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New possibilities using additive manufacturing with materials that are difficult to process and with complex structures

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Abstract

Additive manufacturing (or 3D printing) opens the possibility of creating new designs and manufacturing objects with new materials rapidly and economically. Particularly for use with polymers and polymer composites, simple printers can make high quality products, and these can be produced easily in offices, schools and in workshops and laboratories. This technology has opened a route for many to test ideas or to make custom devices. It is possible to easily manufacture complex geometries that would be difficult or even impossible to create with traditional methods. Naturally this technology has attracted attention in many fields that include the production of medical devices and prostheses, mechanical engineering as well as basic sciences. Materials that are highly problematic to machine can be used. We illustrate process developments with an account of the production of printer parts to cope with polymer fillers that are hard and abrasive; new nozzles with ruby inserts designed for such materials are durable and can be used to print boron carbide composites. As with other materials, complex parts can be printed using boron carbide composites with fine structures, such as screw threads and labels to identify materials. General ideas about design for this new era of manufacturing customised parts are presented.

Supplementary material for this article is available online

Keywords: additive manufacturing, materials, 3D printing, composites

(Some figures may appear in colour only in the online journal)

Introduction—motivation and scope

Additive manufacturing or, more popularly, 3D printing, is a modern manufacturing process that creates products by depositing material where it is needed in the required shape. This process contrasts with traditional fabrication that usually relies on cutting material to the correct form or on casting and moulding that fills defined volumes with materials. Metals
and ceramics can be processed as powders and when the material is deposited it is fused, usually with a high power laser, to reach the required temperature. The highly controlled deposition and the quick transformation of small regions to a solid, allows complex structures to be formed. Processes that are much more common and use only relatively cheap equipment have been developed for production with ‘plastics’ or polymeric materials.

Additive manufacturing provides the possibility of making objects out of new materials and to exploit new designs that cannot be created easily using conventional machining [1]. These advantages are particularly valuable for research apparatus and specialist equipment for which new designs must be tested, in biomedical applications, such as 3D-printed aortic valves [2], or when only a small production series is required. An introduction to the wide variety of techniques that are used in additive manufacturing has been provided by Calvert and Crockett [3]. There have been many advances in recent years and these have also involved a range of strategies using composite materials [4]. Improved functionality arises from the physical properties of particles that can include magnetic, piezoelectric, dielectric and other behaviours [5, 6]. These materials can then be used as antennae, sensors and other active devices. However, perhaps an area that shows the largest growth involves biomaterials and related medical applications where prostheses, implants and medical devices can be tailored to a specific size while incorporating many desirable material properties that may allow for biocompatibility and encourage natural tissue regeneration [7–9].

Many organisations now have their own 3D printers and the most widespread are those that print polymeric materials. Our discussion in this paper will focus on what can be achieved using such simple equipment that is readily accessible. We will give examples using two types of polymeric printing technologies in this work: fused filament fabrication extruders and stereolithography printers. Fused filament fabrication extrusion has become an easily used printing process with a wide range of applications to create objects with complex structures from a range of thermoplastic materials. Stereolithographic printers use resin that is photocurable and solidified with a highly collimated light beam.

Some previous studies have emphasised the rapid or cheap reproduction of standard components or the manufacture of prototypes of objects that will be subsequently manufactured by traditional methods. However, the value of additive manufacturing rises significantly when it is used to produce new devices or if it exploits new materials. Scientists are enthused by these opportunities, both as routes to new materials and new designs or if it exploits new materials. Scientists are enthused by these opportunities, both as routes to new materials and new designs. Recent papers have described components for optics experiments [15, 16] and other laboratory apparatus, e.g. [17, 18]. More substantial advantages can be foreseen with the development of printing entirely new polymers and polymer composites. In a number of cases, the flexibility available in the design and manufacture of products allows new metamaterials to be created that have, by means of a specific microstructure, for example, improved or unusual mechanical [19], electrical [20] or magnetic [21] properties. Improved antennae can be made using optimized composites of dielectric and magnetic particles in polymers [22].

Recognition that optimised design is usually quite different for objects made by additive manufacturing is also important. These areas of process development, creation of materials and new designs are closely related and, when combined, offer a number of new opportunities. Further advantages are that the 3D-printing technology is simple and can be provided at low cost. Objects made of thermoplastics can also be readily recycled.

This paper describes components made by 3D printing that facilitate new applications and, in some cases, use materials that are difficult to machine or to fabricate using alternative methods. The examples are related to various specific requirements, but several general principles are illustrated in this way. The means to improve the capability of printing new composite materials with very hard filler particles are also presented.

Concepts and design

In order to take full advantage of 3D printing, it is important to understand the key conceptual differences between traditional machining and 3D printing. Designs can be optimised by using material only where it is needed. There is no gain in making objects dense by filling volumes completely, for example, unless needed for mechanical strength or some other physical property. Openings and holes in objects are straightforward to create and, in general, depositing less material will give rise to faster fabrication and lower material costs. Complex 3D shapes can be incorporated in designs and used to make products that cannot be prepared by conventional turning on lathes or milling. Fabricated products can combine both relatively large structures and fine details, such as those required for springs, screw threads and clips, in a
single object that requires no further finishing. An example of a demonstration metamaterial [23] with a negative Poisson ratio that is readily made by 3D printing is shown in Figure 1. This would be very expensive to machine and a mould would only be worthwhile if many examples were to be made. This material was produced simply for demonstration purposes but the principles are attracting wider attention, for example, to create objects with negative stiffness [24].

There are several types of research equipment that can benefit from these capabilities and may only require one or a small series of pieces to be made. The simple process for the additive manufacturing of polymers, known as fused filament fabrication, is implemented in a number of different printers. In order to explore the use of a wide range of fabrication materials, including some specifically compounded in small batches, it was desirable to select a system that did not require a filament in specific proprietary forms or containers. Example items described below have been made with an Ultimaker 2 that is widely marketed both for professional use and as a consumer grade printer [25] and can process a broad range of materials. The 0.4 mm nozzle has the capacity to print with a layer thickness as low as 0.02 mm that allows a good resolution of the detailed structure in the components. As we describe, the benefits of different nozzle sizes can be exploited for the benefit of either speed of manufacture or precision. The second method of printing polymers using stereolithography allows higher resolution features to be manufactured with a photocurable resin. The application of this process using a Form 2 printer (Formlabs Inc.) to make rapid and cheap microfluidic devices will be presented in the final section.

A convenient plastic for a number of applications is ABS as it combines good mechanical properties with reasonable operating and processing temperatures. Typically, an injection-moulding grade with high melt flow properties is selected and the present work used either a commercially available filament or plastic provided as chips of Sabic CYCOLAC™ MG94. The layer height was chosen generally to be about 0.1 mm to print fine structures such as screw threads, and 0.15 mm for other objects.

The use of 3D printing has proved to be very efficient for the production of a small series of mounting plates for fused quartz cells. The printed objects are exploited as equipment components and are not just used as prototypes or models. Using designs intended exclusively for manufacture by 3D printing has meant that limitations imposed by conventional machining did not have to be considered. Details are provided in the supplementary information. Several features of the design are important: the ability to form complex 3D objects allows thin, specifically shaped plastic springs to be printed. These are used to hold in place exchangeable aperture plates of different thicknesses. It is difficult to include such parts in a single piece of material by conventional machining. The precision of the printing also allows threads for M5 screws (0.8 mm pitch) to be fabricated directly. Designs for objects with screw threads need to be made so that they are printed in the z-direction, i.e. perpendicular to the printing bed. The mount has been labelled with useful 3D-printed information, such as marks to indicate assembly orientation, as well as to identify the particular material used for manufacture together with the appropriate recycling code.

New materials

Filled plastics provide many possibilities for enhancing the properties of polymers. Anisotropic particles, such as clay (plate-like) or carbon fibres, are used to increase the elastic modulus and toughness. Other fillers can increase the conductivity, make a product ferromagnetic or provide new colours. Mixtures of properties and the exploitation of microfabricated structures can be used to create a range of metamaterials. There is a range of special uses, such as using a large fraction of tungsten to give sufficient heavy metal content to act as shielding for x-rays [26]. It has been reported that wear on the extrusion nozzle is a significant issue when using hard fillers in plastics. An interesting challenge was
posed by the need to use absorbing masks in neutron scattering experiments to define the beam and to prepare shielding to absorb stray scattering. These aspects have been discussed previously and criteria such as the need to meet new environmental constraints and to avoid the use of toxic heavy metals are mentioned in the literature [27]. Boron has a particular advantage for some applications because it does not give rise to activation products with a long half-life. It is also relatively straightforward to block the gamma radiation that arises from neutron absorption in boron. As described in section 1 of the supporting information, a good choice of absorber for many applications is to use boron compounds mixed with polymers. A high density of boron in a stable compound is obtained by using boron carbide, B\textsubscript{4}C.

**Mixing and extruding ABS/B\textsubscript{4}C filament**

We have chosen to work with composites made with mixtures of ABS and B\textsubscript{4}C. Of the two most commonly printed plastics, ABS is easier to extrude than poly lactic acid, PLA, and has better mechanical properties with a higher melting point. ABS can also be dissolved readily in acetone. A test was made to extrude borated polyethylene with 30\% wt boron carbide, which is supplied commercially, but proved difficult to process due to the high viscosity of the grade of high-density polyethylene available.

A significant challenge in the wide exploitation of boron carbide is that it is extremely hard and difficult to machine. It is often sintered as a ceramic, but very high temperatures are required. A number of mixtures with rubbers and plastics are available but these often have a low volume fraction of B\textsubscript{4}C and can be hard to prepare in desirable shapes with adequate precision. Our work has demonstrated the possibility of making a range of components using 3D printing and how to overcome difficulties associated with using extremely hard filler particles.

**Improvements to fused filament printers**

The design of the Ultimaker 2 with replaceable parts allows for the exchange of worn parts and the facile development and test of upgrades. The simple ‘open source’ design of the printer makes the preparation of modifications straightforward, and new components can be tested more readily than with printers that use proprietary parts. The original instrument had an integral hot-end assembly and the entire heater block needed to be replaced when the nozzle was worn. As an example, a simple modification has enabled this to be substituted for a heated brass block with separately replaceable nozzles. A new design of the extrusion head developed in Uppsala (shown in figure S1 of the supporting information, available at stacks.iop.org/PS/92/053002/mmedia) allows widely available nozzles to be exchanged quickly without replacement of the entire heater block. This new design has now been made available commercially [28] and is delivered as standard by the manufacturer. A range of different sizes of nozzle and pieces made from different materials can be exchanged quickly to optimise the printing of different objects or different materials.

Printing composites with B\textsubscript{4}C is not completely straightforward. The particles can clog the nozzle and cause substantial wear. The total wear of the original Ultimaker 2 hot-end assembly after 20 h printing is shown in figure 2. The brass nozzle becomes shorter and the diameter of the orifice becomes larger. A loss of 1 mm in length and an increase in diameter to almost 0.6 mm was observed after 20 h printing a range of composites with weight fractions of B\textsubscript{4}C between 30\% and 60\%.

This poses significant problems as maintaining tight control of the distance above the surface and the positioning of extruded material is crucial for accurate printing with the intended density and fractional fill. In practice, after 4 h, the print quality is inadequate. A simple practical solution has been to use hard inserts made from ruby (supplied by Diamond Technologies Inc.) in the nozzle. The design of this replacement is shown in figure 3 and this has markedly reduced wear. A video illustrating the successful use of the new nozzle is provided in the supporting information. The rapid development in this area is marked by the present availability of such nozzles commercially with a short time interval [29].

Some example components made of boron carbide composites are shown in figure 4. They illustrate that even with loading as high as 60 wt\%, precise fabrication of complex shapes can be achieved. Objects made in this way have found a number of applications: for example, the mask to block background scattering in reflection measurements (figure 4(c)) could improve data (the ratio of signal to background) by approximately a factor of five [30]. Pieces of this composite that are a few mm thick have negligibly small thermal neutron transmission that is difficult to measure because of the consequently very low count rates. However, the performance has been verified in test measurements with a special thin piece and the data are shown in figure S3 of the supporting information.

Further developments of these materials include the use of isotopically enriched 10\textsuperscript{B}B\textsubscript{4}C. This has the advantage of higher neutron absorption and lower scattering when dispersed in common plastics. For the composites used in the present work, particles were blended with the polymer by mixing in solution but it is likely that advances to melt mixing are possible if larger quantities of material are to be produced.

**Scaling objects and mechanical properties—making tools**

Changing the extrusion nozzle on a printer should be performed while it is hot to avoid problems with solid plastic residues. Tightening a replacement nozzle sufficiently for it not to leak without damaging the thread or the rest of the hot-end assembly requires care, and a simple torque wrench is useful. This was the motivation for the simple design shown in figure 5 [31]. The drawings have been made available so that users of the new hot-end assembly can print this tool to...
avoid problems in mounting new nozzles. The printing time is about 2.5 h. Initially the wrench was printed using ABS but it is both useful and interesting to understand how the mechanical properties change with different materials. The torque is limited by the force required for the deformation of the blades. It is expected that this will be correlated with the elastic modulus of the polymer. A range of different materials were used to make examples of the wrench. As expected, the torque that can be applied with the wrench is approximately linearly related to the flexural modulus of the material. This is shown in figure 6(a).

Data for the flexural modulus and the density of various polymers were taken from the manufacturer’s data sheets. The straight line fit shown from the data in figure 6(a) was constrained to pass through the origin and has a gradient of $1.6 \pm 0.3 \times 10^{-4}$ Nm MPa$^{-1}$. The linearity is improved slightly if the modulus is adjusted for the slightly reduced density determined by weighing that is typically about 95% of the bulk density of various polymers, but was found to vary slightly between the various materials and depended on printing conditions.

An interesting further test was made by making wrenches of different sizes using one type of plastic—white Velleman ABS. These were produced by simply scaling the print and using proportionally sized nozzle diameters and layer thicknesses. The variation of torque with size is shown in figure 6(b). The gradient of the fitted straight line is $3.4 \pm 0.15$. This fitted line provides a ready means to predict the torque that can be applied with wrenches of different sizes. A similar correlation has been observed for Colorfabb XT material that is a copolyester resin. A simple model for the force required for the deformation of the blades would give a dependence on the second moment of the area (cross-section) and inversely on the length of the blades. This would suggest a slope of three and so the stronger variation with size suggests that there may be a further small systematic effect on the mechanical behaviour.

A detailed description of the deviation from a simple scaling law would be beyond the scope of a short paper as there are a number of possible influences, such as the gap size between the inner and outer parts of the wrench, as well as variations in density. The layer structure that arises from fused filament fabrication is a natural source of anisotropy in the mechanical properties of a product. Component failure under shear arising from delamination has been described, for
example, by Ahn et al [32]. The tendency to create voids and finished products with a density below that of the bulk material needs to be accommodated in designs and estimates of performance. Particularly in the case of filled polymers, large effects can also be observed in elastic moduli [33] and this can be exploited, particularly for composites formed with anisotropic particles, such as carbon fibres or plate-like minerals.

This development of a torque wrench for use with the printer provides a further useful laboratory tool. Some cells used for neutron reflection studies require large flat crystals to be sealed against a polytetrafluoroethylene gasket [30] and the choice of a suitable, customized, plastic wrench enables this to be done easily. Although there are other 3D printed tools described on the World Wide Web [34], there have been few accounts as to how additive manufacturing is best exploited in this way, or how to vary mechanical properties that are important in their use, and some use fairly traditional designs rather than the innovative possibilities provided by the new manufacturing technologies. Our design, shown above, was intended to be not very sensitive to particular alignment effects.

Microfluidic devices made quickly and cheaply

Some stereolithographic 3D printers, such as Form 2, use a collimated laser in the curing process. The precision of such printers has now reached micrometre scales, enabling the design of small and very precise objects, such as microfluidic devices (called ‘chips’). These chips are used to carry out laboratory procedures on a microscale, effectively downscaling and streamlining laboratory work. The smaller volumes needed reduce the cost of the samples. However the fabrication of traditionally made microfluidic chips using conventional large-facility clean room photolithography is expensive. Creating microfluidic devices using the additive manufacturing technique is a fast and comparatively cheap alternative. Microfluidic chips with practically any features can readily be made, as shown in a recent project within The International Genetically Engineered Machine (iGEM) Foundation [35]. A microfluidic chip and the corresponding drawing are shown in figure 7. The moulds for chips were made with the Form 2 SLA printer.

Discussion and conclusions

The developments with a low-cost, ‘consumer-grade’ fused filament printer have shown that complex and precise components can be made quickly. The high resolution with a print thickness kept at 0.1 mm can produce complicated structures and even include screw threads with a pitch of 0.8 mm or more. The good resolution also facilitates the labelling of products with version numbers and composition. It has been found to be very advantageous to print information such as the composition of composites that may not be readily apparent from simple observation. This good practise can be widely extended outside the range of objects that have been described in the present paper. For example, systematic marking with internationally agreed recycling codes is highly desirable. Stereolithographic printing allows high resolution objects to be printed in cured polymers readily. It has demonstrated applicability in a number of fields that can be of great advantage to society, such as the manufacture of biomedical devices and custom equipment.

The examples and results that have been presented illustrate the value of 3D printing in the development of scientific apparatus. Complex shapes are readily fabricated and several novel, desirable features were easily incorporated in the final products. The ease of fabrication for a composite material is a particular advantage; it is illustrated by the manufacture of complex shapes with an absorber for neutrons that is usually very hard to machine. Objects printed in boron
carbide/plastic composites can be prepared rapidly to accurate dimensions. This composite material can be used to replace cadmium apertures for some neutron experiments and is favoured for a number of safety and environmental reasons.

An advantage of the simple processing of plastics and composites includes the ready ability to recycle materials. Components can be cut into small pieces and re-extruded to provide new filaments for further printing. The low cost of the equipment and quick fabrication allows new designs and materials to be prepared and tested quickly. The possibility to ‘print-on-demand’ with small scale, inexpensive equipment means that stocks of components do not need to be kept or prepared in advance.

The full benefits of additive manufacturing are achieved when using designs that can exploit the ability to produce complex 3D shapes. Rapid production methods and the capability of testing ideas promptly permits the quick development of new devices. New experiments can be performed quickly and small series or unique products can be created in a cost-effective manner. Prospects for other domains of research are wide-ranging when one considers the possibilities available with conducting and magnetic filler particles. Complete devices and sensors could be made using dual head printing, and significant advances in this area are expected soon.

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Supporting information

The supplementary supporting information provides further information about (i) the design features that can be included in simple sample mounts, (ii) criteria for the choice of particular materials, such as neutron absorbers, (iii) preparing a filament of ABS/boron carbide composite, (iv) the details of the modified hot-end assembly for Ultimaker-2, (v) measurements of neutron absorption for printed composites of B₄C, and (vi) the conditions for printing and the scaling of mechanical properties of torque wrenches printed with different size nozzles. A movie is provided that shows the fabrication of an aperture in a composite of boron carbide (40% wt) and ABS that uses the modified ruby nozzle described in the paper to reduce the wear that occurs on the printer hot end when using a very abrasive material. 3D images of the components of the torque wrench shown in figure 5(a) are provided as OBJ files that can be viewed interactively.
References


[31] The drawings for fabrication of this wrench have been made available at https://youmagine.com/designs/nozzle-torque-wrench (accessed 10 April 2017)


[34] NASA https://nasa3d.arc.nasa.gov/detail/wrench-mis (accessed 10 April 2017)