized in Fig. 3A.

In the pursuit of the creation of environmentally friendly additive manufacturing sensors, some researchers are looking for the reuse of PLA-based to develop distinct (bio)sensors [55]. Their method involves the use of conductive materials using carbon black and carbon nanotubes in conjunction with a plasticiser and recycled PLA for filament production. The conductive and non-conductive materials are combined within a heated mixing machine to provide the final composite, which removes any need for additional solvents. Subsequently, the filaments were extruded and passed through a cooling and spooling system, to be used in the additive manufacturing of the sensors. Fig. 3B provides an illustrative representation of the full procedures involved. This approach requires that the polymer being used, it is dried in an oven at a temperature for a set time in order to remove any residual water, as this will affect its extrusion, resulting in poor filament. The conductive part it is mixed with non-conductive (polymer) within a rheomixer at a set-temperature. The resulting polymer composite is allowed to cool to room temperature before being granulated to create a finer granule size using a granulator. The granulated sample was collected and processed through the hopper of a extrusion comprises a single screw with four set heat zones of where the molten polymer was extruded from a 1.75 mm die head, pulled along an Airpath cooling line, through an inline measurement and collected on a spooler. This allows one to ensure that the uniformity in the dimension of the filament it is controlled, and it is consistent.

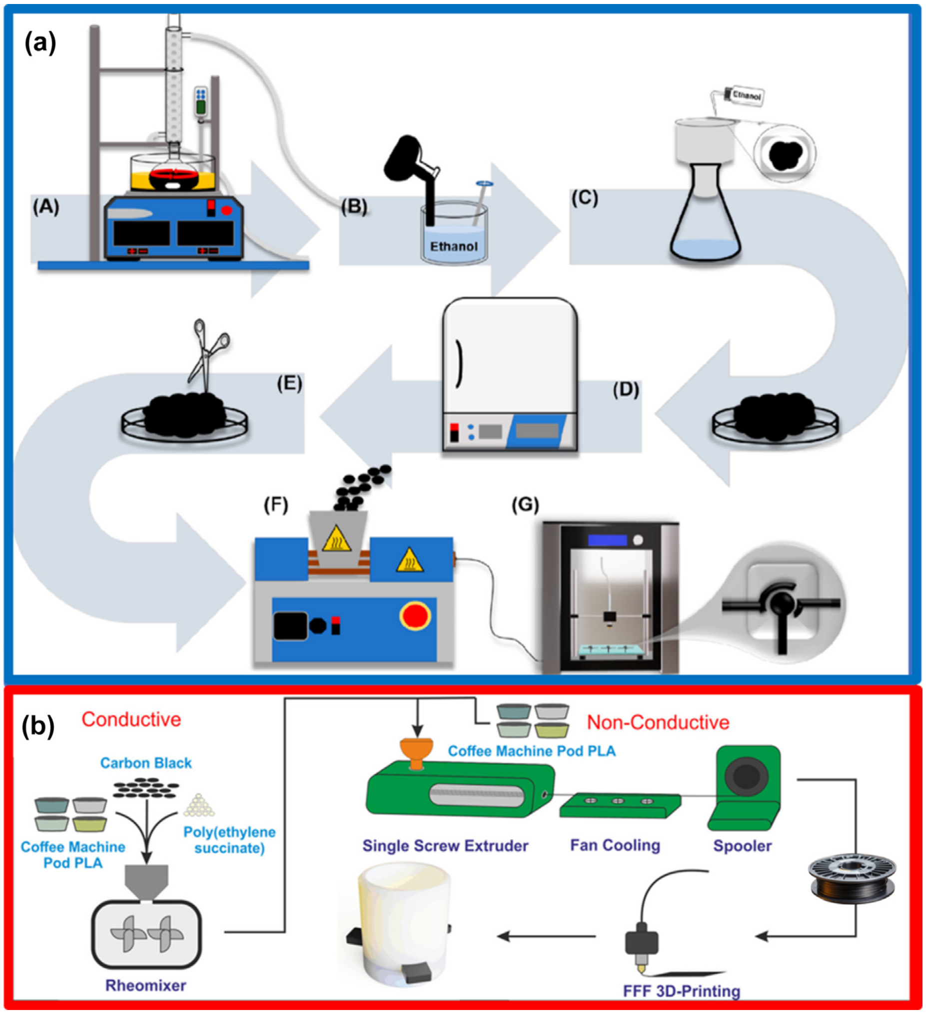


FIG. 3

(A) Illustrative scheme of a procedure based on solvent mixing for the manufacture of bespoke composite and filament, reprinted from [105] with permission. Copyright (2022) Elsevier. (B) General scheme of a procedure for manufacturing conductive bespoke filaments using thermal mixing, reprinted from [55] with permission. Copyright (2023) American Chemical Society.

Bespoke filaments in the literature and their applications

Filament fabrication methods for FFF additive manufacturing have been explored for a wide variety of purposes. In the literature, it is possible to find reports on the manufacture of filaments containing the most diverse compositions, where the polymeric matrix and the fillers can be chosen according to the desired application. For instance, Isakov *et al.* [123] proposed a bespoke filament composed of ABS and $SrTiO_3$ (28 vol%) to manufacture regions of a gradient refractive index (GRIN) lens and horns, enabled by the high relative dielectric permittivity of the final composite. The composite was obtained by solvent dissolution of the polymer using acetone and incorporation of $SrTiO_3$, forming a viscous suspension. After evaporation of the solvent, the composite was milled and inserted into a single-screw hot extruder, giving rise to the bespoke filament [124]. In an interesting work, Cochran and co-authors [125] fabricated a filament for the additive manufacturing of X-ray phantoms (used in medical imaging for quality control tests). Such material requires the same physical properties as the object being simulated, thus, the authors incorporated calcium into PLA to mimic bone. The filament was obtained by the dissolution of PLA using chloroform, and incorporation of 30 wt% calcium into the solution. After evaporation of the solvent, the material was crushed and extruded at 190 °C. The proposed filament showed more realistic bone properties for the attenuation of X-ray photons than pure PLA, indicating the potential of the material. Recently, Shimeta *et al.* [126] developed bespoke filaments for the additive manufacturing of structures with macrofouling properties to prevent the growth of marine biofilms. A filament with antifouling properties, containing polycaprolactone (PCL) mixed with the organic biocide dichlorooctylisothiazolinone (DCOIT) was proposed by the authors. Settlement plates printed with the proposed filament were deployed in coastal marine water for 17 weeks. The authors reported that the additive manufacturing structure remained free of macrofouling, and the use of PCL-DCOIT reduced the microbial diversity, showing great potential. The filament was prepared by melt mixing with the extrusion of PCL pellets coated with DCOIT in a proportion of 10:1 (PCL: DCOIT). The coating was performed in a mixer at 32 °C for 10 min. The extruded filament was spooled and used in the additive manufacturing of settlement plates. As can be seen, many possibilities and materials can be created, however, besides the many possible applications, the use of conductive fillers for obtaining conductive composite filaments has been a challenge. The composite fabrication needs to be carefully performed to ensure that the conductive filler incorporation is uniform. This will avoid agglomerations, capable of causing clogging in the print nozzle, or even increase the percolation threshold, thus demanding higher amounts of conductive fillers to ensure the material's conductivity [127]. In recent years, the incorporation of varied conductive fillers has increased. Among them, carbon-based materials, such as graphene, carbon black, carbon nanotubes, and graphite stand out and have been more explored due to their excellent aforementioned properties. The use of conductive fillers has expanded the applicability of additive manufacturing due to the possibility of giving rise to electrical conductivity in composite filaments, becoming a great ally in the manufacture of materials with applications that include electrical circuits, energy storage devices, and electrochemical sensors [38,127]. Table 3 provides a summary of the fabrication methods and materials used for the obtention of electrically conductive composite materials, in the context of filament fabrication for additive manufacturing.

As can be seen, PLA is notably the thermoplastic most used in the additive manufacturing of conductive filaments, due to its thermal properties allowing for excellent printability, whilst still being a good material for end use [38]. Regarding the conductive filler, carbon allotropes are the most widely explored materials. Carbon black along with carbon nanotubes and graphene are the most popular, followed by graphite. In the work of Leigh *et al.* [96] a composite filament composed of CB (15 wt%) and PCL was proposed. The filament was produced by mixing the components in dichloromethane for 1 h. The final suspension was placed in a watch glass, and after 1 h of solvent evaporation in a fume hood, the formed film was poured into a warmed water bath (80 °C) for 1 min. The filament was formed by rolling the warm film between two glass plates. After 2 h cooling, the filament was ready to be used for additive manufacturing. The new proposed filament was low-cost and accessible according to the authors and was used in the additive manufacturing of a range of functional sensors, including sensors to evaluate mechanical flexing, capacitive sensing devices for Human Interface Devices, and capacitive sensors to sense the amount of liquid in smart vessels. Fig. 4A-C shows the proposed capacitive sensor developed for Human Interface Device. When the user touches the conductive additive manufacturing (3D printed) pad, an increase in the capacitance occurs being sensed by an Arduino board and, consequently, triggering an operation.

The use of graphene was exploited by Wei and co-authors [74]. The authors demonstrated for the first time the manufacturing of a graphene-based composite. The composite was obtained from graphene oxide (GO) since the oxygenated groups present in this compound improved the dispersion of graphene in polymeric phases. Though the electrical conductivity is affected by the conversion of graphene to GO, the subsequent reduction of GO to reduced GO (rGO) restores the electrical conductivity, allowing a conductive composite to be obtained. The new composite was composed of 5.6 wt.% of graphene in an ABS matrix. For the preparation, a dispersion of GO in *N*-methylpyrolidone (NMP) was joined to a mixture of ABS-NMP and homogenized with the aid of a homogeniser. The subsequent reduction of GO was performed by adding hydrazine hydrate and keeping it under homogenizing for 1 h at 95 °C. After dispersion, deionized water was added to the mixture to precipitate the composite, which was washed with ethanol and water, and dried in an oven for 25 h. Fig. 4D-J shows images of the dispersions in each preparation step. The filament was then prepared with the aid of a single-screw extruder and was ready to be used for additive manufacturing, as shown in Fig. 4K and L where it is printed.

Santagar *et al.* [130] developed two conductive filaments, one containing CB and the other CNTs, both on a PLA matrix, and proposed an interesting application for the obtained materials. The incorporation of the conductive fillers in PLA was performed by melt mixing, with appropriate equipment. With the obtained

TABLE 3

A comprehensive table of bespoke conductive filaments for additive manufacturing reported in the literature.

Polymer matrix	Filler (wt%)	Additive	Method	Manufacturing time / h	Proposed application	Ref.
PCL	CB (15%)	–	Solvent dissolution – DCM	2 h + 2 h cooling	Electronic sensors to sense mechanical flexing and capacitance changes	[96]
ABS	CNTs (0.5–3%) and CF	–	Melt mixing – extrusion	–	–	[128]
PCL	Magnetite particles	–	Solvent dissolution – DCM	1 h + drying	Flow sensor	[129]
ABS	rGO (0.4–5.6%)	–	Solvent mixing – NMP	1.1 h + 24 h drying	–	[74]
PLA	rGO (6%)	–	Melt mixing	0.25 h	Flexible circuits	[122]
PP	CB (29.8%)	–	Melt mixing – extrusion	–	Circuits and thermal sensor	[94]
PLA	CNTs or CB (10%)	–	Melt mixing	–	Development of smart textiles	[130]
PBT	CNTs (0.5%) or Graphene (5.2%)	–	Solvent mixing - isopropanol	3 h + 24 h drying	–	[97]
PLA	Graphite (70%)	PC, PEGDME and ATBC	Solvent dissolution – DCM	2 h + 3 h drying	Lithium-ion battery	[131]
PLA	CNTs (1–9%)	–	Solvent dissolution – CFM	14 h + drying	–	[132]
PLA	CNTs or CB (10%)	–	Melt mixing	–	–	[133]
ABS	CNTs (1–8%)	–	Melt mixing	0.5 h	–	[134]
PEEK	CNTs (3–4 %) and GnP (1–5%)	–	Melt mixing – extrusion		–	[135]
PCL	Cu-Ag core-Shell nanowires (50%)	–	Solvent dissolution – DCM	1 h + drying	Electronics	[113]
PLA	Graphene (20%)	–	Solvent dissolution – xylene	6 h + drying	Lithium-ion battery	[100]
PLA	2D-$MoSe_2$ (10%) and CB (15%), or Pt and CB (25%)	–	Solvent dissolution – xylene	6 h + drying	Water splitting	[111]
ABS	CNTs (1–10%)	–	Melt mixing – extrusion	0.08 h	–	[136]
PLA	NC (0–6%)	–	Solvent dissolution – DCM	–	Fabrication of robots	[137]
PLA	NG (25%)	–	Solvent dissolution – xylene	6 h + drying	Electrochemical sensor	[92]
PLA	Graphene and $Ni(OH)_2$ (10%)	–	Solvent dissolution – ACN + CHL	–	Electrochemical sensor	[138]
ABS, PLA, PP, HDPE, LLDPE or PETG	Graphene, CNTs or CB (15%)	–	Melt mixing – extrusion	–	Electronic circuits	[139]
PVA	Graphene (0.1–1%)	glycerol	Solvent mixing – ethanol	–	–	[140]
PLA	Graphene (20%)	–	Solvent dissolution – xylene	3.5 h + drying	Supercapacitor	[24]
ABS	CNTs (1–9.1%)	–	Solvent dissolution – ACN	5.3 h + drying	–	[141]
PLA	Ti(C,N) (45.4 vol%) + nNi (1.4 vol%)	PEG and PEI	Solvent dissolution – THF	–	–	[142]
PLA	Graphite, or AC and CNTs, or AC, CNTs and 2D-MoS_2	PEG	Solvent dissolution – DCN	1 h + 12 h drying	Energy conversion and storage	[53]
PLA	CF (21–25 vol%)	–	Melt mixing	–	–	[143]
PLA	Graphite (40%)	–	Solvent dissolution – ACN + CHL	3.5 h + 12 h drying	Electrochemical biosensor	[105]
PLA	CB (28.5%)	–	Solvent dissolution – ACN + CHL	3.2 h + 12 h drying	Electrochemical sensor	[20]
PLA	GNPs (30%)	–	Melt mixing – extrusion	–	–	[144]
PLA + PCL	GNP (10–25%)	–	Melt mixing – extrusion	–	Circuits	[145]
rPLA	CB (22.5%)	PEG	Melt mixing	0.17 h + cooling	Supercapacitor	[54]
PI-PLA	CB (29.6%)	PES	Melt mixing	0.17 h + cooling	Electrochemical sensor	[55]

(continued on next page)

TABLE 3 (*CONTINUED*)

Polymer matrix	Filler (wt%)	Additive	Method	Manufacturing time / h	Proposed application	Ref.
rPLA	CB (25%)	–	Melt mixing	–	Electrochemical sensor	[146]
rPLA	CB (15%) and CNTs (10%)	PES	Melt mixing	–	Electrochemical biosensor	[98]
rPLA	CB (25%)	Castor oil	Melt mixing	–	Electrochemical sensor	[56]
PLA	Graphite or graphene (15–25 vol%)	PEG	Solvent dissolution – THF	–	Electrodes	[147]
PLA	CB (28.5%)	–	Solvent dissolution – acetone/chloroform	3 h + 12 h drying	Electrochemical biosensor	[148]
rPLA	CB (15%), NG (10%)		Melt mixing	–	Electrochemical sensor	[149]

Key: PCL: polycaprolactone; CB: carbon black; DCM: dichloromethane; ABS: acrylonitrile butadiene styrene; CNTs: carbon nanotubes; CF: carbon fibres; rGO: reduced graphene oxide; NMP: N-Methylpyrolidone; PLA: poly(lactic acid); G: graphene; PP: polypropylene; CB: carbon black; PBT: polybutylene terephthalate; PC: propylene carbonate; PEGDME: poly(ethylene glycol) dimethyl ether; ATBC: acetyl tributyl citrate; CFM: chloroform; PEEK: Polyether ether ketone; GnP: graphite nanoplates; NC: carbon nanoparticles; TPU: thermoplastic polyurethane; NG: nanographite; ACN: acetone; CHL: chloroform; HDPE: high density polyethylene; LLDPE: linear low-density polyethylene; PETG: glycol modified polyethylene terephthalate; PVA: polyvinyl alcohol; nNi: nickel nanoparticles; Ti(C, N): titanium carbonitride; PEG: poly(ethylene glycol); PEI: polyethylenimine; THF: tetrahydrofuran; AC: activated charcoal; GNP: graphene nanoplatelets; rPLA: recycled poly(lactic acid); PI-PLA: post-industrial waste poly(lactic acid) from coffee machine; PES: poly(ethylene succinate).

FIG. 4

A: Additive manufacturing of a capacitive interface device from CB-PCL filament. showing the CAD design proposed, B, image of the printed device, C, a macro image of the printed sensor, adapted from [96] with permission. Copyright 2012 PLOS ONE; Composite preparation and additive manufacturing. Pictures of D, graphite flakes, E, dispersion of GO, F, dispersion of ABS, G, homogeneous mixture of GO-ABS, H, mixture of GO-ABS after chemical reduction by hydrazine hydrate, I, G-ABS coagulations obtained after isolation with water, J, G-ABS composite powder after washing and drying, K, schematic illustration of the 3D printing process, L, additive manufacturing structures with the proposed filament; figures adapted from [74] with permission. Copyright 2015 Springer Nature; A filament comprised of 2 % CNTs within PLA filaments (M, N) and the use of additive manufacturing deposited on a PLA fabric; Figures adapted from [130] with permission. Copyright 2017 Elsevier; A Cu-Ag filament production. P, mixture of Cu-Ag NWs and PCL dissolved in DCM, Q, cut composite, obtained after evaporating the solvent, R, production of the filament by extrusion, S, image of the coiled conductive filament, T, SEM image showing the dispersion of Cu-Ag NWs in the filament, U, a section of the filament of 1.8 mm diameter showing resistance of 0.7 Ω; Figure adapted from [113] with permission. Copyright 2018 John Wiley and Sons.

filament, the authors proposed the development of smart and functional textiles, capable of avoiding unnecessary water, energy, or chemicals. The composite layers were additive manufacturied directly onto the fabrics, as shown in Fig. 4M and N, and did not compromise the flexibility or quality of the fabric. Though carbon materials have been widely explored, a Cu-Ag-based filament has been developed by Cruz *et al.* [113], showing that the incorporation of metallic particles can also be lab-made performed. The composite was fabricated by initially coating Cu nanowires with a thin shell of Ag to protect them from oxidation reactions. Then, the Cu-Ag nanowires were incorporated into PCL using dichloromethane. The evaporation of the solvent showed a solid composite that was further cut in pellets. The extrusion of the fabricated pellets provided the final filament. Fig. 4R–U shows the steps images of the produced composite and filament. According to the authors, this successfully enabled the fabrication of conductive parts capable of withstanding high current densities. Furthermore, the produced parts exhibit conductivity levels 100 times higher than those achieved with commercially available graphene-based filaments. Hence, these filaments possess significant potential for application in electrical devices.

Foster *et al.* [100] proposed the production of bespoke filaments containing graphene and PLA for the additive manufacturing of anodes for lithium-ion batteries. After studying several compositions, the authors showed that 20 wt% graphene shows sufficient conductivity gathered with satisfactory printability for manufacturing the anodes. Fig. 5A-E shows some physicochemical characterizations of the obtained filaments, and the additive manufacturing of the anodes. The fabrication of the filaments was performed by the solvent dissolution of PLA, using xylene as a solvent in a heated reflux system. After 3 h in reflux, a homogeneous solution was observed, and the polymer could be precipitated using methanol, providing a composite that was further extruded. The work demonstrates that lab-made filaments and additive manufacturing technology can be successfully used in the construction of energy storage devices. Kalinke *et al.* [98] produced conductive filaments containing a recycled poly(lactic acid) (65 wt%) mixed with polyethylene succinate (PES, 10 wt%), 15 wt% CB, and 10 wt% COOH-MWCNT, which showed superior performance compared to a commercially available filament. The authors applied the filament in the additive manufacturing of electrochemical sensors, where this composition retains the excellent flexibility but yet it is printable which allows for the enhanced coupling of the biorecognition element to the COOH-MWCNT for the preparation of an electrochemical genosensor for the detection of yellow fever virus cDNA. The preparation of the filament involved the mixture of all components thermally, and subsequent extrusion as schematized in Fig. 4F. The notable flexibility of the proposed filament can be seen in Figure G-H. Stefano and co-authors [20] developed a CB-based filament by the solvent dissolution method. The authors used a mixture of acetone and chloroform for solubilizing the PLA and providing effective incorporation of CB particles. After 3 h under magnetic stirring in a reflux system, the solution was placed in a recipient containing ethanol for precipitation of the polymer. The filaments originated after the extrusion of the formed composite were employed in the additive manufacturing of electrochemical sensors composed of 28.5 wt% CB and 71.5 wt% PLA. To perform an easy and non-enzymatic detection of hydrogen peroxide in milk samples, the authors electrochemically anchored Prussian blue particles at the sensor surface. The filament production process and proposed sensor images are presented in Fig. 5I-L.

To achieve adequate electrochemical performance these electrodes needed to be “activated”, a phrase commonly used in the field to remove polymer from the additive manufacturing electrochemistry platform, which would allow the conductive part being accessed *via* the three-phase boundary, increase the rate of ion transfer, enhanced conductivity, but most importantly, allowing edge plane sites/defects being available for fast electron transfer to occur. A summary of post-print treatments applied to additive manufacturing electrochemistry platforms has been provided by Rocha *et al.* [150] As can be observed from inspection of Fig. 6A-C shows the different methodologies for the activation of additive manufactured graphene electrode where DMF, NaOH and then with DMF and NaOH electrochemical gives rise to the most electrochemical activation creating oxygenated functional groups.

Other approaches are shown in Fig. 6D where an entire additive manufactured sodium ion (full cell) battery produced through the use of PVA, which is processed (dissolving in water), gives rise to a highly porosity surface, promotes electrochemical properties and access to the triple-phase boundary allowing fast ion transfer [48]. Another approach, highlighted in Fig. 6E shows that through a simple chemical pre-treatment can induce porosity resulting in a 200-fold increase in the output of Li-ion anodes within Li-ion batteries [100]. Other work shows the use of NaOH via chronoamperometry, which as shown in Fig. 6FG and H,I are the XPS of the pre- and post-treated electrode and shows that there is an increase in the graphitic carbon peak observed in XPS following treating. This is reflected through the change of morphology, as evidenced by the SEM images where a more porous surface structure is observed. Last, this approach of activation can be made simpler, through the inspection of Fig. 6J, one can observe the sensing of atropine which shows that there is no peak observed at the “no activation”, while in the case of the electrochemical activation (using NaOH), a large signal is seen. Note that this can replicated by simply dropping NaOH on the surface, which is washed, and it is ready to use, gives rise to the largest electroanalytical response. We note that the mechanism likely follows PLA hydrolysis; please see Scheme 1.

One key issue is the reusability of additive manufactured electrodes. In general, such systems are used once which are then are either sent to landfill or energy-from-waste, which is an issue with other disposable electrochemical systems such as screen-printed electrodes produced upon plastics, paper and related substrates [153]. Improving the sustainability of additive manufactured electrodes is of great importance, in line with the UN Sustainability Goals. Currently, most additive manufactured electrodes s are “single-shot” due to the poor chemical stability of PLA in different types of solutions, such as alkaline [46] and the ingress of solution inside the polymer matrix [47]. To combat this problem Sigley *et al.* (2023) [55] have introduced the concept of “*Circular Economy Electrochemistry*”,; please see Fig. 7A. In their approach, they used post-industrial waste poly(lactic acid) from

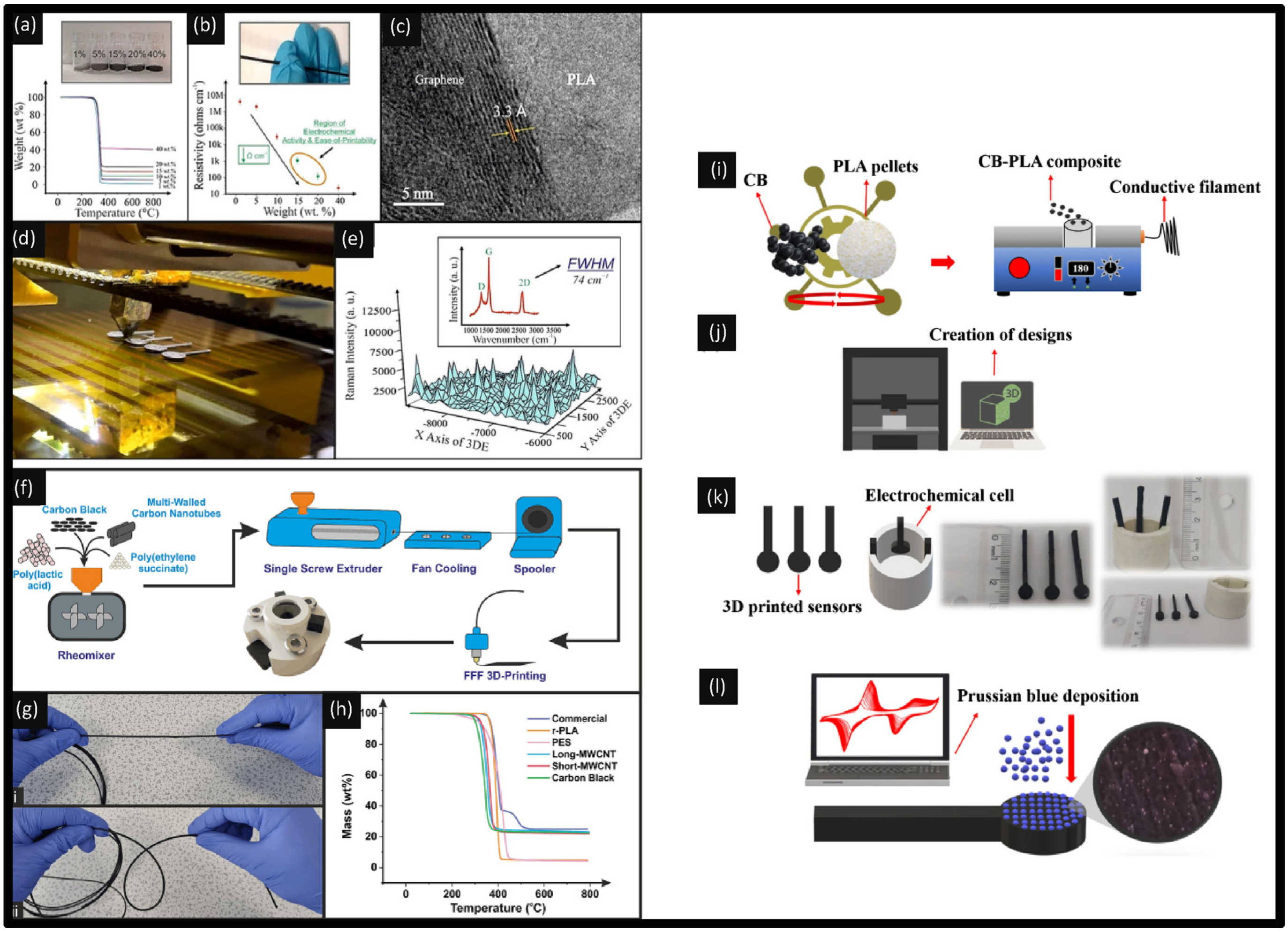


FIG. 5

A: thermogravimetric analysis of filaments with different graphene loadings, B, relation between resistivity and graphene content, C, transmission electron microscopic analysis of G-PLA (20% wt.), D, additive manufacturing of anodes, E, Raman and Raman Mapping of the additive manufactured anodes; Figures adapted from [100] with permission. Copyright 2019 John Wiley and Sons; F, CB and CNT-based PLA filament being fabricated scheme of production, G, photographs of the filament straightened (i) and bent (ii) highlighting the flexibility, H, thermogravimetric analysis results of the filaments explored; Figures adapted from [98] with permission. Copyright 2023 Elsevier. Representative scheme of: i CB-PLA filament production, J, additive manufacturing, K, electrochemical cell, and L, anchoring of Prussian blue particles in the electrochemical sensor; Figure adapted from [20] with permission. Copyright 2022 Springer Nature.

coffee machine pods into electroanalytical sensors for the detection of caffeine in real tea and coffee samples. The post-industrial waste poly(lactic acid) is transformed into both nonconductive and conductive filaments to produce full electroanalytical cells, including additively manufactured electrodes where the cell it is designed utilising separate prints for the cell body and electrodes to increase the recyclability of the system. The cell body made from nonconductive filament was able to be recycled three times before the feedstock-induced print failure. The author report three bespoke formulations of conductive filament were produced, with the post-industrial waste poly(lactic acid) of 61.62 wt% mixed with carbon black, 29.60 wt%, and poly(ethylene succinate), 8.78 wt% which has the equivalent electrochemical performance, lower material cost, and improved thermal stability and ability to be printable. It was shown that this system could detect caffeine which was shown to be able to detect the caffeine content in real and spiked Earl Grey tea and Arabica coffee samples with excellent recoveries (96.7–102%).

This work has been extended in showing how the recycling of old mixed material electrochemical prints into new electroanalytical sensing platforms that match the performance of the original [146] please see Fig. 7B. The authors processed the old prints in four different ways, finding that thermally mixing the prints gave the best dispersion of conductive filler throughout the polymer over that of granulation, ball-milling, solvent mixing, allowing the production of recycled non-conductive filament without the supplementation with any virgin feedstock where the filament was able to be cycled twice before failure. Additionally, they produced a conductive filament through the addition of carbon black into the mixing chamber to meet the same filler quantities as in the original filament. As shown within Fig. 7C, the authors show how to make a highly conductive filament with exceptional flexibility. Also shown is Fig. 7D where thermogravimetric analysis confirmed that the recycled conductive filament had a similar filler content to the original commercially purchased conductive filament, 21 (±2) wt% compared to 21 (±3)

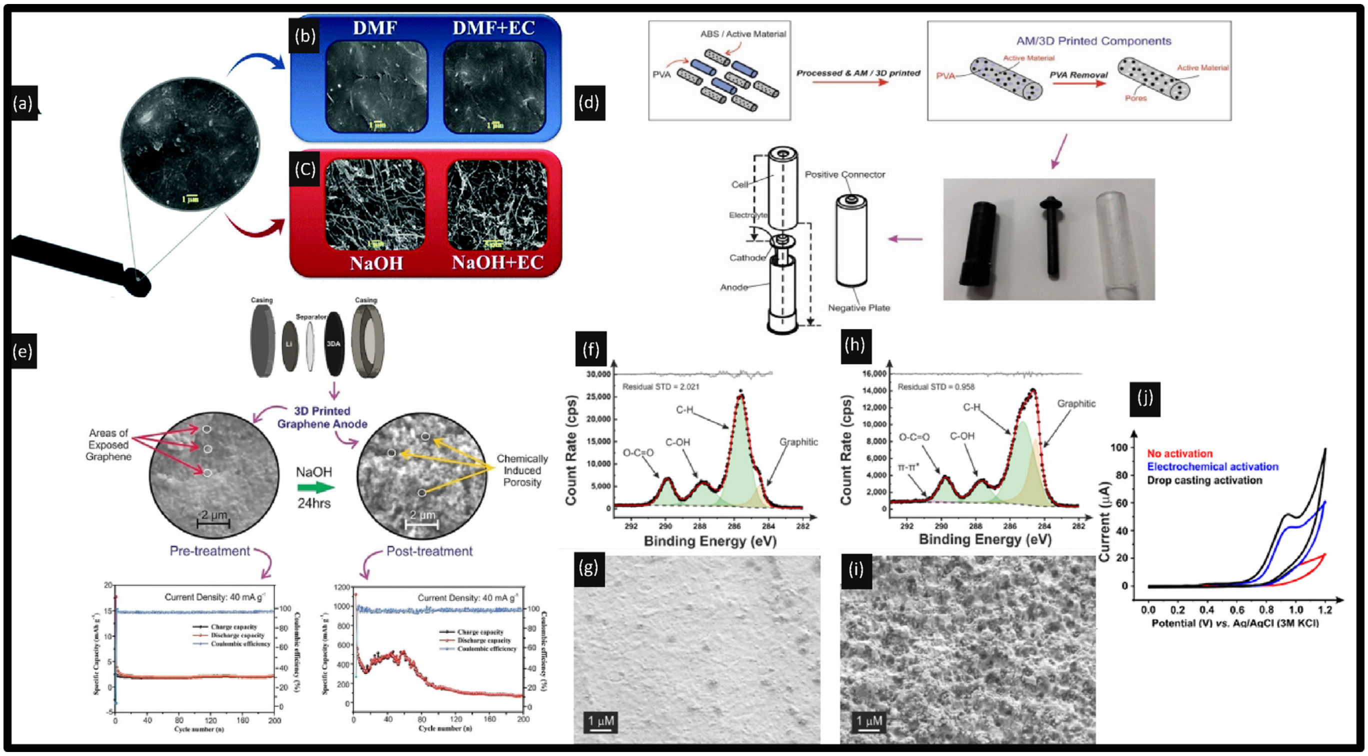


FIG. 6

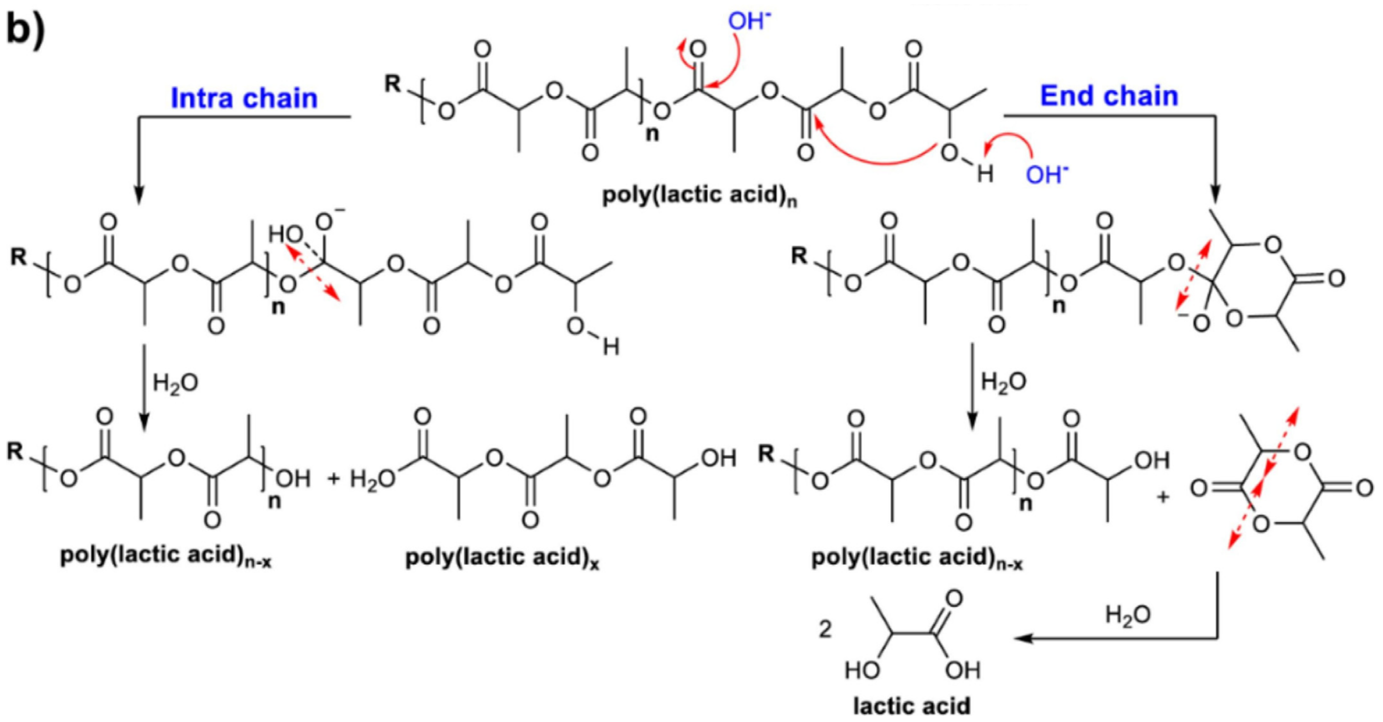
Additive manufactured PLA-graphene electrode design and SEM images with 10, 000X magnification of the electrodes: A: PLA-graphene, B: PLA-graphene in DMF for 10 min and DMF followed by electrochemical treatment (EC), C: PLA-graphene in 1.0 M NaOH for 30 min and NaOH followed by electrochemical treatment (EC). Figure reproduced from reference [102]) Copyright 2020 The Royal Society of Chemistry. D: Schematic illustration and photographs of the fabrication procedure of the complete freestanding fully AM printed sodium-ion battery. Figure reproduced from reference [48] Copyright 2019 Wiley. E: SEM images of a typical graphene additive manufactured anodes pre- and post-NaOH chemical treatment displaying their respective charge–discharge profiles. Figure reproduced from reference [100]. Copyright 2019 The Royal Society of Chemistry. F: XPS C 1 s data for as-printed and SEM image (G) while (H) shows activated CB/PLA/TTM electrode and SEM image (I,J: Cyclic voltammogram (50 mV s^{-1}) of 100 μM atropine (pH 11) with the nonactivated (red) and activated CB/PLA/TTM, both electrochemical (blue) and drop-casting (black) activations using 0.5 M NaOH. Figures reproduced from reference [151] Copyright 2023 American Chemical Society.

wt% where there is no longer a second transition for the recycled conductive filament due to no additional plasticizer being added to the recycled filament. This recycled conductive filament was then used in conjunction with the recycled non-conductive filament to make the electrochemical cell, as shown within Fig. 7E, photographs of the original cell and fully recycled cell from the side and top views where it is hard to see due to both recycled filaments being black, the electrodes are still well defined with the recycled conductive filament having a matt finish compared to the gloss of the recycled non-conductive filament which is due to the significantly increased carbon black filler content reducing the reflectivity of the material. The authors demonstrated that the electrochemical cell could measure acetaminophen in model and real samples, matching the performance of the originals. Last, the storage of filaments need to be considered. Kalinke and co-workers studied the Influence of filament aging and conductive additive into additive manufacturing sensors [31] where they stored their filaments in their original cardboard boxes and hermetic bags with silica gel, protected from light and heat. They found that aging of the filaments negatively influences the performance of electrochemical sensors, leading to a decrease in the response signal and its conductive properties even after the storage of the conductive filaments in the absence of light and moisture; this area needs further research to store conductive filaments for longer but yet they are electrochemical useful.

As can be seen, the production and application of bespoke filaments for additive manufacturing, especially conductive ones, have been studied in recent years, however, there is still much to be explored in this field. So far, very few applications are reported using bespoke conductive filaments. Furthermore, the manufacturing processes remain almost the same, whether requiring expensive equipment or large volumes of solvents, which are in many cases hazardous to health and/or the environment. Improvements in filament manufacturing methods can be investigated, aiming for a decrease in the fabrication time and accessibility to laboratories with poor infrastructure. Furthermore, the use of different materials targeting varied applications, changing or assigning desired characteristics to the material, according to the desired, can contribute to the development of improved materials.

Concluding remarks and future perspectives

We have overviewed the production of bespoke conductive additive manufacturing filaments through exploring at the various factors, which include: polymers, plasticiser, and conductive fil-



SCHEME 1

An overview of a possible mechanism of PLA hydrolysis in alkaline media. Figure reproduced from reference [152]. Copyright 2022 Elsevier.

lers. We have looked at the different methodologies used for the mixing of these materials, summarising the benefits and drawbacks of each, whilst highlighting the work done on improving the sustainability in the area. Following this, a summary of different reports of bespoke filaments in the literature is completed, highlighting the production methods and materials used. Finally, we look to offer our insights into the future of this exciting field.

Great strides have been made in the production of bespoke conductive materials in recent years, with researchers reporting higher loadings of filler, whilst still achieving good low-temperature flexibility and printability. Through the use of suitable approach to form their filament, either solvent or mechanical, the reproducibility of additive manufacturing platforms are easily achieved. To continue this, more research to understand the fundamental interactions between the polymer, plasticiser and conductive filler particles must be undertaken. We expect that the new synthesis of plasticisers is a worthy research field to be taken forward to allow next generation conducting filament to be realised which follows the rules highlighted above, and also ratio in which they are incorporated into the polymer matrix should be undertaken.

There is more scope for the inclusion of additional conductive materials within filaments, or the inclusion of mixed materials to combine beneficial properties while noting the overall cost of the filament. If we consider the overall cost of commercially available filaments, Protopasta®, if we use our "lollipop" design, Protopasta® are £0.02 per electrode but in our case, £0.09 per electrode for our 25 wt% carbon black filament [56], £0.05 per electrode for our 15 wt% carbon black with 10 wt% graphite [149]. Note that these costs reduce where you source cheaper nanocarbons.

Currently, the additive manufacturing materials only contains a fraction of commercially available high-performance polymers due to unique processing constraints since most reported work has utilised PLA as the base thermoplastic polymer, due it is affiliation with additive manufacturing. There is huge scope for the production of conductive filament utilising alternative polymers, to take advantage of their specific properties. Finally, the sustainability of additive manufacturing filament production must be continually monitored and improved. We note that the whole life cycle analysis has be performed on PLA, PETg and ABS filaments [154] which reports that PETg is found be the most environment friendly across all midpoint and end-point parameters, whereas ABS material is the least environment friendly. PLA material has the highest negative impacts on water depletion and freshwater ecotoxicity. There is further scope to extend the LCA upon conductive filaments. Excellent strides have been taken within the use of PLA, by using recycled feedstock, bio-based plasticisers, and solvent-free methodologies. However, the circular economy must be further tested and translated into new polymers when reported. Other areas that need further research are: the negative influence of aging upon on additive manufacturing filaments/electrodes, the negative affect of water ingress of solution inside the polymer matrix and overcoming the poor chemical stability, the departure from the standard "lollipop" approach where unique shapes and geometries can be realised, further use of *Circular Economy Electrochemistry* and further departure from activating the additive manufacturing platforms.

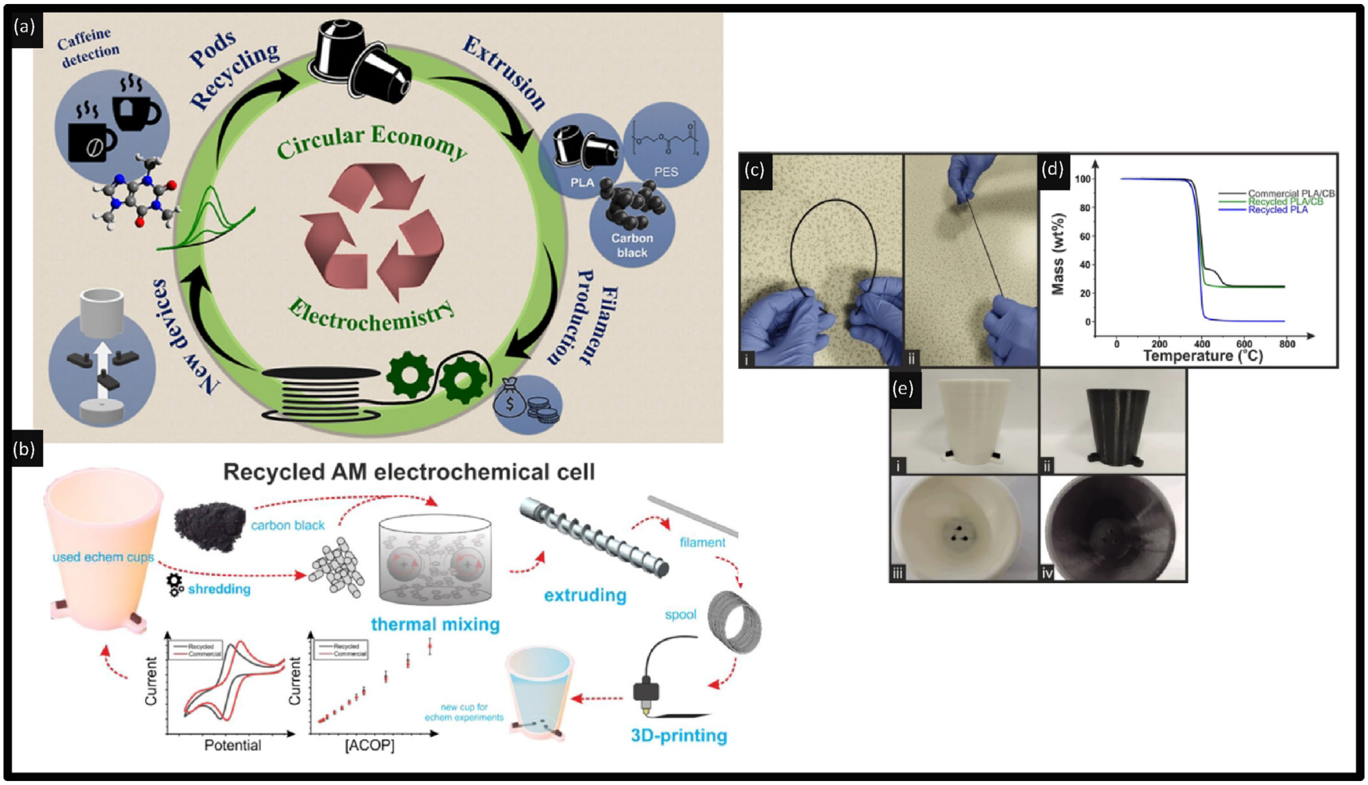


FIG. 7

A: An overview of the recycling of post-industrial coffee pod waste into high-value additive manufacturing feedstocks, introducing the field: Circular Economy Electrochemistry. Figure reproduced from reference [55]. Copyright 2023 American Chemical Society. B: An overview of old additively manufactured one-shot sensing platforms are recycled into new filaments ; this feeds into the concept of an electrochemistry circular economy. C: Photographs of the recycled conductive filament highlighting its flexibility through (i) bending the filament and (ii) straightening the filament. (D) Thermogravimetric analysis of the recycled conductive filament against the recycled non-conductive filament and the commercially purchased conductive filament. (E) Photographs of the original and recycled additive manufacturing electroanalytical cells, showing side views of the cup and connections (i, ii) and the top view (iii, iv) showing the embedded AMEs. Figures reproduced from reference [146] Copyright 2023 American Chemical Society.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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