Received: 29 June 2022 | Revised: 8 October 2022 | Accepted: 13 October 2022
DOI: 10.1002/app.53304

REVIEW

JOURNAL OF Applied Polymer SCIENCE WILEY

Dynamic bond exchangeable thermoset vitrimers in 3D-printing

Balaji Krishna Kumar | **Tarik J. Dickens**

Department of Industrial & Manufacturing Engineering, High-Performance Materials Institute, FAMU-FSU College of Engineering, Tallahassee, Florida, USA

Correspondence
Tarik J. Dickens, Department of Industrial & Manufacturing Engineering, High-Performance Materials Institute, FAMU-FSU College of Engineering, Tallahassee, FL, 32310, USA.
Email: dickens@eng.famu.fsu.edu

Funding information
Florida A&M University NSF CREST Center for Additive Manufacturing, Grant/Award Number: 1735968

Abstract

Dynamic bond exchanging vitrimers have emerged recently due to their malleability, self-heal ability, recyclability, and mechanical stability. Likewise, 3D printing is consciously introduced at different platforms for ease of fabrication, high throughput, cost-effectiveness, and waste reduction. These two distinctive techniques have recently made their consensus performance, resulting from a phenomenal change in the printing field. Conventionally, thermoplastic inks have been primarily used in 3D printing, owing to their effortless processability. At the same time, thermosets were utilized for their superior mechanical strength. However, these two essential properties have been required to be presented in the printed material. In that scenario, thermoset vitrimer materials have been introduced in 3D printing, where malleability and mechanical stability have been observed in the same material. Thus, this article details the recent vitrimer material included with the different 3D printing system systems with their reported results to understand and make them widespread. Eventually, the outlook and perspectives could be helpful to understand and enhance this specific field.

KEYWORDS
3D printing, recycling, self-healing, vitrimers

1 | INTRODUCTION

Layer by layer method perform additive manufacturing systems are commonly known as 3D printing;[1] and this has enriched the polymer construction and fabrication techniques in different fields like automotive,[2] biomedical,[3–5] energy devices, and so forth.[6,7] Significantly, an industrial embracement occurred due to their customized design ability towards the complex structure. As well, this emerging layer by layer method has been performed via "bottom-up" or "top-down" approaches.[8,9] These approaches are compliant by different techniques like fused deposition modeling (FDM),[10–12] direct ink writing (DIW),[13–15] stereolithography (SLA),[16,17] digital light processing (DLP), and so forth.[18–20] Each technique has required the unique property requirements of polymer materials (Figure 1). In addition to that, all the systems could have the capability to produce problematic prototypes with different performance conditions.[21,22] Owing to this, polymer selection and process have been emphasized on every occasion; along with that, the polymer's rheology behavior and curing kinetics have been a significant concern.

Generally, the different aspects of polymer material (like melt rheology, molecular sciences, thermal and inter/intra molecule interactions) need to be considered for better printing outcomes.[23,24] Different polymer/ particle processing methods have emerged to achieve ubiquitous and prominent printed materials. However, different polymer material (multimaterial system) and reprocess

https://doi.org/10.1002/app.53304

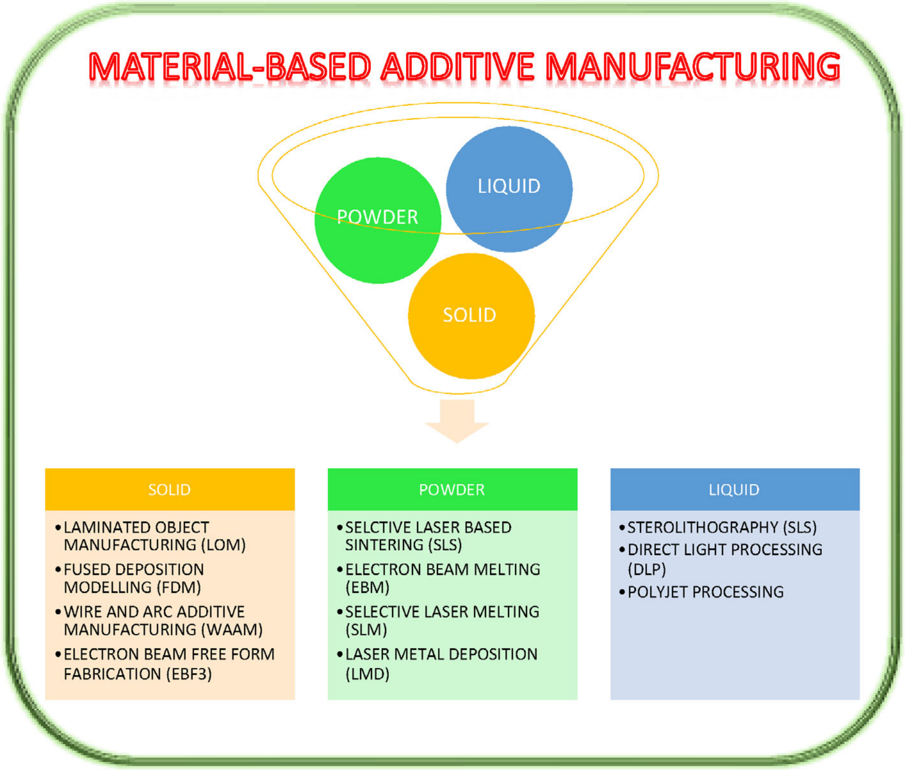

FIGURE 1 Material based additive manufacturing techniques [Color figure can be viewed at wileyonlinelibrary.com]

able ink inclusion is still challenging to overcome the current scenario; the majorly utilized thermoset inks have been unable to reprocess in nature, which could be damaged the environment after their usage. In recent trends, several discussions have been reported on the yield of circular economy alleviating virgin plastic production, where reuse and recycling have been performed with potential energy consumption. Consequently, the concern for printing material sustainability and related interceptions (like a number of repetitions of material, catalyst degradation, waste disposal, etc.) were reviewed in a recent study, where in addition, they mentioned the stringent requirement of 3D printed material recycling, which is important to reduce global pollution. Also, the work described the need for a circular economy promoting reuse/reprocess able materials in the 3D printing field.[25] However, some processing routes could experience reasonable properties and demonstrate some cracks after preparation. Specifically, minor construction defects during preparation and the limitations of modifications (i.e., architectural modification and surface functionalization)[26] have restricted their consumption. Thus, significant demand for reprocessable inks has been investigated to focus on reprocessing thermosetting networks; contemporary malleable thermoset vitrimers are promising materials for that.

Vitrimers demonstrated covalent adaptive network (CAN) formations had been extensively determined the rearrangements of bonds at different conditions without loss of network integrity, where the various chemistries like transesterification,[27–29] transamination,[30] transalkylation,[31] transcarbmoylation,[32,33] disulfide[34–36] and imine exchanges[37,38] have been approached to a large extent. This distinctive approach has been enriching the thermal-based polymer classification, which is helpful providing both (thermoplastics and thermosets) merits of polymer system. Also, vitrimer materials have been included in different applications for specific reasons; especially, 3D printing vitrimer inks have been discussed nascently. Apart from all, the pressing need for a sustainable polymer system has been encouraging the vitrimer ink studies for the future. In addition, the exciting application involvement has been demonstrated with the addition of nanofillers. A vitrimer nanocomposite has been developed that exhibits an excellent mechanical properties and rheology, which is helpful to include the material at different fields. Significantly, various nanofillers like cellulose,[39] silica,[40] nanoclay[41] and carbon allotropies (Carbon nanotube [CNT], Graphene, etc.)[35,42–44] has resulted the prominent outcomes in the recent times. Primarily, the reported functionalized silica (GLYMO [epoxidized] and BARE) based epoxy systems were executed the prevailed covalent transesterification exchanges; also, the 40% addition of filler had resulted the excellent processability without any solvent.[40] And then certain inorganic nanofillers have been performed; and sustainable nanopapers were described with cellulose nanofibrils (CNF)/PDMS with good stretchability and water resistance. Along with that, the performed material had exhibited the interfacial adhesion at 120°C for 1 h.[45] In addition, nanoclay involve nacre- mimetic structured vitrimer material was demonstrated and reported efficient exchanges, reprocessing and recycling.[41] At the same time, several organic nanofillers also discussed widely, due to their adequate property developments. The organic nanofiller CNT has been studied often with different vitrimer; and the incorporation of CNT could be helpful to enhance the light to heat conversion.[46,47] And hence, the inclusion of MWCNT with the epoxy had resulted the evident high performance electromagnetic interference shielding. In that, the addition of 1% had resulted the excellent shielding capability; and through the alcoholysis process MWCNT was segregated and collected at 180 °C for further usages.[42] Similarly, graphene inclusion was detailed with various vitrimer systems; and we have reported the graphene oxide involved epoxy vitrimer with disulfide exchanges. The performed material had determined the self-healing and shape memory at 60°C for 5 min.[34] Substantially, some more biobased nanofiller involve vitrimer investigations have been reported.[48] This outlook explains that the vitrimer is a cross-linked polymer network and the nanoparticles dispersion throughout the material could create a material with high yield stress and viscosity, and which also making it ideal for printing applications.

In overall, till reported 3D printed vitrimer materials have been listed within this manuscript with their chemistries, properties, and advantages. Future prospects, outlooks, and required studies at areas of interest have been mentioned with some critical details for the future interest.

2 | OVERVIEW OF 3D PRINTING AND VITRIMERS

A complex system design manufacturing of the material has been simplified by introducing 3D printing techniques and which were commercialized in 1986- with the effort of Charles Hull- through the stereolithography (SLA) process.[49] Since then, prevailing systems and various techniques have been introduced to ease processing. These sophisticated methods are intrigued to exchange the problematic construction encouraging systems. Besides that, simple computer-based (CAD) 3D design has opened the vast area to application-based utilization.[50] Also, in recent times evolved G-code programming techniques are helpful to prepare the samples via coding.[51]

Conventional subtractive (machine handling manual production) processing systems had been performed to achieve the different geometrics via carving procedures.[52] At the same time, 3D printed system has been manufactured based upon the additive inclusion process method.[53] These remarkable production technique and functional material inclusion have been endeavored the several industrial and research communities to produce high throughput and low cost/material wasting systems (Figure 2).[55–57] However, some more hindrances have been occurred to perform in the major applications field due to their limited polymer usages, curing kinetics, printing constraints, and so forth.[21,58–60] Thus, the material selection in the 3D printing system has always been the primary key to attaining the targeted goals. Altogether, these mass speculative 3D printing material issues have been noticed, and adequate reports have been published recently.[14,16,49,56]

Generally, thermoplastic-based 3D-printed systems have evolved due to their ease of the processing and temperature independence.[61] In contrast, thermoset printed materials have prominent mechanical properties linked to their crosslinked states; however, the nonprocessable and specific curing conditions (i.e., except photopolymer certain temperatures are required for curing the conventional polymers) have restricted their presence in several fields.[62] To mitigate this constraint, Wang et al. have investigated and emphasized the bio-based thermoset in 3D printing materials, which could have degraded effectively via the environmental conditions and provide a sustainable circular bioeconomy; though, the material

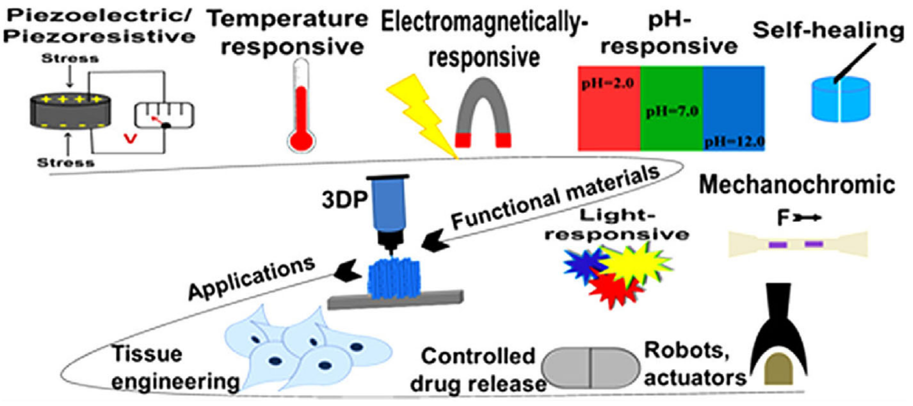

FIGURE 2 Utilization of functional polymers for different applications via 3D printing[54] [Color figure can be viewed at wileyonlinelibrary.com]

properties (like geometrical stability) have not been comparable like a synthetic polymer utilized printed materials.[63] Thus, dynamic chain exchanges such as disulfide, transesterification, trans amination, trans carbonation and other covalent networks demonstrate thermoset materials are needed to be included in the 3D printing system. To this acclaim, substantially emerged a new class of thermoset vitrimer has been recommended. The vitrimer was discovered by Leibler et al. at 2011.[64] Since then, an adequate study has been reported to understand the fundamental dynamic chemical changes and several other factors like a filler addition, functional group, reaction condition, and so forth.[33] Altogether, performed material exhibited silica-like glass behavior, which followed the Arrhenius equation after their topology freezing temperature (T_v). However, if the T_v situates before T_g, that could be restricted their flow and follows William-Landel-Ferry (WLF) equation for a certain period.[65,66] Also, minimum activation energy (E_a) has been required to initiate the bond exchanges.[67] Overall, the vitrimer material performances have been analyzed with different aspects, and various studies could be demonstrated in detail is helpful to include this 3D printed system. Furthermore, advancement in material performance and recently demonstrated vitrimer 3D systems have been detailed in this report with several prospective for future enhancement. Some more material has been discussed for replacing the similar system to attain the same and the significant efficiency.

3 | RHEOLOGY VITRIMER INKS

Rheological studies of polymer (non-newtonian) is helpful to estimate the visco-elastic property of materials.[68] Significantly, vitrimer demonstrating silica-glass like behavior and topology transition temperature (T_v) that has been obtained via the rheological rubbery modulus related extrapolation method.[66,69] Likewise, an efficient 3D printing depends with material rheological properties, where it has been estimated to organize the print parameters.[70] Owing to this, the optimum condition for achieving the vitrimer 3D printing recommends through rheology testing's. However, already the changes in chemical compositions and the filler incorporations have been resulted the prominent changes in rheological conditions of vitrimers, as well as, printing materials.[71,72] Thus, the evaluation of superior printing material rheological behavior would be helpful to adjust vitrimer material rheological behavior with the above-mentioned manner and could result the efficient 3D printing constructions.

Substantially, vitrimer thermosets have been demonstrating the prevailed thermo- mechanical properties, hence that high-yield stress has been observed in the performed materials.[73] At the same time, viscosity drops after the T_v; where the covalent exchanges have commenced and sudden drop of viscosity denotes the transition flow from William-Landel-Ferry to Arrhenius equation.[66,74] Also, rheological studies exhibited tan delta values determine the material deformation; and the reported vitrimer exhibits tan delta values have described the material is flexible and good to perform the printing.[75] Altogether, vitrimers displaying high-yield strength, low viscoelasticity at high temperature and lower tan delta values are supporting that the material can effectively utilized via 3D-printing techniques, and making suitable for an engineering application.

4 | DIFFERENT 3D PRINTED SYSTEMS WITH VITRIMER INKS

Several additive manufacturing techniques have been developed in recent years- to achieve specific properties that contain material components. Significantly, thermoset photopolymer inks have been demonstrated with the specific printing process methods; likewise, nascently reported 3D printed vitrimer systems were performed via particular printing techniques (also specified in Table 1). Accordingly, printed designer-based vitrimer ink studies have been categorized and detailed below with novel insights for a better understanding:

4.1 | Digital light processing

In the current scenario, various vitrimer materials have been demonstrated with a DLP system, where this enrichment has been occurred-due to the ease of printing, high speed, high resolution. However, ink photopolymerization and dynamic reactions would be the key aspects for perfect material outcomes in DLP systems. Significantly, the resulted material remolding and reprocessing need to be comprehended. Thus, an initial study in DLP 3D-printing vitrimer was described through the bond exchangeable TBD catalyst-based epoxy thermoset polymer, where the transesterification mechanism helps to change their networks during the presence of a stimulus. The study demonstrated the hybrid (acrylate- epoxy) thermoset ink, which contained bond exchange reactions based on the ester exchanges (Figure 3a,b). Also, the developed hybrid ink contained photo curable acrylate(P) and thermal curable epoxy(T) in it; and P: T weight ratio were 7:3, respectively. Also, the study mentioned that solvent-based reprocessing of bulk material had achieved through the ethylene glycol and TBD catalyst dissolving process (for 8 h) (Figure 3c). Subsequently, attained

TABLE 1 3D-printed vitrimer materials

Printing technique	Materials	Chemistry	Reprocessing/recycling	Change in efficiency (after first cycle)	Shape memory	Ref
Digital light processing	Photocurable acrylate and thermal curable epoxy with 5,7- triazabicyclo [4.4.0] dec-5-ene (TBD) catalyst	Trans esterification	Dissolved in Ethylene Glycol (EG) at 8 h*	From 46.3 MPa to 37.8 MPa$^{*\sim}$	120°C	76
	Mono-, Bi- and Tri-functional acrylate monomers with Zn(OAC)$_2$, 1,5,7-triazabicyclo(4.4.0) dec-5-ene (TBD), triphenylphos- phine (TPP) and Miramer A99	Trans esterification	180°C for 4 h$^{\#}$	99%$^{\sim}$	180 and 60°C	77
	Thiol- acrylate with triphenylsulfonium phosphate catalyst	Trans esterification	—	—	100°C for 10 min	78
	Methacrylate with di epoxy (BPA epoxy resin (DER331), Ethylene glycol diglycidyl ether (EGDE) and resorcinol diglycidyl ether (RDGE))	Trans esterification	190°C for 1 h with 7 MPa$^{\$}$ 200°C for 30 min$^{\#}$	—	—	81
	Ethylene glycol bis-mercaptoacetate (EGMA), glycerol 1,3-diglycerolate diacrylate (DG2A) and trimethylolpropane tri acrylate (PT3A)	Trans esterification	180°C for 4 h$^{\#}$	100%$^{\#\sim}$	20°C	79
	Diallyl boronate (DABo), pentaerithrytol tetrakis (3-mercaptopropionate) (PETMP) and diallyl phthalate (DAP)	Trans esterification	65°C for 16 h$^{\#}$	—	—	80
Fused deposition modeling	PDMS-based linear elastomer and carbonyl cross-linker	Transamination	Heat gun for a few minutes and then annealed at 70°C.$^{\$\#}$	100%$^{\sim}$	—	82
Direct ink writing	bisphenol A diglycidyl ether (DGEBA), fatty acid, Zn (Ac)$_2$ catalyst and nanoclay	Trans esterification	Dissolved in EG at 180°C for 6 h with high-vacuum condition*	≅100%$^{\sim}$	—	85
Stereolithography	Acrylate prepolymer, hydrogen-bond supplier acrylamide (AM), acrylate monomer tetrahydro-furfuryl acryl- ate, photo initiator Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO), and TBD catalyst.	Trans esterification	Dissolved in EG at 180°C*; 180°C for 1 h with a 1000 psi pressure$^{\$}$; 180°C for 1 h$^{\#}$	—	—	86

Note: *, depolymerization; $^{\sim}$, tensile strength; $^{\#}$, self-healing; $^{\$}$, fragment reprocessing.

material was added to the photo resin (earlier mentioned weight ratio) and extended their reprinting ability several times.

The printed material mechanical properties were discussed regarding the curing conditions, which was more critical in thermoset vitrimer 3D printing systems. The

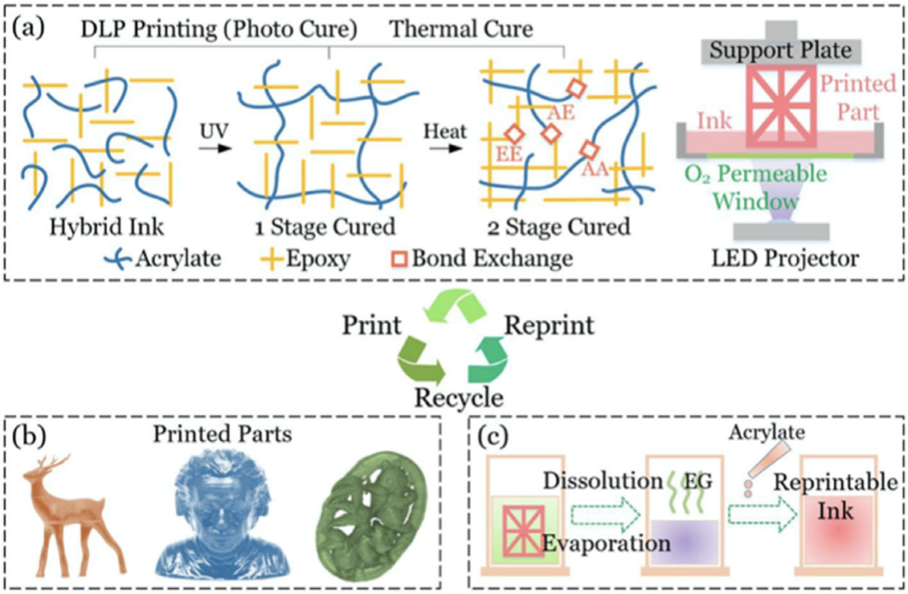

FIGURE 3 (a) Two-stage curing process of DLP 3D printed samples: First stage photopolymerization and second stage thermal curing. (b) Various printed samples. (c) Recycling of printed samples.[76] [Color figure can be viewed at wileyonlinelibrary.com]

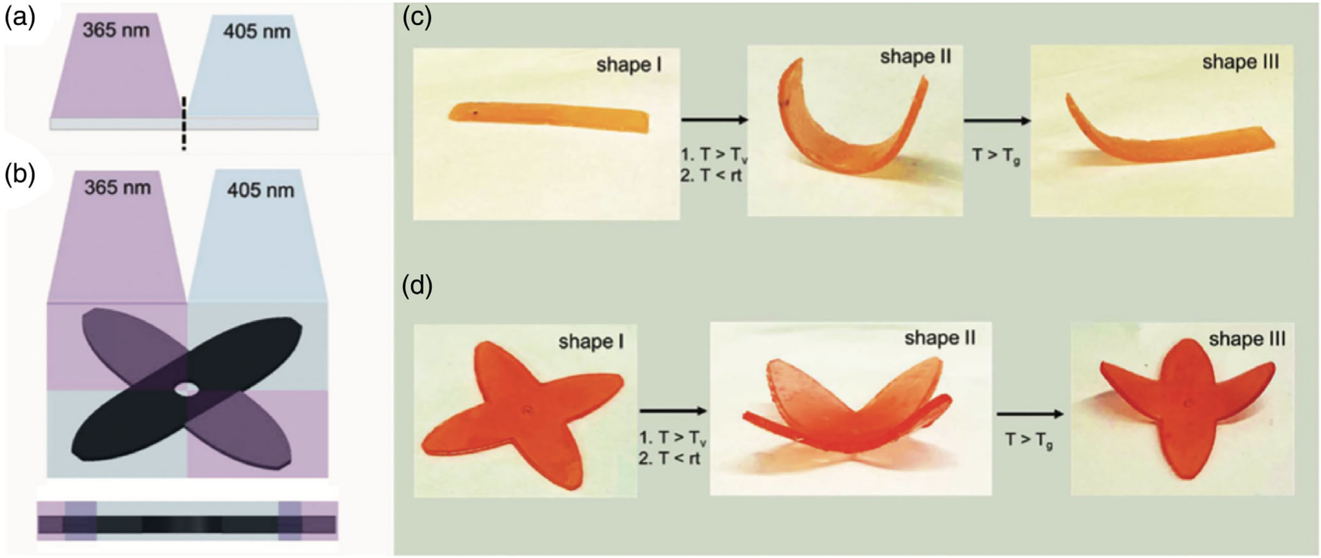

FIGURE 4 Dual-wavelength induced samples structures: (a) rectangular and (b) gripper. Based upon wavelength, the material response has depicted: (c) rectangular sample induced with higher wavelength (405 nm) has regained their position after T_g; though shorter wavelength (365 nm) exposed material retained their position even after reaching T_g- due to the curing and releasing of Bronsted acids. Apparently, higher wavelengths only solidifies the specified portion of the sample, thus, it regains their structure. Similarly, (d) represented based on their wavelength exposure.[78] [Color figure can be viewed at wileyonlinelibrary.com]

first stage photocured 3D printed materials had exhibited mechanical strength (modulus: 10.0 MPa, strength: 1.5 MPa) was lesser than the pristine photoinitiator material (modulus: 249.5 MPa, strength: 12.0 MP); where the epoxy had been behaving as a plasticizer in the network. Though after thermal curing, the performed material had displayed the prominent modulus (2.23 GPa) and strength (46.3 MPa). This enrichment was helpful to construct the actual time conditions involving systems. This kind of curing detailed kinetics study would also be beneficial to understand the ambivalence in this specific field. Additionally, the report described shape memory performed actuator behavior with prevailing explications, instigating further related studies.[76]

Similarly, different catalysts utilized transesterification reaction mechanisms demonstrated with the acrylate monomers DLP 3D printing investigations. Also, experiments were performed with various catalyst-based

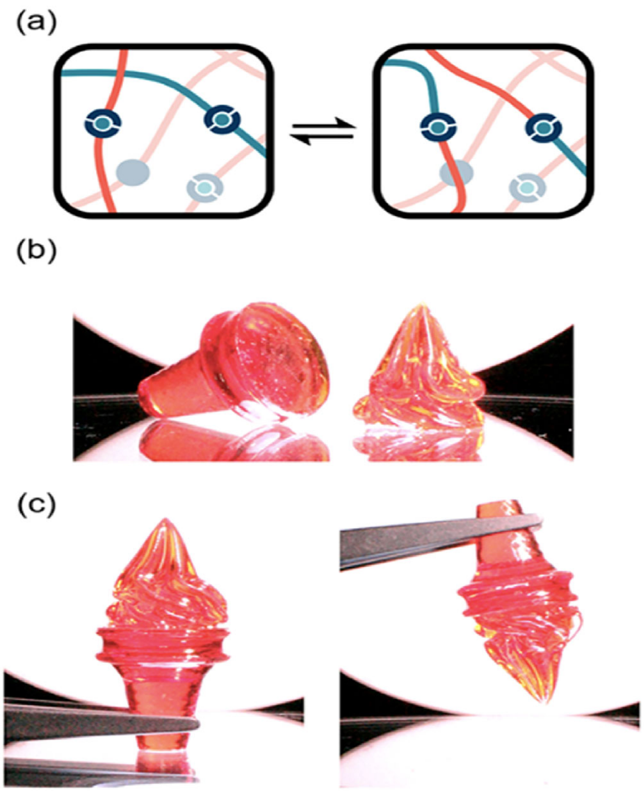

FIGURE 5 (a) Boronate crosslink exchange networks. (b) the printed structure of ice cream cone and ice cream and (c) welded them at 65°C for 16 h.[80] [Color figure can be viewed at wileyonlinelibrary.com]

reaction changes had been notably enhanced the insights about vitrimer reaction at printing system. Similarly, the recent report introduced commercially available Miramer A99 as an esteemed catalyst in place of conventional amine and zinc-based catalysts. Accordingly, the different catalyst-involved system percentages were noted; 15 wt% A99 catalyst provided faster relaxation times (102 min) than the 5 wt% catalyst applied system (634 min). These well-defined optimized results were instigated the different conceptions about the attained material; most importantly, the estimation of catalyst/ free OH groups could be helpful to understand the proficient transesterification covalent exchanges promoted vitrimer system in the 3D-printing system. In addition, the material exhibited self-healing at 180°C for 4 h with 99% recovery; and triple shape memory at 180/60°C.[77] Afterward, photo latent catalyst involved thiol-acrylate vitrimer study had been reported with dual-wavelength DLP 3D printer. Explicitly, triphenylsulfonium phosphate catalyst included thiol- acrylate was cured initially with visible light (405 nm), which had not resulted in the premature release of Bornosted acids. Whereas, during the UV (365 nm) exposure, the photo latent catalyst had rendered to trigger the Bronsted acids in the network; and that was helpful to

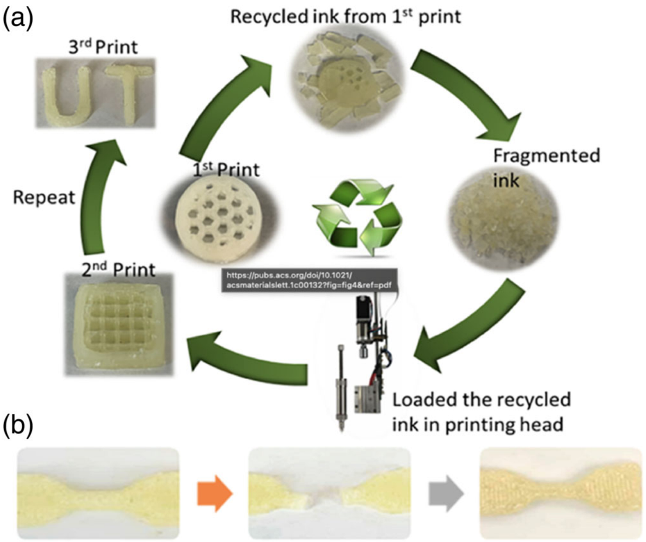

FIGURE 6 (a) Recycling process of recycling polyurea vitrimer ink used 3D printing samples; (b) Repairing of the cut samples with a heat gun.[82] [Color figure can be viewed at wileyonlinelibrary.com]

efficiently catalyze the transesterification reaction. In addition to that, the mentioned photocatalyst effect was determined by the shape recovery test, where the illustrated Figure 4a–d detailed the different wavelength exposed sample areas.

In accordance, higher wavelength (405 nm) exposed area had regained their original structure after heating at 100°C for 10 min (above T_g); however, the shorter wavelength UV (365 nm) exposed area was not retained in the same fixed position even after increasing temperature, which had been described due to their utilized acid-catalyzed topological arrangement. This specific advantage has ensured the possibility to print the defined 3D object without limitations.[78]

Comprehensive studies have been reported about the thiol-acrylate vitrimer for DLP printing. To estimate the impact of molecular structure, functional groups/ester moieties, and structure–property relationship based on the photoreactivity. As a result, it was assumed that the available ester moieties improved the curing kinetics; however, the presence of thiol-acrylate had the opposite effect. The team performed different samples containing diverse acrylate and thiol combinations. In that, EGMA-PT3A (ethylene glycol bis-mercaptoacetate (EGMA), glycerol 1,3-diglycerolate diacrylate (DG2A) and trimethylolpropane tri acrylate (PT3A)) sample had resulted in a complete recovery after healing at 180°C for 4 h and actuating shape recovery behavior at 65/20°C.[79]

In contrast, the traditional catalyst-based vitrimer material printing was superseded with a catalyst-free boronated ester system, which also had promising results. The introduced dynamic boronate (diallyl boronate monomer [DABo]) crosslinkers was helpful to initiate covalent exchanges; however, for the dimensional stability, conventional static phthalate (Diallyl phthalate [DAP]) crosslinkers were included in the thiol-ene systems (Figure 5a). Thus, investigated systems were modulated with different mol% of dynamic and static crosslinkers, resulting in a difference at the printing. Overall, 25 mol% of dynamic DABo inclusion provided the superior fidelity to print the excess complex constructions. Owing to that, complicated constructions had shown precisely; also, the boronate ester rearrangements were helpful to attain the postprinting material had welded together at 65°C for 16 h (Figure 5b,c).[80] This reported system has been intrigued to promote catalyst-free vitrimer studies into a 3D-printing system, where the catalyst complication could be suppressed.

Apart from that, some naturally derived bio-based UV curable dimethacrylate (DMA) synthesized compounds were used as a printing material to restrict nonrenewable feedstock (acrylate and methacrylate monomers) based vitrimer material in 3D printing. Although, the reported study had demonstrated the transesterification reaction and aa good outcome like a conventional vitrimer system. The two-step reaction derived diepoxy MDA vitrimer material was contained the abundantly available dimer acid (DA) in their network with glycidyl methacrylate (≅66–62.5 wt% of biobased content). Also, the resulted material property changes were instituted based upon the chain segmental changes of two methacrylate groups and different epoxy (BPA epoxy resin (DER331), Ethylene glycol diglycidyl ether (EGDE), and resorcinol diglycidyl ether (RDGE)) was used to understand the specific changes. Overall, the DER331 included sample had resulted in superior tensile strength (~9.2 MP) than the control sample. Owing to that, further recycling and 3D printing had been demonstrated with the same sample. The MDA-DER331 sample reprocessing was determined at 190°C for 1 h with 7 MPa pressure and self-healing at 200 °C for 30 min. Moreover, this material was performed for printing and eventually obtained the prescribed 3D object; however, further thermal curing (at 110°C for 2 h) had recommended, and welding of the printed system was described at 160°C for 2h.[81]

4.2 | Fused deposition modeling

In recent years, the most popular additive manufacturing technique, fused-deposition modeling (FDM), has been used with various vitrimer materials due to its ease of use and speed. In general, the FDM system has been used to perform with thermoplastics material, where the extruded sample requires malleability and a high-glass transition temperature for better printing. Significantly,

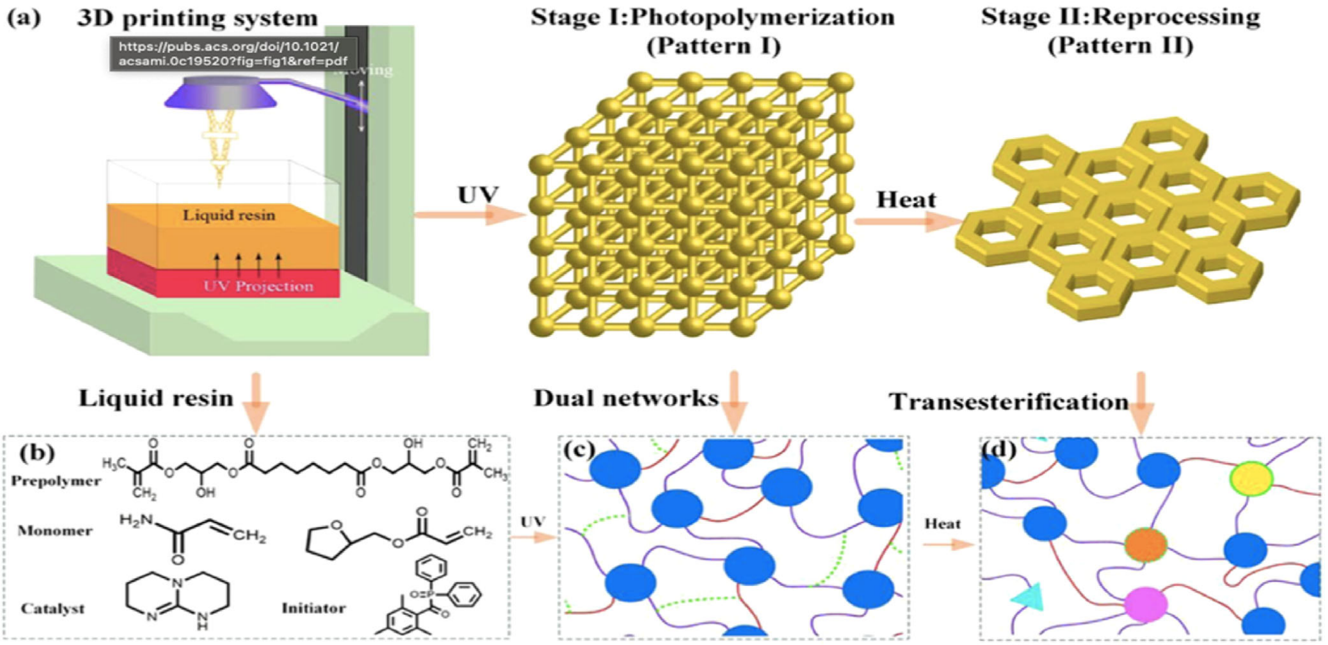

FIGURE 7 (a) Reprocessable and photocurable acrylate vitrimer ink used 3D printing system and the process of photo polymerization and heat curing/reprocessing. (b) Transesterification promoted acrylate vitrimer preparing monomer, prepolymer, catalyst, and initiator chemical structures. (c) Photopolymerized permanent cross link networks (blue) and hydrogen (green). (d) Thermal activated dynamic esterification covalent linkages. (purple, yellow, orange, and green).[86] [Color figure can be viewed at wileyonlinelibrary.com] thermoset materials were not malleable; particularly, FDM printing caused breaks at adjacent lines during continuous printing. In that scenario, the establishment of thermoset has been achieved through the introduction of vitrimer materials in the FDM.[49] Initially, polyurea vitrimer was utilized in FDM studies, where the heat-driven malleability favored the extruding filament for superior layer interfacial adhesion. Also, the topology transition temperature near postannealing conditions (at 70°C for 20 h) had confirmed the good adhesion and 3D object formations with isotropic properties. The performed polyurea material was exchanging their covalent networks via the transamination exchange mechanism, and that study reported five consecutive recycling of the samples (Figure 6a).

The recycled system's resulting efficiency was almost similar to a pristine sample, which had been evaluated based on their tensile studies. And after fifth recycling, the material was exhibited a 19% reduction on their young's modulus, where it was negligible and considerable in vitrimer systems. Along with that, the repairability of the printed material had observed while reattaching two separated parts with a heat gun (for a few minutes) and following annealing (70°C) of the samples (Figure 6b).[82] These remarkable properties presented vitrimer material incorporation at FDM has been intrigued to proceed further research with different vitrimer chemistry describing material; to achieve the high-throughput productions.

4.3 | Thermoplastic vitrimers

This article has solely discussed the thermoset vitrimer material in 3D-printing, where it was predominantly performed at recent times. Whereas some of the thermoplastic vitrimer had been used via FDM printing techniques; the detail of that would be helpful to enhance the overall importance of this article. Owing to that, the newly introduced thermoplastic vitrimer 3D printing studies have been described here:

Primarily, thermoplastic vitrimers were introduced to increase the mechanical strength like a thermoset material. The same strategy has been explored in 3D printing to experiment and obtain fine printing with adequate mechanical stability. Thus, thermoplastic olefins (TPO) crosslinked with covalent networks has been proposed, where it's prescribed due to the TPO's abundant availability and restricted utilization on additive manufacturing. Hence the study reported vitrimer formation by the poly propylene (PP) (TPO) two-stage reaction extrusion process, and their exchanges were performed via transesterification exchange mechanism. Altogether, PP was grafted with maleic anhydride and resulted in material interacted with a multifunctional thiol to acclaim the thio-ester crosslinking bonds. These crosslinking networks were helpful to retain the printed mechanical shape stability-even while increasing the temperature above at their T_m. Owing to this, various amounts of thiol (6%, 20%, and 40%) inclusions were investigated. However, the material containing 6% thiol content had resulted in the prominent printing outputs due to the overall low-additive contents than the other systems.[83]

Subsequently, 4D printable thermoplastic vitrimer material was demonstrated to translate the PCL (ϵ-caprolactone), where it had exhibited a superior heat resistance than the commercial PCL printed material. The reported vitrimer networks had achieved via a two-step reaction process. Initially, the diol contained PCL was transformed to the urethane contained PCL with presence of isocynate and $Zn(acac)_2$ catalyst; then, prepared urethane networked PCL was introduced with the poly (styrene-co- allyl alcohol) (PSA) to achieve transesterification exchanges promoting vitrimer system. After that, prepared material printed via FDM and obtained material has described the self-healing (at 160°C for only 1 min), reprocessing/recycling (170°C under 10 MPa for 30 min), and shape memory properties (at 60°C; shape reconfiguration at 120°C). This shape memory property behavior extended the 3D printed material as a 4D printed material, where the material has an ability to tend towards reversible shape programming.[84]

4.4 | Direct ink writing

Another promising 3D printed system, DIW, was also performed along with the vitrimer thermoset material, which could prevalently promote composite printing. In the same manner, nano clay, including epoxy vitrimer, was printed via DIW. The catalyst-based epoxy vitrimer had described the transesterification reaction, and also 18% of nanoclay filler was added to it. This homogenous epoxy mixture was pre-cured (at 130°C for 30 min under vacuum) and put into the printer. Then the extruded filament derived 3D printed part was first cured at 60°C for 20 h and fully cured at 130°C for 6 h under vacuum conditions. And the material had designed and printed in various shapes to optimize the feasibility of prudent printing; also, the printed material has exhibited self-healing and recycling. The recycling of the printed material was performed by the ethylene glycol (EG) dissolution process. The polymer had immersed in the excessive EG at 180°C for 6 h with the high vacuum condition. Subsequently, polymer dissolved solution containing EG was evaporated for 8 h, the obtained polymer was printed as before the mentioned procedure. However, the curing conditions had changed in both the cycle, where it was performed the pre and complete curing at 80 °C for 20 h and 180°C for 4 h. Further, the efficiency of the recycled sample was evaluated with tensile studies, resulting in pristine material-related strengths with incidental decays.[85] The composite vitrimer 3D printing system has been enhanced the current research towards the vast inductions.

4.5 | Stereolithography

In the current scenario, stereolithography 3D printing is the competitive technique that belongs to other printing technologies; and their substantial-high precision and smooth finish make them essential in this field. In general, monomer or oligomer (low viscosity) photo resins have been used in SLA- to limit the shrinkage at the printed parts. Thus, the photocuring acrylate prepolymer was newly performed for printable dynamic ester exchange and promoted vitrimer material production.

The study reported that the thermoset vitrimer involved a printing system with sacrificial hydrogen bonds, which was helpful to withstand the external mechanical loads. Firstly, acrylate oligomer prepared by one-pot reaction with the β-hydroxyl ester and pendent amide crosslinked networks, after that hydrogen supplied acrylamide (AM) introduced with the catalyst (Figure 7a–d). Overall, the photocuring and heating of the printed material resulted in a smooth and fine printed system; as well as, the addition of different percentage hydrogen supplier AM (0, 5, 10, 15, and 20) had involved, for understanding their mechanical bearing capability (The addition of 20% had resulted in a tensile strength and young's modulus 40.1 and 871 MPa, respectively; and this was 4.4 and 3.85 times higher than the control samples). Moreover, the performed material was described the thermomechanical re-processibility (at 180°C for 1 h with a 1000 psi pressure), and solution-based chemical recycling was detailed with ethylene glycol dissolution at 180°C; also, prominent self-healing behavior (at 180°C for 1 h) was noted.[86] This imparts the SLA printing study for future endeavors and the new vitrimers (Table 1).

5 | OUTLOOK AND PERSPECTIVE

As of now, well-established traditional 3D printed materials have been used in a variety of applications such as soft robotics,[87,88] solid electrolytes,[89–91] dye-sensitized solar cells[92,93] and soft/flexible electronics.[15,94,95] Due to their limited processability after curing, thermoset additive manufacturing studies were avoided. Furthermore, the lack of recyclability/ reprocessability has limited their use in some industrial and high utilized applications, as well as, an inadequate sustainability has reduced their occurrence in recent times. Thus, the prominent vitrimer chemistry mechanism experiencing material has been included in the 3D printing techniques with different formation (Precursors: before curing, UV curing and after curing; Cured: reprocess/ recycle filaments). As well as, most likely thermoset vitrimer 3D printed material would be made them access in the vast area of application with the superior processability. Presenting cohesive advanced, smart, and efficient vitrimer material 3D printing systems has enriched the several studies, which entangled the two different state-of-art systems together to attain the pressing future needs for sustainable smart materials; also, it could be utilized for a several engineering applications. Although, some of the vitrimer materials only have been demonstrated via a 3D printing system; due to their curing kinetics and printing ink preparations. Overall, the data reports presented here would be appropriate for estimating the minimum requirement and comprehending the processing steps prior to/after printing.

The majority of the 3D printed vitrimer systems displayed their exchanges via transesterification mechanisms, which has been heavily emphasized in recent trends in vitrimer materials. And nearly all of the printed materials required a catalyst for their exchanges, whereas newly discussed catalyst-free studies have provided new insights to perform the same type of materials. Aside from that, only a few different chemistries were used in the 3D printed vitrimers. As a result, different evolved vitrimer chemistry executing materials must be performed with various 3D printing techniques. Particularly, room temperature self-healing and presuming disulfide exchange chemistry promoted vitrimer studies could be introduced in this system for promising future outcomes are highly recommended.

Overall, the effect of thermoset vitrimer in 3D-printed has resulted in efficient production, and their inclusion in various fields is expected in the near future. This discussion could be beneficial in achieving sustainable high throughput 3D printed systems, as well as vitrimer chemistry/material establishment, would enrich real-time applications.

AUTHOR CONTRIBUTIONS

Balaji Krishna Kumar: Writing – original draft (lead); writing – review and editing (lead). **Tarik J. Dickens:** Supervision (lead); writing – review and editing (supporting).

ACKNOWLEDGMENTS

The authors acknowledge the Florida A&M University NSF CREST Center for Additive Manufacturing (Award #1735968) for providing support contributing to the research review reported in this publication.

CONFLICT OF INTEREST

There are no conflicts of interest.

DATA AVAILABILITY STATEMENT

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

ORCID

Balaji Krishna Kumar https://orcid.org/0000-0003-4247-272X
Tarik J. Dickens https://orcid.org/0000-0002-1241-023X

REFERENCES

[1] X. Zhang, F. Liou, Additive Manufacturing. in *Handbooks in Advanced Manufacturing* (Eds: J. Pou, A. Riveiro, J. P. Davim), Elsevier, Amsterdam, Netherlands **2021**, p. 1.
[2] Chinthavali, M. In 2016 International Symposium on 3D Power Electronics Integration and Manufacturing (3D-PEIM); **2016**; pp 1.
[3] Y. Bozkurt, E. J. Karayel, *Mater. Res. Technol.* **2021**, *14*, 1430.
[4] C. Culmone, K. Lussenburg, J. Alkemade, G. Smit, A. Sakes, P. Breedveld, *Materials (Basel)* **2021**, *14*, 7910.
[5] K.-W. Cheng, Y. Peng, T. L.-W. Chen, G. Zhang, J. C.-W. Cheung, W.-K. Lam, D. W.-C. Wong, M. Zhang, *Materials (Basel)* **2021**, *14*, 5297.
[6] T. Peng, *Procedia CIRP* **2016**, *40*, 62.
[7] M. P. Browne, E. Redondo, M. Pumera, *Chem. Rev.* **2020**, *120*, 2783.
[8] H. Gojzewski, Z. Guo, W. Grzelachowska, M. G. Ridwan, M. A. Hempenius, D. W. Grijpma, G. J. Vancso, *ACS Appl. Mater. Interfaces* **2020**, *12*, 8908.
[9] P. Katakam, B. Dey, F. H. Assaleh, N. T. Hwisa, S. K. Adiki, B. R. Chandu, A. Mitra, *Crit. Rev. Ther. Drug Carrier Syst.* **2015**, *32*, 61.
[10] A. Alafaghani, A. Qattawi, B. Alrawi, A. Guzman, *Proc. Manuf.* **2017**, *10*, 791.
[11] J. M. Chacón, M. A. Caminero, P. J. Núñez, E. García-Plaza, I. García-Moreno, J. M. Reverte, *Compos. Sci. Technol.* **2019**, *181*, 107688.
[12] M. A. Caminero, J. M. Chacón, I. García-Moreno, G. P. Rodríguez, *Compos. Part B Eng.* **2018**, *148*, 93.
[13] X. Wan, L. Luo, Y. Liu, J. Leng, *Adv. Sci.* **2020**, *7*, 1.
[14] Y. Zhang, G. Shi, J. Qin, S. E. Lowe, S. Zhang, H. Zhao, Y. L. Zhong, *ACS Appl. Electron. Mater.* **2019**, *1*, 1718.
[15] X. Peng, X. Kuang, D. J. Roach, Y. Wang, C. M. Hamel, C. Lu, H. J. Qi, *Addit. Manuf.* **2021**, *40*, 101911.
[16] J. Huang, Q. Qin, J. Wang, *Processes* **2020**, *8*, 1138.
[17] D. Han, C. Yang, N. X. Fang, H. Lee, *Addit. Manuf.* **2019**, *27*, 606.
[18] R. He, W. Liu, Z. Wu, D. An, M. Huang, H. Wu, Q. Jiang, X. Ji, S. Wu, Z. Xie, *Ceram. Int.* **2018**, *44*, 3412.
[19] X. Kuang, J. Wu, K. Chen, Z. Zhao, Z. Ding, F. Hu, D. Fang, H. J. Qi, *Sci. Adv* **2019**, *5*, eaav5790.
[20] H. Wu, P. Chen, C. Yan, C. Cai, Y. Shi, *Mater. Des.* **2019**, *171*, 107704.
[21] S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, *Chem. Rev.* **2017**, *117*, 10212.
[22] A. M. E. Arefin, N. R. Khatri, N. Kulkarni, P. F. Egan, *Polymers (Basel)* **2021**, *13*, 1499.
[23] R. J. Mondschein, A. Kanitkar, C. B. Williams, S. S. Verbridge, T. E. Long, *Biomaterials* **2017**, *140*, 170.
[24] J. Herzberger, J. M. Sirrine, C. B. Williams, T. E. Long, *Prog. Polym. Sci.* **2019**, *97*, 101144.
[25] C. Zhu, T. Li, M. M. Mohideen, P. Hu, R. Gupta, S. Ramakrishna, Y. Liu, *Polymers (Basel)* **2021**, *13*, 744.
[26] Y. Zhang, *Int. J. Bioprinting* **2017**, *3*, 93.
[27] R. Ménard, S. Caillol, F. Allais, *Ind. Crops Prod.* **2017**, *95*, 83.
[28] J. Han, T. Liu, C. Hao, S. Zhang, B. Guo, J. Zhang, *Macromolecules* **2018**, *51*, 6789.
[29] R. Long, H. J. Qi, M. L. Dunn, *Soft Matter* **2013**, *9*, 4083.
[30] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne, F. E. Du Prez, *Adv. Funct. Mater.* **2015**, *25*, 2451.
[31] B. Hendriks, J. Waelkens, J. M. Winne, F. E. du Prez, *ACS Macro Lett.* **2017**, *6*, 930.
[32] D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer, W. R. Dichtel, *J. Am. Chem. Soc.* **2015**, *137*, 14019.
[33] R. L. Snyder, D. J. Fortman, G. X. de Hoe, M. A. Hillmyer, W. R. Dichtel, *Macromolecules* **2018**, *51*, 389.
[34] B. Krishnakumar, R. V. S. Prasanna Sanka, W. H. Binder, C. Park, J. Jung, V. Parthasarthy, S. Rana, G. Yun, *J. Compos. Part B Eng.* **2020**, *184*, 107647.
[35] B. Krishnakumar, M. Singh, V. Parthasarthy, C. Park, N. G. Sahoo, G. J. Yun, S. Rana, *Nanoscale Adv.* **2020**, *2*, 2726.
[36] A. Ruiz de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez, I. Odriozola, *Mater. Horizons* **2016**, *3*, 241.
[37] Z. Feng, B. Yu, J. Hu, H. Zuo, J. Li, H. Sun, N. Ning, M. Tian, L. Zhang, *Ind. Eng. Chem. Res.* **2019**, *58*, 1212.
[38] H. Geng, Y. Wang, Q. Yu, S. Gu, Y. Zhou, W. Xu, X. Zhang, D. Ye, *ACS Sustain. Chem. Eng.* **2018**, *6*, 15463.
[39] L. Yue, M. Amirkhosravi, K. Ke, T. G. Gray, I. Manas-Zloczower, *ACS Appl. Mater. Interfaces* **2021**, *13*, 3419.
[40] A. Legrand, C. Soulié-Ziakovic, *Macromolecules* **2016**, *49*, 5893.
[41] F. Lossada, D. Jiao, D. Hoenders, A. Walther, *ACS Nano* **2021**, *15*, 5043.
[42] H. Fang, W. Ye, K. Yang, K. Song, H. Wei, Y. Ding, *Compos. Part B Eng.* **2021**, *215*, 108782.
[43] Z. Yang, Q. Wang, T. Wang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 21691.
[44] C. Park, G. Kim, J. Jung, B. Krishnakumar, S. Rana, G. J. Yun, *Polymer (Guildf)* **2020**, *206*, 122862.
[45] F. Lossada, J. Guo, D. Jiao, S. Groeer, E. Bourgeat-Lami, D. Montarnal, A. Walther, *Biomacromolecules* **2019**, *20*, 1045.
[46] P. Yan, W. Zhao, Y. Wang, Y. Jiang, C. Zhou, J. Lei, *Macromol. Chem. Phys.* **2017**, *218*, 1.
[47] H. Zhang, X. Xu, *Compos. Part A Appl. Sci. Manuf.* **2017**, *99*, 15.
[48] B. Krishnakumar, A. Pucci, P. P. Wadgaonkar, I. Kumar, W. H. Binder, S. Rana, *Chem. Eng. J.* **2022**, *433*, 133261.

[49] T. D. Ngo, A. Kashani, G. Imbalzano, K. T. Q. Nguyen, D. Hui, *Compos. Part B Eng.* **2018**, *143*, 172.

[50] N. Shahrubudin, T. C. Lee, R. Ramlan, *Procedia Manuf.* **2019**, *35*, 1286.

[51] T. H. Duong, N. I. Jaksic, J. L. DePalma, B. Ansaf, D. M. Daniel, J. Armijo, M. Galaviz, *Procedia Manuf.* **2018**, *17*, 22.

[52] M. Fera, F. Fruggiero, A. Lambiase, R. Macchiaroli, *Cogent Eng.* **2016**, *3*, 1261503.

[53] S. Trzcielinski, W. Karwowski, M. Di Nicolantonio, E. Rossi, *Advances in Manufacturing, Production Management and Process Control: Proceedings of the AHFE 2020 Virtual Conferences on Human Aspects of Advanced Manufacturing, Advanced Production Management and Process Control, and Additive Manufacturing, Modeling Sys; Advances in Intelligent Systems and Computing*, Springer International Publishing, Cham **2020**.

[54] M. Nadgorny, A. Ameli, *ACS Appl. Mater. Interfaces* **2018**, *10*, 17489.

[55] M. N. Nadagouda, M. Ginn, V. Rastogi, *Curr. Opin. Chem. Eng.* **2020**, *28*, 173.

[56] H. A. Colorado, E. I. G. Velásquez, S. N. J. Monteiro, *Mater. Res. Technol.* **2020**, *9*, 8221.

[57] M. Attaran, *Bus. Horiz.* **2017**, *60*, 677.

[58] H. Quan, T. Zhang, H. Xu, S. Luo, J. Nie, X. Zhu, *Bioact. Mater.* **2020**, *5*, 110.

[59] Z. Jiang, B. Diggle, M. L. Tan, J. Viktorova, C. W. Bennett, L. A. Connal, *Adv. Sci.* **2020**, *7*, 1.

[60] J. W. Stansbury, M. J. Idacavage, *Dent. Mater.* **2016**, *32*, 54.

[61] H. Yin, Q. Liang, Y. Duan, J. Fan, Z. Li, *Adv. Mater. Technol.*, **2022**, *7*, 2101479.

[62] B. Wang, Z. Zhang, Z. Pei, J. Qiu, S. Wang, *Adv. Compos. Hybrid Mater.* **2020**, *3*, 462.

[63] M. Shahbazi, H. Jäger, *ACS Appl. Bio Mater.* **2021**, *4*, 325.

[64] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, *334*, 965.

[65] Y. Yang, S. Zhang, X. Zhang, L. Gao, Y. Wei, Y. Ji, *Nat. Commun.* **2019**, *10*, 1.

[66] B. Krishnakumar, R. V. S. P. Sanka, W. H. Binder, V. Parthasarthy, S. Rana, N. Karak, *Chem. Eng. J.* **2019**, *385*, 123820.

[67] S. Dhers, G. Vantomme, L. Avérous, *Green Chem.* **2019**, *21*, 1596.

[68] T. Katashima, *Polym. J.* **2021**, *53*, 1073.

[69] W. Denissen, J. M. Winne, F. E. Du Prez, *Chem. Sci.* **2016**, *7*, 30.

[70] A. Das, E. L. Gilmer, S. Biria, M. J. Bortner, *ACS Appl. Polym. Mater.* **2021**, *3*, 1218.

[71] B. Zhang, C. Yuan, W. Zhang, M. L. Dunn, H. J. Qi, Z. Liu, K. Yu, Q. Ge, *RSC Adv.* **2019**, *9*, 5431.

[72] X. Kuang, Q. Mu, D. J. Roach, H. Jerry Qi, *Multifunct. Mater.* **2020**, *3*, 45001.

[73] H. Wu, B. Jin, H. Wang, W. Wu, Z. Cao, J. Wu, G. Huang, *Front. Chem.* **2020**, *8*, 585569.

[74] F. Snijkers, R. Pasquino, A. Maffezzoli, *Soft Matter* **2017**, *13*, 258.

[75] T. Jain, Y.-M. Tseng, C. Tantisuwanno, J. Menefee, A. Shahrokhian, I. Isayeva, A. Joy, *ACS Appl. Polym. Mater.* **2021**, *3*, 6618.

[76] Z. Chen, M. Yang, M. Ji, X. Kuang, H. J. Qi, T. Wang, *Mater. Des.* **2021**, *197*, 109189.

[77] E. Rossegger, R. Höller, D. Reisinger, M. Fleisch, J. Strasser, V. Wieser, T. Griesser, S. Schlögl, *Polymer (Guildf).* **2021**, *221*, 123631.

[78] E. Rossegger, K. Moazzen, M. Fleisch, S. Schlögl, *Polym. Chem.* **2021**, *12*, 3077.

[79] U. Shaukat, E. Rossegger, S. Schlögl, *Polymer (Guildf).* **2021**, *231*, 29.

[80] L. L. Robinson, J. L. Self, A. D. Fusi, M. W. Bates, J. Read De Alaniz, C. J. Hawker, C. M. Bates, C. S. Sample, *ACS Macro Lett.* **2021**, *10*, 857.

[81] M. Fei, T. Liu, B. Zhao, A. Otero, Y. C. Chang, J. Zhang, *ACS Appl. Polym. Mater.* **2021**, *3*, 2470.

[82] W. Niu, Z. Zhang, Q. Chen, P. F. Cao, R. C. Advincula, *ACS Mater. Lett.* **2021**, *3*, 1095.

[83] M. O. Saed, X. Lin, E. M. Terentjev, *ACS Appl. Mater. Interfaces* **2021**, *13*, 42044.

[84] J. Joe, J. Shin, Y. S. Choi, J. H. Hwang, S. H. Kim, J. Han, B. Park, W. Lee, S. Park, Y. S. Kim, D. G. Kim, *Adv. Sci.* **2021**, *8*, 1.

[85] Q. Shi, K. Yu, X. Kuang, X. Mu, C. K. Dunn, M. L. Dunn, T. Wang, H. Jerry Qi, *Mater. Horizons* **2017**, *4*, 598.

[86] H. Gao, Y. Sun, M. Wang, Z. Wang, G. Han, L. Jin, P. Lin, Y. Xia, K. Zhang, *ACS Appl. Mater. Interfaces* **2021**, *13*, 1581.

[87] T. J. Wallin, J. Pikul, R. F. Shepherd, *Nat. Rev. Mater.* **2018**, *3*, 84.

[88] B. Shih, C. Christianson, K. Gillespie, S. Lee, J. Mayeda, Z. Huo, M. T. Tolley, *Front. Robot. AI* **2019**, *6*, 30.

[89] D. W. McOwen, S. Xu, Y. Gong, Y. Wen, G. L. Godbey, J. E. Gritton, T. R. Hamann, J. Dai, G. T. Hitz, L. Hu, E. D. Wachsman, *Adv. Mater.* **2018**, *30*, 1.

[90] Y. He, S. Chen, L. Nie, Z. Sun, X. Wu, W. Liu, *Nano Lett.* **2020**, *20*, 7136.

[91] A. Chen, C. Qu, Y. Shi, F. Shi, *Front. Energy Res.* **2020**, *8*, 571440.

[92] S. James, R. Contractor, *Sci. Rep.* **2018**, *8*, 17032.

[93] T. El Mogy, D. Rabea, *Proc. Int. Acad. Ecol. Environ. Sci.* **2021**, *11*, 52.

[94] A. D. Valentine, T. A. Busbee, J. W. Boley, J. R. Raney, A. Chortos, A. Kotikian, J. D. Berrigan, M. F. Durstock, J. A. Lewis, *Adv. Mater.* **2017**, *29*, 1.

[95] R. Lin, Y. Li, X. Mao, W. Zhou, R. Liu, *Adv. Mater. Technol.* **2019**, *4*, 1.

AUTHOR BIOGRAPHIES

Dr. Balaji Krishna Kumar received his PhD in chemical engineering from the University of Petroleum and Energy Studies, India. Currently, he is working as a post-doctoral research associate at FAMU-FSU college of engineering, US. His research interests include polymer/vitrimer nanocomposite, additive manufacturing of solar cells and polymer electrolytes.

Dr. Tarik J. Dickens is the founder of the Dickens' research group and principal investigator at HPMI. His group's interest is in advanced manufacturing science and the structuring of materials in design. Next-generation materials and products need novel systems of production, material synthesis, and amalgamation. The Digital center provides for material science experimentation, digital.

How to cite this article: B. Krishna Kumar, T. J. Dickens, *J. Appl. Polym. Sci.* **2023**, *140*(2), e53304. https://doi.org/10.1002/app.53304