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INSPIRED BY NATURE

PRINTING REVOLUTION

EVA BLASCO

More than 500 years after Johannes Gutenberg invented his printing press, we are in the middle of a new printing revolution: 3D printing, also known as additive manufacturing. 3D printing is the process of creating a 3D object from a digital file. Thanks to recent advances in the field, we are now able to print a range of materials including metals, ceramics, polymers and even biological materials. Combining molecular engineering with state-of-the-art 3D printing techniques, materials scientists today are developing new printable materials that emulate the characteristics and behaviour of living systems. Current endeavours at Heidelberg University revolve around 3D printable materials that react to external stimuli like light, heat or electrical/magnetic fields, and that are able to change their properties over time.

MATERIALS SCIENCE



The history of printing began more than 5,000 years ago. Some societies in Asia and the Middle East already used an early form of printing to engrave images onto clay or cloths by using cylindrical rollers or stamps. However, the first printed book known was created many years later (868 AD) in China. At this early stage, printing was limited in the number of editions and books were hand-copied. A real innovation appeared in the 15th century when Johannes Gutenberg, a German craftsman, invented the movable type press, which revolutionised the world of printing. He strongly improved the process by dividing it into two separate steps, typesetting and printing. For the former, the key elements of his invention included: i) a metal alloy consisting of lead, tin, and antimony to form durable reusable types which were cleaned after each printing process and reused to print other documents, and ii) an oil-based ink that was more durable than the previously used water-based inks, sufficiently thick to adhere well to metal, and could be transferred to vellum or paper. Gutenberg's invention is considered to have changed the course of history. It allowed us to print books in a timely manner and at low cost, it opened up access to knowledge and facilitated its transfer between generations. Without printing, we would have missed important progress including, for example, scientific discoveries. It is worth noting that, throughout, the development and success of printing has been linked to the materials accessible in each era - such as wood, metal, paper and so forth.

From 2D to 3D printing

The history of printing did not end with Gutenberg's invention. The concept and technologies of printing continue to evolve rapidly. Three-dimensional (3D) printing has gained much attention over the course of the last years. 3D printing is a manufacturing process that creates a physical object from a digital 3D model file. In other words, while ordinary printers in our homes or offices print graphics and text on two-dimensional (2D) paper with inks, 3D printers convert digital data into 3D objects using different materials.

3D printing has become a promising tool offering a great number of opportunities to society. Above all, it comes with greater freedom in terms of designing and producing personalised and customised products at no additional cost, shortening the time it takes for the finished product to become available on the market! Currently, there are three main types of 3D printing technologies: sintering, melting, and stereolithography. For the two first ones, powdery materials that can be sintered or melted, for example using a laser, solidify after cooling to generate a 3D object. Stereolithography is the original 3D printing technology and was first patented by the US-American inventor and engineer Chuck Hull in 1984. This technol-

ogy is based on a light-induced process that results in the hardening of the ink, usually a mixture of liquid molecules called monomers or prepolymers, in a spatially controlled manner. Depending on the 3D printer, the typical resolution of this technology lies in the range of 100 to 200 microns, i.e. the thickness of one or two human hairs. Subsequently, closely related technologies such as Digital Light Processing (DLP) or Continuous Liquid Interphase Printing (CLIP) have also been developed, allowing for much faster printing while maintaining good resolution and printing quality. Access to 3D printing at the microand nanometre regime - objects so small as to be invisible to the naked eye - has become possible by employing more sophisticated photochemical processes relying on two-photon absorption and, more recently, the so-called "two-step absorption" process. Using the latter, we recently demonstrated the possibility of using more compact and smaller printers, which are less expensive, while achieving remarkable resolution.

Choosing the correct material is as important as choosing a suitable printing technology. The right material, and technology, will always depend on the final application. Among the first properties that need to be adjusted in a printed material are its mechanical properties: black and white in paper printing can be seen as the new hard and soft in 3D printing. The first 3D printing methods focused on polymeric materials - a more general term for what we commonly refer to as plastics - because they are easy to manufacture and handle. However, the field has evolved rapidly and enabled us to use a broad variety of materials including metals and ceramics. Currently, it is possible to print hard materials such as metals for applications in automotive, or materials as soft as a hydrogel (e.g. gelatine) a polymer-based material with a high content of water for biomedicine.

Thus, to bring this field to the next level and exploit its full potential, further efforts need to be made in the development of new advanced functional materials. This is one of the research foci within the Cluster of Excellence "3D Matter Made to Order" (3DMM2O), a joint initiative of Heidelberg University and Karlsruhe Institute of Technology (KIT), where my group works on new features for printed materials such as conductivity, super-resolution or degradability. For instance, we designed new inks that can be erased as needed using laser light - much in the same way that pencil marks can be rubbed out using a rubber eraser. We also developed a new ink that can be deleted with just plain water. This is highly desirable in the context of biological applications, where the use of mild conditions is mandatory. In summary, our goal within the 3DMM20 framework is to open up new possibilities in the fields of optical, engineering and biological sciences, which would be impossible to reach without a

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multi-disciplinary approach combining materials design and cutting-edge technologies.

3D printing in our daily lives

While 3D printing was originally intended as a means of prototyping in industry, among other things, and a lot of research in the field is still ongoing, this technology is already used in different fields including aerospace, automotive or art and design, and it is becoming a popular subject in medicine. One of the fields in which the technology is already quite advanced is dentistry. For example, for dental implants or orthodontics, 3D imaging using computed tomography scans helps to create models that can be 3D printed afterwards. The main advantages of this technology are that it is patient-specific, accurate and that it avoids the use of molds, which means that hardly any material is wasted.

Just as it happened with paper laser printers, 3D printers are also becoming more affordable. It is quite possible that we will have one of them at home in a few years. Nowadays, 3D printers for all kinds of user needs and budgets are available on the market. Indeed, it is possible to buy a desktop 3D printer for less than 300 euros. As a consequence, the number of people who make 3D printing one of their hobbies is increasing more than ever. On the internet one can find different open platforms where the members of the 3D printing community share 3D models and codes for the fabrication of useful, and less useful, objects. Curious examples are castors to repair a broken wobbly chair, screwdrivers or mobile phone cases with incorporated bottle openers.

The benefits of 3D printing do not end in the factory or at home. Education is another area in which 3D printing is starting to be explored. 3D printers in classrooms can be excellent tools to introduce 3D design to art students and also a very valuable instrument for teachers or lecturers in many other disciplines. 3D objects help to visualise a given problem more precisely and with greater ease than

conventional schemes on paper or on the blackboard can, which are limited to two dimensions. This can be advantageous when it comes to explaining complex concepts that require 3D spatial visualisation. Examples of possible practical cases include 3D molecular models in chemistry, mathematical or physics problems or topographic maps in geology.

The future of printing: towards 4D printing and sustainability

Most of the materials and techniques currently employed in 3D printing are limited to the fabrication of static objects with a certain stiffness. But what about printing materials that are as elastic as a blowfish and can react to an external stimulus? Or materials that can change their colour like a chameleon or move towards the sun just like sunflowers do? This is one of the main goals of our research group: to create synthetic materials with "life-like" characteristics and behaviour by combining (macro)molecular engineering with 3D printing technologies. This concept is called 4D printing and the additional dimension refers to the ability of a 3D printed object to change its properties over time. As usual, nature is our best source of inspiration. Natural materials are usually constituted of a limited number of molecular building blocks such as amino acids and carbohydrates, and the underlying hierarchical structure governs their exceptional adaptive properties.

Our group has shown the first examples of adaptive printable materials on a micro- and nanoscale. In particular, we have demonstrated the possibility of controlling the shape of 3D microstructures on demand upon external stimuli such as chemicals, temperature or light. Light is a very attractive stimulus since it allows for spatial and temporal control. Currently, we are making major efforts in this direction to manufacture complex systems that are able to respond to different wavelengths of light. Although there is a long way to go before we reach the level of precision inherent in natural systems, I believe that achieving a



JUNIOR PROF. DR EVA BLASCO has been a professor at the Institute of Organic Chemistry and at the Institute for Molecular Systems Engineering and Advanced Materials of Heidelberg University since October 2020. She previously worked at Karlsruhe Institute of Technology (KIT), first as an Alexander von Humboldt scholarship holder and, afterwards, as a group leader at the Institute of Nanotechnology (INT-KIT). She is a principal investigator at the Cluster of Excellence "3D Matter Made to Order" (3DMM20), a collaboration between Ruperto Carola and KIT. Her research interests include the design of smart functional materials and 3D printing technologies.

Contact: eva.blasco@ oci.uni-heidelberg.de finer control in the design of printable materials will open up new opportunities in promising fields such as (micro) robotics, controlled drug delivery or tissue engineering. Last and certainly not least, we must not forget about sustainability. Even though 3D printing is more sustainable than other manufacturing techniques - it does not require molds and produces less waste - there are still a few issues to be solved. Polymers are key materials for many 3D printing techniques. However, the vast majority of polymers are still derived from petrochemicals, contributing negatively to the greenhouse effect and the depletion of our fossil reserves. Recently, there has been a growing interest in utilising renewable materials such as lignin-derivatives available from many trees and plants and vegetable oils and sugars as feedstock for printable polymer-based materials. In particular, we have successfully demonstrated the use of biobased inks based on five different vegetable oils soybean, sunflower, canola, sesame and olive oil - which

Der Exzellenzcluster 3D Matter Made to Order

Einen stark interdisziplinären Ansatz verfolgt der gemeinsam von der Universität Heidelberg und dem Karlsruher Institut für Technologie (KIT) getragene Exzellenzcluster "3D Matter Made to Order" (3DMM20), der Natur- und Ingenieurwissenschaften verbindet. Er beschäftigt sich mit der Frage, wie digitale Blaupausen durch additive Fertigung - insbesondere 3D-Druck - in Designermaterie mit gewünschter Funktion umgesetzt werden können. Eine wichtige Motivation ist dabei das Vorbild biologischer Systeme, die Moleküle auf der Nanometerskala zusammensetzen können, um damit gewünschte Funktionen auf der Zell- oder Gewebeebene zu erzielen. Für Anwendungen mit biologischen Systemen ist es das langfristige Ziel, industriell fabrizierte Werkstoffe und lebende Systeme miteinander zu integrieren, indem beispielsweise organotypische Systeme durch 3D-gedruckte Strukturen kontrolliert werden. Ziel ist die vollständige Digitalisierung der 3D-Fertigung und -Materialverarbeitung.

Der Exzellenzcluster wurde im Rahmen der Exzellenzstrategie des Bundes und der Länder eingerichtet. Sprecher sind Prof. Dr. Martin Wegener vom KIT und Prof. Dr. Joachim Wittbrodt vom Centre for Organismal Studies (COS) der Universität Heidelberg. Ein zentrales Strukturelement ist die HEiKA Graduiertenschule "Functional Materials", die Masterstudierende und Doktorand:innen in das Forschungsgebiet einbindet. HEiKA steht für die Heidelberg Karlsruhe Strategic Partnership, die alle gemeinsamen bilateralen Aktivitäten des KIT und der Universität Heidelberg umfasst.

www.3dmm2o.de

"As usual, nature is our best source of inspiration."

VON DER NATUR INSPIRIERT

REVOLUTION DES DRUCKENS

EVA BLASCO

Auch wenn die Geschichte des Druckens bereits vor mehr als 5.000 Jahren mit Bildern begann, die in Materialien wie Lehm oder Textilien eingeritzt wurden, war die Erfindung der Druckerpresse durch Johannes Gutenberg im 15. Jahrhundert dennoch eine echte Innovation. Sie sollte jedoch nicht die letzte bedeutende Erfindung in der Geschichte des Druckens bleiben. Derzeit durchleben wir eine weitere Revolution: die des 3D-Drucks, bei dem auf Basis einer digitalen 3D-Modelldatei ein physisches Objekt erzeugt wird. Anders ausgedrückt: Während "normale" Drucker Grafiken und Text mit Farbe auf zweidimensionales (2D) Papier drucken, wandeln 3D-Drucker mithilfe verschiedener Materialien digitale Daten in dreidimensionale Gegenstände um.

Die Wahl des richtigen Materials ist dabei ebenso wichtig wie die Wahl des Druckverfahrens: Analog zum Schwarz-Weiß-Kontrast beim Papierdruck kommen im 3D-Druck harte und weiche Materialien zum Einsatz. Wie beim 2D-Druck auf Papier gibt es aber auch im 3D-Druck nicht nur Schwarz und Weiß, sondern auch viele Grautöne und sogar Farben. Darüber hinaus wäre es höchst attraktiv, über eine große Bandbreite druckbarer Materialien mit unterschiedlicher Funktionalität, beispielsweise Leitfähigkeit, Biokompatibilität oder Abbaubarkeit, zu verfügen. Allerdings ist die Materialauswahl für heutige 3D-Druckverfahren begrenzt. Die meisten der aktuell genutzten Werkstoffe und Techniken eignen sich nur für die Herstellung statischer Objekte.

Könnte man nicht neue Materialien gestalten, die so elastisch wie ein Kugelfisch sind und auf externe Stimuli reagieren? Oder die wie ein Chamäleon ihre Farbe ändern oder sich wie Sonnenblumen nach der Sonne ausrichten können? Das ist eines der Hauptziele unserer Forschungsgruppe: Inspiriert von Phänomenen und Eigenschaften in der Natur wollen wir durch Kombination von makromolekularer Chemie und 3D-Druck synthetische Materialien mit "lebensechten" Eigenschaften und Verhaltensweisen entwickeln.

JUNIORPROF, DR. EVA BLASCO forscht und lehrt seit Oktober 2020 am Organisch-Chemischen Institut und am Institute for Molecular Systems Engineering and Advanced Materials der Universität Heidelberg. Zuvor war sie am Karlsruher Institut für Technologie (KIT) tätig, zunächst als Humboldt-Stipendiatin und später als Gruppenleiterin am Institut für Nanotechnologie (INT-KIT). Eva Blasco ist Projektleiterin im Exzellenzcluster "3D Matter Made to Order" (3DMM20), einem Gemeinschaftsproiekt der Universität Heidelberg und des KIT. Zu ihren Forschungsschwerpunkten gehören die Gestaltung intelligenter Funktionsmaterialien und die Verfahren des 3D-Drucks.

Kontakt: eva.blasco@ oci.uni-heidelberg.de "Aktuell können harte Werkstoffe wie Metalle für den Automobilbau gedruckt werden, aber auch sehr weiche Materialien wie ein Hydrogel für die Biomedizin."

"Polymers are key materials for many 3D printing techniques."

Institute for Molecular Systems Engineering and Advanced Materials

Als Zusammenführung des interdisziplinären Institute for Molecular Systems Engineering (IMSE) und des materialwissenschaftlichen Forschungszentrums Centre for Advanced Materials (CAM) entsteht an der Fakultät für Ingenieurwissenschaften eine neue wissenschaftliche Einrichtung: das Institute for Molecular Systems Engineering and Advanced Materials. Es soll die interdisziplinäre Grundlagenforschung in den beiden Bereichen intensivieren und für die Lehre und Ausbildung sowie den Technologietransfer erschließen. Das umfasst die Forschung an nicht-biologischen und biologischen Materialien und molekularen Systemen sowie deren Anwendungen. Das Institut widmet sich der Grundlagenforschung in den Materialwissenschaften mit einem Schwerpunkt auf Materialien für die organische und gedruckte Elektronik und Optoelektronik sowie Themen an der Schnittstelle der Natur- und der molekularen Lebenswissenschaften, der Materialwissenschaften und des molekularen Engineerings.

are very attractive as a feedstock due to their wide availability and low price. We believe that biobased inks are an essential step towards making 3D printing sustainable; however, they are not the final solution to the problem.

Most 3D printed polymer materials are neither degradable nor recyclable. The terms biobased and biodegradable are often used interchangeably, but they have different meanings. Biobased refers to the origin of a material, whereas biodegradable refers to its compostable characteristics. Also, one should not assume that every biobased material is biodegradable or that every biodegradable material is biobased. Thus, the development of biobased and biodegradable printable materials to reach a sustainable, circular polymer economy is a challenging task that our group is currently pursuing, yet one that is vital for our future.