Composites by Rapid Prototyping Technology

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Abstract

The use of rapid prototyping (RP) technology for rapid tooling and rapid manufacturing has given rise to the development of application-oriented composites. The present paper furnishes succinct notes of the composites formed using main rapid prototyping processes such as Selective Laser Sintering/Melting, Laser Engineered Net Shaping, Laminated Object Manufacturing, Stereolithography, Fused Deposition Modeling, Three Dimensional Printing and Ultrasonic Consolidation. The emphasis of the present work is on the methodology of composite formation and the reporting of various materials used.

Key words: : Rapid Prototyping (RP), Laser, Composites

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1 Introduction

Rapid Prototyping (RP) initially focussed on polymers. These were later replaced/supplemented by ceramics, metals and composites. Composites are used in RP not only to make desired product but also to facilitate the process. For example in Fused Deposition Modeling (FDM), a blend of various polymers may be used, in which different polymers play the role of tackifier, plasticizer, surfactant etc.

There are a number of RP techniques in vogue but only some of them have been used for the production of composites. The processes which have mainly been employed for fabricating composites are: Selective Laser Sintering/Melting

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(SLS/SLM), Laser Engineered Net Shaping (LENS), Laminated Object Manufacturing (LOM), stereolithography (SL), Fused Deposition Modeling (FDM), Three Dimensional Printing (3DP) and Ultrasonic Consolidation (UC) [1–3]. The present paper deals with only the above mentioned RP techniques.

Fibre-reinforced composites have been produced by some of the RP techniques and the paper deals with them. RP techniques which have been mainly used with fibre-based composites are SL, FDM and LOM. In a powder-based RP technique such as SLS [4] and LENS, it is difficult to draw smooth layers of powder-fibre mixture [5]. Using long or continuous fibres instead of short fibres is difficult to incorporate into processing and its use has been limited solely to LOM and SL techniques [6,7]. In FDM and LOM, fabrication of respective fibre-reinforced composite filaments tapes and laminates are required as a pre-step before RP processing, necessitating the need for materials to be formulated and developed.

RP techniques are increasingly used for making biocomposites and a section is devoted to it. Not much work has been done in the area of nanocomposite, the paper nevertheless devotes a short section to it.

2 Selective Laser Sintering/Melting (SLS/SLM)

There are two main reasons for processing composites by SLS/SLM [4]: 1) to facilitate the SLS process using liquid phase sintering (LPS) mechanism and, 2) to combine various materials for achieving properties unachievable by a single material. Examples of first type are the SLS of Fe-Cu, where Cu acts as a melted fluid during processing and binds Fe powders to help form a composite of Fe-Cu [8]. In this case, Cu is not added to enhance the mechanical or other properties of iron product but only to help consolidate the iron powders without difficulty.

The second type is the emulation of formation of traditional composites using SLS/SLM processes, e.g. SLS of PCL/HA, where hydroxypatite (HA) is added to polycapralactone (PCL) for enhancing its strength and biocompatibility [9]. The present section deals only with manufacturing of this type of composites.

In SLS/SLM, composites have been manufactured mainly by using three methods which have been elaborated in the coming subsections.

This is the most common method used for consolidating a composite. Most noticeable application is the formation of a Polymer Matrix Composites (PMC) and the binding mechanism involved is Liquid Phase Sintering (LPS). Polymer powders and ceramics are mixed and laser sintered to form the composites, e.g. PCL and HA [9], Polyether ether ketone (PEEK) and HA [10], PE and HA [11], PA and nano-clay [5] etc. It has been found that Polymethyl mathacrelate (PMMA)-coated HA powder could facilitate better binding of the composite, but uncoated powder is used for the reason of biocompatibility. Coating of a powder has certain other advantages. In case of a nano Al_2O_3 and PS composite, nano Al_2O_3 particles are coated with PS to prevent the agglomeration of nano particles resulting in a uniform distribution of particles in the polymer matrix [12].

The reinforcement powder is used in the form of particulates because fibres as a reinforcement give problems during formation of a smooth powder bed and are not helpful in increasing the final density and strength. Instead of taking a mixture of a polymer powder and a reinforcement powder, a single composite powder can also be used, e.g. glass-filled polyamide (PA) powder, Al-filled PA powder [13,14], HA-filled HDPE powder [15], TCP-glass powder [16] etc. A single composite particle helps overcome the difficulty associated with mixing the powders and yields a uniform spread of composite components in the final product. However, if one of the component of the composite powder is a fiber, problems of manufacturing occur.

The method has also been used to make Metal Matrix Composite (MMC), e.g Fe and graphite [17], WC-Co [18,19], WC-Co and Cu [20,21], Fe, Ni and TiC [22] etc and Ceramic Matrix Composite (CMC) e.g. SiSic [23]. SLS of ceramic and metal, in general, does not give as dense products as is found in the case of PMC. In order to fully consolidate it, an extra material is added to the powder mixture [21] or the porous product is infiltrated [18,19]. Addition of La_2O_3 to the mixture of WC-Co and Cu decreases the surface tension of the melt and consequently increases its sinterability [21]. Strengthening of a WC and Co green product may be done by infiltrating it with bronze [18,19,24,25]. An image of a bronze (Cu and 10% Sn) infiltrated WC-12Co by BSE (Backscattered Electron) mode of SEM is shown in Figure 1 [25].

Table 1 summarizes various materials used for direct fabrication of composites in SLS.

Various customized composite powders are available for processing such as DuraForm GF (polyamide and glass fibre), DuraForm AF (polyamide and aluminium) [34]. A polyamide powder with short carbon fibre reinforcement

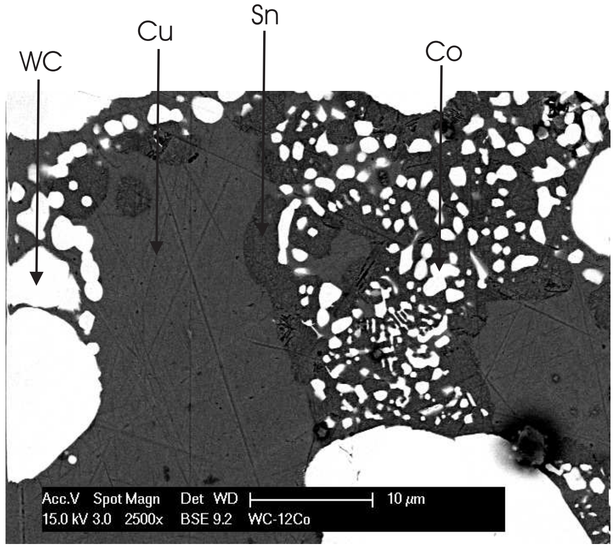

Fig. 1. SEM micrographs of infiltrated WC-12Co

is also available [4].

2.2 Manufacturing of Composites using In-situ Reactions

Laser-induced chemical reactions are used to create in-situ particles during laser sintering. The energy of the laser beam can be used in two ways: 1) to overcome the activation energy of the reactants and to form chemical compounds and 2) to trigger a chemical reaction which will not only form a compound but generate enough thermal energy to propagate chemical reactions. Both types of in-situ formation of compounds are better than the pre-addition of compounds because of the following reasons: fine and uniform distribution of compounds, better wetting, release of exothermic energy helpful to binding.

Examples of 1st type are the formation of Cu-based MMC reinforced with TiB_2 and TiC from a powder mixture of Cu, Ti and B_4C [35]. The 2nd type is a case of Self-propagating High-temperature Synthesis (SHS), e.g. formation of TiC- Al_2O_3 composite from TiO_2, Al and C [28]; Al_2O_3-Cu composite from CuO and Al [36]; NiTi-HA composite from Ni, Ti and HA [37,38]. In the latter case, it has been found that though the product is porous, it could be suitable as an implant material.

Chemical reactions may also help creating a binder material in the case of laser processing of SiC, where disintegration of SiC and subsequent reaction with O_2 gas forms SiO_2 which binds rest SiC powders [39]. This manufacturing mechanism has not furnished strong parts and has not been further used.

Post-processing of laser sintered materials in a furnace is another way for manufacturing a composite. It has been mainly performed in two ways: 1) by using the furnace for infiltration with or without preceding debinding, 2) by using the furnace for chemical reaction and infiltration.

Examples of the first type are treating laser sintered acrylic/glass product in a furnace where the acrylic binder gets de-binded and the glass (SiO_2-Al_2O_3-P_2O_5-CaO-CaF_2) partially changes to ceramic (with apatite and mullite phase) making a glass-ceramic composite [40,41]. In this case, the composite was manufactured using a furnace cycle without using infiltration. In another case, a laser sintered polymer-coated SiC powder was infiltrated with Al in a furnace to form MMC [42]. Other examples are: the formation of refractory Mo-Cu composite [43], silver infiltration of a high-temperature superconducting ceramic $Y_2BaCu_3O_{7-x}$ [44], aluminium infiltration of Al_2O_3 and SiC [45] .

The 2nd type is most common and the most used example is the formation of Si/SiC composites. Laser processed SiC is treated with a phenolic resin. The resin after curing in a furnace gives rise to carbon which reacts with some of the infiltrant Si to form SiC and produces finally Si-SiC composite. The amount of SiC in the composite could be controlled by the degree of treatment of the green product with phenolic resin [46–48]. Another noticeable example of chemical reaction inside a furnace is the use of nitrogen gas for reacting with green product of Al alloy to form AlN. Its infiltration with Al alloy later, produces Al MMC. In this case, successfully manufacturing of Al composite is dependent upon the strength furnished to the meso structure by the formation of nitride [49,50].

3 Three Dimensional Printing (3DP)

Three Dimensional Printing (3DP) is a powder-based RP process in which a polymer binder is jetted onto pre-deposited powder layers. Composites could be made by changing a component of the powder mixture, provided they are compatible with the jetted polymer binder. Here, compatible means that the powders should not be dissolved or chemically react in presence of the polymer.

3DP gives a unique opportunity to control the material composition [51,52] of the product by jetting different materials from different nozzles. These jetting materials can be used either in a molten form or in a slurry form. This can help manipulate various properties such as electrical conductivity, thermal conductivity, reflectivity, magnetic properties and hardness at various places of the product and make Functionally Graded Materials (FGM) or composites [53,54].

Infiltrating porous preform of ceramics, obtained by 3DP with metal or alloy is again an option common to all RP techniques for making composites [55]. A part containing 60 % stainless steel and 40% copper or starch + polyurethane or starch + surgical wax has been successfully made [53].

It is difficult to make fiber-reinforced composite either by jetting the fiber or using a powder-fiber mixture. Infiltration with fiber could help make composite. There is evidence that carbon nano fiber could be infiltrated along with polymer (epoxy resisn) to enhance electrical conductivity [56].

Table 2 summarizes main materials used for fabrication of composites in 3DP.

4 Laser Engineered Net Shaping (LENS)

Laser Engineered Net Shaping (LENS) is similar to SLS as it is also a powder- and laser-based technique; the main difference between the two processes is the way the powder is deposited. The fabrication of composite in LENS is similar to SLS with regard to laser-powder interaction [58–60]. In one variant of LENS named CMB [61], there is an option to use a wire instead of powder as a starting building material [62] giving possibility to make composites without using powders unlike SLS.

LENS is used to create composites having varying degrees of reinforcement composition leading to Functionally Graded Materials (FGM) by using different powders carried using non-reactive gases from different nozzles [58].

Table 3 summarizes various materials used for the direct fabrication of composites in LENS.

5 Laminated Object Manufacturing (LOM)

Fabrication of composites by LOM directly depends upon development of composite laminates. Particulate or fibre reinforced sheets are needed to be produced in order to be further processed for fabricating composites. Fabrication could also be accomplished by infiltrating a preform after a binder burn-out cycle. Pressure is applied during the binder burn-out cycle for avoiding any possible delamination. This could be executed by applying an uniaxial press to an enclosed chamber housing LOM parts covered in silica powders. The powder helps the pressure to be distributed evenly and release degraded binder [68,6].

LOM is unique in the sense that layers of the product could be changed with laminates made up of different materials composition to make varied composites. It has been used to develop a FGM or composite of TiC/Ni with the help of combustion synthesis as post-processing [69]. This possibility has its limitation for automating, as many different sets of laminates need to be integrated into the process.

Fiber-reinforced Composite in LOM

In LOM, there is an example of making a FRC sheet of 0.5 mm by joining layers of ceramic tapes with fibre prepegs. Fibre prepegs are fabricated by joining an unidirectional continuous fibre with a thermosetting resin. During LOM processing, cutting of the continuous ceramic fibres with the CO_2 laser produces burning and heat damage to the adjacent polymer. This problem could be avoided by using copper vapour lasers as it cuts the fibre by photoablation mechanism [68]. In another case, a LOM product is developed from binding a pyrolysed filter paper made up of cellulose fibres with an adhesive tape developed from a slurry containing phenolic resin, polyvinyl butyral, benzyl butyl phthalate and ethanol. The product is then again pyrolysed at 800°C in nitrogen atmosphere to convert the phenolic resin into carbon. The porous carbonized samples were then post-infiltrated with liquid Si in vacuum at 1500°C for making FRC [70].

6 Stereo-Lithography (SL)

In order to fabricate composite by SL, a photopolymer is mixed with particulates or fibres which furnishes enhanced properties. Reinforcing particles give rise to an increase in the viscosity of the photopolymer which consequently complicates the coating process of new layers. Other problems associated with a liquid mixture are: 1) particulate getting settled instead of being suspended in the liquid resin resulting in a non-uniform distribution of reinforcing particles, 2) formation of bubbles in the liquid giving rise to pores after curing which become sources of potential crack initiation, 3) requirement of longer duration of curing due to lower absorption of laser energy by the liquid, arising out of partial reflection of laser rays by the solid particles present in the liquid [7,71,72]. Some of the aforementioned problems can be avoided by using a variant of SL, i.e. the Optoform process in which a paste containing various materials replaces the photopolymer liquid [73].

Using thermal curing in addition to photo-curing also helps make composites by strengthening specially developed polymer mixtures [74].

Fiber-reinforced Composite in SL

Out of all techniques, SL is the one which has been mostly employed for investigating FRC using short fibres [75], continuous fibres [76] and fibre mats [7]. Selection of a glass fibre instead of a ceramic or carbon one decreases its opacity to UV light [77] which makes glass fibre more SL-friendly for making FRC.

Though, continuous fibre is ideal for enhancing mechanical properties, mixtures with short fibres of higher aspect ratio shows more or less comparable properties [77]. Increasing the volume fraction augment the properties but is restrained by the increasing difficulty in the layer formation and the post-processing. However, surface coating of the fibre helps decreasing the viscosity of the mixture [78]. Fibres also support inter-layer bonding by getting partially settled into the uncured regions of a previous layer [75]. The efficiency of short fibres is constrained by their non-uniform distribution in length, random orientation in mixture and fracture during mixing [77].

Table 4 summarizes materials used for fabricating FRC in SL.

7 Fused Deposition Modeling (FDM)

Fused Deposition Modeling (FDM) is capable of yielding strong composite parts as bond forms between successive roads and layers due to partial or full melting of the feedstock composite filaments. In the case an overhanging section is to be produced, a removable support structure of wax has to be created using another nozzle.

Feedstock development is essential for manufacturing a composite product by FDM. The feedstock filament must be of right composition and strength and must furnish a low-viscous extruded material. It consists of a base polymer, a tackifier, a plasticizer and a surfactant besides other metals, polymers or/and ceramics. The base polymer gives strength so that the filament acts as a piston during processing. The tackifier is used for tackiness and flexibility, the plasticizer for improving the flow and the surfactant for an enhanced homogeneous dispersion of metal/ceramic in solution. The development of the filament needs the mixing of right amounts of these components [79,80].

Table 5 summarizes main materials used for the fabrication of composites in FDM.

Fiber-reinforced Composite in FDM

Addition of fibres in case of FDM increases the stiffness of the thermoplastic and decreases the swelling of the tape at the extrusion die head during its production [83]. It also increases its brittleness making it difficult to get wound on a cylindrical drum for getting further operated. Its ductility and flexibility can be improved by the addition of a linear polymer into the mixture. Presence of fibre also enhances the softening temperature and the heat distortion temperature of tapes [84]. Fibres of higher aspect ratio (L/D>100) can be generated during extrusion of tapes by an introduction of droplets of Thermotropic Liquid Crystalline Polymers (TLCP) into the mixture. TLCP can also help overcome problems of extruding fibres of higher aspect ratio through the small diameter FDM die head as they are susceptible to fracture during extrusion. The morphology of TLCP reinforced polymer depends on shear and extensional flow fields during processing and can be tailored to give the required properties. As the processing temperature of TLCP is high and, gives rise to degradation of the base thermoplastic during melting of the mixture, it is necessary to melt them separately and then blend later [85].

8 Ultrasonic Consolidation (UC)

UC is mainly a metallic foil based technique and is suitable for the formation of metal composite structures or metal-matrix composite. The foils are bonded by ultrasonic welding and the bonding parameters are limited by few types of existing UC machines. The foils used are mainly Al, Cu, Fe, Ni etc [86–89].

The process gives following advantages over other RP techniques for making FRC:

(1) Precise placement of fiber in the structure,
(2) Lack of damage of sensitive fibre because of low rise of temperature,

SiC fiber and shape memory alloy fiber have been yet successfully bonded [90,91]. A commercial composite foil named MetPreg (alumina fiber embedded over Al foil) has also been used to observe its bondability [92].

9 Fabrication of Nanocomposites

Polymer matrix nanocomposite have already been made by RP techniques while little work has been done for utilizing nano particles in fabricating metal matrix composites.

There are inherent limitations in using nano particles in powder-based RP techniques such as SLS, LENS and 3DP because it will decrease the tap density and processability. However, nano-structured powder of micron size can be used for nano effect [5,93,67]. Presence of nano-particles into polymer inhibits movement of polymer macromolecules and increases tensile modulus and strength of the polymer without reducing its impact resistance. However, a higher volume fraction is unsuitable as it decreases final green density [5].

In SL and FDM, by using small volume fractions of nano-additives, thermal [83], optical [94] and mechanical properties [95,96] of a matrix polymer can be enhanced without increasing viscosity of the mixture. It eliminates difficulties associated with processing high-viscous materials in SL and FDM. It is also possible to increase the volume fractions by more than 40% [97].

Addition of nano-particles in a resin for SL helps them to get evenly dispersed without constantly agitating the mixture. A material, Bluestone containing nano-ceramic has been developed for SL which makes parts suitable for electrical housing [98].

10 Composites for Bio-medical Applications

Besides the use of RP techniques to produce scaffolds of plain Ti alloys [99–101] or plain biocompatible polymers [102–104], RP has also been used for manufacturing scaffolds [62,105,10,106–109] and custom medical implants [110,111] out of polymer-ceramic composites. These biocompatible composites can be bioactive, bioinert or of various degrees of bio-resorbability. Biodegradable composites are of new interest as implant materials in tissue engineering because: 1) it eliminates the need for a second surgical operation, done for removing implants after healing, and 2) it gives less possibility of a mismatch of the mechanical properties between bones and implants [112,113].

RP has the following special advantages over the conventional techniques for fabricating scaffolds and this explains its increasing acceptability: freedom of shape and size, controlled creation and distribution of global pores of various sizes and shapes, free from toxic binders and solvents and, the capacity for precision and reproducibility. RP has also been combined with conventional techniques to take advantages of both, for the creation of scaffolds. RP has created designed global pores while conventional techniques make local pores necessary for providing potential space for tissue growth. Global pores serve the purpose of nutrient diffusion, fluid and blood flow, control of cell growth and tissue differentiation [107].

The addition of Ca-P ceramic to the polymer makes a composite bone analogue and improves the bone bonding behaviour of unfilled polymers [113]. Calcium phosphate increases the osteoconductivity of the biocomposite [124]. It has been found that the right amount of HA is required to enhance the bioactivity of polymers without making the composites fragile. In case of a PEEK/HA mixture, the right amount of HA is about 40% [10].

Bioactive glasses and glass ceramics are other notable fillers besides HA to polymers [113]. The biocomposite of Titanium nickelide (NiTi) and HA has been synthesized for fabricating bone implants from a mixture of Ni-Ti powder and HA additive through SHS mechanism by the SLS technique [37]. LOM has also been employed to manufacture a custom bone implants from a sheet of 125-150μm consisting of calcium hydroxyapatite and calcium phosphate glass. Pore sizes of post-processed LOM implants depend upon the size of HA and can be enlarged by taking large particles [111]. Table 6 shows the materials used by various RP techniques for fabricating bio-composites.

11 Conclusion

Composites have been fabricated using RP techniques mainly for mechanical applications while its utility for other inter-disciplinary applications namely, optical, electronic and thermal, barring few exceptions, has not yet been extensively investigated. There is need to develop either existing RP techniques (such as increasing the capacity of UC/SLM machine etc.) or search for a new RP technique (such as based on plasma welding etc.) in order to enhance the application domain.

SL and LOM have vast potentials for the fabrication of continuous fiber reinforced composites. However for fast and accurate reproducibility, the techniques need to be further matured. SLS and LENS are capable of producing in-situ ceramics for formation of composites and offers a distinguished area for further exploration. The development of special powders is the easiest way to make composites using SLS/LENS/3DP.

Production of bio-composite specially for manufacturing of scaffolds is another field in which RP has distinct advantages over conventional techniques and with present pace of development, will get more attention in future.

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Figure 1 Caption SEM micrographs of infiltrated WC-12Co

Sl. No.	Materials Used	Composites	References
1	Fe, graphite	MMC	[17]
2	Ti, graphite/diamond	MMC	[26]
3	Ti, SiC	MMC	[26]
4	AlSi, SiC	MMC	[26]
5	AlMg, SiC	MMC	[26]
6	Co, WC	MMC	[18]
7	Cu, Ni, Ti, B_4C	Cu/TiB_2	[27]
8	TiO_2, Al, C	TiC/Al_2O_3	[28]
9	SiC, PA	SiC/PA	[29]
10	Cu, Ni, Ti, C	Cu/TiC	[27]
11	Polycarbonate, Graphite	PMC	[30]
12	Fe, SiC	MMC	[31]
13	ZrO_2, Y_2O_3, Al, Al_2O_3	CMC	[32]
14	acrylic-styrene, SiO_2	PMC	[33]

Table 1
Materials used for the direct fabrication of composites in SLS

Sl. No.	Main Materials Used	Composites	References
1	C, Ti-Cu alloy	TiC/Ti-Cu	[55]
2	WC, Co_3O_4	WC/Co	[54]
3	steel, bronze	steel/bronze	[57]

Table 2
Main Materials used for the fabrication of composites in 3DP

Sl. No.	Materials Used	Composites	References
1	Invar, TiC	MMC	[60]
2	Ti-6Al-4V, B	Ti-6Al-4V/TiB	[59]
3	Ti, TiC	Ti/TiC FGM	[58]
4	Ti, TiB	MMC	[63]
5	NiBSi, Cr_3C_2	FGM	[64]
6	NiBSi, WC-Co	FGM	[64]
7	Ti-48Al-2Cr-2Nb, TiC	MMC	[65]
8	WC-Co	MMC	[66,67]

Table 3
Materials used for the direct fabrication of composites in LENS

Sl. No.	Materials Used	References
1	Carbon fibre, bisphenol A-epoxy,	
	hydroxycyclohexyl phenyl ketone, lauroyl peroxide	[74]
2	glass fibre, acrylic-based polymer	[72]
3	E-glass fibre, epoxy-based resin	[7]
4	E-glass fibre, acrylic-based resin	[7]
5	carbon fibre, acrylic-based resin	[7]
6	Aramid, acrylic-based resin	[7]

Table 4
Materials used for fabricating Fibre-reinforced composites (FRC) in SL

Sl. No.	Main Materials Used	Composites	References
1	Fe, Nylon	Fe/Nylon	[80]
2	Al, Alumina	Al/Alumina	[81]
3	ceramic, polymer	for piezoelectric	[82]

Table 5
Main Materials used for the fabrication of composites in FDM

LM Techniques	Sl. No.	Materials Used	References
SLS	1	Ni, Ti, $Ca_5(PO_4)_3OH$	[37]
	2	PEEK, HA	[10,114]
	3	PVA, HA	[106,115]
	4	PLLA, HA	[110,116]
	5	PCL, HA	[9,117]
	6	PE, HA	[118]
	7	PA, HA	[119,118]
	8	HDPE, HA	[11,120]
LOM	1	Calcium phosphate glass, HA	[111]
SL	1	PPF, TCP	[121]
	2	PPF/DEF, HA	[122]
FDM	1	PP, TCP	[105]
	2	PCL, HA	[109]
3DP	1	PLGA, TCP	[123]

Table 6

Composites fabricated by various RP techniques for bio-medical applications