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Polymers Used for 3D Printing

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Abstract: *3D printing or "additive manufacturing (AM)" is quickly gaining massive attention and adoption as a very flexible and efficient processing technique that is applicable to metal, plastic, concrete, ceramic, and other construction materials. 3D printing is widely used in producing polymeric models and components as several processable polymers are available to choose from.*

There has been a significant growth of 3D printing and several platform technologies have emerged from several prototypic models to customizable models of working parts. Natural fibers are widely used along with their composites in virtually all application areas in this day and age. It is important to enhance natural fiber properties to replace synthetic fibers. In this review paper, we will deeply explore 3D printing technologies and different polymers that can be used to reduce production cost and carbon footprint. The key here is to reduce dependence on synthetic polymers and increase the use of biodegradable polymers.

Keywords **– 3D printing, additive manufacturing, polymers, natural polymers, synthetic polymers, biodegradable polymers**

Chapter 1 - Introduction

3D printers have been dramatically accessible and grown over the past decade for both domestic and industrial uses. There has been a rise in global sales of 3D printers, 3D printing services, and 3D printing materials for consumer and industrial scale by around 33% over the past three years to $4.1 billion in total in the year 2014 (Caffrey et al., 2016). The expiry of early patents for additive manufacturing processes and devices is the major driver behind this growth. A lot of start-ups have developed 3D printers and pushed innovation for their design approaches while lowering the cost, i.e. under $1000 for entry-level machines. Currently, over 300 manufacturers are producing desktop devices that are relatively cheap and units cost under $5000 in this category (Chuang, 2016).

3D printers are placed not only in different industrial settings for this rapid evolution, but also in public libraries, K-12 schools, laboratories, and university classrooms, and even in homes more and more commonly thanks to rapid evolution of 3D printing. Some experts even predict a future where huge digital inventories will be handled by virtual stores, so customers can produce complex or simple products at unexpectedly affordable prices. For 3D printing, biomedical applications are some of the major drivers of growth in a rapidly growing technology. We are already witnessing 3D printing in dental laboratories and clinics. Additive manufacturing is on the verge of exponential growth. Here, we discuss an overview of polymeric materials used in 3D printing while focusing on the growth in materials used and device technology. Filament or powdered polymers are combined to drive significant advancements in this technology.

The term "3D Printing" was related to a detailed additive processing approach initially. Now it is widely combined with a wide-scale use of 'additive manufacturing'. The computer-aided prototyping was enabled and conceived as a process to enable engineers to transform virtual concepts reliably and efficiently to prototypic and physical elements. The significant physical models production are the important enablers for 3D printing while advancements and improvements in materials are going through a rapid change for 3D printing which is being used to generate end-use and tailor-made parts which are supposed to spur significant growth.

The nimble creation of forms making molds is a great aspect of existing printing markets which are indeed used for mass fabrication of production components. The process of additive manufacturing is effective for producing customized, limited-running products having complicated structure. Figure 1 illustrates the use of sheet and filament forms in 3D printing while using powdered polymeric materials. The active polymerization of resins is also used in various additive manufacturing techniques.

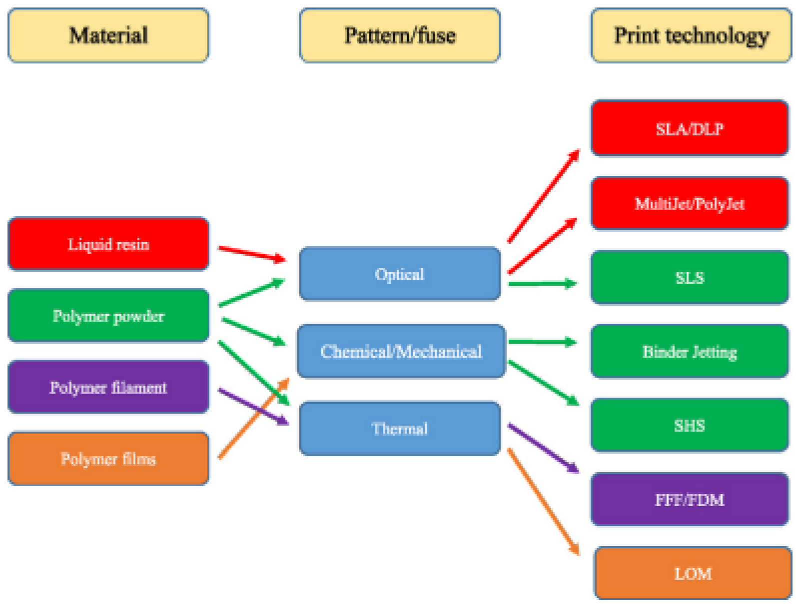


Figure 1 – Use of Polymer/Monomer materials in Print Technology with different patterns (Stansbury **&** Idacavage, 2016)

Dentistry was the first to adopt photo-polymerization and it has remained dependent on it heavily and it is obvious that light-based or UV approaches will be used as dentistry makes the most of this evolving technology. Using 3D printing for photo-curing is especially beneficial for various reasons, such as smooth part surfaces which don't need finishing processes most of the time, high levels of resolution building, solid z axis strength because of chemical bonding around the layers, ability for printing transparent objects, and possible fast builds. The original approach of building layered materials was ultimately based on photo-polymerization. In 1986, 3D printing was first used commercially when stereo-lithography apparatus (SLA) was first introduced in 3D systems where detailed photosensitive liquid resin areas go through the exposure with a rastered UV layer through localized polymerization (Stansbury **&** Idacavage, 2016).

A platform is initially built to handle overhanging structures and anchor the piece. It is possible to modify the exposure of the x/y axis in each different layer as the z axis evolves drastically in the building process. The platform is reduced by 50m after each layer for higher resolution and 200m for lower or standard resolution requirements. The extra resin is reusable and it is drained after completing the part. The extra resin is washed off in the formed parts and the supporting structures are removed manually. There is a possibility to add a post-curing step as per the resin material to drive photopolymer conversion. Usually, the finished parts look like molded parts and they come with small roughness on the surface. Final surfaces are treated with primers, sealants, metallic coatings, or paints for finishing.

Additive manufacturing processes involve the use of various polymerized materials. The "polymer matrix components'', "pure polymers'', "nano-composites'', "polymer ceramic composites'', and "fiber-reinforced composites" are some of the materials that are widely used in this process (Mohan et al, 2017). The "Natural Fiber Reinforced Composite (NFRC)" filaments have garnered a lot of attention in additive manufacturing as these are highly biodegradable and economical materials and they are also less harmful to the environment (Peças et al., 2018). Malaysia had targeted 40% carbon emission reduction by the end of 2020. According to "Roundtable on Sustainable Palm Oil (RSPO)" report on carbon footprint, it is observed that there was 18% rise in carbon emission in the year 2017 since 2014, i.e. from within 350,000 metric ton to 420,000 metric ton carbon emission which should be considered (Kulim carbon footprint report, 2016). Synthetic fibers which are used in manufacturing are harmful to the environment as they raise carbon footprint in their whole lifespan (Meng et al., 2018). On the other hand, PLA and other biodegradable polymers are less harmful to the environment and are an ideal substitute for their petroleum-based counterparts (Choi et al., 2018).

Initially, synthetic fibers were used in additive manufacturing. According to Goh et al. (2019), reinforcements in pure polymers can improve the mechanical properties of composites which are 3D printed. There are some other studies supporting the basis of synthetic fibers for reinforcement. Glass fibers were reinforced with ABS by Zhong et al. (2001) as a matrix with FDM approach and got better strength with ABS-glass fiber as compared to pure polymer. Tekinalp et al. (2014) used ABS to reinforce carbon fibers and found better results with increased tensile strength and modules in fiber content, which is higher than old compression molding.

Chapter 2 - Discussion

2.1. 3D printing of polymer matrix composites

Components can be produced with complex geometries as per the designs by using 3D printing for rapid manufacturing and tooling. Because of limited functionalities and mechanical properties of pure printed polymer parts, it is highly recommended to come up with printable polymer composites with top quality 3D printing and there are several benefits for fabricating composites, such as customized, cost effective, and high precision geometry. **Wang et al. (2017)** review 3D printing with polymer composite materials and performance and properties of composite parts after 3D printing along with their applications in electronics, biomedical, and aerospace engineering. Several widespread 3D printing techniques have been introduced, including selective laser sintering, fused deposition modeling, stereo-lithography, inkjet 3D printing, and 3D plotting. They focused on the performance of fiber-, nanomaterial- and particle-reinforced polymer composites. In the end, they found major limitations to promote further 3D printing research.

Liquid polymer materials or polymers with low melting point are used most commonly in 3D printing because of their low cost, low weight, and flexibility in processing. Some of the challenges with 3D printed polymers are lack of functionality and mechanical strength for wide applications despite having geometric complexity. Combining several materials for functional values and mechanical properties is a great way to fix a lot of issues. Developing composite materials supported with printers available have garnered huge attention over the years. A lot of new composite materials reinforced with nano-materials, particles, or fibers have achieved promising results.

Table 1 – 3D Polymer Printing Techniques and Prototyping

Technique	Starting Materials	Polymer Materials	Applications	Resolution (µm)	Pros	Cons
FDM	Filament	Thermoplastics (ABS, nylon, PC, ABS)	Deposition and extrusion	50-200	Strong, economical, multi-material	Clogging in nozzle, anisotropy
SLA	Photopolymer in liquid form	Photocurable resin	UV curing and laser scanning	10	High quality printing	Costly, cytotoxicity, material issues
3DP	Powder	Any material in powdered form, requires binder	Binder printing	100-250	Affordable, easy removal, supports various materials	Binder contamination, binder jet clogging
SLS	Powder	Polyamide powder and PCL	Heat sintering and laser scanning	80	Strong, easy to remove	Powdery surface, costly
3D	Plotting paste or liquid	Hydrogel, PLA, PCL	UV-assisted or heat-based curing	5-200	Capable of soft materials, high quality printing	Slow, minimal mechanical strength

Source - Wang et al. (2017)

2.2. Polymers for 3D Printing and Customized Additive Manufacturing

3D printing or Additive Manufacturing (AM) turns virtual 3D models made with computer-aided design (CAD) into real objects. AM creates objects one layer after another without using machining or molds, i.e. by using digital slicing of 3D scan, CAD, or tomography data. Additive manufacturing provides customized object fabrication with digital information retrieval and storage. The ongoing movements from prototyping to quick manufacturing add up to new challenges for material scientists and mechanical engineers at the same time. By far, polymers are the most prevalent materials for additive manufacturing. **Ligon et al. (2017)** focuses on developing advanced polymers and polymer processing for 3D printing. There are different techniques of 3D printing, such as aerosol and inkjet 3D printing, powder bed fusion, stereolithography, and 3D bioprinting. Some of the polymers used in 3D printing are thermosets, thermoplastics, hydrogels, elastomers, polymer blends, functional polymers, and biological systems. Table 2 covers additive manufacturing (3D printing) techniques with some pros and cons.

Table 2 - Comparison of AM Procedures and Pros and Cons

Techniques	Resolution (μm)	Materials	Pros	Cons
Exposure of Vat Photopolymerization from above	50-100	Epoxides/acrylates	Accuracy and superior surface quality	Lagging in mechanical strength
Exposure of CLIP from lower end	25-100	Epoxides/acrylates	Low volume of initial vat, high speed in building, improved surface quality	Lacks in mechanical properties and uses low-viscosity resins
Multiphoton Lithography	0.1–5	acrylates	High quality printing	Limited properties and slow build speed
SLS	50–100	PEEK, PA12	Low anisotropy and ideal mechanical strength	Unsintered powder cannot be reused and rough surfaces
FDM	100–150	PLA, ABS, HIPS, PC	Cheap materials and machines	Hot process and rough surfaces

Source - Ligon et al. (2017)

2.3. 3D printing for polymer/particle-based processing

Additive manufacturing or 3D printing is a promising technology for layered micro-manufacturing and rapid tooling. However, in the domain of 3D printing, great fundamental research and study is required to come up with major manufacturing systems and combining multi-materials for multi-functionality and multi-scale behaviors. Particles with diverse electrical, thermal, mechanical, optical, and other properties among these materials can be applicable widely in thermal packaging, structural composites, optoelectronics, electrical devices, energy storage, biomedical implants, purification, and filtration.

Xu et al. (2021) covered the basics of 3D printing along with important factors in particle- and polymer-based printing. They brought forward a lot of printing mechanisms like “powder bed fusion-based”, “material extrusion based”, jetting based, and “vat polymerization-based” mechanisms and other 3D printing approaches that are underrated with some processing parameters, pros and cons, and future challenges in each technique. While discussing 3D printing, they also explained widely-used particles and polymers like viscous inks, liquid monomers, stiff filaments, gels, and loose pellets having nano-scale and microscale particles.

2.4. Filament Extrusion and 3D Printing

Solorio-Rodríguez & Vega-Rios (2019) analyze 3D printing of poly (lactic acid) (PLA) amorphous blend with “Poly(Styrene-co-Methyl Methacrylate)”. The amorphous PLA blends are used for making “PLAx/poly(S-co-MMA)y blends” from 50% “PLA50/poly(S-co-MMA)50”, 75% “PLA75/poly(S-co-MMA)25” and 90% “PLA90/poly(S-co-MMA)10”. The filament extrusion is made with pellets of “PLAx/poly(S-co-MMA)y” blended at 195°C with a prototype extruder. The “fused deposition modeling (FDM)” is done for 3D printing at the same temperature and with the feed rate of 40mm/s. Additionally, the “PLAx/poly(S-co-MMA)y” blends with thermogravimetric curves featured a little bit of thermal decomposition within 0.2% mass loss during 3D printing and filament extrusion.

As compared to amorphous poly (lactic acid) and poly (S-co-MMA) blends, thermal decomposition is lower. On the other side, there is higher "Young's modulus (E)" in the PLAx/poly(s-co-MMA)y blend as compared to amorphous PLA and is closer to "PLA90/poly(S-co-MMA)10". There are better properties in "PLAx/poly(S-co-MMA)y" blends about amorphous PLA with rheological and mechanical characterization.

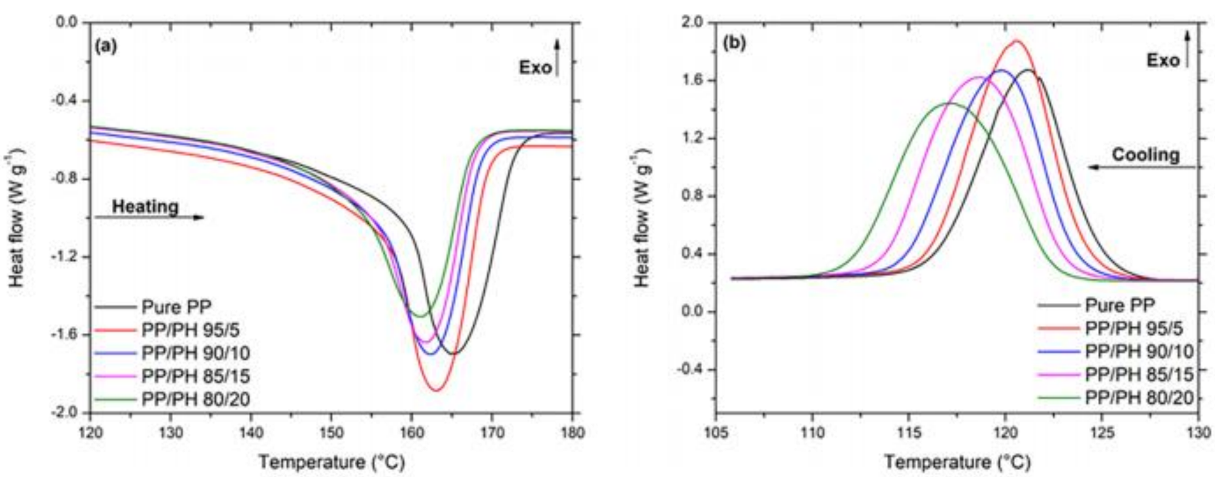
2.5. MEAM with Polypropylene and Hydrocarbon Resin Blends

The MEAM or "Material Extrusion-based additive manufacturing (MEAM)" is one of the most prevalent additive manufacturing (AM) techniques. Along with the significant growth in MEAM, more materials can still be developed and printed. A well-known thermoplastic, isotactic polypropylene (PP) goes through constant volume contraction and crystallization. It can cause the buildup of remaining strain in PP elements when it is routed with MEAM process and it causes deprived hold to mechanical performance, printing platform, and arithmetical lenience. **Das et al. (2019)** investigated the effects of several compositions of hydrocarbon resins with low molecular weight in PP. The crystallization, thermal behavior, printability, and morphology of blends have been considered for this study.

- **The concept of "Differential Scanning Calorimetry (DSC)"**

This procedure was conducted to analyze the crystallization of polypropylene blends in ideal circumstances for MEAM aspects. From the next heat cycle of "non-isothermal DSC '', the melting and "cooling profiles" for "PH/PP" blends are defined in Figure 2. Both blends and pure PP have homogenous melting points in heating scans and they suggest no individual "crystalline phases" in blends and they likely come from solubility of resins. In melting endotherms, the temperatures are lowered with rising resin in the blends. Elevating resin levels in blends for both "PP/PH" and "PP/FH '' blends raise the driving force in comparison to pure PP behind crystallization and the crystallization window is expanded for the blends. Considering these results, the crystallization is delayed by the resins and it is corroborated further by the peak crystallization and peak melting temperatures and melting enthalpy and "crystallization of pure PP/PH, PP/FH, and PP blends''.

Figure 2 – (a) Melting endotherms of DSC for various PP/PH compositions (b) Cooling exotherms of DSC for various PP/PH compositions

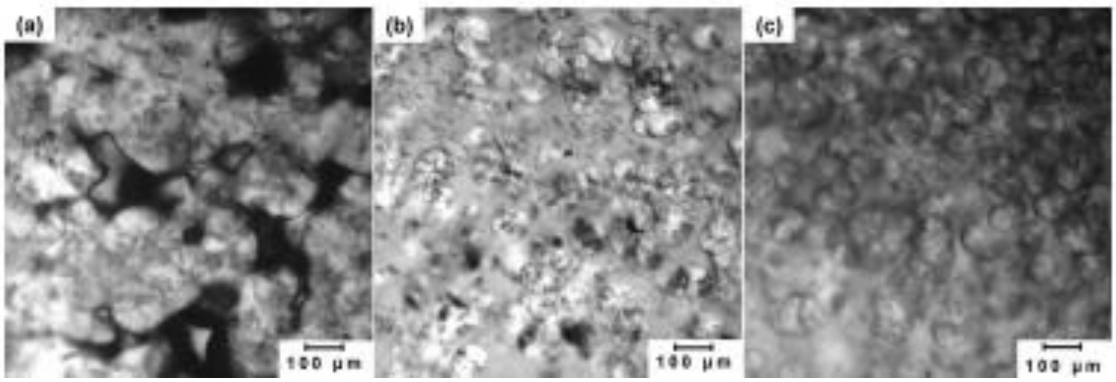


Source: Das et al. (2019)

- **Hot Stage Polarized Light Microscopy (HS-PLM)**

On a hot-stage light polarized microscope, isothermal crystallization tests were done with the blends of hydrocarbon/PP resin to test the resin addition impact on various conditions of crystallization at temperatures and crystallization was expected to take place during the process of printing. The process of printing is truly non-isothermal and there are further challenges in thermal history in developing "morphology analysis". The key here is to know the specific effect of resins on "morphology" to figure out the changes in morphology of printed components between the examined works. The "Compositional Extremes" are considered to analyze the range of effects that have been expected. Figure 3 presents pure PP micrographs and 80/20 blends with hydrocarbon resins. The morphology is affected with hydrocarbon resins by cutting down the spherulite sizes and crystallization process. It shows the change in results of spherulite sizes from the events of nucleation conducted at various times at the right temperature.

Figure 3 – Heated optical polarized micrographs for (a) pure PP, (b) 80/20 PP/PH blends, and (c) 80/20 PP/FH resin blends collected after cooling from melting at 120°C which is held isothermal

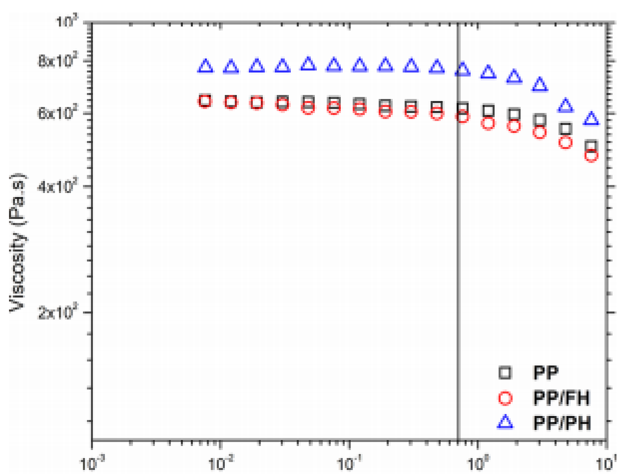


Source - Das et al. (2019)

- **Shear Rheology of "Pure PP/FH and PP/PH Blends"**

On compression-molded 80/20 and pure PP blends, shear rheology was conducted with hydrocarbon resins. The rheometer was used to collect and correct raw data with single-point correction (Carvalho et al, 1994). Both blends and PP feature shear-thinning and classical behavior given in Figure 4 with shear rate of around 0.7 and shear thinning. Hence, the longest time for relaxation is around 1.4s for materials, irrespective of shear rate at the occurrence of shear thinning at the onset. The printing speed is tuned to tie the scale this time with the printing process during MEAM in a way that the ratio of relaxation time scale or Deborah number (De) to the time scale of the process is ~1. It is important to relax the blended materials properly during the process of printing in a way that effects induced with orientation don't play a vital role in crystalline models.

Figure 4 – Shear thinning with PH and FH resins of PP and 80/20 blends at 180°C under TA ARG2 rheometer. Vertical line shows shear thinning at 0.7 s-1

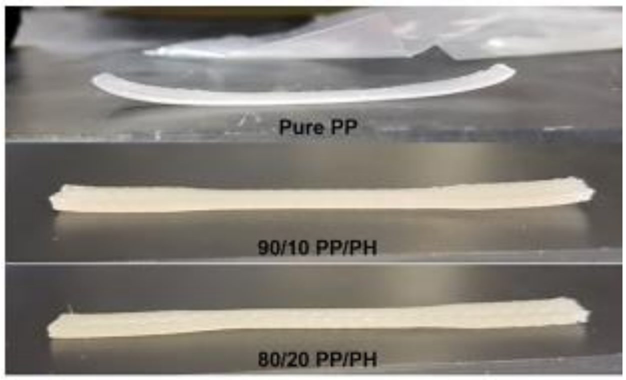


Source - Das et al. (2019)

- **Printing Experiments with Warpage and Adhesion**

PP blend was used for printing experiments to set up the baseline to compare the same with PP/resin performance. There is a risk of poor dimensional accuracy and huge warpage with pure PP. On the other side, there was a great improvement in printing tests with PP/PH blends with dimensional stability and low warpage (Figure 5) for 80/20 and 90/10 PH blends. It is possible to have improvements in printing with PP/FH blends but it is not possible to eliminate warpage completely, even though it cuts down drastically as compared to pure PP print. The printed part was lifted off to measure the warpage from the printed bed when the printing process finishes.

Figure 5 – 80/20 (PP/PH), 90/10 (PP/PH) and pure PP blends after printing. There was a huge warpage in pure PP parts due to a rise in resin content.



Source - Das et al. (2019)

2.6. Additive Manufacturing with Poly(Caprolactone)/Epoxy Blends

Dorigato et al. (2020) developed a combination of thermosetting/thermoplastic systems with Poly(Caprolactone) or PCL structure produced and designed with epoxy matrix and fused filament fabrication. The fracture toughness, mechanical strength, and heating capabilities of Poly(Caprolactone)/Epoxy (PCL-EP) blend were compared with the strengths of melt mixed EP-PCL blend. In the EP-PCL blend, the fine PCL dispersion caused significant toughening effect while there is an independent behavior in the 3D EP-PCL structure in two phases and progressive yielding followed the fracture propagation in epoxy of PCL domains. The PCL phase expressed its complete potential with this peculiar EP-PCL (3D) behavior as the absorber of energy under impact situations. Toughness tests the crack and propagates the same in the phase of epoxy during fracture as noticed in the optical microscopic images. The PCL played its role for absorption of energy with deformation of plastic. With the PCL in the 35% blends and discrepancy in constituents' mechanical properties, there was limited efficiency of both systems.

2.7. Properties of 3D Printable "PLA/PBAT Blends" and "Nano Talc Composites"

There has been widespread use of biodegradable PLA filaments in 3D printing and "fused deposition modeling (FDM)" technology. PLA is known to have low thermal resistance and sturdiness affecting printability and limiting its industrial use cases. **Prasong et al. (2020)** compounded PLA with poly(butylene adipate-co-terephthalate) blend with 0-40 wt% and varied nano talk content at twin screw extruder of 0 to 40 wt%. The capillary rheometer is used to re-extrude the filaments. The PLA/PBAT or "Poly(lactic acid)/Poly(butylene adipate-co-terephthalate)" blend and filaments were 3D printed with FDM technology. The researchers tested the rheological behavior, morphology, surface roughness, thermal characteristic, and mechanical strength of 3D printing of blends as well as their composites. Composites and complex viscosity of blends was increased with the rise of nano-talc and PBAT contents.

The crystallization temperature is enhanced with nano talc and coefficient of expansion of volume is reduced on the composites. It was observed that composites and PLA/PBAT blends were good in both dimension stability and printability of 10-30 wt% of PBAT and 10wt% of nano talc. They could print composite filaments at 75^{o} angles without a supporter in the overhang test. The roughness of the surface is improved from vertical samples by having nano talc. The composites and tensile strength were reduced in the blends and elongation rose at the break when nano talc and PBAT contents were improved. Tensile strength can be reduced with agglomeration of dispersed PBAT stage and less adhesion was observed between the matrix and nano talc. It is worth noting that the 3D printing composites had great elongation at 410% of breakup by adding 1 wt% of nano talc. Hence, the PLA/PBAT ductile printable blend and the composites of PLA/PBAT-based nano talc can be made with commercialized potential.

2.8. Additive Manufacturing for Acoustic Panel

Natural fibers and composites are used widely in virtually all applications in this day and age. It is important to improve the properties of natural fibers to contend with synthetic ones. **Sekar et al (2019)** discuss additive manufacturing as a novel approach to make acoustic panels with composites of natural fibers with improved acoustical and mechanical properties. It will be an alternative to synthetic acoustic absorbers in acoustic uses with biodegradable composite panels. They also cover the polymer matrix of PLA and its benefits and types of natural fibers to reinforce acoustical and mechanical properties. They also elaborated the filaments based on natural fibers in acoustic panels and additive manufacturing made of natural fibers available. They present the benefits of additive manufacturing and its uses to come up with novel acoustic panels which are based on agricultural waste.

2.9. 3D Printing of Polylactic Acid /clay Nanocomposites

Coppola et al (2018) investigated the use of silicate-reinforced and layered PLA in additive manufacturing. They studied the effect of temperature in the process of 3D printing of "PLA/clay nanocomposites". A twin screw extruder is used with 4032D and 2032D PLA grades with 4wt% of layered silicate. They produced the PLA/clay and PLA feedstock filaments with the diameter of 1.75mm with a single screw extruder. They conducted 3D printing of prismatic and dog-bone specimens with FDM technique at varied temperatures that were raised from melting temperatures. They characterized PLA/clay and PLA specimens with "thermo-gravimetric analysis (TGA)", "differential scanning calorimetry (DSC)", "dynamic mechanical analysis (DMA)" and tensile tests.

Additionally, they tested morphology of 3D printed samples with contact angle and optical microscopic dimensions. The diverse matrix of the polymer and the resultant nano-composite morphology predisposed the properties of 3D printed samples. There was a rise in storage modulus in PLA/clay and DMA filaments at ambient warmth and over the glass change as compared to clean PLA strands. In addition, thermal stability was also increased with the presence of nanoclay as defined by TGA and it worked as a nucleating agent.

The researchers observed different behavior with rising temperature in printing for 3D printed specimens for the two PLA grades and nano-composites. There was high elastic modulus in 3D printed nano-composite specimens as compared to clear PLA samples. But there was a rise in elastic modulus for PLA 4032D+C30B grade at rising temperature while it decreased slightly for PLA 2003D+C30B grade. Diverse nano-composite morphology and macromolecular structure can explain this difference in behavior.

Chapter 3 - Related Studies

There is a lack of research in 3D printing of composites reinforced with natural fiber which is extracted from plants and fruits. Stoof & Pickering (2017) tested 3D printing of composite reinforced with natural fibers. They have 3D printed the composite successfully by reinforcing hemp and harakeke fibers using a polymer matrix of PLA. They found raised tensile strength with 10% fiber of hemp as compared to polymer matrix. When fiber content is increased, tensile strength starts declining. Tensile strength was reduced for 10% fiber with harakeke fibers initially. Later on, tensile strength rose for 20% of fiber (Stoof & Pickering, 2017). Mazzanti et al. (2019) discussed the research studies on nano-fiber composites after 3D printing and the factors affecting mechanical strength. It is observed that mechanical properties are improved in certain cases with the rise in reinforcements.

They also found that the rise in natural fiber to PLA reduces the composite strength but its stiffness has no effect. Elongation and impact strength is also reduced by adding natural fibers. It is also observed that mechanical properties are not increased dramatically on an overall basis in comparison to pure polymers. It is possible to further improve the mechanical strength of composites after 3D printing by improving filament diameter, nozzle diameter, infill geometry, printing rate, melting warmth, infill thickness and geometry, etc. It is observed that a 3D printed composite surface has cracks, gaps, and pores on 3D printed composites made of natural fiber. The formation of gap, crack, and pore is known to be a limitation in several studies and research about 3D printed composites reinforced with fiber (Mazzanti et al., 2019). Some of the research and earlier studies on 3D printing using polymers on natural fillers are illustrated in Table 3.

Table 3 – Other studies on 3D printing with polymers and fillers

Polymer used	Natural filler composites	Studies and their purposes	Formation of void (crack, pore, gap, if any)	Reference
PLA	Flax and Bamboo	Investigation of length over dia ratio of fibers	Yes	(Depuydt et al., 2019)
PLA	Harakeke and hemp	3D printing of natural fibers	Yes	(Stoof & Pickering, 2017)
PLA	Wood	Testing the thickness layer effect of printing on mechanical properties and water absorption	Yes	(Ayrilmis et al., 2019)
Polyethylene	Thermomechanical pulp	Testing polyethylene-based filament for additive manufacturing	Yes	(Filgueira et al., 2018)
PHB	Sawmill	Composite warpage by adding fillers	Yes	(Vaidya et al., 2019)
PLA	Sugarcane	Study on orientation of printing on mechanical sturdiness of composites	Yes	(Liu et al., 2019)
Polypropylene	Harakeke and hemp	To investigate natural fiber-based filaments of polypropylene	Yes	(Milosevic et al., 2017)
Polyurethane	Wood flour	Mechanical and rheological properties of composite	Yes	(Bi et al., 2018)
bioPE	TMP	Discussion of composite's mechanical properties	Yes	(Tarrés et al., 2018)

The formation of void in 3D printing can be beneficial in acoustic applications as perforation is needed for acoustic devices on the surface for its proper absorption. Currently, mechanical properties, physical properties, rheological properties and warping, water absorption, and morphology have been tested. Additive manufacturing was started with pure polymers which are made of various monomers or small molecules. Polymers are formed by combining monomers with a polymerization process. Polymers are categorized on the basis of thermal response, occurrence, formation mode, physical properties, and online structures. Several polymers can be used in composite as matrix, such as polypropylene (PP), polyester, polyethylene (PE), polyurethane (PU), polycarbonate, and polystyrene.

Fused deposition modeling (FDM) has a working temperature of over 300^{o}C due to which only a few polymers can be used in additive manufacturing (Mohan et al., 2017). Thermoplastic polymers can be molded over the given temperature limit and turned solid when it is cooled down (Pucci, 2018). Some of the best examples of these polymers are polystyrene, polypropylene, polyethylene, PVC, nylon, Teflon, acrylic, and "acrylonitrile buta-styrene (ABS)". Petroleum-based polymers cannot be used as they raise carbon footprint (Narayan, 2011). This way, only PLA and PHA are the biopolymers that can be used but PHA can increase the production cost (Możejko-Ciesielska & Kiewisz, 2016). Rodríguez-Panes et al. (2018) produced samples with PLA and ABS with FDM AM process and found higher tensile strength, rigidity, and bonds between PLA layers in specimens which are made with PLA. Hence, PLA is found to be the best suited polymer for 3D printing.

PLA is thermoplastic polyester and is extracted from raw materials like corn, rice, and sugar beets. It is known for better compatibility and renewability than other biodegradable materials (Abd Alsaheb et al., 2015). As a polymer matrix, PLA is non-toxic (Gonçalves et al., 2017) and is reinforced with natural fibers that make it more economical and effective for several applications (Zhao et al., 2011). It is also an eco-friendly polymer with higher degradation when it goes to landfills and costs less energy in the production process. Bioplastics cause less carbon footprint as compared to traditional plastics (Gironi, F.& Piemonte, 2011). Overall, PLA filaments can be reused and recycled with some strength (Math et al., 2018). But pure polymers have some drawbacks. PLA is known to have low impact strength and is naturally brittle (Daver et al., 2018). To deal with this issue, polymer-reinforced fibers can be helpful in several applications for lighter weight, high durability, and cost-savings (Yashas Gowda et al., 2018).

Chapter 4 - Conclusion

Poly(lactic acid) or PLA has turned out to be an effective polymer as a matrix because it is non-toxic, biodegradable, eco-friendly and recyclable. It is possible to reinforce with natural fibers as per the availability and requirements. Best compounding techniques can be used to produce composites and turn them into filaments with the right spinning techniques. 3D printing can be done on filaments reinforced by natural fiber with FDM technology. Minor voids can be formed in 3D printed composites between deposition lines. Minor range of pores is needed for sound absorption making void formation essential.

With the expansion of 3D printing, several practical factors like material costs, processing costs, production volume and speed, electricity costs etc. are now considered well apart from the conventional processes. It is also worth considering the performance, properties, recycling potential and lifespan of printed parts. It will definitely be worth looking forward to 3D printing living up to its hype for bringing the third industrial revolution and whether polymer materials would be the cornerstone of this emerging technology with technological advances.

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