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3D printing of CNT- and graphene-based conductive polymer nanocomposites by fused deposition modeling

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A B S T R A C T

Fused deposition modeling (FDM) is limited by the availability of application specific functional materials. Here we illustrate printing of non-conventional polymer nanocomposites (CNT- and graphene-based polybutylene terephthalate (PBT)) on a commercially available desktop 3D printer leading toward printing of electrically conductive structures. The printability, electrical conductivity and mechanical stability of the polymer nanocomposites before and after 3D printing was evaluated. The results show that 3D printed PBT/CNT objects have better conductive and mechanical properties and a better performance than 3D printed PBT/graphene structures. In addition to that, printing more than one material (multimaterials) and challenges in using abrasive conductive fillers (i.e., CNT and graphene) are also discussed. Overall this study demonstrates that a commercially available desktop 3D printer can be used to fabricate low-cost functional objects.

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1. Introduction

Additive manufacturing, also known as 3D printing, is revolutionizing the world, mainly because computer designed objects fabricated by 3D printers can be more complex than conventionally machined parts [1]. This allows for larger design flexibility and enables improved performance, often at reduced weight. From the ever increasing number of additive manufacturing approaches, fused deposition modeling (FDM) has pervaded most into science, education and home use. In FDM, the feedstock is a thermostatic polymer filament, which is heated above its glass transition temperature \(T_g\) and extruded through a movable nozzle in the X-Y plane to form a 3D structure by layer-wise addition [2]. While almost every base material, that is, metals, ceramics and polymers, can be 3D printed into complex shapes, nowadays a strong demand exists for 3D printable materials having additional functionality [3]. Significant progress has been made in 3D printing materials with functionality, such as electrochemical electrodes [4], photochromatic materials [5], chromatographic devices [6], membrane modules [7], conductive composites and blends [8–14]. With these developments unique possibilities for creating multifunctional devices, implants, and even organs, by 3D printing come into scope [15,16].

Desktop 3D printing of functional devices opens the next level in the market. The cost of manufacturing small series or unique parts can be reduced significantly, facilitating easy manufacturing even to the small-scale private sectors. However, the main limitation is the availability of application specific functional raw materials for specific 3D printers and the optimized printing conditions to obtain good esthetics (without surface roughness) as well as sufficiently good functional properties. Desktop 3D printing of polymer nanocomposites (PNCs) with a relatively low amount of layered silicate fillers or conductive nanofillers, such as carbon nanotubes (CNT), graphene and metal particles, allows one to build objects with multifunctional properties having good electrical conductivity, thermal conductivity, mechanical strength, and stiffness at a relatively low cost [10,12,17]. In conductive PNCs, the electrical conductivity is governed by electrical percolation, which requires a minimum filler content (volume fraction) to convert an insulting polymer matrix into a conductive composite [18]. This minimum volume fraction of nanofillers, referred as percolation threshold, strongly depends on factors like, shape and size distribution of the nanofillers [19,20], attractive interactions [21], and processing methods (dispersion and agglomeration of nanofillers) [22]. Several studies have been reported on 3D printing of conductive PNCs, based on conventionally used 3D printing polymers like poly lactic

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acid (PLA) and acrylonitrile butadiene styrene (ABS) [2, 9, 12, 13, 23]. However, development of new conductive PNC materials for a desktop 3D printer is highly desirable to achieve better printability, mechanical properties and electrical conductivity.

Several factors need to be considered while printing conductive composite materials. One of the major bottlenecks is nozzle jam, caused by agglomeration of the nanofillers and resulting in poor printability and surface roughness [23]. Hence, in order to control these effects, the size and size distribution of the conductive fillers as well as the printing parameters/conditions, such as printing temperature, printing speed, residence time and printing bed temperature, need to be optimized for printability. In addition to that, certain physical properties of the polymer matrix and the subsequent conductive PNC are required to obtain suitable printability and functional behavior. The conductive PNC filament should have enough flexibility to be spooled after melt extrusion and fed through the Bowden tube of the 3D printer without breaking for 3D printing. The 3D printed object should also have sufficient mechanical strength, stiffness, and chemical resistance to ensure the durability of the end-product for the specific application. The polymer material needs to withstand appropriate temperature during composite fabrication via melt extrusion and subsequent printing. A material with a higher storage modulus requires 3D printing at slower speed, or using a higher nozzle temperature. However, if the printing temperature is too high or the residence time of the polymer in the hot end at slower printing speed is too long, polymer degradation may occur, typically resulting in voids in the printed structure [24]. This also results in a lower electrical conductivity of the composite materials. Most importantly, the chosen printing temperature of the material (conventionally slightly above the melting temperature of the polymer) should match with the 3D printer’s temperature regime. For instance, the Ultimaker 2 FDM printer used in this work has a processing window of 150–260 ◦C. Based on these criteria (see SI, section I and II), we chose polybutylene terephthalate (PBT) as the base polymer matrix for the development of conductive PNC for 3D printing applications and investigated the change in electrical conductivity, crystallinity, morphology and viscoelastic properties of PBT/CNT and PBT/graphene structures fabricated using the aforementioned commercially available 3D printer (Ultimaker 2). Surface modification of the CNTs or the graphene could lead to a better dispersibility but will also affect the conductivity adversely and, hence, we opted for using non-modified materials. In addition, we extend the scope of printing multi-materials and discuss the potential degradation of 3D printer parts (such as printer head and nozzles) upon 3D printing of abrasive materials like CNT and graphene.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (CNT, ρ∼2.1 g/cm³) were supplied by Nanocyl, Belgium (Product No. C7000). Thermally expanded graphite (graphene, ρ∼2.1 g/cm³) was prepared by microwaving hydrolyzed graphite bisulphite for 1 min at 2450 MHz (700 W) as explained by Arapov et al. [25]. Polybutylene terephthalate (ρ∼1.32 g/cm³, Tg∼55 ◦C) was supplied by Sabic Innovative Plastics, The Netherlands.

2.2. Sample preparation

CNT and graphene dispersions were prepared by adding 50 mg of CNT in 100 ml of isopropanol and sonicating for 2 h in an ice bath (Bransonic 1510) to prevent any rise in temperature. Appropriate amounts of PBT powder were added to the mixture and further sonicated for an hour. Subsequently, isopropanol was allowed to evaporate at 90 ◦C using a water bath while stirring the solution vigorously to avoid macroscale inhomogeneity and phase separation. However, some degree of inhomogeneity could not be avoided, especially in the last stages of drying due to the higher viscosity of the mixture. Nevertheless, this method is proven to result in a good dispersion [26]. The resulting PBT powder coated with conductive fillers was dried at room temperature for 24 h. The composite powder was fed into a DSM Xplore 15 ml mini extruder. The temperature of the mini extruder was set to 240 ◦C and allowed to mix for 5 min at 50 rpm. Thereafter the melt mixed composite was
extruded via a die with a diameter of 3 mm and allowed to quench to room temperature.

An Ultimaker 2 3D printer was used for 3D printing the composite filaments. The composite filaments were printed into squared monolayers with dimension of 3 cm × 3 cm × 0.3 mm. Brass nozzles with 0.4 mm diameter were used. The printing head was set at the rate of 20 mm/s. The nozzle temperature varied between 240 °C and 260 °C depending on the amount of conductive filler content (see SI, section III). Double-sided tape was used as a printing substrate with the printing bed temperature set at 70 °C to prevent the printed material from warping (see SI, section IV). While printing, multi-materials using dual extrusion head, the nozzle temperature of PLA and PBT/CNT was set at 200 °C and 260 °C, respectively, and the printing bed temperature was varied between 65 °C and 80 °C.

2.3. Characterization

DC conductivity measurements were carried out using a four-point setup with parallel electrodes separated by 5 mm. The current was applied through the outer electrodes by a Keithley 237 source measure unit, and the potential difference was measured between the inner electrodes by a Keithley 6517A electrometer. Detailed information on the electrical measurements is given in the SI, section V. Scanning electron microscopy (SEM) images were acquired using a Quanta 3D SEM (Thermo Fischer Scientific) operated at 5 keV on a secondary electron detector. Profiometry measurement was performed on a Veeco Dektak 150 surface profiler instrument at a speed of 80 μm/s. Thermal stability and the transition temperatures were determined using a differential scanning calorimeter at 10 °C/min (DSC Q2000 – TA Instruments) and thermogravimetric analysis (TGA Q500 – TA Instruments) at 2 °C/min. The viscoelastic properties were measured using a dynamic mechanical analyzer (DMA Q800 – TA Instruments) at a constant frequency of 1 Hz. All wide-angle X-ray scattering experiments were performed on a SAXSLAB’s Ganesha instrument equipped with a GeniX-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of 1 × 10⁸ photons/s. Scattering patterns were collected using a Pilatus 300K silicon pixel detector with 487 × 619 pixels and with a pixel size of 172 μm² placed at a sample-to-detector distance of 91 mm. The beam center and q-range were calibrated using the diffraction peaks of silver benenate. Conversion of 2D into 1D data was carried out with Saxsgui V2.13.01 using an automated beam stop mask. Samples were exposed to X-rays for 1800 s. Electron transparent samples were prepared by microtoming the 3D printed samples into ∼500 nm thick sections using a Diatome 35° 3.0 mm diamond knife mounted on a Reichert-Jung Ultracut-E ultramicrotome and collected on a continuous carbon film coated 200 mesh copper TEM grid. All scanning transmission electron microscopy (STEM) images were acquired using a Titan electron microscope (Thermo Fischer Scientific) operated at 300 keV with a convergence angle of 4 mrad on a Fischione HAADF-STEM detector at camera length of 450 mm.

3. Results and discussions

3.1. 3D printing of conductive PBT composites

Several PBT composite filaments with varying volume fractions of CNT and graphene were prepared by melt extrusion process and subsequently 3D printed to monolayers to determine the electrical percolation threshold. Images of prepared composite filaments and 3D printed monolayers are shown in Fig. 1. All the graphene-based filaments and 3D printed monolayers appeared to be rough and brittle as compared to CNT-based composites. No difference in surface quality was obtained by slightly changing the nozzle temperature or the printing speed. Low convergence angle scanning transmission electron microscopy (LC-STEM) imaging of the PBT/G composite (Section 3.3) reveals that the graphene platelets were dispersed finely in the PBT matrix without any significant agglomeration. However, during processing at elevated temperature, the evaporation of moisture in the thermally expanded graphite platelets leads to formation of voids along the surfaces of the printed material, thereby causing surface roughness and brittleness.

The surface of the 3D printed samples was examined by SEM. Multiple 3D printed layers are clearly seen and uniformly placed with layer width closely matching to the nozzle diameter. The interface of the neighboring layers was merged to form ridges between the layers. This is caused by the nozzle touching the printed layers and pushing the printed material aside. Such discrete interfaces were distributed at some regions in some of the graphene-based monolayers as the molten material spreads across covering several layers as shown in Fig. 1E. This can be avoided by further reducing the temperature (slightly increasing the viscosity); however, it may cause the nozzle jam and results in loss of printing resolution.

3.2. Electrical conductivity analysis

Fig. 2 shows the electrical conductivity plotted as a function of volume fraction of conductive fillers for the various 3D printed monolayers. The minimum amount of conductive filler (φp) required to form conductive composite can be estimated by electrical percolation theory [27,28]. A detailed analysis of electrical percolation is given in the SI, section VI. Based on the analysis of film formation and electrical percolation, we suggest that at least ~0.49 wt.% of CNT (~0.31 vol.%) and ~5.2 wt.% (φp ~ 3.3 vol.%) of graphene is required for the FDM fabrication of PBT/CNT and PBT/G conductive filaments, respectively. Previous studies using conventionally used polymer matrices reported a similar level of about φp ~ 0.67 wt.% for PLA/CNT composites [12] and of about φp ~ 2 wt.% for ABS/G composites [23]. The differences could be related to the use of different preparation methods and/or different raw materials. The difference in PBT/G and PBT/CNT composite behavior is mainly caused by the dimensionality of the filler particles (1D for CNT, 2D for graphene) [29] and potential aggregate formation for graphene which increases the electrical resistance [26], possi-
bly reinforced by air entrapment between the exfoliated graphite flakes [25].

The anisotropy in distribution of the conductive fillers was observed by measuring conductivity at various angles between the deposition direction of the FDM print head and the measuring probes. For instance, by placing the 4 probes in line with the printed layers – parallel measurement, 90° to the printed layers – perpendicular measurement, and also at intermediate angles (see Fig. S4). In PBT/CNT composites the anisotropy in conductivity is a factor of ~7 at the percolating volume fraction (\( \varphi = 0.0062 \)), decreasing to a factor of ~1.3 well above the percolating volume fraction (\( \varphi = 0.036 \)). This factor converges to 1, as a result of a conductive network formed across the printed layers that results in a lesser effect of additional CNT paths to the overall conductivity. Here it needs to be mentioned that ridges were formed between the connecting interfaces of the layers during printing, which may cause the observed variation in conductivity. Therefore, the precise variation in the thickness and the profile of the 3D printed monolayers were measured using a surface profiler (see, SI, section VII). For the 3D printed PBT/CNT \( \varphi = 0.036 \) monolayer, the thickness increases by a factor of 1.38 due to the ridges on the top surface. This factor matches closely with the variation in conductivity (\(~1.3\)). This shows that the apparent increase in conductivity while measuring parallel to the printed lines is due to the uncorrected increase in thickness of the ridges at high volume fraction composites. At the percolating threshold of conductive fillers, the electrical conductivity is limited by network connectivity across the interface between neighboring deposition lines. The change in resistance as a function of angle of the measurement (angle between the probes and the sample) is shown in Fig. S7. The slope of the curve changes depending on the angle of the measurement. For small angles, the resistance increases slowly, but above about 45° the slope significantly increases. This shows that the connectivity at the interfaces of the neighboring printed lines was limited and the interface between the 3D-printed layers predominantly acts as series resistors. By changing the angle of measurement, the network acts like parallel resistors (layers), connected by several series resistors (interface between layers). This also suggests that, in order to get a uniform connectivity across the FDM deposition lines, it is advisable to have concentrations (of conductive nanofillers) far above the percolating volume fraction. Hence, we chose 2 3D printed composite monolayers that are percolating as well have nearly the same amount of conductive fillers – PBT/CNT \( \varphi = 0.036 \) and PBT/G \( \varphi = 0.041 \) – for further analyses.

3.3. **Morphological analysis**

The distribution of conductive fillers within the 3D printed structures was characterized by low convergence angle scanning transmission electron microscopy (LC-STEM) [30,31] of relatively thick (~500 nm) sections with large area imaging toolbox [32]. Detailed information on large-scale LC-STEM imaging and the acquired representative images is given in the SI, section IX. A detail from the large-scale images of 3D-printed samples of PBT/CNT
Fig. 5. (a) Cooling scans of DSC measurements. (b) Heating scans of DSC measurements. Arrow indicates the recrystallization. (c) Crystallinity as calculated from melting enthalpies for various samples.

Fig. 6. (a) TGA curves of PBT/CNT (ϕ = 0.036) and PBT/G (ϕ = 0.041) composites. (b) Storage modulus E' and loss modulus E'' plotted as a function of temperature for 3D printed PBT/CNT (ϕ = 0.036) and PBT/G (ϕ = 0.041) composites.

(ϕ ~ 0.036) and PBT/G (ϕ ~ 0.041) composites is shown in Fig. 3a and b, respectively. The graphene platelets (marked in circles in Fig. 3b) produce very low contrast as compared to the CNTs. Both graphene and CNTs were uniformly distributed and no large agglomerates were found. The light regions represent the crystalline part of the PBT matrix. The amount of crystallinity appears to be roughly same for both PBT/CNT and PBT/G composites despite the slightly higher volume fraction of graphene in PBT/G composite. It is known that in semi-crystalline polymers like PBT, interactions between the graphic rings of the conductive filler (CNT and graphene) and the benzene rings of the terephthalate moiety induces crystalline stacking of polymer chains [33,34]. In the PBT/CNT composites, the CNTs were predominately located within the crystalline regions, indicating the strong tendency of PBT to crystallize on CNT walls.

The morphology of the 3D printed composites was characterized by wide-angle X-ray scattering (WAXS). Fig. 4 shows the WAXS diffraction patterns of 3D-printed samples of PBT/CNT (ϕ ~ 0.036) and PBT/graphene (ϕ ~ 0.041). Because of the very low concentration of conductive fillers, their characteristic peaks (for instance, 002 plane of graphene at 26.5°) are not visible. The peaks associated with the crystalline lattices of PBT are sharper in PBT/CNT than in PBT/G. During the 3D-printing process, at each pass of the nozzle in the X–Y plane, the already printed layers were reheated. This allows for uniform heat transfer and relatively less super-cooling and induces the crystallization. However, such a phenomenon was not observed in PBT/G composites. This suggests that CNTs possess a higher nucleation ability as compared to graphene. A possible explanation is that the polymer chains require more time to adjust their conformations across the surface area of the graphene sheets as compared with the CNTs and therefore the rate of crystallization and the percentage crystallinity decrease [35]. In addition, the isotropic distribution of intensities along the diffraction rings (Fig. 4b) suggests that the flow conditions in the micro-compounder and the 3D printer do not induce preferentially oriented morphologies [22].

3.4. Crystallization behavior

To access the change in crystallinity during the 3D printing process, differential scanning calorimetry (DSC) analyses of the 3D printed samples were carried out and the results are shown in Fig. 5. Fig. 5a shows the cooling curves where a shift of the crystallization peak toward higher onset temperatures for the 3D-printed composites as compared to pure PBT is observed. This clearly illustrates the above mentioned phenomenon that the conductive fillers act as nucleating sites and induce crystallization of the polymer matrix [36,37]. The increase in crystallization temperature is not proportional to the amount of CNT added (see SI, section X), illustrating that above a certain critical filler content, the onset of crystallization levels off with further increase in filler content. Fig. 5b shows the corresponding heating curves. The crystals of the pure PBT melted at lower temperatures than the 3D-printed composites, which indicates a difference in the distribution of crystalline lamellae thickness in the 3D-printed composites. In addition, simultaneous
melting and recrystallization of the pure PBT filament was observed (shown by an arrow), i.e., the thinner lamellae melted, resulting in thicker remaining lamellae with higher melting point. This phenomenon was not observed in the 3D-printed composites; instead a broad shoulder is observed indicating the broad size distribution of the lamellae. The degree of crystallinity was calculated from the melting enthalpies [38], and the results are shown in Fig. 5c. By increasing the conductive filler content, for the PBT/CNT composite the crystalline fraction shows a maximum. At higher volume fraction both composites show a decrease in crystallinity. This decrease suggests that the presence of large number of nucleating sites dispersed over the entire polymer matrix immobilizes the polymer chains and limits the formation of crystalline lamellae. Moreover, an increase in conductive filler content could increase the probability of agglomeration, which probably decreases the degree of crystallinity as well.

3.5. Thermal stability and viscoelastic behavior

To assess durability, thermal and mechanical stability, thermogravimetric analysis (TGA) and dynamic mechanical analyses (DMA) of 3D-printed samples were conducted and the results are shown in Fig. 6. Fig. 6a shows the TGA curves of pure PBT and the 3D-printed composites performed under oxidative conditions. Degradation of PBT occurred in two steps. A weight loss of 5% occurs at 303 °C, 339 °C, and 332 °C for the PBT, PBT/CNT, and PBT/G composite, respectively, while they completely decompose at about 450 °C. The addition of conductive fillers, not surprisingly, improves the thermal stability, as both the onset and the maximum degradation temperature shift to a higher value. The presence of the conductive fillers facilitates the heat conduction and acts as barrier to inhibit the emission of decomposition products during the combustion [39]. The total mass loss of the PBT/CNT and PBT/G composite was 94% and 99.5% at 550 °C, respectively. This shows that the PBT/CNT composite has higher thermo-oxidative stability than the PBT/G composite.

Fig. 6b shows the storage \( E' \) and loss modulus \( E'' \) of the 3D-printed composites. The stiffness of the PBT/CNT 3D-printed monolayer was significantly higher than that of the PBT/G composite; more precisely, the storage modulus was 28% higher for the PBT/CNT at 25 °C. Since the crystalline fraction is higher for graphene composites (see Fig. 5c) as compared to CNT composites, the observed inverse relation in storage modulus was unexpected. Often the formation of an interphase between the surface of the conductive fillers and the polymer chains is referenced for outstanding mechanical properties [40,41]. In addition, reinforcement is usually described in terms of the critical filler length \( l_c \), below which the filler cannot transfer its stiffness or strength properties to the polymer matrix, and results in premature failure of the composite. It is generally accepted that, in order to obtain a good reinforcement, the filler length should be at least 10 times \( l_c \) [26]. In addition, the loss factor \( E''/E' \) was observed to be \( \sim 0.1 \) for both the PBT/CNT and PBT/G samples. Previous studies on 3D printed graphene-based ABS composites reported \( E''/E' \sim 0.5 \) at comparable volume fraction. This shows that our PBT-based composites behave more elastically.

4. Further discussions

4.1. 3D printing of multi-materials

Printing multiple materials would take the development of functional devices to the next level. Recently, Gonzalez et al. [8] showed printing electrical circuit like structures of a conductive polymer nanocomposite on an insulating base of the same polymer. Here we show the printing of 2 of different materials, which we call “integrated printing”. This requires the use of a multi-extrusion head and the printing parameters/conditions are very critical as they need to be optimized for more than one material, especially when the T_g of the materials are significantly different. For proper necking, diffusion, and adhesion between polymers of different T_g, the temperature of the printing polymer should be higher so that it heats the already printed polymer layer (usually the printing temperatures should be higher than the T_g of the already printed polymer) [42].

For our multi-materials printing tests, we used our PBT composite and conventionally used pure PLA. Using the same printing parameters as used for printing monolayers, significant thermal stress at the interface of the materials (indicated by the arrow in Fig. 7, left sample) arise due to the difference in the coefficient of thermal expansion of different materials. Hence, a variable printing bed temperature (from 65 °C to 80 °C upon increasing layer thickness) was used to overcome these difficulties (Fig. 7, right sample). The resulting electrical resistance was also measured and appeared to be more than 2 times lower (\( \sim 600 \) Ω) for the constant bed temperature sample (\( \sim 1350 \) Ω). We also observed that PLA becomes softer and tends to sag at 100 °C printing bed temperature, while the PBT/CNT composite does not bond with PLA at a printing bed temperature as low as 50 °C. Hence, choosing an appropriate printing bed temperature while printing multi-materials is crucial.

4.2. Nozzle wear

The exceptionally high specific Young’s modulus of CNTs and graphene (higher than that of diamond) is expected to lead to nozzle wear during the 3D printing process [43,44]. Fig. 8 shows the 3D printer’s nozzle surface before and after printing several CNT- and graphene-based composite materials. Upon prolonged printing, the brass nozzle was abraded both inside the nozzle as well as on the front surface where it touches the printed object (Fig. 8c). A SEM image of the surface of the corresponding 3D printed PBT/G composite material is shown in Fig. 8d. The surface is clearly rough and the ridges were irregularly placed with loss of printing resolution due to the degradation of the nozzle and this effect potentially degrades the aesthetics and the functional properties. Therefore, for printing abrasive materials like CNTs and graphene, FDM nozzles made from harder materials, such as silicon carbide, may be required; however, because of the difference in the thermal con-
ductivity of harder materials, the printing conditions need to be optimized appropriately [45].

5. Conclusions and outlook

Desktop 3D printing has an enormous potential to fabricate complex structures that can be applied for large-scale manufacturing at low-cost. In this work, we have shown the preparation, filament extrusion and FDM-based 3D printing of CNT- and graphene-based conductive polymer nanocomposites into functional 3D model structures. More specifically, PBT was used as a base polymer, as compared to the commonly employed polymers PLA and ABS, in order to obtain highly functional as well as mechanically robust structures. The printability, electrical conductivity, crystallinity, morphology and viscoelastic properties of the 3D printed structures were evaluated. The analysis showed that PBT/CNT 3D printed structures have better functional properties (elastic behavior and conductive properties) as well as esthetics than the PBT/G 3D printed structures. The optimum printing parameters/conditions do not change much for the PBT/CNT and PBT/G composites due to the very low volume fraction dispersed in the PBT matrix.

We illustrated the use of multiple printing heads such that more than one material can be printed at once. We expect that this will become the standard for the fabrication of functional devices. For instance, it shows the potential to print conductive structures like electrodes within a 3D-printed insulating matrix. We have also shown that care must be taken while printing abrasive materials that could potentially damage the printing nozzle, resulting in loss of printing resolution and causing undesirable properties. There are several research questions that still need to be addressed. New materials need to be optimized for 3D printing grades, such that they have the proper flow rate, crystallization and shrinking properties, in addition to their functional properties. Significant progress is required in nozzle design for printing abrasive materials and also to reduce the chance of clogging of conductive fillers. Co-extruding nozzles instead of double nozzles could take the development to the next level, but there are several issues that require attention upon using co-extruding nozzles. For instance, the nozzle has to be purged while switching to a different material and only materials with similar printing temperatures can be used. In addition, the nozzle material and nozzle geometry is probably limited to one design, which forces one to print, for example, abrasive material and conventional 3D-printing material with the same nozzle. Finally, and more importantly, health and safety issues upon printing ultra-small nanoparticles need to be assessed. Overall, we believe that this study demonstrates that 3D printing is a viable technology for manufacturing functional structures at very low-cost, and shows that unconventional polymers/materials can be exploited and optimization to obtain better printability (esthetics) and functional properties, and will push our materials selection process and applications.

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Appendix A. Supplementary data

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References
