



Exploring the advantages and applications of nanocomposites produced via vat photopolymerization in additive manufacturing: A review

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Received: 10 April 2023 / Revised: 21 November 2023 / Accepted: 3 December 2023 / Published online: 20 December 2023
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Abstract

Additive manufacturing (AM) also known as 3D printing (3DP) has become a popular technology with a wide range of applications, from which vat photopolymerization is a technique for producing nanocomposites with controlled mechanical, thermal, and electrical properties. This technology uses a UV light laser to cure a liquid resin into a solid object, layer by layer, allowing complex three-dimensional (3D) objects with intricate details of manufacturing and excellent finishing. Nanocomposites produced by vat photopolymerization have been used in aerospace, automotive, and medical industries, due to their superior mechanical strength and dimensional accuracy. In this article, we will discuss the advantages and other aspects of nanocomposites made with vat photopolymerization, exploring potential applications, and discuss the research by different areas, such as their AM technologies and materials properties.

Keywords Nanocomposite · 3D printing · Additive manufacture (AM) · Stereolithography (SLA) · Digital light processing (DLP)

1 Introduction

Nanocomposite materials belong to a category of composite materials in which at least one component has dimensions below 100 nm. These materials can be superior in their mechanical, electrical, and thermal properties with respect to their micro or macro materials, due to the unique properties at the nanoscale, such as high surface area and almost perfect crystal order. Some common types of nanocomposite materials include polymer matrix, metal matrix, and ceramic matrix nanocomposites [1], which are being researched for a wide range of applications, including electronics, aerospace, biomedical, and energy storage.

Nanomaterials display very distinct surface effects compared to micro and bulk materials, primarily due for three reasons: (a) dispersed nanomaterials possess a significantly larger surface area and a higher particle count per unit mass, (b) the proportion of surface atoms in nanomaterials is greater, and (c) surface atoms in nanomaterials have fewer immediate neighbors. These differences lead to enhance chemical and physical properties useful for multiple applications [2]. Some of the key properties of nanomaterials include high surface area: due to their small size, nanomaterials have a large surface area relative to their volume, which can lead to increased reactivity and improved catalytic activity. Increased strength and stiffness: due to their small size and the ability of atoms to bond more closely, the strength and stiffness of nanomaterials can be significantly higher than those of bulk materials. Improved electrical and thermal conductivity: the electrical and thermal conductivity of nanomaterials can be much higher than those of bulk materials due to the increased surface area and the ability of electrons to move more freely at the nanoscale. Enhanced optical properties: the optical properties of nanomaterials, such as absorption, reflection, and transmission, can be significantly different from those of bulk materials due to the quantum confinement of electrons and photons at the nanoscale. Increased reactivity: the increased surface

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area of nanomaterials can lead to increased reactivity with other materials, which can be useful in applications such as catalysis and sensing. Increased chemical reactivity: due to the high surface area and high surface energy, the chemical reactivity of nanoparticles can be much higher than that of bulk materials. Of course, that all these properties can be highly dependent on the specific material, size, shape, and surface chemistry.

In general, nanocomposites contain nanostructures such as those summarized in Fig. 1: nanowires, nanoparticles, graphene, nanoplatelets, carbon nanotubes, and nanofilms. Nowadays, there is a wide range of research in nanocomposites, in fields such as, drug delivery [3, 4], tissue engineering [5, 6], and biosensing applications [7, 8]. In energy storage, there are nanocomposites developed for use in batteries [9, 10], supercapacitors [11, 12], and fuel cells to improve energy storage capacity and performance [11, 13, 14]. In electronics, there are nanocomposites explored for use in electronic devices such as transistors [15, 16], solar cells [17, 18], and sensors to improve their performance and reduce their cost [19, 20]. In environmental, there are nanocomposites for water filtration [21, 22], air purification [23, 24], and waste treatment [25, 26]. In aerospace, there are lightweight nanocomposites [27, 28] and high-strength materials for aircraft and spacecraft [29, 30]. In automotive industry, there are lightweight nanocomposites [31, 32], high-strength materials [31, 33], and other developments aiming improved fuel efficiency [34, 35]. For textiles, there are nanocomposites with improved flame-resistance [36], anti-bacterial, and UV-protection characteristics [37, 38]. In packaging, there are nanocomposites working as barrier films to improve the shelf life of food products [39, 40].

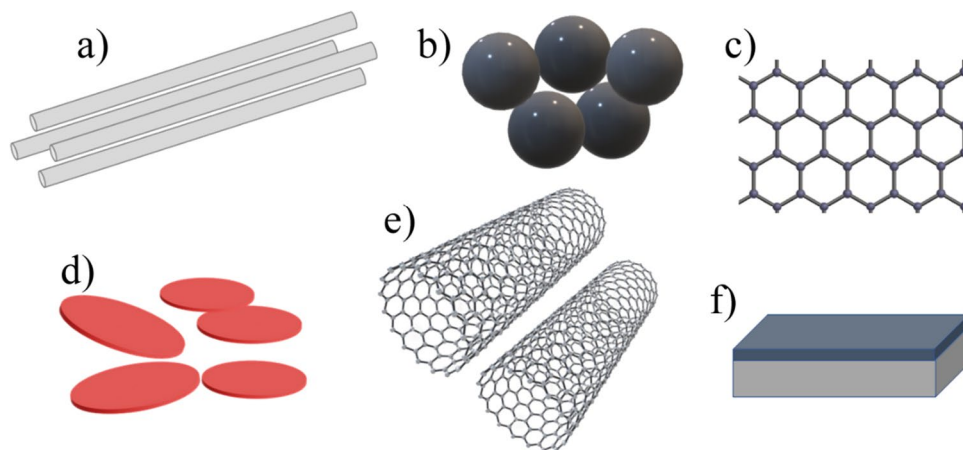
Recent research has extensively covered various facets of advanced nanocomposite materials and technologies. Xie et al. [41] introduced a carbon-based “meta-composite” to overcome limitations in unit size for metamaterials, showcasing tunable electromagnetic properties. Li et al. [42] concentrated on synthesizing high-performance cobalt nickel

bimetallic oxides to enhance electromagnetic wave absorption. Li et al. [43] introduced a hydrogel with capabilities for self-powered devices, with potential applications in wearable electronics. Wang et al. [44] conducted a comprehensive review of metal-organic frameworks and their magnetic composites for contaminant adsorption. Ruan et al. [45] delved into the role of microstructure design in optimizing electromagnetic interference shielding for biomass-derived carbon materials. Lin et al. [46] provided a summary of fabrication methods and recent progress in MXene/LDH composites for supercapacitors. Kang et al. [47] proposed a biochar-enhanced photocatalytic method for antibiotic treatment in aqueous ecosystems. Chen et al. [48] investigated the effects of hydrophobic nano-silica and a β -nucleating agent on the crystallization and mechanical behaviors of polypropylene. de Macedo et al. [49] discussed kaolinite clay intercalation techniques for polymer nanocomposites, and Wu et al. [50] reviewed metal nanoparticle composites for non-enzymatic glucose detection. Lastly, Naik et al. [51, 52] emphasized the significance of composites in sectors like aerospace, automobile, and defense, underlining the importance of green technology for environmental sustainability.

Additive manufacturing (AM) is a set of fabrication technologies by which a 3D digital model is transformed into a real object by adding layer over layer in a computer-controlled process, and it is opposed to subtractive technologies such as traditional milling processes. AM also belongs to the so-called Industry 4.0. Also known as 3D printing, AM has the potential to disrupt traditional manufacturing methods by offering several advantages over them, such as injection molding, casting, and machining. Some remarkable benefits of this technology are as follows:

1. Customization: AM allows for the rapid and cost-effective production of customized parts and products, which can be difficult or impossible to achieve with traditional manufacturing methods [53, 54].

Fig. 1 Nanomaterials typical shape configuration, **a** nanowires, **b** nanoparticles, **c** graphene, **d** nanoplatelets, **e** carbon nanotubes, **f** nanofilm



2. Speed: AM can produce parts and products quickly, which can be beneficial in applications where time-to-market is critical [55].
3. Complex geometries: AM can create parts with complex geometries and internal structures that are difficult or impossible to produce with traditional manufacturing methods, enabling products with unique properties [56].
4. Material flexibility: AM allows the use of a wide range of materials, including but not limited to metals, plastics, ceramics, and composites, which can be a limitation with traditional manufacturing methods [57].
5. Reduced waste: AM can reduce material waste by only using the exact amount of material needed to produce a part or product, as opposed to traditional manufacturing methods which may require excess material to be removed [58, 59].
6. Reduced tooling costs: AM eliminates the need for costly tooling and molds, which are required in traditional manufacturing methods such as injection molding or CNC milling [60].
7. Faster changes: AM technologies can provide quicker adjustments in the final product as shown in the critical time of pandemic COVID 19, showing a high technology adaptability [48].

However, it's important to note that the displacement of traditional manufacturing methods by AM depends on the application and the specific product. For example, traditional manufacturing methods are still more cost-effective and efficient for the mass production of simple parts, while AM is still more suitable for low-volume, complex, and customized products.

AM enabled the democratization of production by making the manufacture of certain objects accessible to companies or individuals because limited access to manufacturing technologies or high production costs. On the other hand, the AM allowed the possibility of personalization ("customization") of the product, since it allows adaptation to the needs of each user, sufficiently competitive in terms of quality and price [61]. Likewise, AM has led to the increasing decentralization of production, in which large manufacturing centers seek to reduce transportation costs and maximize scale economies. It is noteworthy that the advantages of AM on demand can be exploited not only by the final consumer but also by other actors within the supply chain, being particularly useful for users who can design their own solutions [62].

The restricted selection of available materials has been one of the main obstacles to the industrial use of 3D printing resins. Initially, the materials available were acrylate oligomer-based resins, usually with low molecular weight, which were noted for their extreme brittleness and poor mechanical and thermal characteristics [63].

However, with the introduction of new technical resins with improved qualities created in recent years, this has significantly changed, and this technology is now in the limelight in numerous industries. The development of new resin-based 3D printing, have lowered prices and speed up the printing process, providing a competitive option that may even outperform existing AM processes in some production sectors. There are currently multiple options for high-quality light-curing resins on the market, compatible with both stereolithography (SLA) and digital light processing (DLP). They stand out for combining little residue, little thermal expansion, and sufficient precision [64].

In both commercial and residential environments, 3D printing photocurable resin has been gaining ground to overtake fused deposition modeling (FDM) technology as the most common 3D printing method. This boom is the result of two significant elements: on one hand, 3D printing resin has become cheaper thanks to the development of new technologies, placing them in the same price range as FDM printers. On the other hand, new materials such as dental, flexible, or engineering resins have emerged, making possible to create resin components that were previously only feasible using FDM or selective laser sintering (SLS).

The main advantage of 3D printing with resins is the resolution, which is usually 0.05 to 0.1 mm, while the resolution of FDM printing is usually 0.3 to 0.5 mm [65]. This makes resin printing with very good esthetic quality in comparison to other AM technologies, with very good surface finishing and degree of detail.

Additionally, in recent years, nanomaterials have attracted great interest, since extraordinary optical, magnetic, electrical, and mechanical properties improved at this scale [66]. These emerging properties enable these materials to have potential applications in various fields such as electronics, medicine, biology, and energy production. In addition, nanomaterials can be classified according to the dimension of the structural elements that compose them: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures. Nanomaterials include 0D quantum dots, 1D nanowires and nanofibers, 2D nanoplatelets, and 3D nanospheres, among others [67]. However, nanomaterials tend to agglomerate, which limits the use of their intrinsic properties and, consequently, their performance in final applications. Nevertheless, many studies and strategies have recently been carried out to obtain increasingly efficient and affordable materials [68]. An alternative that has been developed to take more efficient advantage of the excellent properties is by assembling them in 3D structures until obtaining macroscopic structures in the form of hydrogels, foams, sponges, aerogels, and nonwoven fabrics [69]. For this, various strategies have been implemented, such as the self-assembly method, electrospinning, emulsion, 3D printing, and spray drying [70].

Similarly, current technological development points to a trend towards progressive miniaturization, and AM techniques are proving to be a very effective tool for working at micro and nanoscale dimensions in crucial fields like artificial organs, microfluidics, microelectronic devices, scaffolds for tissue engineering, or devices for the controlled drug release [71, 72]. In recent years, the demand for increasingly smaller devices has been growing exponentially, for applications involving micro engines and micromachines, medical micro inserts, and techniques for minimally invasive surgery [73].

3D printing is proving to be a very effective tool for the development of these technological advances, considering the trend towards progressive miniaturization. This technology enables fabrication at scales below the micro and nano dimensions [74]. Similarly, the development of new materials with extremely precise characteristics and properties will be possible thanks to these new technologies, such as advanced textiles that allow the implementation of UV filters, antibacterial and/or repellent properties, and biodegradable garments [75].

The present topic highlights the feasibility of exploring various active areas in nanocomposite research. These areas encompass a broad spectrum of studies, including investigations into the influence of hydrophobic nano-silica agents on the crystallization and mechanical properties of polypropylene random copolymers [48]; the development of electrostatic self-assembly strategies for combining cellulose nanofibers, MXene, and nickel chains to create highly stable and efficient systems for seawater evaporation [76]; the utilization of metal-organic frameworks and their magnetic composites for pollutant removal [44]; the exploration of polymer nanocomposites for non-enzymatic glucose detection [50]; and the advancement of high-performance conducting nanocomposites featuring polyaniline with enhanced antimicrobial properties, specifically designed for biomedical applications [77]. Additionally, the research extends to bioinspired materials and processes [78], innovations in cements and ceramics fabrication utilizing additive manufacturing techniques [79–82], the investigation of circular materials [83, 84], and materials under hard conditions of high loading and high temperatures [85, 86].

Based on the above, this review aims to present recent advances in the development and use of novel composite materials based on the incorporation of nanoparticulate materials in photocurable 3D printing resins.

2 Specific objectives of the review

The review of nanocomposites synthesized through vat polymerization comprises several noteworthy papers. For instance, Andjela et al. [87] have delved into the utilization

of vat photopolymerization within the realm of dentistry. In a similar vein, Al Rashid et al. [88] conducted an analysis focusing on the challenges and prospects inherent to vat polymerization techniques, shedding light on issues and gaps pertaining to polymeric composite materials and the vat polymerization process. Medellin et al. [89], on the other hand, offered insights into the influence of reinforcing materials on nanocomposite properties, also covering various preprocessing and post-processing methods. Furthermore, Taormina et al. [90] provided a comprehensive survey of the approaches employed for manufacturing components via vat photopolymerization (VP) processes. They also provided an extensive overview of additive manufacturing technologies and the diverse polymer-related technologies available.

This article provides an updated review of the advantages of nanocomposites produced by VAT photopolymerization, analyzing their potential applications, research in various fields, and the properties of the materials obtained with this technique.

The specific objectives of this review are the following:

- Summarizing recent advances and research on diverse types of nanofiller materials, their characteristics, and applications
- Supplying comprehensive information on trends in developing new materials and their improved characteristics through incorporating nanomaterials
- Revealing recent advances in the development of polymerization processes

This document would provide a better understanding of the perspectives and trends on the application of nanomaterials in the development of new composite materials using AM techniques based on photocurable resins. In addition, provide original and creative suggestions based on recent findings that can be used in future research projects. This article will also serve as a reference point for experienced researchers to envision new possibilities for the creation and use of novel materials, allowing them to suggest future lines of research.

3 Review methodology

3.1 Sources of information and techniques of searching

The review was conducted following the guidelines and framework presented by Moher et al. [91] known as Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA). PRISMA is a well-accepted standard that aims to improve the reporting and quality of systematic reviews. The review followed the PRISMA approach, which

included conducting literature searches, selecting relevant articles, and extracting data. The PRISMA declaration website provides standard flowcharts and additional resources for conducting comprehensive reviews [92].

3.2 Keyword-based search

From this preliminary search, it could be established that the potential use of nanoparticles in composite applications manufactured by AM methods is a growing topic of interest in the scientific community. First-level databases (such as ScienceDirect or Scopus) compile a variety of studies about new materials and their applications; however, issues such as the associated health and environmental risks are little investigated.

All scientific data included in this study were collected using the PRISMA method. First, a literature search was performed using the combined results from the ScienceDirect database. Additional results were retrieved using the Scopus database. Only articles in which the title, abstract and full paper were published in English were considered for this review. The keywords of the searches were “(vat photopolymerization) OR photopolymerization) AND nanocomposite.” The search was limited to only for research publications, leaving out review articles and book chapters. Relevant literature related to the keywords served as the basis for this search. The chosen keyword combinations, such as “printing” OR “(SLA OR stereolithography)” OR “DLP” formed the basis of the search approach. These search terms were selected to look for more accurate data and information on the procedures for creating materials using nanocomposites and their most current uses. Figure 2 shows the results of an initial query conducted to determine the annual publication count in the ScienceDirect (SD) database related to the subject of this review. The figure also illustrates the increasing interest and research activity in this field of study.

However, only studies published after 2012 were considered for this review, with a focus on those from the previous

five years because the authors felt that they were the most pertinent for the current study.

3.3 Article selection process

The second phase consisted of categorizing the published articles and eliminating irrelevant data. The results were analyzed by examining titles, abstracts, and full articles. The scope of the study was expanded to include only relevant publications and data published between 2012 and 2022 were collated. Figure 3 shows the flow of information in the distinct phases of this systematic review.

3.3.1 Review process

In the last review phase, the content of each published article was evaluated, and useful information was extracted from them.

4 Vat photopolymerization (VPP)

Photopolymerization is a photochemical process that involves linking small monomers to form a chainlike polymer with the aid of a catalyst. Adequate crosslinking of the polymers is necessary to prevent the polymerized molecules from dissolving back into the liquid monomers [93]. In the realm of 3D printing, photopolymerization offers a wide range of possibilities as it enables the solidification of liquid resin through radiation. This process utilizes photosensitive polymer resins that are selectively cured layer by layer using either a laser or digital light projection source [94].

VPP stands out as a highly favored 3D printing method among the different types of AM technologies. It has garnered significant interest from a wide range of industries and fields. VPP involves the use of light to solidify or cure photocurable resin, also known as photoresist, in the process of creating three-dimensional objects [95]. The most popular methods for resin AM in terms of printing techniques are stereolithography (SLA), digital light processing (DLP), and

Fig. 2 Research articles published per year in the SD database about this review

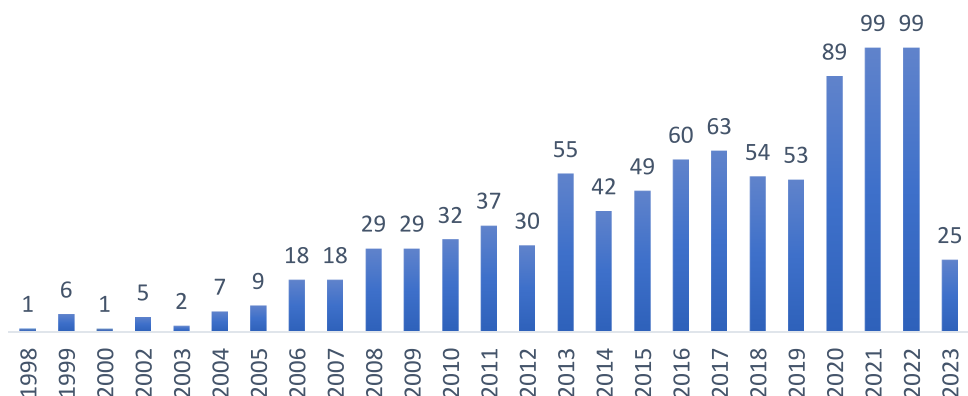
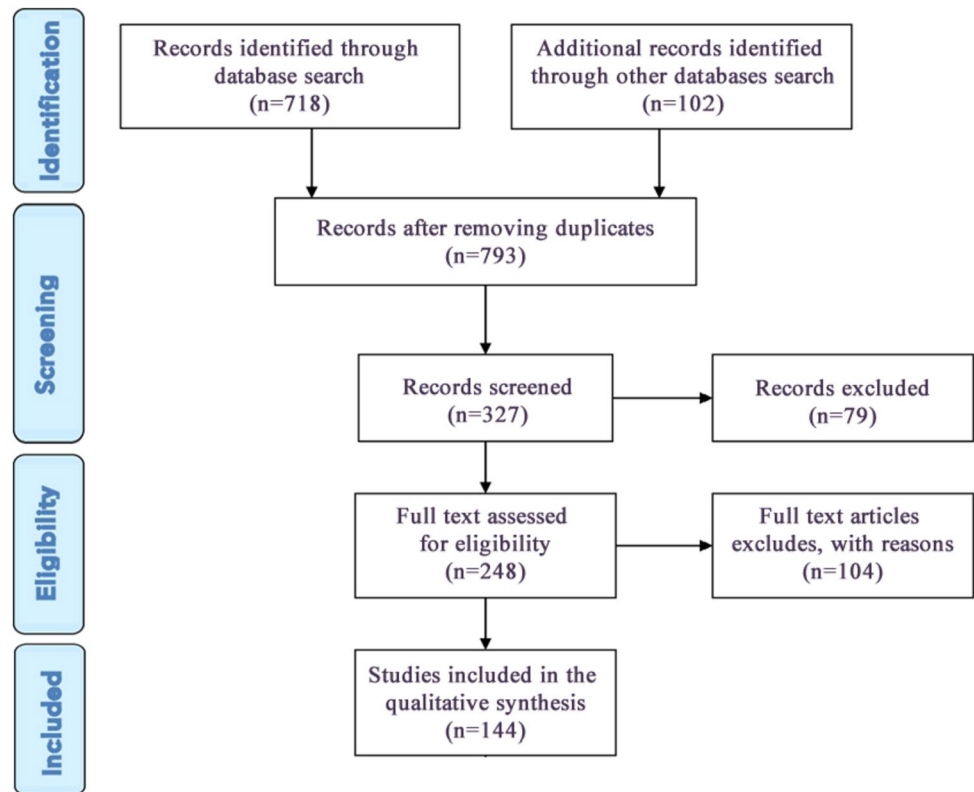


Fig. 3 Flow of information through the different phases of this systematic review



liquid crystal display-light emitting diode (LED-LCD), due to their ability to produce high-precision, isotropic, and airtight components and prototypes using a variety of sophisticated materials that enable the fabrication of fine details and a smooth surface finish [96].

Previously, these technologies were complex and expensive, but today, desktop and small-format SLA and DLP 3D printers produce industrial-quality parts at an affordable price and with unparalleled versatility, thanks to a wide variety of options of materials [97].

To produce very thin with these two methods, solid layers of plastic that overlap to form solid objects are based on the selective exposure of liquid resin to a light source (a laser in the case of SLA and a projector in the case of DLP). Despite having a very similar concept, these two methods can lead to completely different results [98].

4.1 Stereolithography (SLA)

SLA is a 3D printing technique that uses a laser to convert liquid resin into solid parts. Because it allows precise control of the dispersion of nanoparticles within a polymer matrix, it has become increasingly popular in the field of nanocomposites. As a result, the materials exhibit improved qualities, such as increased strength and toughness. SLA can also be used to create complex geometries and structures that are difficult to fabricate

using conventional production processes. This makes it a method with great potential for creating sophisticated nanocomposites for various applications. In general, SLA has a UV laser light positioned with mirror galvanometers for scanning and producing the photopolymerization in a plane (see Fig. 4a). Some of the industries that find SLA particularly relevant and valuable include:

- Aerospace and defense: SLA is used for rapid prototyping, creating intricate components, and producing functional parts for aircraft and defense applications [99, 100].
- Automotive: SLA enables the production of high-precision prototypes, concept models, and customized parts for automotive design, testing, and manufacturing [101, 102].
- Medical and healthcare: SLA is utilized for creating surgical guides, patient-specific models, dental appliances, prosthetics, and other medical devices with intricate geometries and high accuracy [103, 104].
- Consumer products: SLA is employed in the development of consumer goods such as electronics, household appliances, toys, and fashion accessories, enabling rapid prototyping and customization [105, 106].
- Industrial manufacturing: SLA finds applications in various industrial manufacturing processes, including creating molds, tooling, jigs, and fixtures with complex geometries and high precision [107, 108].

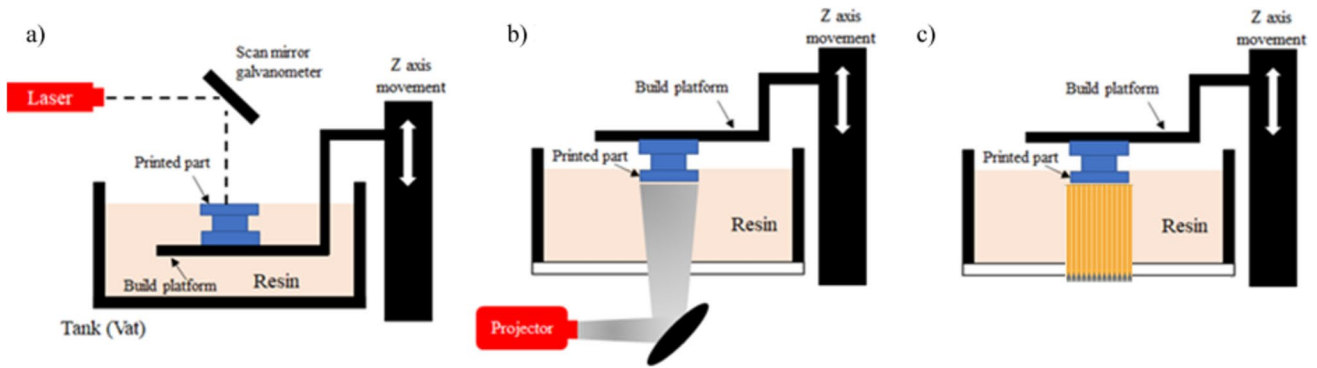


Fig. 4 Widespread light-curing technologies, a SLA, b DLP, c LED-LCD

- Engineering and architecture: SLA is used in the fields of engineering and architecture for creating detailed architectural models, prototypes, and scaled-down replicas [109, 110].
- Education and research: SLA is employed in educational institutions and research laboratories for teaching, research projects, and exploring new applications of additive manufacturing [111, 112].

4.2 Digital light processing (DLP)

DLP is a popular technique for creating parts with high resolution and fine details. DLP technology uses a digital light projector to cure liquid resin layer by layer, creating a solid object. The resolution of the final part is determined by the resolution of the projector, which can be as high as 25 microns, creating of parts with very fine features. DLP is particularly useful for creating small, precise parts such as dental models, jewelry, and figurines. In addition, DLP is faster than some other 3D printing technologies such as FDM, which is an advantage for high-volume production of small parts. Figure 4b shows a projector illuminating a wide area, which enables faster printing speeds.

4.3 Liquid crystal display-light emitting diode (LED-LCD)

LED-LCD technology emerged as an advancement over DLP technology and has largely supplanted it in contemporary times. The functionality of LED-LCD technology is like DLP, but instead of utilizing a digital micromirror device (DMD) to reflect light, it employs an LCD device where each pixel acts as a miniature window, controlling the passage or blocking of light. Refer to Fig. 4c for a visual representation.

One of the main advantages of LED-LCD technology is its high printing speed and low cost. Furthermore,

it surpasses DLP technology in two fundamental aspects. First, as mentioned earlier, the perpendicular projection avoids distortions that can occur due to the oblique projection provided by lenses used in DLP systems. Second, LCD devices not only block or allow light to pass through but can also filter it, independently varying the light intensity in each pixel. This enables the use of anti-aliasing processes that reduce the stair-step effect and achieve surface qualities very close to those obtained through SLA.

However, LED-LCD technology also has some drawbacks. One of the main concerns is the high heat generated by the LED matrices used, which necessitates the implementation of effective cooling systems to prevent resin overheating during long printing sessions.

SLA and DLP are the most widely used resin 3D printing technologies. This is in part because resin 3D printers are currently a popular option that allows producing high-precision, isotropic, and hermetic parts, and prototypes with a portfolio of advanced materials for fine detail and smooth surface finish, as well as desktop and small-format SLA and DLP 3D printers that produce industrial quality parts at an affordable price.

5 Examples of nanocomposites

5.1 Nanofillers materials used in nanocomposites

Nanofillers, with particle sizes ranging from 1 to 100 nm, have garnered significant interest in the field of polymer composites. They offer unique properties and functionalities that can enhance the performance of polymer matrices. New nanofillers, including nanoclays and needle-shaped nanowhiskers, have emerged and are commercially available [113].

VPP can be greatly enhanced by the inclusion of nanofillers in the photocurable resin. Nanofillers bring numerous benefits to VPP, improving the mechanical strength, thermal stability, and dimensional accuracy of printed objects.

Nanoparticles like nanoclays or nanosilica reinforce the resin matrix, resulting in higher tensile strength and reduced shrinkage. They also contribute to a better surface finish and reduced warping, enhancing the overall quality of the printed objects. Additionally, nanofillers can introduce additional functionalities such as electrical conductivity or unique optical properties, further expanding the range of applications for VPP technology. Achieving optimal performance requires proper dispersion and compatibility of the nanofillers, which can be achieved through surface modification techniques. By integrating nanofillers, VPP offers exciting possibilities to produce advanced 3D printed objects with enhanced properties, opening up new opportunities in various industries.

Classifying nanoparticles based on their number of dimensions is a helpful approach, which extends the concept of aspect ratio. Nanofillers can be categorized into three groups according to their dimensions: one-dimensional (1D), two-dimensional (2D), and three-dimensional (3d) nanofillers [114]. 1D nanofillers, such as montmorillonite clay and nanographene platelets, possess shape-dependent characteristics and find applications in microelectronics, biosensors, sensors, and coatings [115]. 2D nanofillers, including carbon nanotubes and graphene, offer excellent mechanical properties, flame retardancy, and reinforcement capabilities [116]. They are utilized in energy, sensors, electronics, and optoelectronics. 3D nanofillers, such as nanosilica and nanotitanium oxide, possess specific properties that make them valuable in various applications, including coatings, separation and purification, and biomedicine [115].

Hybrid polymer nanocomposites combine nanofillers from different sources to further enhance the properties of polymer matrices. Carbon-based nanofillers, such as graphene and carbon nanotubes, are commonly used in these composite designs. Hybrid nanocomposites with multiple carbon-based fillers exhibit improved tribological properties, load-bearing capacity, wear resistance, and interfacial bonding strength. Adequate loading of nanofillers is crucial to minimize agglomeration and phase separation, ensuring longer wear life cycles [117].

Electrospun nanofibers, produced through the electrospinning method, offer advantages such as continuity, controlled diameter/structure, and mass production capability. These nanofibers are emerging as reinforcing fillers

in polymer matrix composites. Their performance strongly depends on the interphase strength, which is an important area of development and study [118].

Nanofillers play two crucial roles in polymer blends. First, they improve various properties such as mechanical strength, barrier properties, thermal stability, flame retardancy, and electrical conductivity. Second, they modify the miscibility and morphology of polymer blends. The effectiveness of nanoparticles in altering the blend's properties depends on their localization, interactions with polymer components, and dispersion within the blend [118]. Some of the properties that can be improved with nanofillers are shown in Table 1. It should be noted that, when creating nanocomposites for specific applications, the integration of nanoparticles can also alter other characteristics of the final materials, such as their thermal and electrical properties.

5.1.1 Graphene-based nanocomposites

Graphene is a two-dimensional material with exceptional electrical conductivity and mechanical strength and has been incorporated into various polymer matrices to create graphene-based nanocomposites. These nanocomposites have improved electrical conductivity [9], mechanical properties [129], thermal stability [130], and barrier properties [131].

5.1.2 Carbon nanotube-based nanocomposites

Carbon nanotubes (CNTs) have also been used to create nanocomposites with improved mechanical properties, electrical conductivity, and thermal stability. CNTs can also contribute with improved barrier properties [132] and enhanced electrical conductivity [133, 134].

5.1.3 Metal nanoparticle-based nanocomposites

Metal nanoparticles such as gold, silver, and copper are being used to create nanocomposites with improved electrical conductivity, mechanical properties, and thermal stability [135–138]. Also, some of the most used nanofillers according to recent literature and their study topics identified in this review are shown in Table 2.

The use of polymeric nanomaterials also raises certain questions regarding the potential health and environmental

Table 1 Nanofillers and enhanced properties when incorporated into a polymer matrix

Nanofillers	Enhanced properties	References
Graphene fibers	Improved strength, stiffness, and toughness	[119, 120]
Carbon nanotubes	Carbon nanotubes, stiffness, and toughness	[121, 122]
Clay nanoparticles	Improved mechanical behavior	[123, 124]
Silica nanoparticles	Improve the stiffness and toughness	[125, 126]
Metal powders	Improve mechanical and optical properties	[127, 128]

Table 2 Nanofillers used in nanocomposites

Material	Technique	Study	Ref.
ZnO	DLP	Influence of UV irradiation	[139]
ZrO ₂	SLA	Viscosity characterization	[140]
		Translucent and biocompatible resin	[141]
		Rheological properties	[142]
		Performance of epoxy composites	[143]
TiO ₂	UV-DIW		
Silver	SLA	Enhance the thermal conductivity	[144]
		Thermal–mechanical properties	[145]
		Electrically conductive resin	[146]
Silica	SLA	Reinforcing and toughening	[147]
		Material viscosity	[148]
Silica	DLP	Printing adaptability	[149]
		Temperature sensing	[150]
Magnetic particles	DLP	fabrication of polymeric composites with embedded magnetic particles	[151]
		Controlled production	[152]
		Control of magnetic microstructure	[153]
		Fabrication of functionally graded materials	[154]
Magnetic particles	SLA	Fabrication of porous composite scaffold	[155]
Hydroxyapatite	DLP	Bone reconstruction	[156, 157]
Hydroxyapatite	SLA	Exfoliation and dispersion in a vinyl monomer	[158]
		Viscoelastic and strain rate response	[159]
Graphene	DLP	Friction and wear characteristics	[160]
		Controlled production of aligned polymer	[152]
		Nano-reinforcement polymeric matrix	[161]
		Reinforced medical-grade resin	[162]
Cellulose	SLA	Mechanical reinforcement and thermal stabilization	[163]
		Development of natural-based composite	[164]
Cellulose	DLP	Curing kinetics and printing parameters	[165]
Carbon nanotubes	DLP	Electrical properties	[166]
		Electrically conductive resin	[133]
	DLP/SLA	Sensitizers for the cure of epoxy resins	[167]
		SLA	Electrical and mechanical tuning
	Nanoclays	SLA	Enhance the thermal conductivity
Composites reinforced			[169]

issues they may generate, and that further studies are required to understand and address these issues.

5.2 Biodegradable polymers

Biodegradable polymers are a type of polymer that can be broken down by natural processes such as bacteria or enzymes. These materials are used in a variety of applications such as packaging, agriculture, and medicine. Biodegradable matrix polymers are designed to degrade into non-toxic by-products and can be an environmentally friendly alternative to traditional plastics. Some examples of biodegradable matrix polymers include:

5.2.1 Nanocellulose-based nanocomposites

Nanocellulose is a natural material extracted from plant fibers and has been used to create nanocomposites with improved mechanical properties, barrier properties, and biodegradability [170, 171].

5.2.2 Layered double hydroxide-based nanocomposites (LDHs)

LDHs have been used to create nanocomposites with improved mechanical properties, thermal stability, and flame retardancy [172, 173]. Recent advances in nanocomposites

demonstrate that it is possible to develop new materials with improved capabilities for various applications. However, it is essential to keep in mind that, when creating nanocomposites for specific applications, the type of nanoparticles used, their concentration, and the synthesis technique can have an impact on the final characteristics of the materials depending on the application.

5.3 Trends in the development of new nanomaterials for VPP

The development of new nanomaterials for VPP has seen several advances in recent years. New nanomaterials have been developed for VPP to reduce costs and increase efficiency. Some of these include the following.

5.3.1 Improved mechanical characteristics

Recent development show nanomaterials that can be used to create parts with improved mechanical properties such as increased strength, stiffness, and toughness, for example, the incorporation of carbon nanotubes [174, 175], graphene [159, 176], and other nanomaterials to improve the mechanical performance of printed objects [70, 177, 178].

Among the recently reported developments of materials with improvements in their mechanical properties, Hyun et al. [142] prepared UV-curable 3Y-ZrO₂ zirconium nanoparticle resins with 50 volume % ceramic content for supportless stereolithography printing. Based on the rheological behavior of the ceramic nanocomposites such as photo curability, viscosity, fluidity, and printability, they obtained high relative densities (99.90%) and flexural strengths above 930 MPa. On the other hand, Eng et al. [169] studied montmorillonite nanoclay fillers (plate-shaped) considering the dispersion, alignment, size, and charges of the nanoclays by dispersing them homogeneously in the photopolymer through various mixing processes, including sonification. In this study, the nanoclays were immobilized during photopolymerization after ultraviolet (UV) exposure, thus maintaining their orientation and alignment, which significantly improved their elongation (more than 100%), as well as their tensile strength and Young modulus. Similarly, Younes et al. [152] investigated nanocomposites with polymer fillers and magnetic Fe₃O₄@graphene using the DLP method for the controlled production of highly aligned 3D printed nanocomposites, which showed a significant improvement in Young's modulus of the nanocomposites with 0.4–0.8 wt.% Fe₃O₄@graphene of the printed parts by varying the angle of the magnetic field. In contrast, Dizon et al. [179] investigated the mechanical and swelling characteristics of silica/poly (ethylene glycol) diacrylate nanocomposites and contrasted them with unreinforced samples. They found that

the addition of 1% SiO₂ increased the poly (ethylene glycol-tensile)'s and compressive strength by 30%.

Additionally, Taormina et al. [180] investigated the possibility of generating silver nanoparticles (AgNPs) from a liquid system with a dispersed silver salt, which was reduced to metallic silver through a stereolithographic process. They reported that simultaneous photoinduced crosslinking of acrylic resin produces a thermosetting resin with significantly improved thermomechanical properties over unfilled resin, even at very low AgNP concentrations, achieving an improvement in Young's modulus of over 120%. Similarly, Feng et al. [176] developed A polyurethane resin, in which trimethylolpropane trimethacrylate was used as a diluent and phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (Irgacure 819) as a photoinitiator, achieving a 62% increase in tensile strength over samples fabricated by direct casting. Tsang et al. [181] studied the development of modified flexible polymeric nanocomposites based on graphene oxide/elastomer; however, the addition of graphene oxide resulted in a decrease in the mechanical strength, as well as in the elongation of the resulting nanocomposite. Correspondingly, the thermal properties were also negatively affected by the addition of graphene oxide. Similarly, Li et al. [182] characterized a photosensitive acrylate resin reinforced with graphene nanosheets, obtaining a composite material with better mechanical and thermal properties. Additionally, Hu et al. [144] employed nanofillers, such as silver, copper, halloysite, and other nanoclays, to increase the thermal conductivity of resins for stereolithography. The fillers were applied to a photopolymer resin, allowed to cure, and then assessed using scanning electron microscopy, contact angle, hardness, thermal conductivity, and mechanical characteristics. They found that the addition of 3% by weight of halloysite nanoclay produced a 6% increase in the thermal conductivity of the resin.

5.3.2 Improved electrical characteristics

The incorporation of conductive or semi-conductive nanoparticles such as graphene, carbon nanotubes, and metal nanoparticles into the polymer matrix is being explored to create parts with improved electrical properties [144, 166, 183]. Nanocomposites made of a polymer matrix and nanoparticles can have enhanced electrical properties compared to the pure polymer matrix. These properties can be achieved by incorporating nanoparticles made of conductive or semi-conductive materials such as carbon nanotubes (CNTs), graphene, or metal nanoparticles (such as gold or silver) into the polymer matrix. Carbon nanotubes, for example, have excellent electrical conductivity and can be used to create nanocomposites with improved electrical conductivity and thermal stability. Similarly, when used to improve the electrical characteristics of nanocomposites,

graphene, a two-dimensional material with exceptional electrical conductivity, can be used. Metal gold or silver nanoparticles can also be used to create conductive nanocomposites with improved electrical conductivity and mechanical properties. In this sense, several studies have recently been carried out in which carbon nanotubes are added to evaluate and optimize nanocomposite materials. In this sense, Lim et al. [133] studied the printing of polymeric compounds based on carbon nanotubes by applying a solution intercalation method to promote the dispersion of nanotubes, thus contributing to high electrical conductivity and precision in the stereolithography process. For their part, Chavez et al. [168] studied the dispersion of carbon nanotubes in polymers, assisted by an electric field, for three-dimensional fabrication using stereolithography techniques, obtaining a significant increase in electrical conductivity (26%). Additionally, Gonzalez et al. [166] developed photocurable acrylic formulations containing CNTs (up to 0.3% by weight) with improved electrical conductivity for the construction of 3D structures with electrical properties. Likewise, Charoeythornkhajhornchai et al. [143] studied the effect of coatings of the aromatic compound carbazole on nanoparticles of titanium dioxide (TiO₂) as a photosensitizer, through their characterization by their photo-absorbency, morphology, and surface properties, and used a UV curing technique to fabricate flexible epoxy composites/multi-walled carbon nanotubes (MWCNTs) which showed low thermal expansion with good electrical properties. Similarly, recent research has been carried out to improve the electrical conductivity of composite materials by adding other nanoparticulate materials. For instance, Tan et al. [146] created silver nanowires (Ag NWs) and combined them with liquid thermoplastic polyurethane (TPU) resin to create an electrically conductive resin. Similarly, Moriche et al. [161] investigated the photocuring-induced modifications of Bis-GMA/TEGDMA by adding graphene nanoplatelets to electrically conductive nanocomposites.

5.3.3 Enhanced optical properties

The most important optical properties of a polymer resulting from radical polymerization include its absorption and refraction characteristics, as well as its light transmission, reflection, and scattering features. These properties are determined by the type of monomers used in the polymerization process, the molar mass and molecular weight distribution of the polymer, and the arrangement of the atoms and molecules in the polymer structure. For their part, researchers are exploring the use of metallic nanoparticles to create parts with increased transparency and color stability [184, 185]. Likewise, the use of quantum dots to manipulate the

electronic and optical properties of materials is also being investigated [186].

5.3.4 Ceramic additive manufacturing

Ceramic additive manufacturing has evolved with the advancements in additive manufacturing technology [187]. This technology produces intricate ceramic structures that are challenging to produce via traditional milling processes. Moreover, it holds immense potential for integrating ceramics with complex architectures, high-temperature resistance, exceptional wear resistance, and other functional properties into everyday applications. Currently, ceramic AM offers significant advantages, including high precision in forming, process flexibility, cost-effectiveness, and extensive research [188]. The fundamental principle of ceramic vat photopolymerization involves the exposure of a high-solids ceramic paste to ultraviolet (UV) light, initiating the process of photopolymerization. Following this, the green parts undergo post-processing steps such as debinding and sintering to achieve densification [189].

Harnessing the potential of light-curing for ceramics opens a multitude of possibilities across a broad spectrum of applications. Table 3 provides an overview of the broad versatility of vat ceramic additive manufacturing, showing its suitability for various nanofillers in ceramic nanomaterials.

5.3.5 Multi-functionality

Researchers are exploring the development of nanocomposite materials that exhibit multiple functionalities such as improved mechanical properties, electrical conductivity, and thermal stability [17, 37]. These trends are driven by the growing demand for advanced materials with improved properties for various applications such as aerospace, automotive, healthcare, consumer goods, and the need to move towards more sustainable and environmentally friendly materials.

The development of composite materials with improved electrical, mechanical, and thermal properties for the development of materials for biomedical and dental applications, and improvements in the polymerization

Table 3 Fillers used in ceramic nanomaterials in VPP

Nanomaterial	Functional properties	Reference
SiO ₂	Optical properties	[190]
Fe ₃ O ₄	Piezoelectric properties	[191]
SiC	Mechanical strength	[192]
Al ₂ O ₃	Mechanical strength	[135]
CaP	Bone repair	[193]
TiO ₂	Antibacterial	[193, 194]
Bi _{0.5} Sb _{1.5} Te ₃	Thermoelectric	[195]

properties of composite materials are the most discussed topics in the field of applied nanocomposites, according to the literature review conducted for this study. Likewise, studies have been developed aimed at the elaboration of medicines for the controlled administration of drugs.

5.4 Hazards associated with VPP processes

According to the present review, there is a gap in recent literature in relation to studies aimed at evaluating the risks associated with the extended use of VPP processes. However, some aspects that in the opinion of the authors should be considered when opting for the use of this technique.

VPP is a process in which monomers are polymerized in a liquid medium, typically using a photosensitizer and light as an initiator. Although this process has the potential to produce high-quality polymers with well-defined properties, it also presents some potential health and environmental hazards.

Exposure to photosensitizers used in vat polymerization, a potential health risk, can result in skin irritation and other adverse effects if not handled properly [196]. These chemicals can be toxic. Moreover, the process of vat polymerization generates harmful by-products such as formaldehyde and acrolein, which can be detrimental to human health if inhaled. Similarly, Xu et al. successfully demonstrated the viability of SLA 3D printing in creating modified-release tablets as oral dosage forms. However, it is crucial to note that these printed tablets do not degrade but maintain their structural integrity upon elimination from the body. This characteristic carries the potential risk of intestinal obstruction or raises concerns within specific patient populations [104].

Another potential environmental hazard is the release of harmful chemicals into the environment, especially if proper disposal methods are not followed. This can lead to soil, water contamination, and likewise damage wildlife and ecosystems.

Furthermore, the process of 3D printing, particularly with existing commercial DLP printers, generates substantial heat and light, which can contribute to the greenhouse effect and global warming. Additionally, the utilization of UV light or near-UV light as light sources in these printers poses potential hazards, such as DNA damage, particularly when employed in bioprinting applications [197].

It is important to note that the potential risks associated with VPP can be minimized by using proper handling and disposal methods, as well as by employing less harmful initiators and photosensitizers. In addition, research should focus on the development of alternative polymerization

methods that are more sustainable and have a lower environmental impact.

6 Conclusion and perspective

Due to their distinct characteristics and prospective uses in a variety of disciplines, 3D printed polymer-based nanomaterials have received a lot of attention in the last years. In the present review, the most active research areas in the field of nanocomposite materials used in the VPP technique were addressed, considering the filler materials that have been reported in the literature, as well as their uses in different applications, the trends in the development of new materials, and the most recent studies aimed at improving the polymerization processes.

Nanofiller materials can be used to enhance the properties of the polymer, such as increasing its strength or thermal stability. A homogeneous distribution of nanofillers in VPP can be an effective way to improve the properties of polymer matrix composites.

This review has focused on advances and trends in the development of composite materials, envisioning those available in relation to the possibilities in the limited materials tested so far. This opens not only opportunities for new materials and parts made with SLA and DLP but also prospects for modification of manufacturing technology, modification of process parameters on a large scale, and new business.

However, in the opinion of the authors, there is still a need for studies to evaluate and to improve the safety of the commercially available resins, considering the exothermic nature of VPP processes. Another aspect that still needs to be explored in depth is related to the use of waste and the recycling of parts after their useful life, since the aspects of circularity and the life cycle of the products are aspects that must be considered from the preliminary stages of design, to avoid future problems of contamination and pollution of the environment. It is important to note that the use of polymer-based nanomaterials also raises some concerns about their potential health and environmental risks, and more research is needed to understand and mitigate these risks. Another aspect that is not usually raised in evaluated works is related to the costs of raw materials and the manufacturing process, which is a fundamental aspect to evaluate the feasibility of future implementation.

Finally, although there are now many research and developments in 3D printing of nanocomposites, certainly it is a new and limitless of possibilities to explore, not only from the materials side point of view, but also from the manufacturing innovation, with high impact in electronics, medicine, energy, and armor, and transportation.

Author contributions Henry A. Colorado L.: Conceptualization, methodology, investigation, supervision, funding acquisition. Elkin I. Gutierrez-Velasquez: methodology, writing—review and editing. León D. Gil: methodology, investigation. Italo Leite de Camargo: methodology, writing—review and editing, funding acquisition.

Funding Open Access funding provided by Colombia Consortium

Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare no competing interests.

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