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Advances in 3D printing with eco-friendly materials: a sustainable approach to manufacturing

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Additive manufacturing or 3D printing has revolutionized production techniques across industries, offering unprecedented flexibility and customization potential. However, with growing environmental concerns, the focus has shifted towards enhancing sustainability within 3D printing processes by utilizing eco-friendly materials. This review elaborates different 3D printing processes that are useful in printing biodegradable, biocompatible and other eco-friendly materials. Additionally, recent advancements in biodegradable polymers, bio-composites, and hybrid materials compatible with 3D printing technologies have also been discussed. Moreover, applications of ecofriendly materials in different fields have been elucidated in detail. This article will assist in understanding the role of eco-friendly materials in fostering a sustainable manufacturing landscape. The findings emphasize the need for further material optimization to balance sustainability with functionality, marking a crucial step toward environmentally benign 3D printing.

Sustainability spotlight

The global challenge of reducing environmental pollution produced by conventional plastics is directly addressed by this effort, which emphasizes the integration of eco-friendly materials in 3D printing to support sustainable manufacturing solutions. The use of biodegradable polymers, bio-composites, and recycled materials supports UN Sustainable Development Goals (SDGs) 12 (Responsible Consumption and Production), 13 (Climate Action), and 9 (Industry, Innovation, and Infrastructure). While preserving functionality and adaptability in production, sustainable innovations include cutting down on material waste, reducing carbon footprints, and improving air quality. By encouraging responsible industrial growth and bolstering a circular economy, this change positions 3D printing as a key factor in attaining sustainability across a range of industries, including the biomedical, automotive, packaging, and aerospace sectors.

1. Introduction

3D printing has emerged as a viable alternative to conventional manufacturing for making prototypes, complex geometries and manufacturing products in a diverse range of industries such as aerospace, medical and automotive sectors.¹ AM uses computer-aided design (CAD) drawings for designing an object. A slicing program is then used to slice the object, generating a G-code which contains information related to geometry that has to be traced. The 3D printer reads the G-code and melts, fuses or deposits (depending on the process) the material layer upon layer to form the object.² The various types of 3D printing processes as per ASTM 52900 along with their advantages/disadvantages and applications are illustrated in Table 1. 3D printing is quite innovative in the sense that it enhances the manufacturing process and creates opportunities for fabricating intricate shapes and designs. While AM has revolutionized prototype design and ready to use part production, it also plays a pivotal role in the advancement of Industry 4.0 and has the potential to align with sustainable development goals. Aligning AM practices with

sustainable development goals is essential for fostering long-term ecological balance and responsible industrial growth.

The increase in demand for sustainable practices has significantly transformed various sectors, including manufacturing, in recent years.⁹ In light of global environmental issues, the inclusion of eco-materials has become increasingly imperative in manufacturing processes.¹⁰ 3D printing, renowned for its adaptability and ingenuity, has the potential to lead the way in this eco-friendly revolution. It will enable a more sustainable future by utilizing eco-friendly materials, resulting in environmental and economic advantages.¹¹ Table 2 shows some of the 3D printing materials used in various 3D printing processes. Due to the high energy usage and lack of biodegradability, traditional printing materials such as ABS and ordinary plastics frequently contribute to environmental damage. Eco-friendly materials, on the contrary, provide a sustainable substitute by lowering waste and preserving precious resources. Examples of these materials are recycled plastics and biodegradable filaments extracted from renewable resources. Additionally, these materials commonly produce near to nothing harmful substances, leading to healthier working conditions and improved air quality. Use of environmentally friendly materials not only supports worldwide attempts to slow down climate change but also establishes

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S. no.	Process	Advantages	Limitations	Applications	Ref.
(a)	Vat photopolymerization				
(i)	SLA	Excellent surface finish and high resolution	Needs support and has cleaning issues	Clear aligners and prop making	3
(ii)	DLP	High speed process	Less accurate	3D printed jewellery	4
(b)	Material extrusion				
(i)	FDM	Cost effective and fast process	Average surface finish	Pharmaceuticals, jigs and fixtures	5
(c)	Material jetting	High accuracy, low waste, multi-material parts and colors	Limited to polymers and waxes only	Bioinspired composite structures, soft robotics and 4D printing	4 and 6
(d)	Binder jetting	Multiple binders and powders can be used	More post processing required	Casting patterns, cores and molds, and full color decorative objects	3
(e)	Powder bed fusion				
(i)	SLS	Low cost, accurate, good mechanical strength, no support structures, and complex geometries	Less choice of available materials, rough surface, and higher waste	Prosthetics and orthotics and surgical tools	3
(ii)	SLM/DMLS	Metal printing, light weight, durable and complex structures	Limited choice of materials	Mold inserts for die casting and patient-specific prostheses and implants	3
(iii)	EBM	Unused powder is 95–98% recyclable and few supports are required	Limited print volume and material selection and powder removal problem in closed cellular structures	Biomedical, automotive and aerospace applications	3 and 7
(g)	DED	Denser parts and enhanced features	Poor surface finish and time consuming	Multi-material structures, large structure fabrication and repairs	3 and 8
(f)	LOM	Less manufacturing time and larger structures	Inferior surface quality, higher post processing required, and limitations for complex shapes	Paper manufacturing and foundry industries	3

This review discusses the integration of eco-friendly materials in 3D printing, examining their potential to create sustainable solutions across a variety of industries. As the need for sustainable practices in manufacturing becomes critical, this review highlights the transition from conventional, environmentally harmful plastics to biodegradable, biocompatible, and recyclable alternatives. The article discusses the various

2. Biodegradable polymers in 3D printing

The development of biodegradable polymers has gained more attention in recent years as worries about the damage that

Table 2 Different materials used in 3D printing processes

S. no.	Process	Material	Ref.
(i)	SLA	AB 001, DC 100, DC 500, and DL 350	3 and 12
(ii)	DLP	Rubber and thermoplastics	12
(iii)	FDM	Acrylonitrile butadiene styrene (ABS), High Density Polyethylene (HDPE), Polylactic acid (PLA), Polyethylene terephthalate glycol-modified (PETG), and Polycarbonates (PCs)	13
(iv)	Material jetting	ABS, HDPE, PC, Polypropylene (PP), PS, and PMMA	14 and 15
(v)	Binder jetting	Polymers: PC, ABS, and PA, ceramics: glass, and metals: stainless steel	14
(vi)	SLS	Nylon, polyamides, fused silica, and borosilicate glasses	3,16 and 17
(vii)	SLM/DMLS	Cobalt chrome, copper, nickel (inconel), tool steels and stainless steel	14 and 18
(viii)	EBM	Titanium and cobalt	3
(ix)	DED	Titanium, copper, stainless steel, ceramics, and aluminum	3
(x)	LOM	Polymers, paper, ceramics and metal fills	3

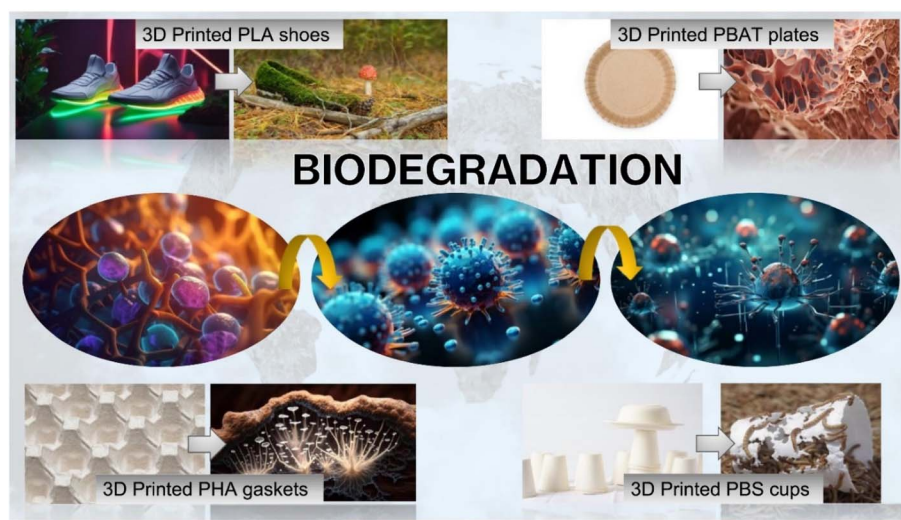


Fig. 1 Commonly available biodegradable polymers in 3D printing (reprinted with permission from ref. 22 Dananjaya S. A. V., Chevali V. S., Dear J. P., Potluri P., and Abeykoon C., 3D printing of biodegradable polymers and their composites-current state-of-the-art, properties, applications, and machine learning for potential future applications, *Prog. Mater. Sci.*, 2024, 101336. Creative Commons Attribution 4.0 International License CC BY-NC-ND, <https://creativecommons.org/licenses/by-nc-nd/4.0/>).

synthetic plastics made from petroleum pose to the environment have grown. Because bioplastics are biodegradable and made from renewable resources, they provide a sustainable substitute. Despite over a century of research, large-scale production of bioplastics is still in its infancy. 2.11 million tons of bioplastic were produced worldwide in 2019, according to the European Bioplastics association, accounting for only 0.6% of all plastic output. Higher production costs, comparatively poor mechanical qualities as compared to traditional plastics, and problems with recycling and competition for food resources are some of the barriers preventing their widespread use.^{15,18} The characteristics of bioplastic materials have improved dramatically in recent years, including improved optical characteristics, higher strength, decreased thickness, and improved breathability, all of which contribute to improved performance. Notable biodegradable polymers include polylactic acid (PLA), polybutylene succinate (PBS), polycaprolactone (PCL), polyhydroxyalkanoates (PHA) and others that have been used for various applications (Fig. (1)).^{23–27}

Because of their ease of use, adaptability, and compatibility with different kinds of 3D printers, biodegradable polymers are ideal for 3D printing. These characteristics increase its usefulness in a variety of sectors by making it possible to produce intricate designs and precise prints. In addition to promoting sustainable behaviours, the combination of biodegradable polymers with 3D printing technology opens the door for creative production techniques. A comparison of several bio-based and fossil-based polymers that are appropriate for 3D printing is shown in Table 3.

2.1 PLA (polylactic acid)

One of the most popular biopolymers is polylactic acid (PLA), which is made up of lactic acid monomer units obtained from renewable resources such as tapioca roots, corn starch, and sugarcane. Because of the convenience of processing, biocompatibility, and environmental friendliness, PLA has gained popularity for a variety of uses. However, obtaining lactic acid



Table 3 Various bio-based and fossil-based 3D printable-compositions, properties and applications

S. no.	Bio-based	Fossil-based	Bio-degradability	Composition	Properties	Application	Ref.
1	PE	✓	✗	Polyethylene-ethylene monomer (C ₂ H ₄)	LDPE: flexible HDPE: high strength UHMWPE: high impact resistance	Personal care, food packaging and automotive applications	28
2	PET	✓	✗	Polyethylene terephthalate-polymer matrix of ethylene terephthalate monomers with alternating (C ₁₀ H ₈ O ₄) units	Good tensile strength and higher chemical resistance	Packaging, textiles and bottles	29
3	PA	✗	✗	Polyamides-characterized by the presence of amide linkages (–CO–NH–) in their molecular structure	Excellent tensile strength and toughness	Electronics, textile and automotive industries	30
4	PTT	✗	✗	Poly(trimethylene)-synthesized from terephthalate-1,3-propanediol (a diol), terephthalic acid	Good thermal stability and low moisture absorption	Insulation materials, mechanical components such as bearings and seals	31
5	PLA	✗	✓	Poly(lactic acid)-primarily corn starch or sugarcane	Better processability and higher encapsulation efficiency and stability	Toys, stationery and kitchen utensils	32
6	PHA	✗	✓	Polyhydroxyalkanoates-hydroxy fatty acids	Biocompatibility and excellent barriers for moisture and gas	Surgical sutures and implants, eco-friendly packaging and mulch films	25
7	PBS	✗	✓	Synthesized from 1,4-butanediol and succinic acid	Better blending compatibility and balanced strength and flexibility	Light packaging materials and biodegradable films and coatings	33
8	PP	✓	✗	Polypropylene-propylene monomers (C ₃ H ₆)	Ease of moulding and fabrication and light weight and good impact resistance	Containers, pipes, fittings and automotive components such as dashboards <i>etc.</i>	34
9	PBAT	✓	✓	Poly (butylene adipate terephthalate)-synthesized from terephthalic acid 1,4-butanediol and adipic acid	Moisture resistant and high crystallinity	Packaging	35
10	PCL	✓	✓	Made through the ring-opening polymerization of a cyclic ester and ε-caprolactone	Solvent compatibility, lower glass transition temperature and remarkable rheological characteristics	Tissue engineering, biomedical devices and controlled drug delivery	23

requires complex fermentation and purification processes that account for almost half of the manufacturing cost; its production is more expensive than that of petroleum-based polymers. PLA's beneficial qualities have allowed its application in a variety of industries, including consumer items, construction, medical equipment, food packaging, and artistic works, despite these increased costs. PLA, which is renowned for its extreme strength and durability, degrades in a single step between 250 °C and 450 °C when heated at a rate of 10 °C per minute.³⁶

In the field of AM, PLA is especially significant. It is one of the most commonly used materials for 3D printing due to its

ease of use, low melting point, and compatibility with a wide range of 3D printers. This versatility, combined with its biodegradability, makes PLA an attractive option for sustainable manufacturing processes, contributing to the development of eco-friendly and innovative solutions in various industries.

2.2 PHA (polyhydroxyalkanoates)

A class of aliphatic polyesters known as polyhydroxyalkanoates (PHAs) are produced by specific bacteria in environments with minimal nutrients and are spontaneously biodegradable. These biopolymers are becoming more widely acknowledged as



environmentally friendly alternatives to conventional plastics, especially for use in biomedical equipment, packaging, and agriculture. PHAs are used in products such as food packaging, plant pots and agricultural mulch films. Because they naturally decompose, they significantly reduce plastic waste, which benefits the environment.²⁵ In the agricultural sector, for instance, PHAs can replace polyethylene (PE) in mulch films, decomposing at the end of the season and minimizing labour costs and waste. Despite their promising properties, PHAs face limitations in broader applications, such as odour issues that require additives, and their relatively high production costs due to energy-intensive processes.

PHAs offer significant potential as a biodegradable material that aligns with the growing demand for sustainable manufacturing. PHAs can be effectively used with various 3D printing technologies, with printing parameters deciding the final characteristics of the printed part. This synergistic relationship between PHAs and 3D printing technology makes them suitable for diverse applications owing to enhanced material properties. As sustainability becomes a critical concern globally, the use of PHAs in AM provides an eco-friendly solution that contributes to reducing plastic waste while advancing innovative manufacturing techniques.

2.3 Polycaprolactone (PCL)

Polycaprolactone (PCL) is a flexible and adaptable semi-crystalline biodegradable aliphatic polyester. Its molecular weight affects its crystallinity because larger molecular weights cause chain folding, which reduces crystallinity. Because of its high chain segment mobility and low intermolecular interactions, PCL has a low melting point (60 °C) and a glass transition temperature of −60 °C. PCL is extensively used in biomedical applications, including drug delivery systems, prosthetics, and sutures, and has FDA approval for human use. Its superior processability, thermal stability, and compatibility with a wide range of other polymers are what make it so appealing.²³ It is easily melt-processed into various structures and forms, contributing to its versatility in different applications. Furthermore, PCL's biodegradability is a significant advantage, as it undergoes slow degradation through hydrolysis, making it ideal for long-term implants and devices. In addition to biomedical uses, PCL has applications in 3D printing, where its mechanical flexibility and ability to be functionalized make it useful for producing customized, biocompatible scaffolds. PCL's combination of processability, biodegradability, and biocompatibility positions it as an environment friendly material especially useful in the medical field.

2.4 Polybutylene succinate (PBS)

Polybutylene succinate (PBS) is a biodegradable semi-crystalline polymer known for its versatility and structural characteristics. Its physicochemical properties are comparable to those of polyethylene terephthalate, making it useful across various industries. PBS exhibits robust elongation properties, and its biodegradability is triggered by the hydrolytic breakdown of ester groups, particularly when exposed to water or elevated

temperatures.²⁶ This makes PBS a highly attractive material for applications where environmental sustainability is crucial.

The polycondensation of succinic acid with 1,4-butanediol yields PBS, and the monomers can be obtained from both fossil and renewable sources. This synthesis process enhances PBS's thermoplastic processability, mechanical, and thermal characteristics. However, while bio-based synthesis methods hold promise for reducing environmental impact, they are often more costly than petroleum-based alternatives. Recent advancements in microbial processes have shown promise in producing succinic acid more sustainably, though challenges with instability remain.

Owing to PBS's biodegradability, combined with its mechanical properties, it is being used in packaging, agriculture, and biomedical fields. Surface modification techniques, such as plasma treatment, have further expanded its utility by enhancing surface hydrophilicity and biocompatibility. With the rise of 3D printing, PBS has gained attention as an ideal material for creating customized, eco-friendly products. Its adaptability to various processing conditions makes it a key material in the growing field of ecofriendly material 3D printing.

2.5 Polybutylene adipate-co-terephthalate (PBAT)

Adipic acid (AA), terephthalic acid (PAT), and 1,4-butanediol (BDO) are polycondensed to create polybutylene adipate-co-terephthalate (PBAT), a flexible and biodegradable polyester. Pre-mixing, pre-polymerization, and final polymerization are the three main processes in its manufacturing. Typically, the production of PBAT requires high temperatures (over 190 °C) and vacuum conditions to facilitate the removal of lighter molecules such as water. Organometallic catalysts such as zinc, tin, and titanium compounds are used to enhance the polycondensation process.²⁴ In order to improve crystallization and decrease tackiness, nucleating agents such as mica, chalk, and silicon oxides are frequently added during the polymerization of PBAT. Colour stabilizers such as phosphoric acid may also be incorporated to prevent the degradation of film quality. For the production of ultra-thin films, the polymer backbone's melt strength can be effectively increased by incorporating long-chain branching (LCB). The uses of PBAT have increased as a result of this modification, especially in agricultural films and packaging.

PBAT is a compostable material, making it an attractive choice for industries seeking sustainable alternatives to traditional plastics. By adding multifunctional branching agents, such as alcohols, acids, and epoxides, LCB PBAT can be synthesized, further improving its properties for various applications. The composting process allows PBAT films to degrade naturally, contributing to its growing popularity as a biodegradable polymer in environmentally cognizant industries.

3. 3D printing technologies for eco-friendly materials

Recent advancements in AM have significantly expanded its applicability to biodegradable polymers, particularly biopolymers and bio-based polymers. AM enables the layer upon layer



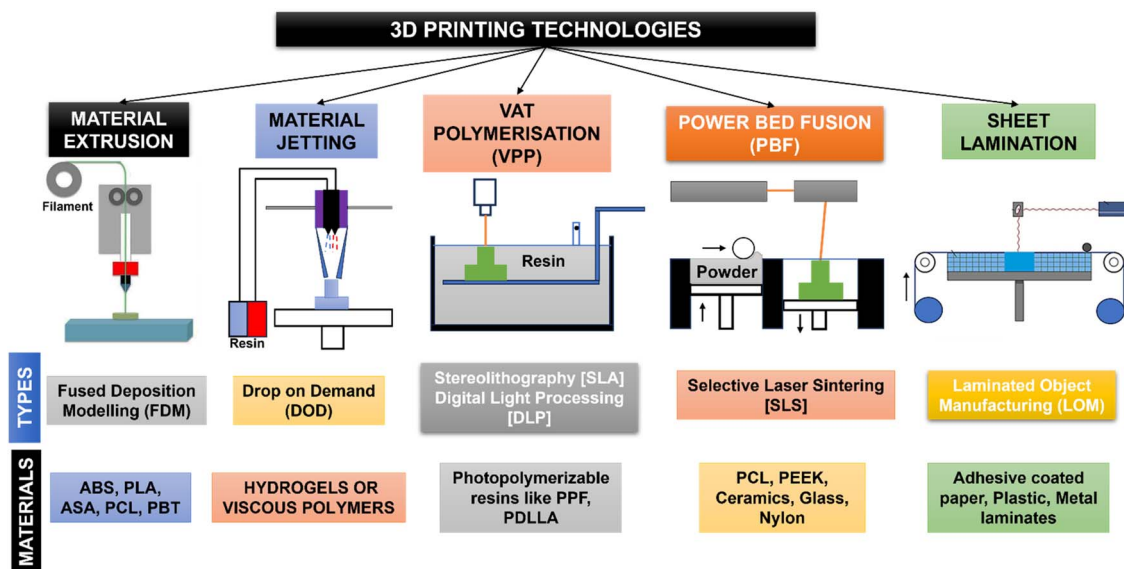


Fig. 2 Schematic illustration of various 3D printing processes for biodegradable material printing.

development of complex objects with biodegradable materials, offering distinct advantages over traditional manufacturing processes.^{27,37–39} These advantages include greater design freedom, improved flexibility, customization, and reduced material wastage, making it an ideal choice for sustainable manufacturing. Five main steps are usually involved in AM for biopolymers: creating a model with computer-aided design (CAD) software, converting the CAD file into a compatible format, such as .stl, setting up build parameters, slicing the model into layers, and then carefully fusing, melting or depositing the biopolymer material. New file formats, such as .amf, *etc.*, are increasingly being used in AM, particularly for multi-material and multi-color designs, enhancing the choice of biopolymer 3D printing. Specific AM technologies, including material extrusion methods such as Fused Deposition Modelling (FDM or FFF), vat photopolymerization processes such as stereolithography (SLA), and powder bed fusion techniques, are widely utilized for biopolymer applications (Fig. 2).⁴⁰ Each technique is adapted to suit the material's properties, ensuring that biopolymers maintain structural integrity and biodegradability. FDM is particularly popular for its ability to extrude thermoplastic biopolymers layer by layer, while SLA and SLS offer precise detail and surface finish, critical for biomedical and environmental applications. These processes allow for the creation of biodegradable products ranging from medical implants to sustainable packaging solutions. As research in biopolymer-based 3D printing progresses, new innovations are driving the optimization of material properties, thereby expanding the use of eco-friendly, high-performance products in numerous industries.⁴¹

3.1 Material extrusion

The most popular AM method for biopolymers is material extrusion, especially Fused Filament Fabrication (FFF). FFF is particularly well-suited for prototyping since it builds items

layer by layer by extruding the material through a nozzle. This technique is frequently used with bio-based materials such as cellulose nanoparticles and lignocellulosic compounds. However, die swell—a phenomenon where highly viscous materials, including biopolymers, expand upon exiting a small-diameter nozzle, affecting the dimensional accuracy of printed objects—makes it difficult to produce smaller-diameter filaments for extrusion-based 3D printing. Improving the printability and quality of biopolymer-based 3D-printed components requires addressing these problems.²⁷

Material extrusion covers many techniques beyond FFF, such as Direct Ink Writing (DIW). DIW is particularly versatile for printing biopolymers, as it enables the direct deposition of highly viscous materials, including hydrogels, to create intricate 3D structures. Furthermore, material extrusion technologies can accommodate the simultaneous use of multiple materials, provided the printer is equipped with multiple nozzles. This multi-material capability allows for more complex designs and expands the applications of biopolymers in fields such as tissue engineering and eco-friendly packaging. As advancements continue, optimizing material flow and extrusion precision remains critical for enhancing the performance and sustainability of biopolymer-based 3D printing.⁴²

3.2 Material jetting

Material jetting is an AM technique that functions similarly to 2D inkjet printing. It involves the precise deposition of liquid droplets, typically polymers, onto a substrate layer by layer. The nozzle releases these droplets under the influence of thermal or acoustic forces, allowing for the creation of highly detailed structures.⁴³ After deposition, UV light is used to solidify each layer, building up the final product. This process is particularly well-suited for polymers, making it a versatile method for complex part production.



In terms of biodegradable materials, material jetting has shown significant promise in bioprinting applications. Polymers such as PLA and PHA have been explored for material jetting, offering biodegradability and biocompatibility. This technique is widely recognized for its use in the fabrication of tissues and organs, making it a valuable tool in the medical field.^{44,45} Moreover, laser-induced forward transfer (LIFT), another method in this group, is used to fabricate both 2D and 3D biodegradable forms.⁴⁶ As research in sustainable materials continues, biodegradable inks designed for material jetting are being developed to reduce environmental impact while maintaining precision and functionality. These materials are increasingly employed in the production of eco-friendly prototypes, packaging solutions, and biomedical devices, reflecting the growing demand for sustainable and biodegradable manufacturing solutions.

3.3 Vat photopolymerization

A flexible AM method that is being utilized more and more to print biodegradable and bio-based products is vat photopolymerization (VPP). This method creates thermoset polymer based objects by employing light with a particular wavelength to cure and solidify liquid monomers or oligomers.⁴⁷ The growing interest in sustainability led to development of biodegradable photopolymerizable resins for eco-friendly applications that can be processed using VPP. These materials undergo selective curing, one layer at a time, allowing for the creation of intricate and highly precise 3D structures, often used in medical and environmental applications.

Traditional resins, such as acrylate-based polymers, were the pioneers in VPP, but there has been significant progress in introducing biodegradable and biocompatible resins. Polyethylene glycol diacrylate (PEGDA), for example, is a biodegradable material that has been successfully utilized in VPP processes. Additionally, bio-based photopolymers, derived from natural sources, are being integrated into VPP workflows, further expanding the choice of materials available for sustainable manufacturing.¹⁸ Digital Light Processing (DLP) technology, which exposes entire layers of liquid resin at the same time, has enabled faster production of biodegradable objects without compromising precision. This capability makes VPP an excellent choice for applications requiring eco-friendly, high-resolution components, such as in tissue engineering, medical implants, and environmentally conscious product design. As advancements in biodegradable resin formulations continue, the potential of VPP in sustainable manufacturing is set to grow further.

3.4 Powder bed fusion

An advanced AM process known as Powder Bed Fusion (PBF) uses laser or electron beams to selectively melt and fuse powdered materials into solid objects. Using a blade mechanism from a hopper, a thin layer of powder is first evenly applied throughout the build platform. The object is then created by scanning and sintering the powder layer by layer using a laser or electron beam. The process is repeated until the product is completely produced, spreading a fresh coating of

powder after each layer is finished. PBF is well known for its extreme precision and works especially well for producing complicated structures and intricate geometries.⁴⁸

For biodegradable materials, PBF has demonstrated significant potential, especially with materials such as PLA and PCL.^{23,36} These polymers, when processed using PBF, retain their biodegradability while benefiting from the high resolution and structural integrity that the technique provides. This opens new avenues for the production of eco-friendly products, including biodegradable medical implants, scaffolds for tissue engineering, and sustainable consumer goods. The potential to recycle the unused powder material in subsequent builds reduces material waste, aligning PBF with sustainable manufacturing goals.

3.5 Sheet lamination

An AM technique called sheet lamination joins small material layers to produce a seamless three-dimensional object. Laminated Object Manufacturing (LOM) and Ultrasonic Consolidation (UC) are its two main subcategories. In LOM, sheets with adhesive backing are fused together, and the extra material is cut out to form the finished product.^{27,37,40} Conversely, Ultrasonic Consolidation (UC) bonds metallic sheets without the need of heat or adhesives by using ultrasonic vibrations and pressure. The accuracy and adaptability of sheet lamination, which can be applied to a variety of materials, such as metals, polymers, and paper, are demonstrated by both techniques. Furthermore, sheet lamination has the potential to be used in sustainable manufacturing since it can contain biodegradable polymers such as PLA and PCL, though binding these materials may require specific processes. Bio-based polymers are predicted to be used more often in sheet lamination as research progresses, especially for packaging and biomedical fields.

4. Ecofriendly polymer based composites, blends, and hybrid materials

The integration of composites, blends, and hybrid materials in 3D-printed biodegradable polymers is advancing sustainable manufacturing. These new materials address the limitations of traditional biodegradable polymers, which, while being environmentally friendly, often lack the necessary strength, flexibility, or durability for broader applications. By enhancing properties such as mechanical strength, elasticity, and thermal resistance, these innovations enable biodegradable polymers to compete with non-biodegradable alternatives across various industries. This not only expands their practical uses but also maintains their eco-friendly nature, contributing to greener, more efficient manufacturing solutions. Table 4 shows different 3D printable biodegradable polymer composites, blends and hybrid materials.

4.1 Composite materials

Two separate materials with differing physical and chemical characteristics are combined to create a composite material.



Table 4 3D eco-friendly polymer-based composites, blends and hybrid materials

S no.	Polymer matrix	Reinforcement/ fillers	3D printing process	Application	Outcomes	Ref.
(a) Polymer composites						
1	PP	Rice husk	FDM	Electronic casings	Reduced warping and weak interlayer bonding	49
2	PET	Textile waste	FDM	Furniture and interior design	Reduced viscosity and improved impact resistance	50
3	PP	Cocoa bean shells	FDM	Seat belts and agricultural tools and equipment	Lower processing temperature, increased water absorption and decreased tensile strength and Young's modulus	51
4	HDPE	Sawdust	FDM	Sustainable decking and outdoor furniture	Improved dimensional accuracy	52
5	PLA	Anchovy fishbone powder	FDM	Landscaping and garden products Dental materials such as temporary crowns, molds, or aligners	Increased flexural modulus	53
(b) Blends						
1	PLA/PEG	—	Material extrusion	Tissue engineering and scaffolds	Increased surface roughness and wettability	54
2	PLA/PHA	—	FDM	Agricultural mulch films, biodegradable utensils and straws	Increased degradation in marine environments	55
3	PET/PP/PS	—	FDM	Feedstocks for manufacturing in remote environments	Performance on par with commercial HIPS filaments	34
4	PLA/PET	—	Material extrusion	Bottles and containers and compostable bags	Increased tensile strength (68 Mpa)	56
5	PLA/PC	—	Material extrusion	Medical devices and equipment and sports equipment	Increased melting temperatures (240–265 °C)	57
(c) Hybrid materials						
1	PLA blend (bioplastic)	Carbon from waste coconut shells	FDM	Water filtration systems and medical applications	Increased tensile strength	58
2	PLA	Hemp and harakeke	FDM	Textiles and customised tableware	Decreased tensile strength and increased Young's modulus	59 and 60
3	PP	Wastepaper and wood flour	FDM	Automotive parts such as dashboard and packaging materials	Improved stiffness and weaker interfacial strength	61
4	PLA	Wood, bamboo and cork	FDM	Furniture, decorations, and automotive parts	Improved impact strength and increased temperature sensitivity	62
5	PLA	Nona and soy	FDM	Enhanced lightweight structures	Enhanced durability and tensile strength	63

This combination creates a novel material that is intended to carry out particular tasks, including being more electrically resistant, lighter, or stronger.^{64–66} In biodegradable substances, either nanoparticles or natural fibres are incorporated into a polymer matrix as reinforcements.^{67–70} This results in materials that possess increased strength and durability, alongside a commitment to making them suitable for various sectors, environmental responsibility, aerospace, construction and consumer products.⁷¹ Non-biodegradable polymers can be modified to become partially biodegradable by blending them with biodegradable fillers. This approach enables the degradable nature of the fillers, which serve as initiators for the breakdown of the composite structure. The mechanisms of partial biodegradability in these composites depend on the

nature and compatibility of the biodegradable filler with the polymer matrix.

A polymer composite with PP with cocoa bean shells as a filler was fabricated by researchers. The inclusion of the filler enhanced the tensile strength and modulus (Fig. 3(c)), reduced warping, provided dimensional steadiness (Fig. 3(a) and (b)) and lowered the processing temperature. This shows how different fillers enhance different properties of composites.⁵¹ In another study, PLA and biodegradable co-polyesters Mater-Bi(MB) reinforced with anchovy fishbone powder (EE) were printed using an FDM based 3D printer. The addition of the filler decreased tensile strength and modulus, increased flexural strength and modulus, and improved impact strength in comparison to neat polymers.⁷² Another example of a polymer



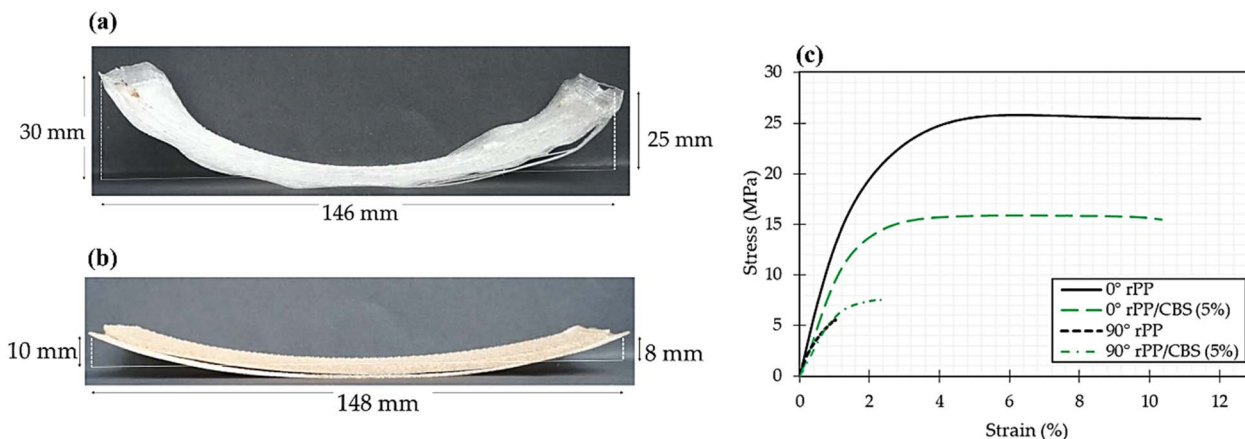


Fig. 3 Warping behaviour of 3D printed (a) neat polypropylene (PP) and (b) PP reinforced with cocoa bean shells (CBSs) and (c) stress–strain curve of a PP and PP–CBS composite printed at 0° and 90° raster angles (reprinted from ref. 51 Morales M. A., Maranon A., Hernandez C., and Porras A., Development and characterization of a 3D printed cocoa bean shell filled recycled polypropylene for sustainable composites, *Polymers (Basel)*, 2021 Sep 18, 13(18), 3162). Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

composite is PET with reinforcement textile waste; this composite is printed using the FDM method and is used in furniture and interior design. The inclusion of hydrolysed cotton fibres efficiently reduced the viscosity of PET, and the composite exhibited improved impact resistance.⁵⁰ The process of 3D printing polymer composites presents a number of difficulties. Finding the right materials is a big challenge, and it's still difficult to strike a balance between the materials' biodegradability and the required mechanical characteristics such as strength and flexibility. To get consistent and trustworthy results, researchers must additionally adjust variables including printing speed, temperature, and layer height. Furthermore, evaluating the environmental impact of 3D printing using biodegradable materials is difficult and necessitates a thorough analysis of the whole product lifespan, from the extraction of raw materials to disposal. To overcome all these difficulties machine learning can be a viable tool for diversifying the use of 3D printable eco-friendly materials.^{73–76}

4.2 Blends

To develop a new material, two or more polymers are combined to generate a polymer blend. In this technique, several polymers are strategically mixed in a well-planned manner. It is possible to create materials with specific qualities by combining different polymers, striking a balance between strength, sustainability, and other desired characteristics.^{77,78} This adaptability makes it possible to produce biodegradable materials that satisfy certain requirements, such as those found in flexible packaging, medical devices, and agriculture.^{79–82} By addressing environmental issues while preserving functionality, biodegradable polymers are bringing about a new age in sustainable materials innovation.

In one study PLA/PEG blends were fabricated for tissue engineering applications. The inclusion of 5% PEG and 5% bioglass (G5) resulted in the fabrication of high-resolution PLA scaffolds at low temperature and the highest compressive

strength.⁵⁴ In one study mechanical properties of 3D printed PC and PLA blends with compatibilizers were explored. Results demonstrated the maximum tensile and impact strengths of PC/PLA (70 : 30 by weight %) and SAN-*g*-MAH (@5%) as the compatibilizer.⁸³ In another instance mechanical behaviour of 3D printed PLA/PET blends was investigated.⁸⁴ Results revealed an improvement in tensile moduli with the increase in percentage PLA (up to 0.5%) and after that it started decreasing. Researchers studied the behaviour of PLA and PLA-PHA in marine environments, printed using the FDM process. Compared to non-blended PLA, the PLA-PHA blend showed a 24% increase in UTS after 15 days but experienced a sharper decline after 30 days (Fig. 4(a)). Its Young's modulus decreased significantly (35% for 80% infill and 16% for 40% infill), indicating greater embrittlement over time (Fig. 4(b)). Also, there was a slight increase in yield strength (Fig. 4(c)). While PLA-PHA initially exhibited increased elongation at break after 30 days, both materials showed a loss in elongation after 45 days (Fig. 4(d)). Overall, PLA-PHA degraded faster than non-blended PLA, with more pronounced changes in mechanical properties, making it more suitable to be used in marine environments in terms of biodegradability.⁵⁵

In another study researchers used recycled PP blends as new 3D printing materials. Their study suggested that blends of recycled PP with PET or PS offer promising and practical options as feedstocks for FFF 3D printing, exhibiting tensile strengths on par with certain lower-end commercial filaments such as HIPS. Although compatibilizing these blends with SEBS elastomers did not lead to significant improvements in tensile strength, it still presented a viable alternative for sustainable printing materials.³⁴

The use of biodegradable polymer blends in 3D printing is limited in high-stress environments due to issues with mechanical strength, different breakdown rates, and limited thermal instability. It's still quite challenging to maintain environmental stability and print quality as time passes. Despite these limitations, it is anticipated that future



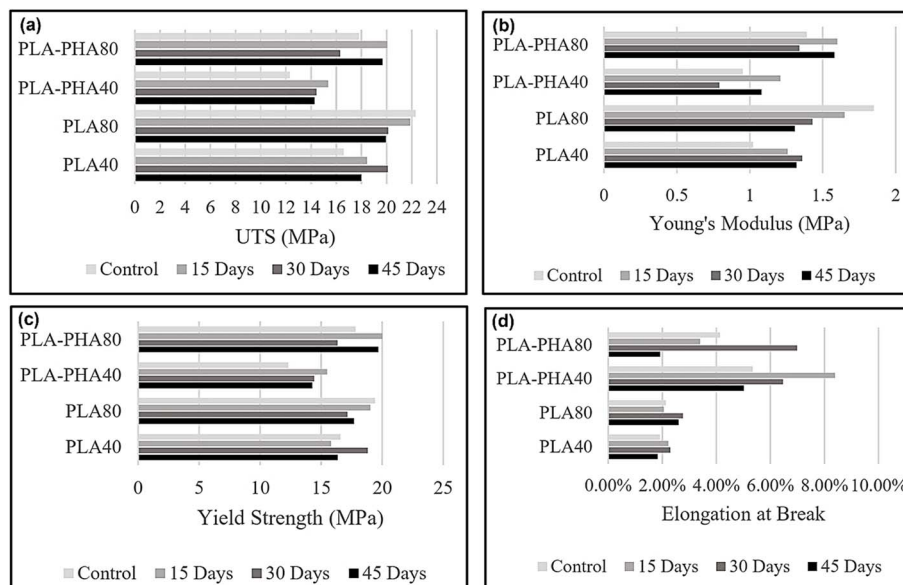


Fig. 4 Mechanical properties of the 3D printed samples over the various marine submersion periods, (a) ultimate tensile strength, (b) Young's modulus, (c) yield strength and (d) elongation at break (reprinted from ref. 85 Montalvão G. R., Moshrefi-Torbati M., Hamilton A., Machado R., and João A., Behaviour of 3D printed PLA and PLA-PHA in marine environments, *IOP Conf. Ser. Earth Environ. Sci.*, 2020, **424**(1). Creative Commons Attribution 3.0 licence. <https://creativecommons.org/licenses/by/3.0/>).

developments in polymer science and 3D printing methods will enhance the usability and variety of biodegradable materials, opening up new applications in industries including consumer

products, packaging, and medical devices. Biodegradable polymers could turn into essential parts of sustainable manufacturing as an outcome of these advancements.^{86,87}

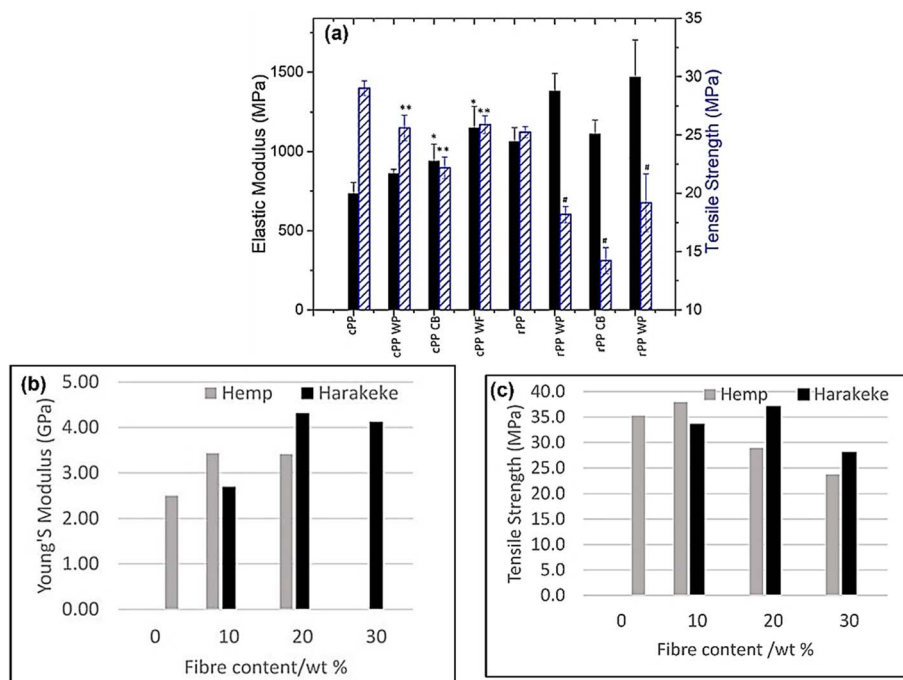


Fig. 5 (a) Tensile strength (black) and elastic modulus (blue) of printed PP and PP composites, WP = waste paper, CB = cardboard, and WF = wood flour. (b) and (c) Young's modulus and tensile strength of PLA/Hemp/Harakeke hybrid composites respectively (reprinted with permission from ref. 59 and 91 (Copyright (2019), American Chemical Society), Stoof D., Pickering K., and Zhang Y., Fused deposition modelling of natural fibre/polylactic acid composites, *Journal of Composites Science*, 2017, **1**(1) and Zander N. E., Park J. H., Boelter Z. R., and Gillan M. A., Recycled cellulose polypropylene composite feedstocks for material extrusion additive manufacturing, *ACS Omega*, 2019, **4**(9), 13879–88. Creative Commons Attribution 4.0 International License CC BY-NC-ND, <https://creativecommons.org/licenses/by-nc-nd/4.0/>).



4.3 Hybrid materials

To improve their properties, bio-based polymer matrices are combined with other fiber or filler reinforcements to create biodegradable hybrid polymers. These combinations provide materials with desired properties that enable them to compete with conventional polymers derived from petroleum. One fascinating new area is the creation of hybrid materials for 3D-printed biodegradable polymers. Biodegradable polymers are increasingly being combined with non-polymeric materials, such as metals or ceramics, using sophisticated 3D printing techniques.⁸⁸ These hybrid materials combine the environmental benefits of biodegradable polymers with the properties of metals or ceramics, such as electrical conductivity or heat resistance.⁸⁹ This creates a lot of opportunities, including lightweight medical implants and environmentally friendly, sustainable electronic components. With the ongoing advancement of research and development in these fields, the future of environmentally friendly looks increasingly promising.⁹⁰

Usually in the form of fibers, particles, or other structures, reinforcements are substances that are added to polymers to increase their strength and functionality. The strength and other allied properties of the composite are enhanced by these reinforcements. The choice of reinforcing materials is influenced by elements including processing simplicity, biocompatibility, and the necessary strength. An example of a biodegradable hybrid is a bioplastic (BP)/PLA blend with carbon from waste coconut shells. It is printed using the FDM method and gives a 50% increase in tensile strength compared to neat BP up to a certain weight fraction of fillers and decreases afterwards due to the agglomeration of fillers.⁵⁸ The mechanical characteristics of 3D printed PP reinforced with wastepaper and wood flour were investigated in another study. The fabricated composite demonstrated enhanced stiffness, tensile strength, and elastic modulus and a storage modulus increase of roughly 20–30% compared to pristine PP (Fig. 5(a)). Additionally, it was discovered that the strength of the filler itself was stronger than its interfacial strength.⁶¹ Researchers developed natural fiber reinforced PLA composites using the FDM process.⁵⁹ Results demonstrated improved tensile strength and Young's modulus (Fig. 5(b) and (c)).

There are several limitations of printing with hybrid materials, which include lower thermal stability and mechanical strength as compared to conventional plastics, thus limiting its use in high stress applications. Hybrid polymers may degrade, unpredictably under different environmental conditions. Achieving uniformity in dispersion of fillers in hybrid materials remains a challenge, affecting print quality. Biodegradable polymers also tend to absorb moisture, which can alter their properties and compromise printing precision. These factors limit their use in industrial 3D printing.^{92–94}

5. Applications of eco-friendly materials in 3D printing

3D printing is revolutionizing many industries and has found groundbreaking and diverse applications in a wide range of

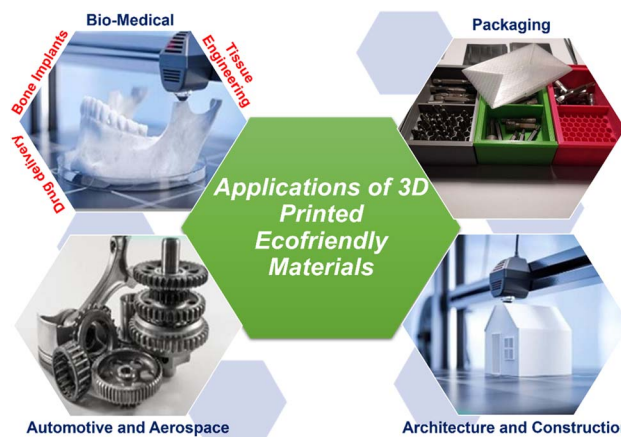


Fig. 6 Applications of 3D printed eco-friendly materials in different fields.

industries. As concerns about climate change, scarcity of resources and pollution increase, the need for 3D printing with ecofriendly materials increases. Eco-friendly materials such as bio-plastics and polymer composites are gaining interest and are being actively researched. The addition of eco-friendly materials with 3D printing has various applications in the bio-medical field, healthcare, construction and other different sectors, where reducing environmental impact is increasingly essential (Fig. 6).⁹⁵ As AM technology advances, innovations in sustainable material development are likely to increase, further amplifying the environmental benefits and practical uses of 3D printing.

5.1 Bio-medical applications

5.1.1 Bone implants. Bone implants are medical devices used in orthopaedic surgeries where they are used to hold or support injured or fractured bones.⁹⁶ These are customised based on the type of bone and injury.⁹⁷ A large range of materials are utilised to make bone plates, which are used to repair bone fractures. Bone plate applications frequently use materials including stainless steel, titanium and its alloys, cobalt-chromium alloys, hybrid composites, and bioabsorbable polymers (especially for paediatric fractures). The mechanical characteristics of various polymer-based hybrid composites (PBHCs) are similar to those of real bone. Numerous factors influence the utilization of PBHCs in bone plate applications. By bridging the mechanical gap between conventional metallic bone plates and natural bone, these composites seek to address the problem of “stress shielding” and lower the risk of long-term consequences. The improvement of biocompatibility is the main objective of polymer-based composites since they also reduce adverse reactions and improve implants' overall biocompatibility.^{98,99} The polymer matrix of PBHCs is reinforced with fibers, particles, or other structural components to increase the material's mechanical qualities. These reinforcements give the material strength, stiffness, and toughness, which improves its usefulness. These reinforcements are crucial for increasing the composite's strength and load-bearing



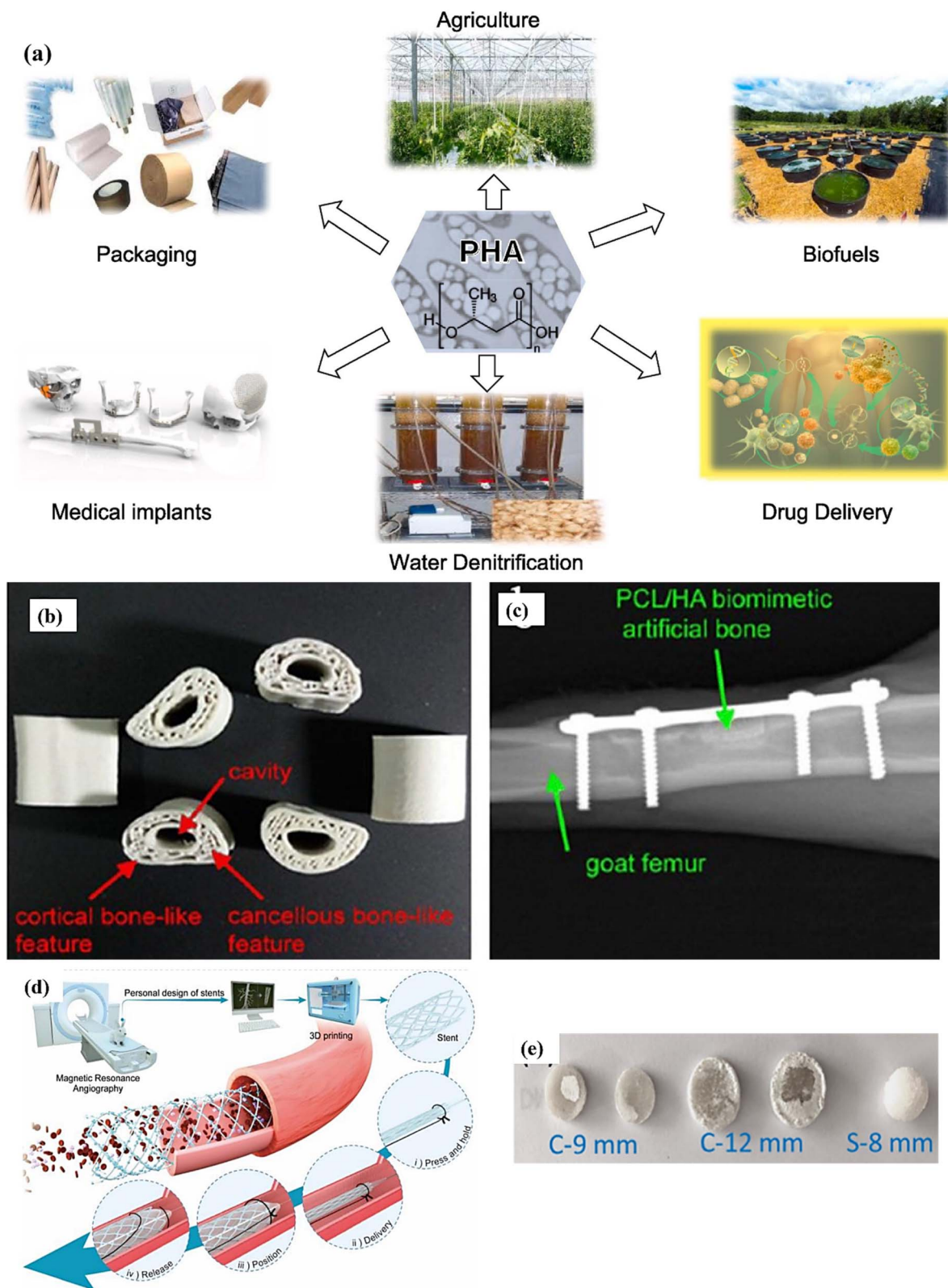


Fig. 7 (a) Applications of PHA and its composites in various fields. (b) PCL/HA stent, (c) computed tomography image of implantation,¹⁰³ (d) a customized coronary artery stent and (e) 3D printed PLLA implants (reprinted with permission from ref. 18, 103, 104 and 105 (Copyright, 2014, ACS), Dananjaya S. A. V., Chevali V. S., Dear J. P., Potluri P., and Abeykoon C., 3D printing of biodegradable polymers and their composites – Current state-of-the-art, properties, applications, and machine learning for potential future applications, *Prog. Mater. Sci.* [Internet], 2024, **146**(March), 101336; Wang Y., Sun L., Mei Z., Zhang F., He M., Fletcher C., *et al.*, 3D printed biodegradable implants as an individualized drug delivery system for local chemotherapy of osteosarcoma, *Mater. Des.*, 2020 Jan 15, **186**, 108336; Shen Y., Tang C., Sun B., Zhang Y., Sun X., EL-Newehy M., *et al.*, 3D printed personalized, heparinized and biodegradable coronary artery stents for rabbit abdominal aorta implantation,



performance in bone plate applications. For usage in bone implants, PBHCs—which are renowned for their superior mechanical qualities and biocompatibility—can be created utilizing techniques such as FDM, SLA, or SLS. For bone plate applications, PBHC combinations come in a variety of forms, each with unique benefits based on demands.^{100–102} Researchers²⁵ investigated PHA/PHB-based implants in growing rats, finding high resistance to *in vivo* degradation even after 36 weeks. Using μ CT, they analysed femoral bone healing and implant resorption. Surface roughness was examined by SEM and EDX to assess bone ingrowth potential. Four PHB composites with ZrO₂ (for contrast) and Herafill (to increase degradation) were tested. Implants remained largely intact, though the ZrO₂/30% Herafill composite showed the best bone accumulation. No significant surface changes were observed. However, improvements in mechanical properties are needed for effective load-bearing applications in custom 3D-printed implants. Fig. 7(a) shows various applications of PHA and its composites.

Researchers¹⁰⁶ used β -TCP and bio-glass powders in varying amounts for 3D-printed scaffolds. Study demonstrated that these scaffolds facilitated the growth of osteogenic MG-63 cells without significant cytotoxicity and demonstrated superior biocompatibility and mechanical strength. Researchers¹⁰⁷ produced PCL/HA composites for bone scaffolds which proved compatible and mechanically robust (Fig. 7(b) and (c)). In another study¹⁰⁸ PCL and β -TCP composite scaffolds with controlled porosity, degradability, and mechanical strength were developed, observing higher *in vivo* degradation rates than *in vitro*. In another instance¹⁰⁹ researchers designed a 3D-printed PLGA scaffold aimed at craniomaxillofacial bone defect treatment, showing promise for clinical applications. Another researcher¹¹⁰ utilized low-temperature deposition printing to create PLGA scaffolds with exceptional properties and non-toxicity, highlighting their potential for bone tissue engineering applications.

5.1.2 Drug delivery. Bio-based polymers may be made to adapt to the needs of the body as they are becoming more and more helpful in medication delivery systems. Drugs are added into bio-based polymer structures to build devices that answer to particular biological signals and release medication in a targeted manner with precision and control. Apart from 3D printing, 4D printing is also useful in this situation. By including the element of time, 4D printing expands on 3D printing and enables objects to modify, adapt, or even mend themselves after printing. This is made feasible by the materials' ability to alter their form, dimensions, or characteristics in response to outside factors, opening up opportunities for administering medications.^{111–113} A study that used PHB made by *Alcaligenes eutrophus* H16 (now *C. necator* H16) examined the utilization of PHB tablets in mouse fibroblast cells and *in vivo* in mice. The findings showed that PHB might be used as a controlled-release, biodegradable drug carrier without negatively impacting *in vitro* cell growth. *In vivo*, subcutaneous PHB

implants caused connective tissue capsule formation and inflammation, which aided in implant degradation. Despite using placebo pills, this study marked a pioneering *in vivo* application of PHA/PHB in drug delivery.²⁵ A 3D printing technique was developed by researchers¹⁰⁴ for osteosarcoma treatment using personalized chemotherapy. *In vivo* trials showed poly-L-lactic acid (PLLA) implants (Fig. 7(e)) that were 3D printed to be excellent drug carriers with customizable morphologies and micropores, ensuring effective biodegradability, biocompatibility, and anti-cancer properties. Local chemotherapy using PLLA implants proved more effective against osteosarcoma than traditional methods, allowing individualized treatment, multi-drug delivery, sustained release, and eradicating the need for reoperation. This method highlights the capability of 3D printing in osteosarcoma treatment and its adaptability for localized chemotherapy in other cancers.

5.1.3 Tissue engineering. Biodegradable polymers are perfect candidates for tissue engineering applications owing to their degradability, biocompatibility and potential to replicate the matrix. These may be used as scaffolds, providing a structural framework that supports cell attachment, proliferation, and differentiation. These may not need to be surgically removed because of the degradation rates which can be tuned to match tissue regeneration timelines. Additionally, advancements in polymer modifications enhance their mechanical properties and printability, expanding their applicability across a wide range of tissue types, including skin, cartilage, and bone.^{114,115}

3D printing offers innovative and promising solutions for creating tissues such as scaffolds, personalized to one's needs, for each patient. In one study¹¹⁶ a bioink combining hyaluronic acid, tricalcium phosphate, silk fibroin and gelatine was used to 3D print hybrid scaffolds. Human platelet-rich plasma (PRP), which was applied to the scaffolds *via* dual crosslinking, promoted the growth and multiplication of human adipose-derived mesenchymal stem cells and elevated the expression of genes linked to bone formation. Alkaline phosphatase (ALP) activity was only marginally enhanced by the coating, though. This method of integrating PRP therapy with silk fibroin scaffolds has a lot of potential to advance bone regeneration and healing in tissue engineering applications. Research proposed using patient blood-derived biomaterials for safer, biocompatible wireless micromachines.¹¹⁷ They developed multi-responsive, 3D-printed micro-swimmers and micro-rollers made of nanocomposites (magnetic) from serum albumin, blood plasma and platelet lysate which respond to magnetic fields and pH changes for controlled cargo delivery. Their enzymatic degradability reduces long-term risks, paving the way for biocompatible autologous medical robots. In another instance researchers created 3D-printed, PCL-based vascular stents (Fig. 7(d)) functionalized with heparin for improved biological activity. These heparinized stents showed reduced platelet adhesion and did not activate platelets, as confirmed by



platelet adhesion and clotting tests. In rabbit trials, these stents achieved full endothelialisation within one month and remained patent for three months, showing promise for use in abdominal aorta implants.¹⁰⁵

5.2 Packaging

3D printable eco-friendly materials can potentially change the entire packaging sector, tackling environmental issues such as overfilled landfills, plastic in oceans, *etc.* by enabling manufacturers to create personalised, biodegradable, and resource efficient packaging. The materials that may be used (potato starch, cornstarch and cellulose) are inexpensive, generate profit and produce smaller carbon footprint. This method guarantees that the materials are biodegradable after use and enables the use of food and beverages in disposable packaging

that benefits from 3D printing. Additionally, it makes it easier to create distinctive, personalized, and one-of-a-kind packaging, which improves customer interaction and product branding. Companies can rapidly create eye-catching packaging that works well for marketing. The appropriateness of sugarcane bagasse for creating customized three-dimensional food packaging casings and its biodegradability, printability, and water absorption qualities were examined in a study by Nida *et al.* Furthermore, as a sustainable choice for 3D food packaging, they evaluated the printability of rice husk (RH) fractions, including milled (MRH) and mixer ground (MGRH), with and without guar gum (GG).¹¹⁸ Only MRH with GG was extrudable, allowing steady printing under optimal conditions at 2100 mm min⁻¹, 300 rpm, and 4 bar pressure. Additionally, they studied sugarcane bagasse (SCB) for its printability and biodegradability in custom food packaging. With a 1.28 mm nozzle,

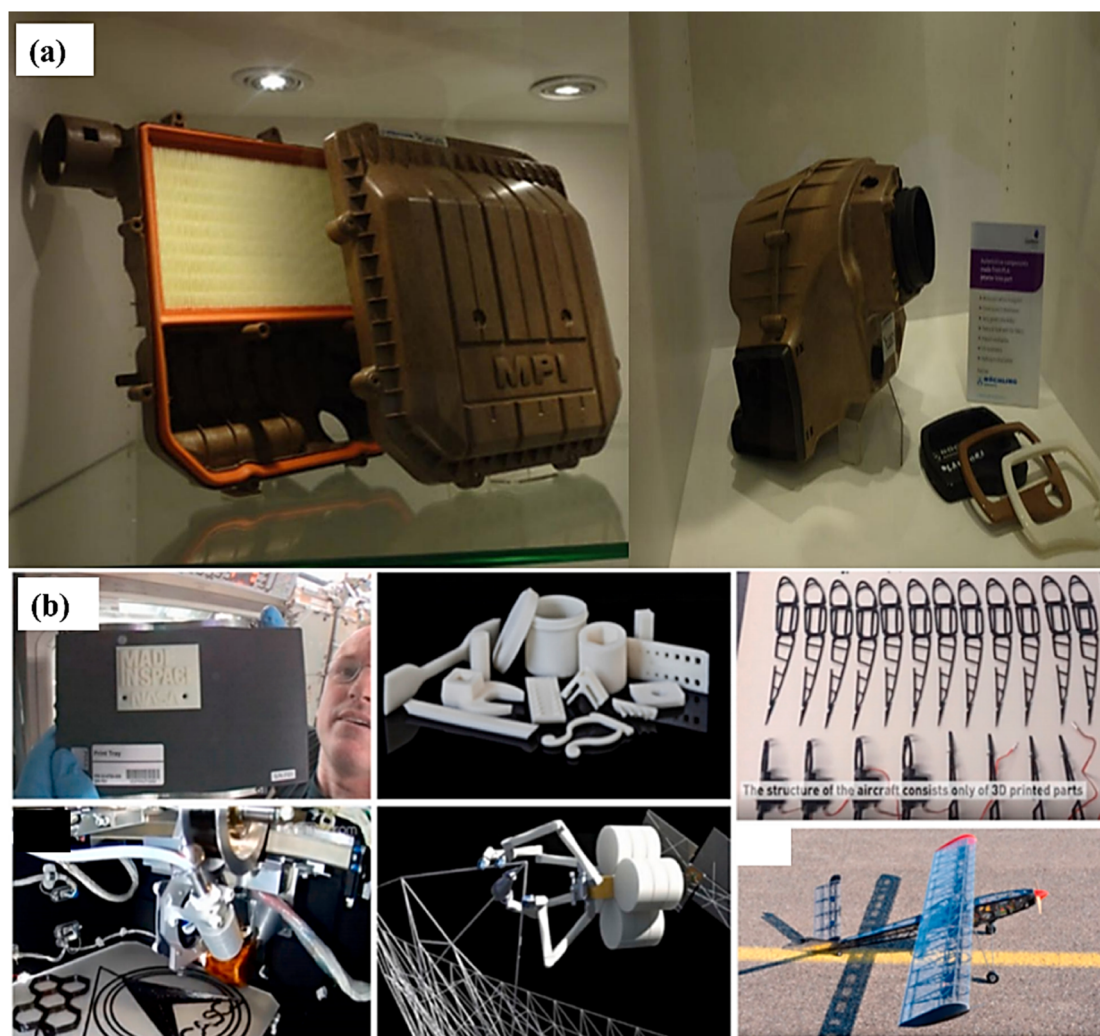


Fig. 8 (a) 3D printed air filter box and (b) space 3D printing and 3D printer parts from NASA's SpiderFab (reprinted with permission from ref. 18 and 123 Dananjaya S. A. V., Chevali V. S., Dear J. P., Potluri P., and Abeykoon C., 3D printing of biodegradable polymers and their composites-current state-of-the-art, properties, applications, and machine learning for potential future applications, *Prog. Mater. Sci.*, 2024, 101336 and Tuli N. T., Khatun S. and Rashid A. B., Unlocking the future of precision manufacturing: a comprehensive exploration of 3D printing with fiber-reinforced composites in aerospace, automotive, medical, and consumer industries, *Heliyon*, 2024, 10(5), e27328. Creative Commons Attribution 4.0 International License CC BY-NC-ND, <https://creativecommons.org/licenses/by-nc-nd/4.0/>).



3.2 bar pressure, and 500 mm min⁻¹ speed, SCB was extrudable and showed soil degradation and water sorption over 0.07 (g water per g solids) at humidity above 50%. SCB packaging proved suitable for low-moisture foods, offering an eco-friendly alternative to single-use plastics. Businesses now have an exciting opportunity to embrace eco-friendly packaging methods, improve their brand image, and contribute to a greener future at the same time by leveraging 3D printed biodegradable polymer materials and the global push for sustainability.

5.3 Automotive and aerospace applications

Eco-friendly polymers and their composites have gained more attention for application in automotive and aerospace applications due to their many advantages, including their biodegradability, renewability, and relative affordability in comparison to conventional petroleum-based polymers. PLA nanocomposites are useful in the automotive sector owing to their many advantages, such as light weight, higher corrosion resistance, durability, outstanding thermomechanical properties, ease of manufacture, and relative cost. Custom auto parts, quick prototyping, and even the manufacture of complete automobiles have all benefited from the use of 3D printing.^{119–122} Corbion Purac has introduced an innovative air filter box for the automotive industry named Plantura (Fig. 8(a)). These parts are crafted from high-heat PLA (polylactic acid) compounds made from Corbion Purac's lactides. The Plantura material family offers a PLA-based solution designed for long-lasting use in both durable goods and automotive applications. These materials can tolerate temperatures as high as 140 °C and are resistant to hydrolysis, or the breakdown of water, thanks to the inclusion of fiber reinforcement. They are perfect for enduring wear and exposure in cars since they also show excellent scratch and UV resistance. This development shows the industry's increasing dedication to sustainable innovation as it moves towards more resilient, environmentally friendly materials for forthcoming car designs.¹²⁴ Tungsten inert gas (TIG) welding has traditionally been employed to repair dies for vehicle engine manufacturing, but these repairs only last about around 20% of the lifespan of an original die before requiring another fix. A new hybrid repair method was established, which involves eradicating damaged areas and rebuilding them with a powder-blown Directed Energy Deposition (DED) process. Dies repaired with DED now last as long as the original, reducing the necessity for frequent emergency repairs and unexpected downtime. This innovation allows DED-restored dies to achieve the full lifespan of the original dies, enhancing efficiency on the production line.¹²⁵

The aerospace industry has leveraged 3D printing technology for producing complex geometries with quick turnaround. 3D-printed products in aerospace are prized for their low production volumes, superior quality, lightweight nature, and high-temperature resistance. One advantage of 3D printing of composite materials is its ability to create lightweight structures using topology optimization, which is often used in the aerospace industry.^{126–128} Another advantage of 3D

printing is the ability to create multimaterial multifunctional structures.^{129–131} Continuous fibers are incorporated into composites to create lightweight structures with remarkable strength-to-weight ratios, which makes them appropriate for use in the automotive and aerospace industries. NASA produced more than 20 pure PLA samples on board the ISS in 2014, marking the first in-space 3D printing milestone. Building on this, scientists from China's Academy of Space Technology conducted the country's first in-space 3D printing experiment in 2020 using PLA composites reinforced with continuous carbon fiber. Under SpiderFab design (by NASA), a space robot used continuous carbon fiber-reinforced PEEK composites to build a massive helical structure (Fig. 8(b)). Using 3D-printed continuous fiber-reinforced composites (CFRCs), the CMASLab at ETH Zurich created a morphing drone that could only be controlled by morphing surfaces in terms of pitch, yaw, and roll. The 3D-printed CFRCs used in aerospace applications are designed to endure harsh conditions such as high vacuum, sharp temperature changes, and prolonged radiation exposure.¹³²

5.4 Architecture and construction

Renewable resource-based materials that naturally break down over time, such as PLA and PHA, substantially mitigate their long-term environmental effect and minimize harm from building. Complex, personalized structural elements, architectural components, and decorative embellishments can be fabricated with little waste generation by using 3D printing technology. In line with the industry's emphasis on sustainable building practices, this AM technology has the potential to improve construction efficiency, lower carbon footprints, and reduce material waste. The remarkable structural stability of PLA-reinforced concrete has been shown by research, underscoring its potential for use in environmentally friendly building applications.¹³³ When comparing PLA-reinforced concrete to plain concrete samples, a noteworthy increase in tensile and flexural strength was observed, reaching 2.7 Mpa and 10.8 MPa respectively. Also, water absorption was reduced around 4% when compared to the normal concrete sample. This newly developed PLA-reinforced concrete demonstrated great mechanical performance and improved moisture resistance relative to both sisal fibre-reinforced concrete and traditional concrete used as a reference. Some of the other instances where 3D printed ecofriendly materials were used include Gaia House (Italy) which uses a 3D printed mixture of earth, straw and rice husk for sustainability and insulated walls.¹³⁴ Another example is The Ashen Cabin (New York), designed by Hannah; this cabin uses locally sourced ash wood and 3D-printed biodegradable bioplastics, demonstrating the viability of sustainable materials in small-scale construction.

Although 3D printed biodegradable polymers have great potential, there are still challenges related to cost, meeting regulatory standards, and ensuring the long-term strength of printed parts. To increase the viability of biodegradable polymers for building, researchers and industry experts are striving to enhance these materials and procedures. It is anticipated



that 3D printed biodegradable polymers will play a bigger role in creating distinctive and sustainable structures when these problems are resolved and technology advances.¹³⁵

6. Challenges and limitations

While additive manufacturing (AM) offers numerous advantages, including material efficiency, design flexibility, and reduced production waste, it still faces several challenges that hinder its widespread adoption as a truly sustainable technology. Despite its potential, AM is not inherently eco-friendly, as it relies on energy-intensive processes, non-recyclable materials, and costly sustainable alternatives.^{136,137} Additionally, industries adopting AM must navigate economic, regulatory, and material constraints. Addressing these limitations requires advancements in materials science, energy efficiency, and policy frameworks. The key challenges can be categorized into four main areas: environmental concerns, economic viability, industry-specific constraints, and material diversity (Fig. 9).

6.1 Environmental concerns

Additive manufacturing (AM), commonly known as 3D printing, has transitioned from a tool to prototype products to production technology across industries such as aerospace, healthcare, automotive, and consumer goods. As its applications expand, sustainability has become critical. Initially, AM prioritized efficiency and customization, often overlooking environmental concerns. However, increasing ecological awareness has highlighted the necessity of integrating sustainable practices.¹³⁸ Although 3D printing generates less waste than subtractive manufacturing, managing post-printing plastic waste and enhancing material circularity remain a challenge.¹³⁹ Initially, the advancement of 3D printing progressed without considering environmental impacts. Many materials, including plastics and metals, originate from non-renewable sources and have

limited recyclability. Large-scale AM operations have high costs, slow printing speed, weak strength, and limited part sizes¹⁴⁰ and require a lot of energy, resulting in considerable carbon emissions.^{141–143} Despite its advantages, AM is not truly sustainable. A key challenge is the dependency on non-recyclable materials, which leads to waste accumulation. Additionally, the energy-intensive nature of certain AM methods increases electricity consumption and emissions. In some cases, AM's energy demands may exceed those of traditional manufacturing, diminishing its environmental benefits.^{140,144,145}

6.2 Economic challenges

Economic and technological constraints cause hindrances in increasing sustainable AM. The development of recycled, biodegradable, and renewable materials remains costly, limiting widespread implementation. Moreover, energy-efficient AM technologies are still evolving and are not viable yet. A lack of standardized regulations for sustainability complicates efforts to transition towards environmentally responsible AM practices. Without clear guidelines on material selection, energy efficiency, and waste management, industries struggle to adopt sustainable approaches.^{141–143,146} Recent advancements in AM materials offer potential solutions. Researchers are developing biodegradable plastics, recyclable metals, and renewable composites to reduce reliance on fossil fuels. Integrating these alternatives into AM processes could significantly enhance sustainability.²⁷

Sustainable AM also increases economic benefits. As consumer demand for environmentally friendly products increases, companies that implement green practices gain an upper hand. Businesses investing in sustainable AM can attract ecological customers and strengthen market positioning. Additionally, government incentives, including tax benefits and subsidies, encourage the usage of sustainable AM technologies, making environmentally responsible production more financially viable.

6.3 Industry-specific challenges and adaptations

Various industries have integrated sustainable AM initiatives. The automotive sector employs recycled materials for non-essential components, reducing production costs and environmental impact. Additionally, AM facilitates the development of lightweight vehicle components, improving fuel efficiency and lowering emissions. In construction, AM is utilized to fabricate structures using recyclable and biodegradable materials, contributing to sustainable building practices.¹³²

The healthcare sector also benefits from sustainable AM innovations. The production of biodegradable medical implants and eco-friendly prosthetics reduces medical waste while enhancing patient-specific treatment solutions.¹⁴⁷ Furthermore, research in biomaterials has led to the development of biodegradable components that naturally degrade over time, eliminating the need for surgical removal and minimizing environmental harm. Similarly, the consumer goods and electronics industries have adopted biodegradable packaging and

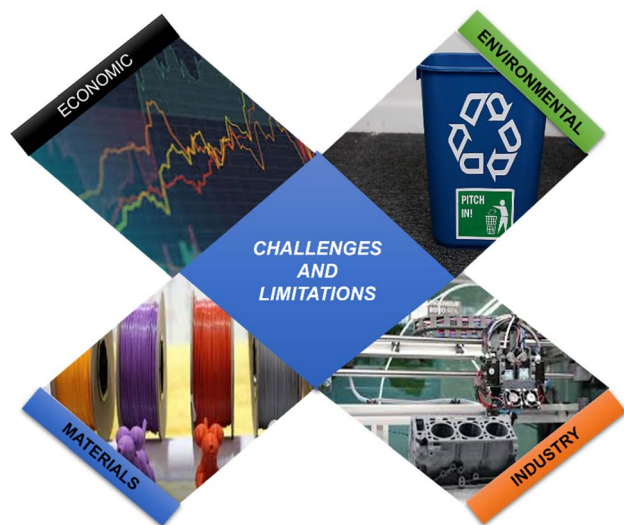


Fig. 9 Challenges and limitations in 3D printing of ecofriendly materials.



recycled materials to reduce electronic waste and promote sustainability.^{148–154}

The shift toward sustainability in AM is imperative. With growing environmental concerns and increasingly stringent regulations, the AM industry must address challenges such as excessive material consumption, high energy usage, and the absence of standardized sustainability frameworks. However, ongoing advancements in biodegradable materials, energy-efficient processes, and waste reduction strategies offer promising solutions. Industries such as automotive, construction, healthcare, and consumer goods are at the forefront of sustainable AM adoption, setting a precedent for broader implementation.

6.4 Material diversity and availability

Despite advancements in AM, material diversity remains a significant limitation. The range of eco-friendly AM materials is still limited compared to traditional manufacturing.¹⁴⁰ Many sustainable alternatives, such as biodegradable polymers and recyclable metals, lack the mechanical strength and durability required for industrial applications. Additionally, integrating renewable feedstock into AM processes poses technical challenges related to printability, consistency, and performance, expanding the portfolio of sustainable AM materials while ensuring that their functional viability is essential for broader adoption. Research in biomaterials, nanocomposites, and bio-based polymers offers promising solutions, but further innovation is needed to develop materials that balance sustainability with mechanical performance.¹³²

7. Conclusion and future scope

This review highlights the important role that eco-friendly materials play in advancing sustainable manufacturing practices in 3D printing. By leveraging materials derived from renewable resources, industries can mitigate the environmental impact associated with conventional plastics. Materials such as PLA, PHA, and PBS and their blends/composites not only reduce waste but also meet the structural and functional demands of various applications. The incorporation of natural fibers and bio-based fillers further enhances the performance of these eco-friendly materials, making them viable alternatives for high-stress applications. Although challenges remain, particularly in balancing biodegradability with mechanical strength, the ongoing development of bio-composites and hybrid materials holds promising potential to minimize these limitations.

Future research should emphasize on optimizing the properties of biodegradable polymers to expand their usability in demanding applications. Developing novel biopolymer blends and composites with improved mechanical and other properties will be essential for their broader adoption. Additionally, integrating machine learning and data-driven approaches to predict material performance and streamline the selection of sustainable 3D printing materials could accelerate progress in this field. Furthermore, in order to measure the environmental

impact of eco-friendly materials and aid in the shift to a circular economy in manufacturing, lifetime assessments of these materials and their uses in additive manufacturing will be crucial.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Kavya Agrawal: conceptualization, visualization, and writing. Asrar Rafiq Bhat: supervision, review, writing and editing.

Conflicts of interest

There is no conflict of interest.

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