

Additive manufacturing of natural fiber reinforced polymer composites: Processing and prospects

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ABSTRACT

Throughout the world there have been alarming concerns over the use of nonrenewable resources during manufacturing of goods and associated environmental legislations. Therefore, the use of natural materials and fabrication of composites therefrom, particularly, development of natural fiber reinforced polymer composites is gaining significant attention. Although natural fiber reinforced composites (NFRCs) show strong application prospects, various materials and processing related challenges needs to be addressed to achieve long-term stability and performance. In this review, we attempted to provide an overview of different types of natural fibers, their characteristics and properties enabling them to be used as reinforcing agents in different polymers. Then the unique requirement of fiber surface modification to achieve enhanced fiber-matrix bonding is discussed. The article also discusses conventional processing routes and critical issues associated with NFRCs processing. The use of different additive manufacturing (AM) technologies in processing polymer composites is also discussed. At the end, we have critically analyzed the challenges and opportunities associated with AM of NFRCs.

1. Introduction

Environmentally friendly processes, products and recycling or use of waste are greatly acknowledged not only by scientific community but also by several industries due to mounting concerns over the use of nonrenewable resources. These are critical to the key principles of sustainable manufacturing; namely, reduce, reuse, recycle, recover, redesign, and remanufacture. Environmental legislation such as end-of-life vehicles must be 85% reusable/recycled, 10% used for energy recovery and balance for landfills implemented in Europe since 2015 is a very good example to address these environmental concerns [1]. Extensive research is underway at various parts of the world to meet environmental concerns by exploiting materials and composites prepared using renewable resources [2]. In this context, composites comprising polymer matrices and natural fibers are of great interest which can provide desirable properties and performance at affordable cost. Although natural fiber reinforced composites (NFRCs) show strong future potential

and prospects, various materials and processing related challenges needs to be addressed to achieve long-term stability and performance. Currently, several synthetic polymers are being used as matrices to fabricate NFRCs, which find applications in automotive, electronic, packaging, construction and biomedical sectors [3]. Natural fibers in these composites provide several economic and environmental benefits as they are abundant, recyclable, biodegradable and more importantly they are relatively inexpensive than synthetic reinforcements such as glass fibers [3]. Recently there has been growing interest on thermoplastic-based NFRCs for high-performance engineering applications [2,3]. However, these non-biodegradable synthetic polymers pose significant disposal problems and therefore, complete environmental compatibility of NFRCs is still a great challenge. In this context, the best approach would be to produce NFRCs using biodegradable polymer matrices which are produced using non-renewable/renewable resources or current non-biodegradable polymers produced using renewable biological resources [4,5]. However, such bio-composites are not popular

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due to inadequate mechanical, thermal and other physical properties [6].

The main purpose of using natural fibers in polymer matrix composites is to reduce feed stock material cost, and to achieve high stiffness-to-weight ratio, recyclability, biodegradability, thermal insulation, and CO₂ neutrality compared to their conventional counterparts that include glass fibers and carbon fibers [7]. Although NFRCs properties, in some cases depending on the matrix and fiber combination, are inferior to composites made using synthetic reinforcements they are gaining significant importance due to above benefits. Furthermore, the production of natural fibers always require less energy (9.55 MJ/kg for flax) compared to synthetic fibers such as glass fibers (54.7 MJ/kg) [8]. The authors of this study [8] also compared complete life cycle of natural and glass fiber reinforced composites, and revealed that NFRCs enable incorporation of high amount of natural fibers thus reducing the overall consumption of synthetic polymer matrices, light weight and energy recovery after end of life incineration. Several natural fibers such as hemp, wood, kenaf, jute, rice husk, flax are being used to reinforce thermosetting polymers (Epoxy, Urethane, Vinyl Ester, Phenolic, Polyester, Polyimide, Polyurethane (PU)) [9,10], and thermoplastics (Polyethylene (PE), Polypropylene (PP), Nylon, Polycarbonate (PC), Polyvinyl chloride (PVC), Polyether-ether ketone (PEK), Acrylonitrile-butadiene-styrene (ABS)) polymers [11,12] and elastomers [13]. Thermoplastics offer better design flexibility and simple processing techniques compared to thermosets and elastomers with complex cross-linked structures. However, relatively less research has been reported on the use of agricultural residues such as soy hulls, pineapple, banana leaf fibers as reinforcement in these polymer matrices. Since majority of natural fibers become unstable at temperatures ≥ 200 °C, matrices that required high processing temperatures are not suitable to manufacture NFRCs [14].

Recent forecast indicates that the global market for NFRCs grow at a compound annual growth rate (CAGR) of 11.8% during the period 2016–2024 [15]. In 2016 the market size was valued at USD 4.46 billion with dominating consumption from construction segment (56.0%) [15]. In automotive industries several light-weight components such as door panels, dash boards, headliners, and seat backs, are currently being manufactured using NFRCs based on wood, hemp, flax, cellulose with ~20% lower cost than conventional composites. Variety of other products such as laptop/mobile cases, bicycle frames are also popular. While increased awareness about environment-friendly, biodegradable, recyclable products has positive influence on the market growth, challenges such as supply logistics, moisture sensitivity and weak interfacial bond of NFRCs are potentially detrimental to market growth. Another important factor is natural origin of these fibers, which result in inherent variations in their properties leading to large variations in properties, long-term stability and durability of NFRCs [16]. Among most popular natural fibers (wood, flax, cotton, hemp and kenaf), wood found to dominate the market and predicted to continue its dominance till 2024 due to its low cost and supply logistics. NFRCs based on kenaf fiber are popular in construction, food packing, oil and chemical sectors. Although inorganic matrices account 43.4% of market share in 2015, it has been estimated that natural polymer matrices (25.1% in 2015) will have relatively more growth and demand compared to synthetic polymers during next five years.

2. Natural fibers composites, properties and their applications

2.1. Types and characteristics of natural fibers

Natural fibers are often classified based on their origin such as animal fibers, plant fibers and mineral fibers [17]. A major difference between animal and plant fibers is that the former consists of protein as major constituent while the latter composed of cellulose. The fibers derived from plants can be categorized based on their origin as shown in Table 1. From Table 1 it can be seen that natural fibers tend to be

light-weight with densities between 1.1 and 1.6 g/cm³ and are low-cost as their price ranges from \$0.25 to \$4.2/kg that makes them suitable materials as filler in engineering and non-engineering applications. Contrary to price and density, the cellulose content, and cellulose crystallinity vary as the natural fiber type changes from bast, leaf, and fruit to agricultural residue. For instance, kenaf, bast fibers have cellulose crystallinity of 50–90% whereas the sisal fiber that is obtained from leaves has cellulose crystallinity of 50–70%. Often bast fibers are used to achieve high mechanical properties (modulus, strength, stiffness) of products such as automotive components, or fiberboards [18]. Plant fiber constituents typically include cellulose (60–80%), hemicellulose and lignin (5–20%), while the rest constitutes waxes, pectin, moisture (up to 20%) and water-soluble organic components, which found to vary widely depending on their type and origin [19]. More details on composition of natural fibers can be found in Ref. [20].

It is known that natural fiber is a composite composed of rigid crystalline cellulose microfibrils in soft, amorphous matrix which is mixture of lignin and hemicellulose. The properties of fibers, and in turn NFRCs properties, depends on its composition, microfibril angle, crystallinity and internal structure [27]. Cellulose, the major component of natural fiber, has strength and stiffness of >2 GPa and 138 GPa, respectively [28]. However, the stiffness of these natural fibers depends particularly on microfibril angle and therefore, fibers with high cellulose content and low microfibril angle are found to provide high reinforcing effect in polymer composites. From various types of natural fiber sources, shown in Table 1, fibers obtained from bast, tend to have higher cellulose content (~30–76 wt%) and lower microfibril angles (2–8°). Other constituents of natural fibers such as pectin and hemicellulose dictate other properties such as water absorption, wet strength, swelling and integration of fiber bundle [29]. Therefore, complete characterization of natural fibers is of utmost importance to achieve desired strengthening in NFRCs.

Important characteristics of natural fibers such as fiber diameter, fiber length and cell wall thickness are summarized in Table 2. It can be seen that natural fibers have wide range of fiber diameters (5–76 μ m), fiber bundle widths (10–1000 μ m) and lengths (1.2–300 mm), in addition to fiber shape, which results in large variations in properties of polymer composites prepared using these fibers. Further, these characteristic variations in natural fibers also pose significant challenges in optimizing manufacturing processes where the fibers are used as reinforcement materials. Therefore, precise feedstock material assessment and control is extremely important to achieve desired performance in NFRCs.

The large variations in natural fiber structure and dimensions, such as fiber density (cell wall-lumen ratio) and microfibril angle (MFA), directly affects their mechanical properties. The mechanical properties of NFRCs depend on inherent mechanical properties of these natural fibers [31]. As shown in Fig. 1a, fibers with high density often exhibit high strength and stiffness compared to those with low density. Similarly, elastic modulus of natural fibers strongly depends on MFA and low MFA results in stiffer fibers, Fig. 1b–c. This is intuitive, as low MFA enable orientation of cellulose fibrils almost parallel to loading axis and therefore can sustain more load leading to enhanced stiffness. However, these low-MFA fibers characteristically exhibit brittle behavior due to their high stiffness. On the other hand, natural fibers with high MFA typically exhibit large plastic deformation and therefore high toughness [32,33]. Other factors that control mechanical properties of natural fibers include fiber diameter and degree of cellulose polymerization. Table 3 provides brief summary of mechanical properties of different natural fibers as well as synthetic fibers. While the properties of synthetic fibers do not vary much, the properties of natural fibers clearly show large variation, within and across different fibers. Such a large variation in mechanical properties of natural fibers can pose critical concerns on overall mechanical reliability of composites made using these fibers. Further, it is not clear whether these mechanical properties (Table 3) were measured on single fibers or fiber bundles, as the

Table 1
Characteristics and composition of natural fibers [2,21–26].

Fiber	Density, g/cm ³	Cellulose, wt.%	Cellulose crystallinity, %	Lignin, wt.%	Microfibril angle, °	Moisture, wt.%	Price, US\$/kg
Bast							
Hemp	1.47	70–74	50–90	4–10	2–6	6.2–12	1.0–2.1
Flax	1.5	64–71	50–90	2.2–2.5	5–11	8–12	2.1–4.2
Jute	1.3–1.5	61–72	50–80	12–13	7–9	12.5–13.7	0.35–1.5
Kenaf	1.5–1.6	31.39	–	9–17	9–15	6.2–12	0.26–0.52
Ramie	1.5–1.6	68.6–76.2	–	0.6–0.8	7.5–8	12.17	1.5–2.5
Leaf							
Sisal	1.45–1.5	66–78	50–70	8–10	10–25	11	0.6–0.7
Pineapple	0.8–1.6	70–82	44–60	8–13	8–14	11.8	0.4–0.55
Abaca	1.5	56–63	–	7–12	20–25	15	0.34
Banana	1.35	44–64	45–55	7.5	10–25	10.71	–
Fruit/Seed							
Coir	1.2	32–43	27–33	40–45	30–49	11.3	0.25–0.5
Kapok	1.3	13–35	–	13–21	5	–	–
Coconut	–	–	–	–	–	–	–
Cotton	1.6	82.7–91	–	0.75	20–30	7.85–8.5	2.1–4.2
Grass/reed							
Bamboo	0.6–1.1	20–60	40–60	21–31	8–11	9.16	0.45–0.5
Switchgrass	1.4	32	–	–	–	–	–
Miscanthus	1.41	38	–	–	–	–	–
Agriculture residue							
Wheat straw	–	38–45	–	12–20	–	–	–
Soy hull	–	41–57	–	8–19	–	–	–
Corn stover	–	38–40	–	7–21	–	–	–

Table 2
Important characteristics of natural fibers [20,26,30].

Fiber	Shape	Dia./width, μm	Bundle width, μm	Length, mm	Cell width/dia., μm
Wood	Rectangular to round	5–50	–	1.2–3.6	10–30
Flax	Polygonal	5–76	40–620	4–140	–
Hemp	polygonal or ribbon-shape	5–40	25–500	8–55	4–60
Jute	Rectangular to Polygon	5–30	25–200	1–5	–
Kenaf	Round to polygonal	12–50	30–247	1.5–11	–
Abaca	Polygonal to round	6–46	10–1000	2–12	–
Sisal	Polygonal to round	4–47	9–460	0.5–8	–
Coir	Round to oval	10–30	50–460	150–300	10–30

properties of fiber bundles can be significantly different from those of single fibers. The data shows that natural fibers have more or less similar density, but large variations in mechanical properties could be seen. For

example, spider silk found to exhibit extremely high tensile strength between 875 MPa and 972 MPa. Although flax fiber can have highest strength of 1834 MPa its strength can be as low as 343 MPa. Similarly, the elastic modulus of flax covers wide range (8–100 GPa). Overall, it can be said that natural fibers have large variation in mechanical properties and their tensile strength is significantly lower than synthetic fibers. Some of the natural fibers, for example, flax, pineapple, ramie, can cover the elastic modulus of synthetic fibers.

Both processing and properties of NFRCs depends on inherent mechanical properties and other characteristics of natural fibers, which are summarized in Table 4. Some of these characteristics have direct influence on many NFRCs properties such as fiber-matrix bonding, interactions, thermal stability, moisture sensitivity, etc. [35,36]. For example, fiber-matrix compatibility is compromised due to hydrophilicity and hydrophobicity of natural fiber and matrix, respectively, which can reduce mechanical performance of these composites [4,29]. Therefore, variety of chemical and physical methods of fiber modification [29] and addition of coupling agents during processing [35] have been developed.

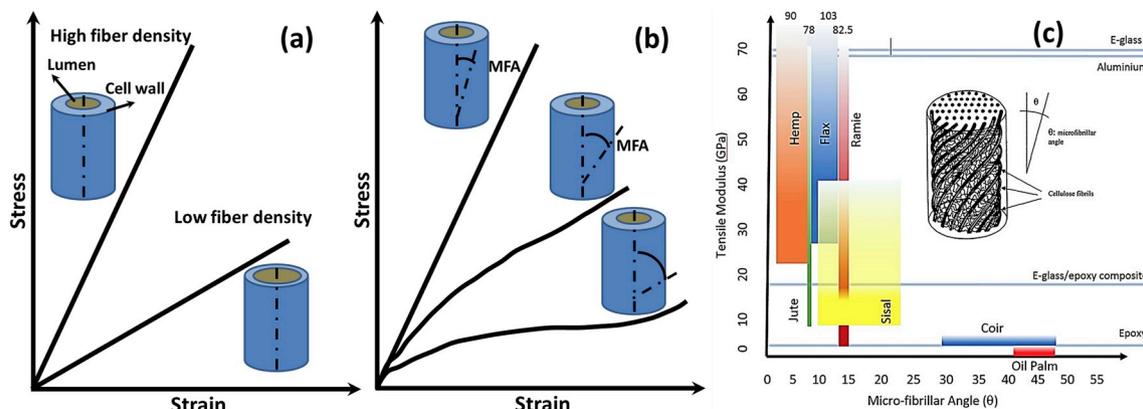


Fig. 1. Influence of fiber density (a) and microfibril angle (MFA) (b) on stress-strain behavior and mechanical properties of natural fibers (adapted from Ref. [23]). (c) Tensile modulus of different natural fibers as a function of their microfibrillar angle [34].

Table 3
Mechanical properties of natural and synthetic fibers [2,20–23,25,26].

Fiber	Density	Elongation, %	Tensile strength, MPa	Young's modulus, GPa
Natural fibers				
Jute	1.3–1.5	1.5–1.8	187–800	3–64
Sisal	1.5	1.9–14	80–855	9–38
Banana	–	1–10	430–914	7.7–42
Flax	1.5	1.2–4	343–1834	8–100
Kenaf	1.45	1.5	215–930	35–53
Pineapple	0.8–1.6	0.8–14.5	170–627	2–128
Cotton	1.5–1.6	2–10	220–840	4.5–12.6
Coir	1.2	30	160–250	3.3–6
Hemp	1.48	1.5–51.4	95–1735	2.8–90
Ramie	1.5	1.2–4.6	290–1060	5–128
Wool	–	25–35	120–174	2.3–3.4
Spider silk	–	17–18	875–972	11–13
Kapok	1.3	1.2–4	45–93	1.7–4
Abaca	1.5	1–12	12–980	12–72
Bamboo	0.6–1.1	3.8–5.8	140–230	11–17
Synthetic fibers				
E-glass	2.5	2.5	2000–3500	70
Aramid	1.4	3.2–3.7	3000–3150	63–67
Carbon	1.4–1.7	1.4–1.8	4000	230–240

Table 4
Summary of important characteristics of natural fiber that can influence processing and properties of NFRCs.

Category	Property
Geometrical	Length, Diameter, Cross-section, Surface shape and structure
Mechanical	Single fiber strength/modulus, Fiber bundle strength/modulus, Poisson's ratio, Flexural properties, Elastic modulus
	Yield strength, Elongation, Fatigue properties
Chemical	Concentration of different constituents, Impurities due to processing and cultivation, Degree of polymerization
Physical	Density, Texture, Coefficient of thermal expansion, Thermal conductivity, Degree of crystallinity, Microfibril angle, Wettability
Thermal	Moisture content, Water absorption, Swelling

2.2. Advantages, properties and applications of natural fiber reinforced composites

Natural fibers are being widely used in different industries as reinforcement in polymer composites and some of the important advantages of these NFRCs include [2,4,8,37–39]:

- First and foremost benefit of natural fibers is environmental friendliness due to their renewability, CO₂ neutrality and biodegradability. For example, 3 ton CO₂/ton of material can be achieved if synthetic glass fiber is replaced with natural hemp fibers [40].
- Abundantly available and harmless residues after enhanced energy recovery by incineration.
- Natural fibers are inexpensive and can reduce overall cost of polymer composites.
- Reduce the use of petroleum based products by replacing them with up to 50% natural fibers in injection molding and more than 50% in compression molding.
- Provide relatively safer manufacturing process and better occupational safety (reduced dermal and respiratory irritation).
- NFRCs manufacturing processes and disposal routes are environmentally benign.
- Natural fibers are soft and therefore increase overall life and efficiency of processing equipment/tool.
- Natural fibers offer best alternative to E-glass fibers as the latter pose disposal issues.
- Natural fibers are light-weight and therefore provide significant weight savings and fuel efficiency for automotive applications

- Some natural fibers exhibit relatively high specific strength, modulus, toughness and ductility than E-glass.
- NFRCs exhibit excellent acoustic absorption properties.
- Effective utilization of agricultural residues generates income and job opportunities.
- Relatively low processing temperature and NFRCs provide good insulation against sound and heat.

Natural fibers and NFRCs also suffer from following disadvantages [17,35,41–43]:

- High moisture absorption (depends on fiber type) leading to swelling, thereby effecting products' performance and reliability.
- Poor wettability (hydrophilic fibers and hydrophobic matrices) of natural fibers often results in weak fiber-matrix interfacial bonding and decreases mechanical properties.
- Some fibers are not compatible with some polymer matrices.
- Large variations in fiber characteristics and properties directly contribute to large scatter in NFRCs properties.
- Readily susceptible to fungal and insect attacks.
- Relatively low degradation temperature and easily flammable.
- Large variations in natural fiber quality/characteristics depending on weather and cultivation conditions (harvesting time, solid quality, fertilization, geographical location, climate, etc.).
- Thermal conductivity of NFRCs is relatively less than glass fiber reinforced composites.
- Complex supply chain, geographical availability.
- Price and supply variations due to weather and crop yield.
- NFRCs are often limited to non-structural components and due to their low thermal stability their service temperature is ≤ 200 °C.

NFRCs become very attractive, after its first production in 1908, in building and automotive sectors primarily due to their light-weight, low-cost and other properties [43]. Several natural fibers such as hemp, sisal, jute, coir, flax, wood, kenaf, bamboo have been used to produce NFRCs with variety of polymer matrices that include thermoset, thermosetting, elastomers and proteins. The fiber and matrix combination primarily depends on the final component, mechanical and other functional property requirements. As shown in Tables 3 and 4, fiber or fiber bundle characteristics and properties have strong influence on quality, production processes and properties of NFRCs. For uniform mechanical properties, primarily for automotive applications, the fiber length and their distribution within the polymer matrix are extremely important. Typically, combination of natural fibers such as flax + kenaf or hemp + sisal with different size distributions are used to achieve desired mechanical performance without hampering molding process [44]. For series production in automotive industries, currently only wood fibers pretreated with acrylates are in use and the process for other fibers (hemp, flax, jute, etc.) is not yet established. Several leading automobile manufacturers such as Audi, BMW, Volkswagen, Toyota, Daimler-Benz, Volvo, Ford use NFRCs for variety of components that include seat back, boot lining, interior door paneling, noise insulation panels, instrumental panel support, engine insulation, and internal engine cover, due to their light-weight and consequent improvement in fuel efficiency and reduction in greenhouse gas emission. For example, banana fiber reinforced composites have been used for under floor protection trim of Mercedes A class [45]. Typical NFRC parts for automotive applications are presented in Fig. 2. Polypropylene and polyurethane-based composites are popular for automotive part manufacturing due to their easy processability, low-density and excellent mechanical properties. Other matrices such as polyethylene, polystyrene and nylon are also widely used. Currently industry is aiming at replacing synthetic polymer matrices with biodegradable matrices such as polylactic acid (PLA) and Poly(butylene succinate) (PBS) reinforced with hemp, cellulose, cotton and kenaf fibers, to manufacture parts like tailgate trim and tire covers [35,46]. Alternatively, these biodegradable



Fig. 2. Typical NFRCs products used in automotive and other applications [49]. [Sculpture and small-scale rotor blade are from Ref. [49] Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium with proper citation].

natural fiber reinforced composites are also used to make wind turbine rotors, laptop and cellular phone covers [46], and kayaks. The properties of such biodegradable composites found to be comparable to polycarbonate-based composites. Therefore, it appears that durable automotive parts can be manufactured using 100% biodegradable materials derived from natural resources. Other applications of NFRCs include packaging, household and furniture, sport equipment, electrical and musical instruments [28], as shown in Table 5. Hybrid composites reinforced with carbon and flax fiber showed excellent vibration damping and mechanical properties as a result they are used to make snowboards, and bicycle frames [17]. Example sporting goods include flax-carbon (25:75) composites for tennis rackets and 80:20 flax:carbon

Table 5
Summary of typical applications of NFRCs in different industrial sectors [compiled from Refs. [25,47,48]].

Industry/Sector	Example parts
Automotive, transport and aerospace	Interior door panels, body panels, seat backs, headlines, dash boards, instrument panel, floor mats, noise insulation panels, engine insulation, engine cover, trunk liners, decking, parcel shelves, spare type covers, spare-wheel pans, automobile and railway coach interior, boats, interior carpets, architectural moldings
Construction and building	Railing, bridge, roof tiles, panels for partition and false ceiling, partition boards, wall, floor, windows and door frames, mobile structures which can withstand natural calamities,
Electronics	Mobile and laptop cases
Sports	Tennis racket, ball, bicycle, frames, snowboards, fork, seat post, boats
Household	Tables, chairs, fencing elements, door panels, interior panels, door-frame profiles, food trays, partitions, lampshades, suitcases, helmets, shower and bath units, pipes, ropes, hessians, sacking, mats and carpet.
Materials handling and storage	Storage silos, post-boxes, fuel containers, bio-gas containers,

composites for bicycle frames and flax composites for snowboards [17].

Depending on the matrix and reinforcement combination the properties of NFRCs can vary (Table 6): Tensile strength – 17–92 MPa, Young’s modulus – 0.8–10 GPa, Tensile elongation – 0.8–3%, Flexural strength – 21–70 MPa, Flexural modulus – 0.8–6 GPa, Impact strength – 4–35 kJ/mm². Thermal degradation temperature can range between 281 and 305 °C. Processing, mechanical and other functional properties of NFRCs depend on large number of parameters including fiber aspect ratio, fiber-matrix bonding, fiber concentration, fiber orientation and distribution, stress transfer between fiber and matrix, fiber selection (type and harvest time), extraction method, fiber treatment, manufacturing process, etc. [22,50]. Further, mechanical and thermal properties of NFRCs strongly depend on fiber structure/geometry, matrix properties and manufacturing processes used. Further the chemical constituents of natural fibers, such as cellulose (crystalline and non-crystalline), hemicellulose, lignin, wax, etc. [51], have direct influence on their tensile strength and modulus [34]. Therefore, composition of natural fibers directly affects mechanical properties of NFRCs. For example, fiber with high concentration of crystalline cellulose and low amount of hemicellulose provide high strength to fiber and composites. From design point of view the critical parameter is fiber-matrix interfacial interactions and bonding [52]. However, the most important technical drawbacks of NFRCs include [17,35,41–43] (i) High moisture absorption (depends on fiber type) leading to swelling and deterioration of performance and reliability. (ii) Inherently large variations in fiber characteristics and properties contributing to large scatter in NFRCs. (iii) Poor wettability (hydrophilic fibers and hydrophobic matrices) of natural fibers often results in weak fiber-matrix interfacial bonding leading to decrease in mechanical properties. (iv) Relatively low degradation temperature and easily flammable. Further, there exists very limited data on moisture absorption behavior of natural fibers although some data on NFRCs is available. Since moisture absorption behavior of natural fibers primarily depends on their hemicellulose and the process is reversible, fiber-matrix interface modification via fiber treatments is extremely important.

Table 6
Summary of mechanical properties of some NFRCs (compiled from Refs. [35,44,50,53,54]).

Matrix	Fiber/%	Strength, MPa		Modulus, GPa		Impact strength
		Tensile	Flexural	Tensile	Flexural	
Epoxy	Sisal/37-77	183–410	290–320	6–20	22–27	–
Epoxy	Flax/46-54	280–279	–	35–39	–	–
PLA	Wood flour/40	60.24	–	7.40	–	–
Acrylic resin	Wood	–	30–45	–	3–3.3	20–30 kJ/mm ²
PP	Flax/30	29.1	–	5	–	–
PP	Hemp or Kenaf	–	45–55	–	2.3–2.7	25–35 kJ/mm ²
High-modulus PP	Wood powder	–	30	–	2.0	4
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)	Jute/30	35.2	–	7.0	–	–
Poly-L-lactic acid (PLLA)	Flax/30	98	–	9.5	–	–
PLA	Jute/30	81.9	–	9.6	–	–
PP	Jute/30	47.9	–	5.8	–	–
PP	Jute	23–29	45–54	1.6–2.4	1.7–2.8	30–51 J/m
PP	Palm	21–30	44–55	1.1–1.6	1.6–2.6	39–53 J/m
PP	Abaca	23–27	46–48	1.6–2.6	1.4–2.6	39–46 J/m
Polyhydroxybutyrate (PHB)	Flax/30	40	–	4.7	–	–
PLA	Flax/30	53	–	8.3	–	–
PLA	Flax/20	64.4	–	6.9	–	–
PLA	Ramie/30	66.8	–	–	–	–
PP	Coir	25–28	47–49	1.7–2.7	1.6–2.8	41–54 J/m
PP	Banana	36–41	–	0.82–0.98	–	10.2–12.8 kJ/m ²
PP	Hemp	27–29	–	1.6–1.8	–	–
PP	Bagasse	17–22	21–34	1.2–1.4	0.8–1.6	3.3–6.2 kJ/mm ²

3. Processing of natural fiber reinforced composites

3.1. Pre-processing of natural fiber reinforcements

It is known that natural fibers with high concentration of hydroxyl groups on their surface results in hydrophilicity and therefore their wettability with hydrophobic polymer matrices is very poor. The distribution of fibers within the matrix would also become non-uniform due to this fiber-matrix incompatibility [55]. Poor flax fiber-PE matrix interface with large number of interfacial porosity has been reported by Kakroodi et al. [56], which resulted in significant reduction in tensile strength (~39% reduction). As a result fabrication of NFRCs with effective load transfer between the fiber and matrix, resulting in high

mechanical properties, has always been a challenge. Fiber-matrix interfacial incompatibility of NFRCs also found to increase moisture absorption of composites leading to swelling, residual stresses, increased biological degradation and deterioration of strength [57,58]. Fiber size and their concentration in the NFRCs have direct influence on their ability to absorb moisture [59]. Further, thermal stability of natural fibers can also be tailored by improving fiber-matrix interfacial bonding. Therefore, most important step in manufacturing NFRCs is pre-processing of natural fibers before their incorporation in to polymer matrices which include (i) surface modification of fibers, and (ii) modification of polymer matrix by adding compatibilizing agents.

Surface modification of fibers: The approaches to modify natural fiber surface characteristics can be categorized as chemical, physical and

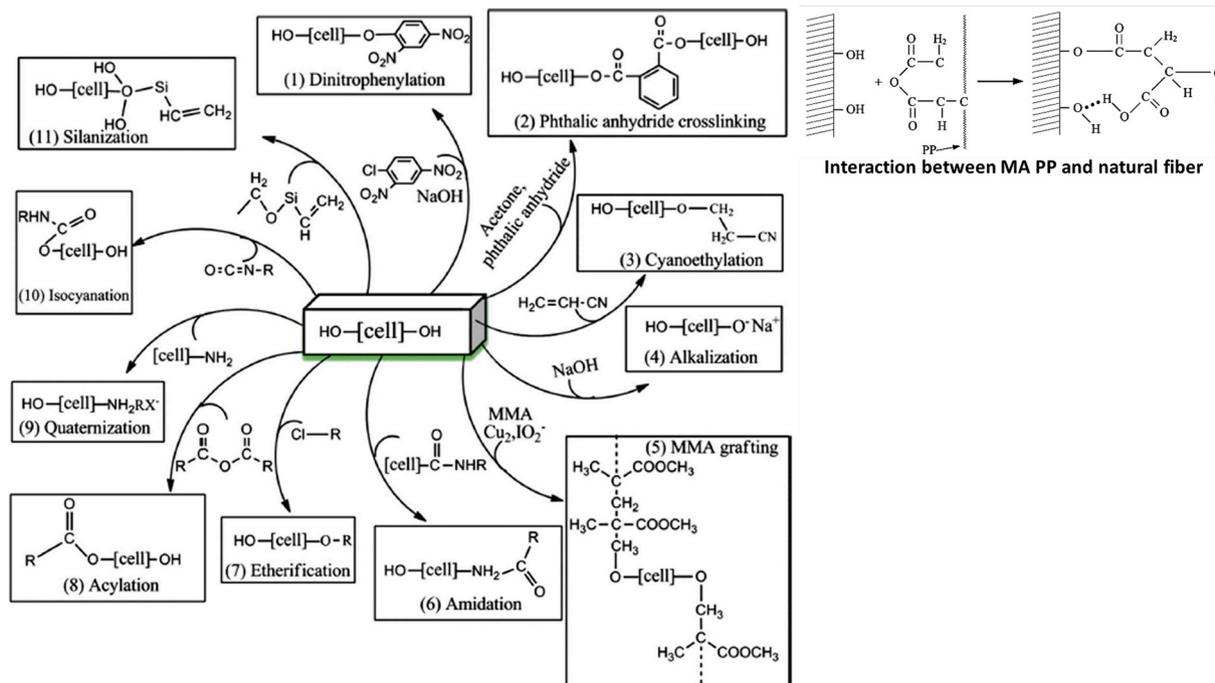


Fig. 3. Summary of methods used to modify fibers' surface [50,54].

mechanical (rolling, swaging) methods. Among these physical methods are relatively more environmentally friendly and decreases the polarity difference between fiber and matrix. Chemical methods can also help in reducing degradation due to moisture absorption. A summary of different fiber treatments is schematically shown in Fig. 3. Important physical methods include steam explosion, autoclave treatment, corona-discharge, high-energy radiation. Approaches such as alkalization, silanization, dewaxing, graft copolymerization, isocyanate treatment, benzylation, etc. are popular chemical treatments for different natural fibers. Type of treatment depends on type of fiber and matrix combination.

During chemical treatments, hydroxyl groups of natural fibers react with chemical agents and their number decreases significantly leading to reduction in hydrophilicity. Some chemicals react with fibers and from chemical bonding with the matrix. Alkaline treatment (mercerization), due to its cost-effectiveness, is one of the most popular chemical treatments. This treatment removes fiber constituents such as wax, pectin, oil, lignin (weaker than cellulose) and hemicellulose from the surface and also increases the surface roughness (form porous surface) thus improves bonding with the matrix [60]. As shown in Fig. 4, mercerization converts hydroxyl group to alkoxide by ionizing the nature fiber. The success of treatment depends on treatment time, temperature and type of alkaline solution and its concentration [61]. It can be seen from Fig. 4a, that as-received hemp fibers have surface protective layer primarily consisting of oil and wax. However, after NaOH treatment these impurities were removed from the fiber surface and therefore enhance its compatibility with polymer matrices [62]. Mercerization also found to either increase or decrease the crystallinity of cellulose depending on the severity of treatment and increased crystallinity can enhance fiber strength [63–65]. Sawpan et al. observed increased crystallinity of PLA matrix due to crystalline cellulose in the alkaline treated hemp fibers, which acted as nucleating sites [66]. Improved interfacial compatibility by alkali treatment reported to improve mechanical properties (tensile and flexural), thermal stability and moisture resistance [67–69]. However, due to high concentration of exposed cellulose usually increase hydrophilicity and therefore, this treatment often precede with other chemical treatments such as acetylation, silanation.

Another popular fiber treatment involves the use of Silanes (alkyl, amino, glycidoxy, methacryl), which can bond with fiber on one side and the other with polymer matrix. These are also used to improve

compatibility between glass fibers and polymer matrices. In this treatment, the interaction between silane and water results in formation of Si–OH groups on it, Fig. 3, which bond (covalent or hydrogen) with hydroxyl group of fibers [72,73]. When the bonding is covalent the improvement in the strength of NFRCS found to be maximum [72,74]. Significant improvement in tensile strength of low-density polyethylene reinforced with cellulose fiber was observed with γ -methacryloxypropyltrimethoxy treatment [75]. The hydrophobicity of natural fibers can also be increased, for better bonding with hydrophobic polymers, using acetylation after alkaline treatment. Although this treatment can help in enhancing mechanical, thermal and moisture resistance, small cellulose degradation and fiber cracking can have negative effects [76, 77]. Acetylation found to reduce impact strength of NFRCS. Other chemical treatments used for natural fiber surface modification include acryl, peroxide, zirconate, titanate, isocyanate, and enzyme treatment [47].

Physical treatments for natural fibers include corona-discharge, gamma-ray irradiation, plasma treatment, electron beam treatment, ultraviolet treatment, autoclave treatment, seam explosion and fiber beating. Gamma-ray or UV irradiation of natural fibers has been found to improve thermal stability of fibers which is very essential during processing and use of NFRCS [78–80]. Similarly the free radicals formed during electron beam irradiation can improve fiber-PP bonding (21–53% improvement) due to increased crosslinking between the reinforcement and matrix [81]. The simplest physical treatment of natural fibers is heat treatment in appropriate atmosphere where the fibers are heated to temperatures to reduce their moisture content, change chemistry, polymerization, and cellulose crystallinity. Additionally, heat treatment conditions (temperature, time, and atmosphere) have strong influence on physical and chemical changes of fibers that can occur during this treatment. Heat treatment induced improvement in the cellulose crystallinity of kenaf and sisal fibers, and removal of impurities, resulted in significant increase in the strength of these fibers [82,83]. However, concomitant improvement in composite mechanical properties could not be achieved. Plasma treatment in appropriate atmosphere found to increase hydrophobicity, increased contact angle with water, and surface roughness leading to enhanced fiber-matrix interfacial adhesion [84]. Seki et al. subjected jute fibers to low-temperature oxygen plasma and studied the influence of plasma power on the mechanical properties of jute-high density polyethylene (HDPE) composites [85]. It was observed that inter-laminar shear strength and flexural strength of these composites increased up to 35% and 30%, respectively, when the fibers were treated with 60 W power for 15 min. Fiber defibrillation related increase in the surface area of the fiber and their interlocking also results in small increase in the strength of kenaf-PP composites [86]. Recently there has been gaining interest in the eco-friendly fiber treatment methods using enzymes, fungi and bacteria [87–89]. Such treatments found to be economical, less energy intensive, improve thermal stability of natural fibers [90] and found to have selectivity towards pectin and hemicellulose removal. For example, defibrillation of hemp fibers using enzymes and chelators can improve thermal resistance by increasing fiber crystallinity [91]. Atomic force microscopy study [92] demonstrated that enzyme treatment along with steam explosion exposes secondary cell wall of the hemp fibers by removing hemicellulose, thus increasing their wettability and adhesion. Fiber treatment with fungi resulted in increased crystallinity index due to its ability to remove amorphous lignin [88]. In general, removal of surface impurities, increased fiber fineness and fiber individualization can be achieved with enzymatic treatments [93,94].

Modification of polymer matrix by adding compatibilizing agents: Modification of matrix is another popular approach to improve fiber-matrix interactions, which include chemical modification of matrix using maleic anhydride (MA) and addition of maleated polymer to the matrix. Both approaches results in active interaction between MA with hydroxyl group of natural fiber to reduce their hydrophilic nature. Typically MA is grafted to PP to make PP-based NFRCS and this MAPP

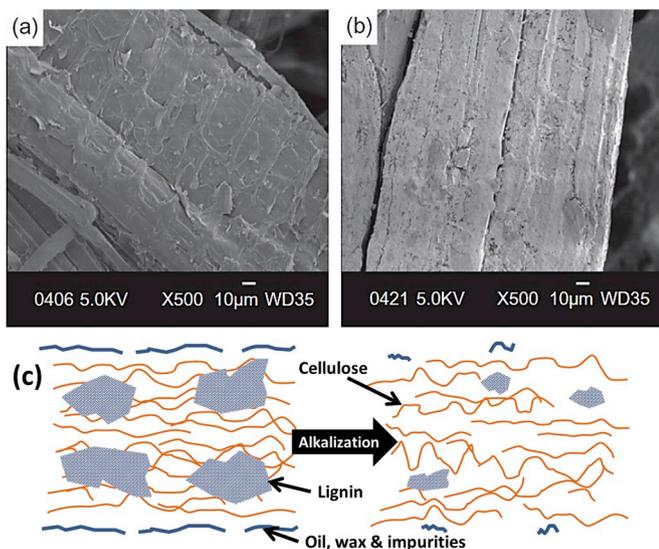


Fig. 4. Surface morphology of hemp fibers before (a) and after (b) NaOH treatment [70], (c) Schematic showing the changes in fiber structure due to alkali treatment [adapted from Ref. [71]].

form covalent or hydrogen bonding with hydroxyl groups present on the surface of natural fibers. Sometime fibers have also been impregnated with maleic anhydride using MA solution or MA grafted polymers to enable bonding with the matrix [95] leading to considerable improvements in mechanical properties (tensile, flexural and impact) of PP-based NFRCs [96]. Further, this treatment has been demonstrated to increase the strength by two times compared to silane treatment [65] due to enhanced fiber-matrix bonding and fiber dispersion.

During service NFRCs are exposed to humidity, heat, radiation and their combination, which results in loss of mechanical and functional properties including color primarily due to moisture absorption, changes in polymer structure, and formation of gas molecules. Moisture absorption of NFRCs is a serious concern due to increased biological degradation, swelling, internal stresses, cracking and loss of mechanical properties. Appropriate fiber treatment or matrix compatibilization can address these issues. For example, HDPE-rice husk composites compatibilized with ethylene and glycidylmethacrylate found to improve resistance to water absorption of these composites when exposed to freeze-thaw cycles (-21°C for 24 h) and therefore the degradation in mechanical properties was also reduced [97]. Another study of Stark and Matuana [98] reported that addition of stabilizers (zinc ferrite and UV absorber) to HDPE-wood flour composites can improve photo-degradation resistance while restricting the mechanical property degradation. Table 7 gives overview of different treatments used to improve fiber-matrix adhesion and properties of NFRCs.

3.2. Conventional processing of NFRCs

Majority of current manufacturing processes used to make NFRCs include compression molding, resin transfer molding, injection molding, hot pressing, vacuum infusion molding [51]. The low stability of natural fibers during processing always poses challenges in processing NFRCs using these conventional manufacturing processes as these are primarily designed/developed based on synthetic fiber reinforced composites. Therefore, pretreatment (chemical/physical) of natural fibers becomes integral part of NFRCs processing using conventional molding processes. Pretreatment of fibers improves fiber-matrix interfacial interactions thereby improves processability and properties of NFRCs. Some of the popular processes (Table 8) such as compression molding, injection molding and extrusion are found to be suitable and extensively investigated to make NFRC parts (short fiber reinforced) [2,126], which are briefly described here.

3.2.1. Compression molding (CM)

This process is very popular in automotive and transport sectors where complex components with deep impressions up to 20 cm are readily made using this technique. Typically the process is well suited for large parts in medium to large quantities and the cost of tooling is always less than that of injection molding. Typical CM process can be carried out either cold or hot and uses thermosetting matrix with sheet or bulk molding compounds, which are also thermosetting-based compounds (Fig. 5a). The process can be used with thermoplastic matrices, which uses glass mat thermoplastics as molding compounds. Cold CM uses only pressure (as the curing takes place at room temperature), whereas the hot molding involves simultaneous use of pressure and temperature (to cure and densify) on the preforms placed in a mold cavity. Typically alternatively stacked fibers between polymer matrix sheets are used and careful control of viscosity is important to achieve good bonding and impregnation between the fibers and the matrix, especially thick parts [129]. At the same time, it is extremely important to ensure fibers do not break/degrade during hot CM due to excessive heat and pressure. Therefore, there always exists compromise between fiber degradation and good bonding/wetting with the matrix with CM temperature and pressure, which depends on type of matrix and natural fiber being used. Further, distortion of parts is major drawback of this process. One unique advantage of this process is that it can take 35–90%

Table 7

Overview of treatments used to improve fiber-matrix adhesion and properties of NFRCs [compiled from Refs. [54,61,64,87,99]].

Treatment	Fiber-matrix combination	Observations
Chemical treatments		
NaOH (0.5–20%)	Banana-epoxy	1% NaOH treatment provide better properties [100]
5% NaOH; 0.5% Silane	Hemp-PLA	NaOH and Silane treatment increased adhesion by 100% and 45%, respectively, but fracture toughness decreased [101]
Chromium sulfate and sodium bicarbonate in acid media	Coir-PP	Hydrophobic conversion of fiber surface, improved adhesion and mechanical properties [102]
Mercerization	Jute-epoxy	4% NaOH increased strength up to 30% [61]
Silane, NaOH, etherification	Coir-HDPE	Improved tensile/torsional properties, ductility (Silane and etherification) [103]
Alkali, dilute epoxy, acetone and silane	Flax-epoxy	Highest flexural properties improvement with combination of alkali and dilute epoxy treatment [104]
Alkali treatment	Agave-epoxy	Improved fiber-resin interface and fracture strain [105]
Alkali treatment	Palm leaf stalk-jute-polyester	Addition jute fiber and alkali treatment improved storage and loss modulus [106]
Alkali + tetramethoxy orthosilicate	Coir-PP	Improved adhesion, mechanical properties and moisture resistance [107]
Permanganate (KMnO ₄) treatment	Banana-PP	Increased polarity and roughness of fiber, enhanced tensile (5%) and flexural (10%) properties [108]
Acetylation treatment	Flax-PP	Enhanced thermal properties (50%) and 25% improvement in tensile and flexural strength [77]
Benzoylation, peroxide, mercerization, silane treatments	Flax-HDPE, Linear low-density polyethylene (LLDPE), HDPE/LLDPE mix	Achieved uniform fiber distribution, improved mechanical and physical properties [109]
Oligomeric siloxane	Jute-polyester and epoxy	Treated fibers (1% siloxane) improved tensile, flexure and interlaminar shear strength of composites [110]
Physical treatments		
Autoclave (0.5–2 bar)	Flax-organic resin	Improved moisture resistance [111]
Corona discharge	Miscanthus-PLA	Significant enhancement in fiber-matrix adhesion [112]
Argon and air plasma (60 W, 30s)	Wood-PP	Marginal increase in tensile strength and modulus [113]
Plasma treatment	Coconut fiber-PLA	Increased thermal stability and decreased shrinkage [114]
Flame, corona discharge (CD), mechanical abrasion (MA)	Wood-polymer	MA + CD treatment increased the strength 0.2 MPa–3.4 MPa [115]
Gamma-ray irradiation (up to 2.0 MGy)	Basalt-epoxy	Irradiation induced polymer chain scission and oxidation of epoxy, achieved stable tensile and flexural properties, interlaminar shear strength increased [116]
UV radiation (up to 50)	Jute-PE-PP	Tensile (18%) and bending (20%) strength increased [117]
Corona treatment	Miscanthus-PP, Miscanthus-PLA	Surface oxidation and etching of fibers, enhanced

(continued on next page)

Table 7 (continued)

Treatment	Fiber-matrix combination	Observations
		interfacial interaction, homogeneity, static and dynamic mechanical properties and decomposition temperature [112]
Plasma (air and argon; 100, 200, 300 W)	Flax-polyester	Air plasma treatment (300 W) improved tensile strength (34%), flexural modulus (66%), flexural strength (31%) and interlamellar shear strength (39%). Argon plasma treatment with 200 W resulted in better properties [118]
Laser, ozone and plasma	Jute	No reduction in mechanical and thermal properties of fibers, increased surface roughness, potential use of lasers and ozone treatment [119]
Matrix modification		
Maleated polypropylene (MAPP)	Wood flour-HDPE	MAPP addition improved dimensional stability and strength [120]
MAPE, MAPP, acrylic acid grafted PE, maleated SEBS	Wood flour-HDPE	Enhanced tensile strength and modulus, best improvement with maleated LLDPE [121]
Graft-copolymerization	Cellulosic polymer	Improved physical, chemical and thermal resistance [122]
Maleated HDPE	Jute-HDPE	Improved dynamic (storage modulus, loss modulus) and static (tensile, flexural and impact) mechanical properties with 1% MAPE [123,124]
Eco-friendly treatments		
Enzymatic treatment (hemicelluloses, pectinases, oxidoreductase)	Flax and hemp	Removal of surface contaminants, reduction of hemicellulose, individualization of fibers with crystalline cellulose and improved thermal stability [90]
White rot fungi (<i>Schizophyllum commune</i>)	Hemp-PP	Improved tensile strength of composites (28%) [125]
Fungal treatment	Hemp-PP	Achieved 22% higher composite strength, which is 32% higher than that of alkali treated fibers [88]

fiber loading in the composites. Thermosetting polymer matrices such as vinyl ester, phenolic, polyester, and thermoplastics such as polyurethane, polypropylene, polyetheretherketone (PEEK), polyamide are popular. Although expensive than thermoplastics, currently more than 35% of NFRCs made for automotive applications are processed using thermoset matrices due to their superior thermal properties. Variety of fibers including wood, flax, hemp, sisal, kenaf and their mixtures can be easily processed using this technique. The natural fibers are often impregnated with thermoset resins and then pressed to shape. Mixing fine fibers with large surface area can improve adhesion with matrix and coarse fibers assist in felts saturation and eliminate resin pockets. During CM the pressure, holding time, temperature and viscosity of the material must be precisely controlled to achieve good fiber wetting, impregnation, fill die cavity and avoid spurting. Typical defects include voids, fiber breakage, sink marks, warpage and residual stresses, which can significantly reduce mechanical properties of NFRCs produced using

Table 8

Popular manufacturing techniques used to make NFRCs [compiled from Refs. [54,127,128]].

Fiber-matrix combination	Processing method	Typical process characteristics
Flax, Sisal, Bamboo, Hemp, Pine wood, Date palm leaves, Rice husk	Compounding (single or twin-screw) + Injection molding	Fiber content (wt. %): <40 Fiber length (mm): 0.1 to 1 Anisotropy: Medium Part complexity: High
Sisal, Jute yarn, Pineapple leaf fiber, Hemp, Kenaf, Coir, Saw dust	Compression molding	Fiber content (wt. %): >40 Fiber length (mm): >10 Anisotropy: Low Part complexity: Low
Sisal, Hemp, Rice husk	Extrusion	Fiber content (wt. %): <40 Fiber length (mm): 1 to 25 Anisotropy: High Part complexity: Low

CM. Thicker parts always suffer from large temperature gradients from surface to core of the parts. One most important attribute of CM is alignment of the fibers, which are typically aligned along the polymer flow direction. Processing parameters vary depending on the type of resin, fiber and matrix being used to make the composites. However, typically the pressures can vary between 10 and 20 MPa, temperatures between 130 and 250 °C, and pressing time can range between 30 s and 5 min.

3.2.2. Injection molding (IM)

Although new in the area of NFRC processing this process can produce relatively more complex parts in high quantities than other molding techniques. The requirement of low molding temperatures for NFRCs, typically between 175 and 190 °C, can pose problems with melt flowability while offering short cycle time, low energy consumption and damage/wear to molds and screws. Since the feedstock for IM is in granule form the natural fibers used in this process are often short fibers or short fiber bundles to enable compounding during IM [28]. Generally, the feedstock material is dried, due to hygroscopic nature of natural fibers, before feeding to the machine. The granules are then heated, compounded and then transported towards the mold using twin screw extruder. Generally, during this mixing stage the damage to the natural fiber is maximum due to friction (inter-fiber, fiber-matrix, fiber-extruder). Other potential areas where fiber damage can occur include die orifice and mold gates. The depth of the screw channel decreased with screw length, which accumulates and compact the material at the end of the screw. When sufficient quantity of material is accumulated the molten materials is injected in to the preheated mold to form composite part (Fig. 5b). The pressure is maintained in the mold (500–2000 bars) till the part solidified and cooled. Fiber agglomeration and lack of fiber-matrix bonding are important challenges in IM, which are being addressed using additives and pretreatment of fibers. Further, maximum fiber content that can be processed in this technique can range between 40 and 50 wt%. Important process parameters of IM are injection and screw speed, injection pressure, mold and melt temperature, which not only control overall part quality but also their mechanical properties and residual stresses. Residual stresses in IM parts found to reduce strength [51] and effect dimensional accuracy. Due to inherent material flow of IM, the fibers and matrix exhibit preferred orientation along the flow direction. The orientation of fiber across the part cross section also changes due to friction between material and

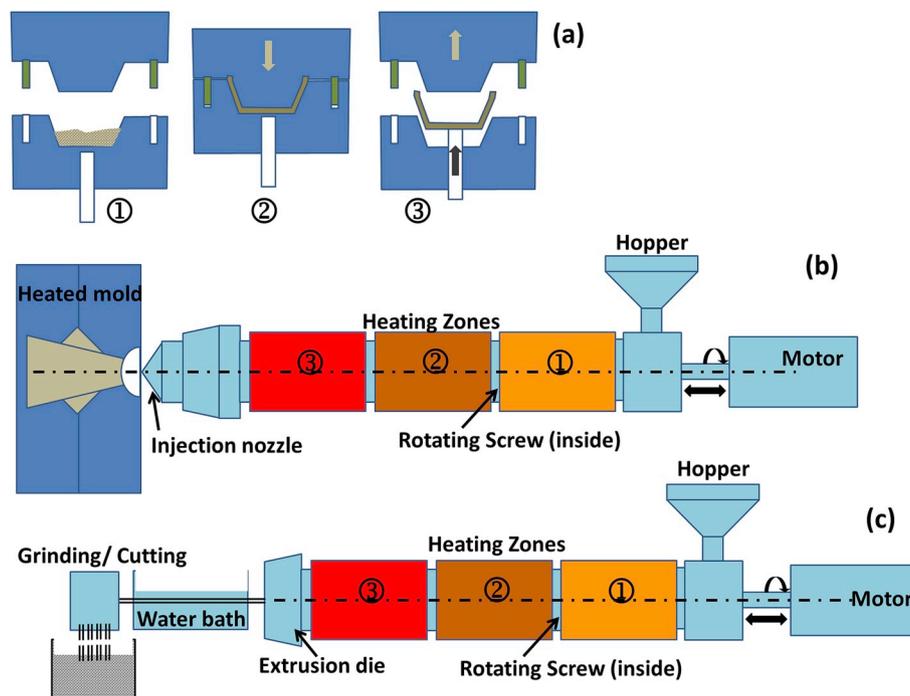


Fig. 5. Schematic diagram showing (a) compression molding, (b) injection molding, and (c) extrusion of NFRCs.

mold [130]. Further, the process is often limited to NFRCs with fiber content $\leq 40\%$ and always results in fiber length reduction during processing. However, IM provide several advantages [131] in the production of NFRCs such as (i) complex shapes with inserts/cores and high repeatability, (ii) minimum warpage and shrinkage, (iii) low material loss, (iv) high production rate (20–60 s cycle), and (v) high surface finish with near-net shape or net-shape. The only concern with this process is its high capital cost and large number of process parameters. So far IM has been used to produce NFRCs using bast fibers only (hemp, flax, jute, kenaf).

3.2.3. Extrusion

In this process granules compounded with natural fibers and polymer matrix are fed into a heated extruder. The heated mass is then mixed to achieve a homogeneous mixture using a screw and then forced through a die of defined cross section (Fig. 5c) to produce long composite rods, plates, and profiles. Although various varieties of extruders are in use, for NFRCs twin-screw extruders are most popular. This process can be used to make feedstock for IM or actual parts and twin-screw extruders provide good fiber distribution and hence mechanical properties. Similarly, the extrusion process is widely used to make wood fiber/flour reinforced composites as these composites meet the required properties of extruded profiles for the construction sector at lower costs, compared to relatively expensive fibers such as bast or leaf fibers. As with other techniques to process NFRCs, the fibers must be dried ($<1\%$ moisture) before final extrusion. Therefore, the fiber loading in the composite must be carefully controlled in the extrusion chamber. Since extrusion is popular with wood fibers, the processing temperatures are usually between 140 and 150 °C (below the blackening temperature of wood fibers) which restricts the polymer matrix flowability and the type of matrix that can be used. To minimize the damage to fibers from the shearing forces of the extrusion screw, the process must be carefully controlled below the critical value. Further, excessively high extrusion speeds can result in fiber damage, air entrapment, and high melt temperatures.

3.3. Critical issues in the processing of NFRCs

To achieve desired mechanical and functional performance in NFRCs

it is important to control the distribution of fibers within the matrix, concentration and length of fibers to achieve the desired strengthening effect, interaction/bonding between fiber and matrix, and defects such as porosity. In general, the amount of fiber and its characteristics such as length, L/D ratio, and composition have a strong influence on NFRC processing. Therefore, critical issues related to the processing of NFRCs directly originate from the inherent characteristics/properties of natural fibers. The important processing issues include (i) thermal stability of natural fibers, (ii) hydrophilicity of fibers, (iii) low strength of fibers leading to damage/breakage, (iv) water/moisture absorption, (v) distribution of natural fibers in the matrix, and (vi) machining.

3.3.1. Thermal stability

It is an important concern for the effective processing of NFRCs as most of the natural fibers degrade with an increase in the processing temperature. Fiber degradation occurs due to chemical and physical changes with heating between 100 and 300 °C [132]. Some of the important changes include dehydration, discoloration, recrystallization, hydrolysis, oxidation, decarboxylation, depolymerization [132]. These changes, due to high temperature exposure during NFRC processing, can have a negative influence on the composites' mechanical properties, color, and odor [133, 134]. A study on jute and flax fibers showed that temperatures above 170 °C significantly decreased mechanical properties and polymerization of these fibers [132]. Similarly, a rapid decrease in the strength and modulus of cotton has been reported after heating above 160 °C for 20 min [135]. Even very short thermal exposure to high temperatures can degrade the properties of flax fibers [136]. Several other studies also demonstrate detrimental effects of high processing temperatures on the mechanical and other functional properties of natural fibers [137–139]. It can be seen that the properties of natural fibers strongly depend on their composition, such as concentration of cellulose, lignin, and hemicellulose (Tables 1 and 3). Similarly, thermal stability or degradation of these fibers is also dictated by their composition and structure. Typical degradation temperature ranges of constituent phases of natural fibers are presented in Fig. 6. It has been observed that initial thermal degradation of natural fibers starts with the degradation of hemicellulose and is also associated with moisture content [140]. As a result, natural fibers with high concentration of hemicellulose can degrade at lower

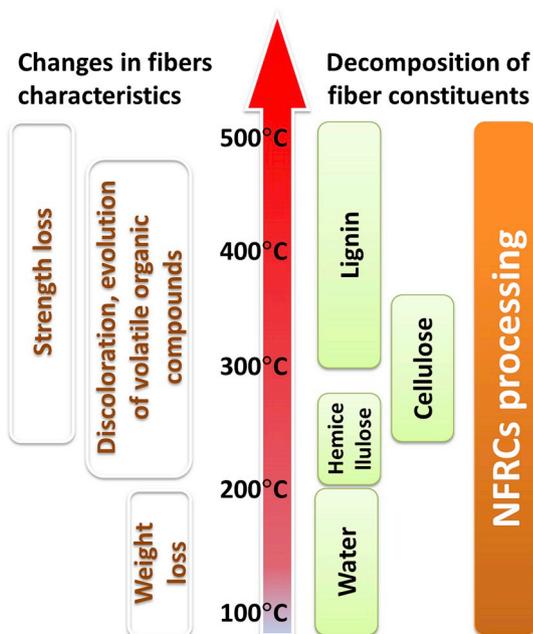


Fig. 6. Schematic showing the degradation temperature ranges for different constituents of natural fibers [adapted from Refs. [34,144]].

temperatures, due to their high moisture absorption tendency, compared to those with low hemicellulose. Thermal stability of fibers can also decrease with high amount of extractives [141]. It was observed that high crystalline cellulose in the fiber can improve thermal stability and strength [142]. While increasing the crystallite size and crystallinity index of cellulose found to increase decomposition temperature of natural fibers [137,143]. From these studies it is clear that the thermal degradation behavior of natural fibers must be assessed, based on their composition and structural characteristics, and must be improved before they can be used to manufacture NFRCs with desired mechanical performance. The stability of natural fibers can be improved by variety of chemical and physical treatments as discussed earlier.

3.3.2. Hydrophilicity of natural fibers

The presence of hydroxyl groups on the surface of natural fibers makes them highly hydrophilic and therefore their wettability with hydrophobic polymers is very poor, which leads to lack of good bonding between the fibers and matrix, difficulties in mixing during NFRCs processing and thus poor mechanical properties. Additionally, natural fibers are prone to moisture absorption and hence microbial degradation as well due their high hydrophilicity. Therefore, the fibers must be dried before they can be fed to processing equipment or during processing. At the same time, the dried fibers must be carefully stored and handled to avoid moisture absorption and dust explosions. If they are dried during processing, the amount of fiber loading must be carefully controlled. Excessive moisture of the fibers can lead to formation of water vapor and porosity in the NFRCs during processing. The water absorption tendency can be addressed by increasing cellulose crystallinity and removing hemicellulose from the fibers using hydrothermal treatment [145,146]. Alternatively chemical treatments such as photo-curable monomer coatings on the fibers can also found to improve moisture resistance of fibers [147,148]. Variety of physical and chemical treatments have been developed to reduce fibers' moisture absorption [149].

Another important consequence of fibers' hydrophilicity is inability to achieve effective bonding with hydrophobic polymer matrices. Since the fiber-matrix interface plays decisive role in transferring stress to matrix through the fiber, the mechanical performance of NFRCs also depends on this interface. Therefore, to achieve desired mechanical properties in NFRCs the fibers must be treated or polymer matrix must

be added with compatibilizers/coupling agents to improve fiber-matrix interfacial adhesion [150,151]. Popular fiber treatments include grinding, acetylation, steam explosion, electron beam irradiation, gamma-ray irradiation, plasma irradiation, alkali treatment (mercerization), silanization, graft copolymerization of monomer or polymer on to fibers. For example, decreased hydrophilicity and enhanced thermal stability can be achieved with acetylation in vapour phase.

3.3.3. Fiber breakage leading to degradation of composite strength

Fiber breakage during compounding/mixing is another important concern in the processing of NFRCs. The reinforcing effect of natural fibers (depending on the finer aspect ratio and orientation) strongly depends on type of manufacturing process used to make NFRCs. As discussed above fiber breakage occurs in all stages of IM of NFRCs. For example, during initial steps fiber ruptures due to simultaneous action of temperature and pressure. Use of too small fibers causes attrition, during IM of NFRCs, due to high shear rates existing in the barrel and sprue nozzle. Further, natural fibers can also break in length due to collision between fibers, between fiber and tool/mold. Therefore, fiber length in the final composites becomes less than critical length leading to significant drop in strengthening effect of fibers and in such cases, the short fibers can also act as defect in the composite. Sometimes, fiber entanglement can also occur due to relatively more flexibility of natural fibers compared to synthetic fibers. Typical fiber lengths between 0.1 and 1.2 mm with aspect ratios <20 can result in significant reduction in strengthening effect of natural fibers [28]. Understanding on natural fiber breakage during NFRCs processing is relatively very poor [152] than synthetic fibers [153]. However, high processing temperatures, long mixing times and high rotor speeds during compounding often results in sever fiber breakage. Another critical issue noted with IM of NFRCs is decrease in the reinforcing effect with increase in the injection cycles and consequent decrease in the breaking strength as shown in Fig. 7. Such decrease in the strength is possibly due to separation of fiber bundles, changes in the polymer properties such as glass transition temperature and molecular weight [154].

3.3.4. Water/moisture absorption

Natural fibers typically have high moisture absorption ability, during storage or after processing, which can lead to fiber swelling and loss of dimensional stability. Moreover, swollen fibers decrease fiber-matrix adhesion and hence mechanical properties of NFRCs. Therefore, to process high quality NFRCs the moisture content of fibers must be reduced below 3 wt%. Any increase in the moisture is converted to water vapor during processing and results in porous composites [51]. Natural fibers can absorb moisture at elevated and room temperatures through hydrogen bonding due to their strong polar groups on the surface. The moisture content of the fibers depends on relative humidity [155] of processing/storage and type of fiber [156] being used. For example,

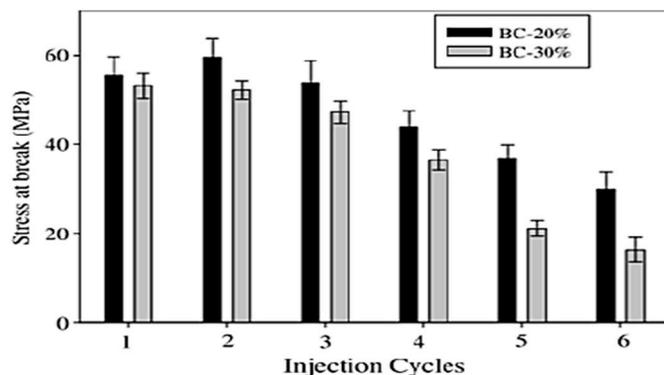


Fig. 7. Influence of injection cycles on the strength of poly-L-lactide (PLLA)/flax composites [154].

composites reinforced with pennywort fibers have moisture content of 57% at 90% relative humidity compared to composites made with bamboo fibers, as a result the former composites are inferior to the later in terms of moisture related degradation [2]. As discussed above appropriate surface treatment of fibers can reduce moisture content and rate of absorption significantly. Alternatively extruders with high L/D ratio screws and barrel redesigning enable degassing during NFRCs processing leading to low moisture in the composites [2]. Moisture absorption of natural fibers is not well studied although several

investigations report degradation of NFRCs due to moisture [157].

3.3.5. Distribution of natural fibers in the matrix

In case of NFRCs, it is difficult to control fiber distribution, although size-dependent, due to their hydrophilicity. Poor fiber distribution manifests itself in to fiber-deficient or fiber-rich regions which are weak and prone to cracking, respectively. Different chemical and physical treatments of fibers can improve their distribution in the final NFRCs. Alternative approaches include addition of coupling agents such as

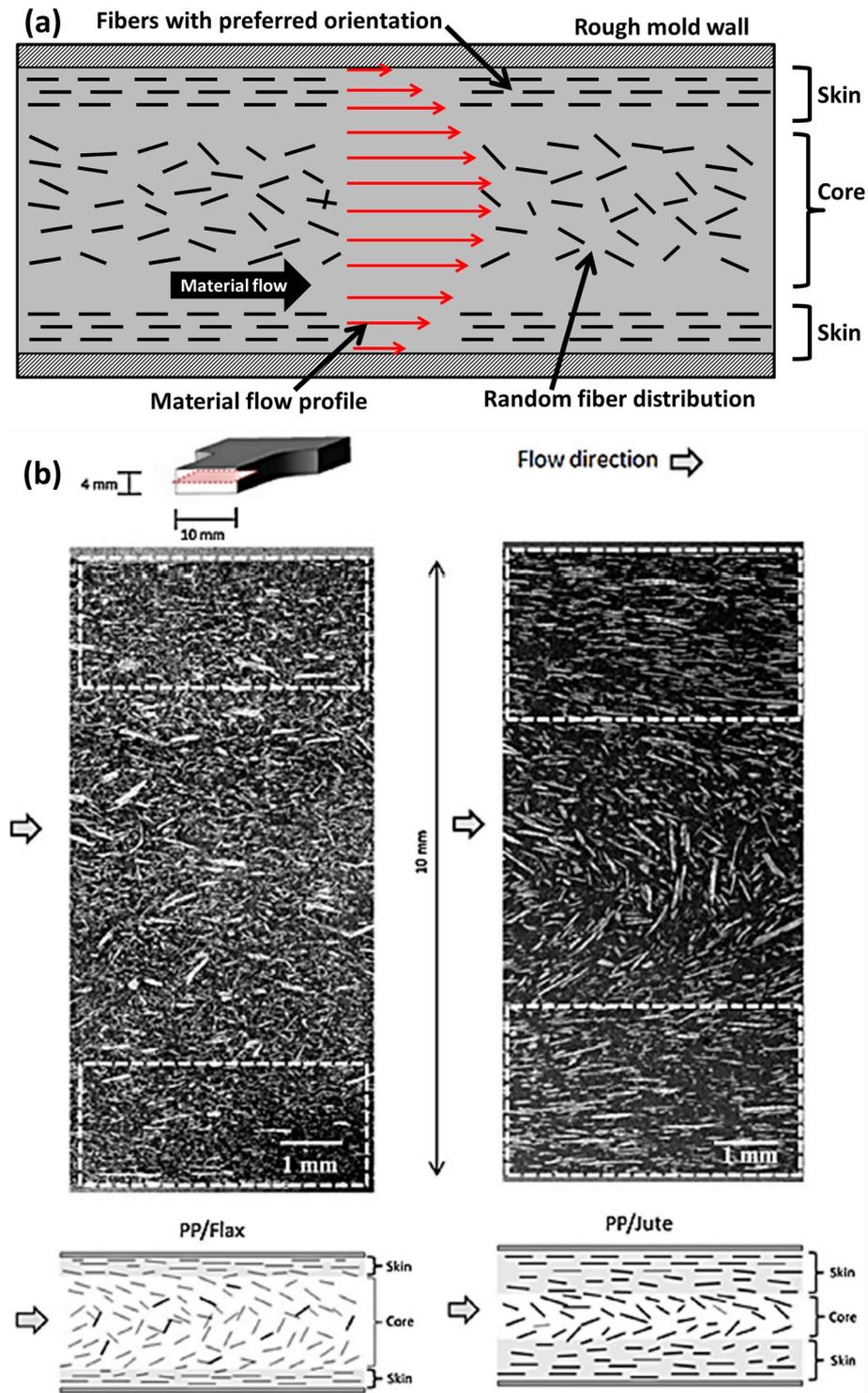


Fig. 8. (a) Schematic variations in fiber orientation and distribution due to material flow during NFRC processing [adapted from Ref. [34]], (b) Microstructures of PP/flax and PP/jute composites showing variations in fiber concentrations and orientation in core and skin [162].

miner oil, stearic acid which can improve fiber distribution by reducing fiber-fiber interactions and fiber entanglement. Simple alkali treatment can dissolve pectin from the fiber surface and reduce fiber clumping. Fiber bundles with large diameter reduces interfacial bonding area with matrix and thus detrimental to stress transfer between fiber and matrix. Therefore, fiber bundles must be separated to achieve strong NFRCs with uniform distribution of individual reinforcements. Fiber bundles can be separated by appropriate selection of process parameters ensuring high energy of mixing, while avoiding fiber breakage.

Majority of NFRCs, processed using different techniques, often show some preferred orientation of fibers [130]. The orientation of fibers depends on shape of the part, material flow, material viscosity, wettability and surface roughness of mold. Generally fibers align themselves along material flow and shear direction, which are severe along the mold walls, as shown in Fig. 8a. This region is known as skin and covers a central region (core) of part with random fiber orientation [158]. The surface roughness of mold or barrel strongly influences the material velocity across the cross section and the velocity is more in the central region, Fig. 8a. Increasing the length of the fiber increases the skin layer thickness as it is relatively easy to orient long fibers compared to short fibers. Due to strong fiber alignment along the direction of material flow in the skin region their mechanical properties are always higher than that of core region with random fiber distribution [159]. Composites with high concentration of fibers can decrease severity of fiber orientation due to increase in the melt viscosity and fiber-fiber interactions [160]. The severity of skin-core effect depends on injection pressure, temperature, speed, gate location in the molds, part size and type of natural fiber [161]. For example, the changes in the severity of fiber orientation in PP/Flax and PP/Jute composites are shown in Fig. 8b, which are attributed to the large diameter and high lignin of jute fibers [162].

3.3.6. Machining related challenges

Machining of composites, in general, is relatively more complex than conventional materials due to their inherent microstructural and property heterogeneity. Often several operations such as milling, turning, grinding, and drilling are regularly used to assemble and finish complex NFRC components. Poor surface finish and high tool wear are typical in machining NFRCs. High cutting speeds can lead to matrix melting and the surface finish depends on fiber orientation with respect to cutting edge. On the other hand, any grinding operation could lead to fiber pull-out, burrs, burning and delamination. For better surface finish the fiber orientation must be normal to the grinding direction. Currently, several

NFRC parts are assembled by riveting and fastening to make complex shapes, which require drilling causing burrs around the hole. Recent study on NFRCs showed feed rate and cutting speed are critical in reducing machining induced damages such as peel-up or push-down delamination [163]. Increasing the feed rate increased delamination in banana fiber-epoxy composites and its effect is relatively more than that of drilling speed [164]. Tool geometry also found to have strong influence of quality of drilled holes in NFRCs [165]. The severity of defects caused during machining, such as burrs, delamination, overheating, debonding (Fig. 9a), cracking, depends on several machining parameters and composite characteristics such as fiber type, amount etc. Any manufacturing related defects (voids, cracks, matrix imperfections, and debonding) can lead to more severe damage to NFRCs during machining. Typically machined holes in composites exhibit burrs along the edges, Fig. 9b, due to which overall damaged area would be larger than actual hole. Circularity and deformation of holes is also an important consideration in NFRCs.

4. Additive manufacturing (AM) of composites

Additive manufacturing, also known as three-dimensional printing (3DP) or solid freeform fabrication (SFF) or rapid prototype (RP), is a process in which 3D components, with high precision and complexity, are made by depositing materials in layer-by-layer fashion as opposed to conventional machining or forming methods [168]. Typically the process starts with a 3D computer-aided design (CAD) model of the part to be manufactured, which is electronically sliced in to number of horizontal cross-sections. This data is sent to AM machine where each cross-section is built one over the other to create 3D part represented in 3D-CAD model. Usually the parts are net-shape or near net-shape and are ready to be used or require small amount of finishing/machining or cleaning operations. Several thermoplastics (Acrylonitrile Butadiene Styrene [ABS], Polycarbonate [PC], ABS + PC blends, Polylactic Acid [PLA], Polyetherimide [PEI], Polyetheretherketone [PEEK], Thermoplastic polyurethane [TPU], Polyphenylsulfone [PPSF]), thermosetting polymers (Acrylics, Acrylates, Epoxies) and other plastics (Polymides (Nylon), Polystyrene, Polypropylene) have been processed using different AM technologies [169]. However, AM technologies such as fused filament fabrication (FFF), stereolithography (SLA), selective laser sintering (SLS), direct-write (DW) and binder jetting (BJ) are currently popular for processing single polymeric components. This is primarily due to availability of feedstock materials that are compatible with existing commercial printers. Although multiple printing heads, in some

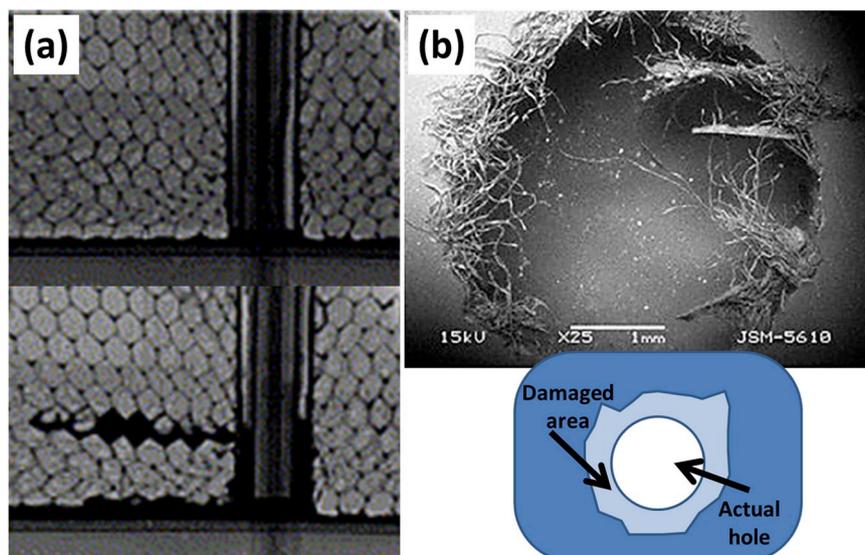


Fig. 9. (a) Debonding [166], (b) Burrs and drilled hole in composites [167].

of the printers, allow fabrication of composite structures, development and use of premixed feedstock materials reinforced with particles, fibers and nanomaterials in variety of AM machines is gaining significant attention [170]. Therefore, preparation of feedstock and their stability during processing is very critical. For example, distribution/agglomeration of reinforcements, microstructural uniformity, reinforcement-matrix adhesion, feature resolution, blocking and wear of print heads, changes in the hardening/curing, etc. are potential issues to be addressed before fabrication of polymeric composite parts using AM [170]. However, use of AM to manufacture polymer composites can provide several benefits [168] such as (i) custom and complex geometrical parts, (ii) near net-shape or net-shape parts with high accuracy, (iii) flexible processing to make parts with high performance, (iv) tailorable and precise control of site-specific mechanical, physical, thermal and other properties, (v) significant savings in terms of time and cost.

4.1. AM technologies for polymer composites fabrication

Currently polymers are available in the form of filaments, powder, resins and reactive monomers, which are being used by different AM technologies to make pure polymer and polymer matrix composites. The most widely investigated AM technologies to make polymer matrix composites are FFF, SLA, SLS, DW and BJ processes. Depending on feedstock materials, part geometry/complexity, processing limitations in terms of resolution, and multi-material deposition, different AM techniques have been used. Characteristics of these technologies are summarized in Table 9. FFF uses feedstock in the form filament and variety of polymers reinforced with particles and fibers have been successfully processed with this technique. This is most popular technique for polymer composites due to its low-cost and ability to process multi-materials. Similarly, SLS is another technique which is widely used to process semi-crystalline polymers reinforced with glass, carbon and ceramic powder. Compared to FFF feature resolution is significantly better in SLS and also complex parts with high strength can be manufactured. However, this process is relatively more expensive than FFF. SLA is limited by polymers that are photo-curable. Similarly, BJ process depends on binder-polymer compatibility without hampering mechanical properties of final parts. More detailed discussion on these processes is provided in the following sections.

4.1.1. Fused filament fabrication (FFF)

It is also known as fused deposition modeling (FDM) and is the most popular technique to fabricate polymer composites. In this process, the feedstock material in the form of filament is melted, extruded through a nozzle and then deposited on a build sheet as per desired path to complete the part represented in 3D CAD model. Amorphous thermoplastics, as listed in Table 9, are commonly used in FFF due to their temperature range and high viscosity, which enable easy processing with extrusion nozzles with diameter (\varnothing) 0.2–0.5 mm. The process uses two different materials i.e., one for actual part and the second one for support structures, which are removed manually or by melting or dissolving. As shown in Fig. 10a, the process begins with feeding the feedstock filament (\varnothing 1–2 mm) to the extrusion head, which is then heated and extruded (using solid filament and roller mechanism) through a nozzle in semi-solid state and then deposited on to a build sheet. Specialized softwares have been developed to create support structures and desired tool paths, which are essential to reduce support build time, tailor internal architecture and improve mechanical properties of parts. The extruded material solidifies by bonding with surrounding and previous deposits in a temperature controlled build chamber (which keeps the existing deposits warm and ensure good bonding). Once a layer is completed the build platform moves down by layer thickness (0.1–0.5 mm) and the next layer deposition is completed. The support structures for each layer are also built at the same time using a separate extruder. The width of the extruded material (0.25–2.5 mm) is controlled by filament feed rate. The part quality and properties depends on deposition speed, filament feed rate, nozzle diameter, deposited road width, deposition head temperature (to control the viscosity), build chamber temperature and build material properties. The most important concerns of FFF to make composites are uniform distribution of reinforcements, inter-track porosity, wavy surface finish and inaccurate parts due to unpredictable shrinkage of thermoplastics. Addition of different reinforcements to polymers changes their viscosity and poses significant processing challenges. Therefore, not all polymers are suitable for FFF. Inherent elliptical shape of the deposited material track results in wavy surface, which can be addressed using thin layers and small extrusion nozzles. Similarly, part accuracy can be improved by using appropriate deposition strategies and shrinkage compensation. In addition to merits of this AM technology listed in Table 9, the process enable deposition of multiple materials (through multiple extrusion heads) thus one can fabricate multi-functional composites with different materials.

Table 9

Characteristics of AM technologies currently being investigated to manufacture polymer matrix composites [compiled from Refs. [168,169,171–173]].

Technology	Feedstock form	Matrix materials	Reinforcement	Resolution (X–Y&Z, μ m)	Merits	Demerits
FFF	Filament	Amorphous Thermoplastics: ABS, PC, PLA, Polyethylenimine (PEI), Polyether ether ketone (PEEK), Thermoplastic polyurethane (TPU)	Particles: Fe, W, Cu, graphene, Carbon nano tube (CNT), Hydroxyapatite (HA), Tricalcium phosphate (TCP), Al_2O_3 , TiO_2 , $CaTiO_3$, $BaTiO_3$, Polymer blends (PC + ABS) Fibers: Glass, Carbon, Continuous Carbon fiber	250-500&50-750	Low-cost, strong parts, multi-material deposition, simplicity, high deposition speed	Only thermoplastics, Nozzle wear/clogging, inter-raster porosity, wavy surface finish, anisotropy, unpredictable shrinkage of thermoplastics result in part inaccuracies
SLA	Photocurable liquid	Acrylics, Epoxies, Acrylates	Al_2O_3 , CNT, Graphene oxide, TiO_2 , $BaTiO_3$,	200-300 & 10-762	High resolution and quality	Feedstock must be photocurable, expensive, slow printing, toxic materials
SLS	Powder	Semicrystalline polymers: Polyamide, PP, PEEK,	Glass, Carbon, Al, Al_2O_3 , TiO_2 , HA, TCP, Silica, $CaSiO_3$,	70-500 & 76-500	Strong parts, complex parts, easy support removal, high surface finish and resolution	Expensive, slow process, loose powder surface, porosity
DW	Slurry	PLA, Polycaprolactone (PCL), elastomer, Epoxy, hydrogel	Short C fiber, Graphene, Fe_3O_4 , bioactive glass, CNT, SiC whisker, Silica, TCP, HA,	250-500 & 5-200	Soft and delicate material printing, high resolution	Slow and inferior strength
BJ	Powder	All polymers in powder form with compatible binder		120-500&70-250	Inexpensive, complex parts, easy support removal	Matrix-binder compatibility, lack of inter-layer adhesion, coarse resolution, porosity, poor powder workability, print head clogging

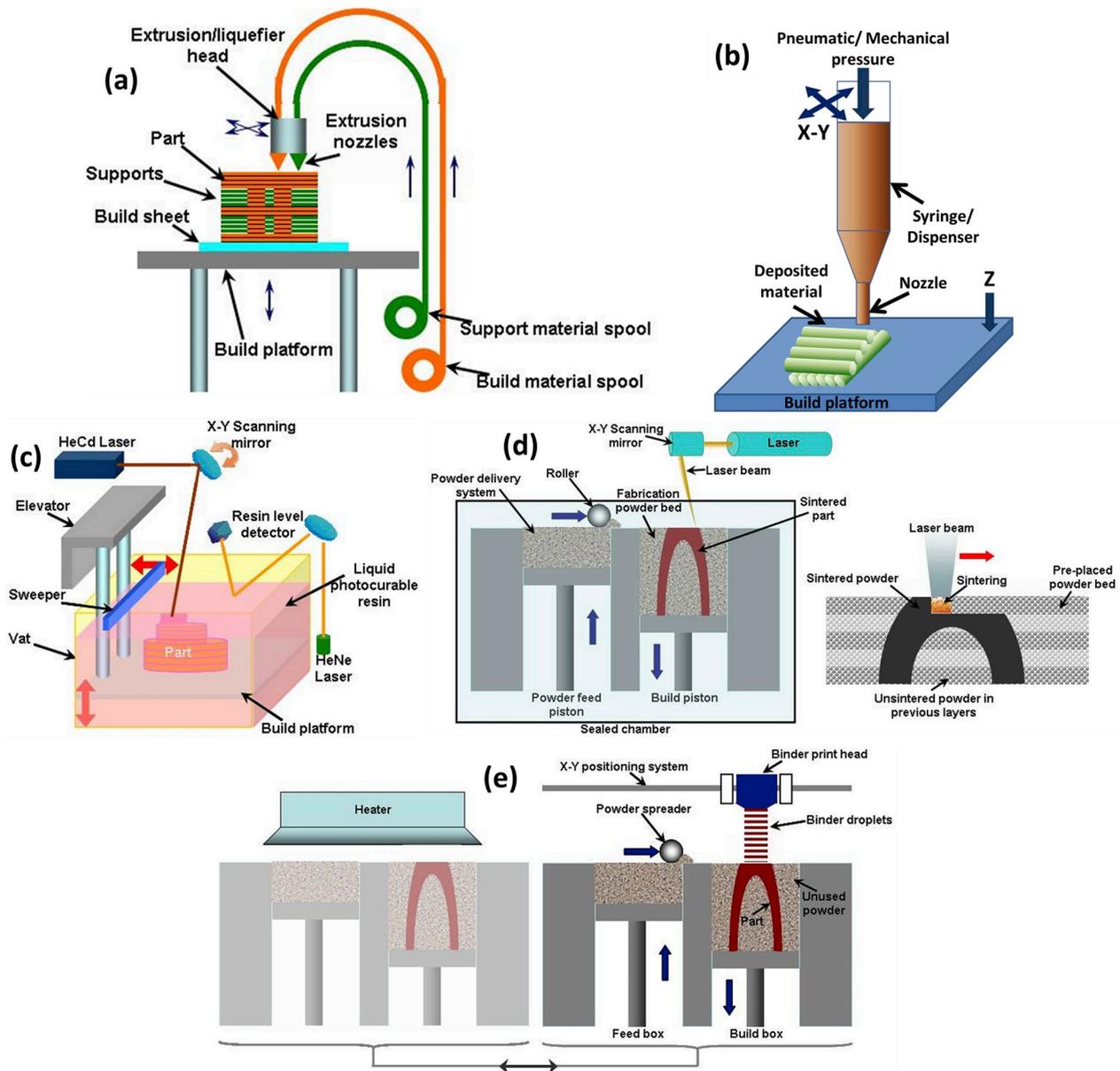


Fig. 10. Schematic representation of different AM technologies used to fabricate polymer and polymer composites (a) FFF [168], (b) DW, (c) SLA [168], (d) SLS [168], (e) BJ [168].

4.1.2. Direct-write (DW)

The technique is also known as 3D plotting, robocasting and direct ink writing. The process is very similar to FFF, where a viscous solution is dispensed through a computer controlled fine syringe as per CAD model, Fig. 10b. The nozzle openings can range between $1\ \mu\text{m}$ and $>1\ \text{mm}$ and therefore high resolution and build speeds can be achieved [174]. The deposited part is hardened [175,176] by (i) post-fabrication heating, (ii) post-fabrication UV light, (iii) using reactive feedstock. The feedstock materials could be in the form of solution, slurry/paste or hydrogel and therefore the process is highly flexible. However, building overhang structures is difficult as the deposited material will be too soft and can collapse. Therefore, support structures may be required if parts have complex features [177]. The extrusion pressures in this process are relatively less than FFF and no heating or solidification is involved. In case the extruded material is monomer then the substrate can be heated therefore immediately upon deposition the monomer polymerizes and strengthens. Another unique advantage of DW process is its ability to produce parts with functional and compositional gradients [178]. The most critical requirements for success of this process are the composition

and properties of solution, slurry/paste or hydrogel being used. The feedstock must be free of air entrappings, agglomeration homogeneous and in case of composite fabrication the reinforcement concentration must be as high as possible. Viscosity of the printed material also should be sufficiently high to retain its shape and must have sufficient stiffness to become self-supporting after printing on substrate.

4.1.3. Stereolithography (SLA)

This process relies on polymerization of liquid resin or monomer exposed to electromagnetic radiation such as UV-laser or electron beam. The polymerization takes place, at room temperature, point-by-point, line-by-line and finally layer-by-layer. Initially the build platform will be lowered, equivalent to layer/cure thickness, below the liquid resin/monomer and focused laser beam is directed on to the liquid surface to cure, as shown in Fig. 10c. By rastering the beam a single layer/cross section, as per CAD model, will be completed and then the build platform is lowered by layer thickness, and the process is repeated. For efficient bonding (interlayer and interscan) the cure depth ($25\text{--}500\ \mu\text{m}$) and width must be controlled by using appropriate beam size and scan

speed. As opposed to other AM techniques, in SLA the part is built in bottom-up fashion, Fig. 10c. After completing the build process, parts are processed using heat or photo-curing to complete the curing and improve mechanical properties, as ~80% polymerization takes place during actual SLA process. The curing process is highly complex and therefore the light source, exposure speed and time are to be precisely controlled to achieve high resolution and quality parts [179]. Important process parameters include laser power, wavelength, spot size, layer thickness, scan speed, post-curing, etc. Polymerization or cure depth of liquid monomer/resin can be tailored by adding UV absorbers and photoinitiators [180]. However, feedstock resin/monomer characteristics such as high wettability with polymerized resin, high curing speed, low viscosity, shrinkage and curling tendency, long shelf life provide high quality parts. The most distinguishable feature of SLA is its high resolution (~10 μm) and absence of nozzles and related problem when processing composites. However, available resins/monomers that are photocurable are very limited and some of the photoinitiators are toxic. Parts made using SLA often mechanically inferior compared to the parts made using other processes [181]. But, SLA has been used to fabricate complex and strong polymer composites reinforced with nano-scale reinforcements [182].

4.1.4. Selective laser sintering (SLS)

In this process a thin layer of loose powder is spread on a build platform, usually in controlled atmosphere build chamber, using a spreader. This powder layer is fused using a high-power laser beam scanned (using X–Y scanner) over the bed surface according to CAD model cross-section, as shown in Fig. 10d. The interaction between laser and powder generate sufficient heat to melt the powder creating solid cross section. The unaffected loose powder can act as support for overhang structures. The process is repeated for all cross sections after spreading fresh layer of powder on build platform by raising and lowering the feed box and build platform by one layer/slice thickness (~100 μm), respectively. Once all layers are built the parts are cooled in the controlled atmosphere chamber and loose powder is removed. Sometimes to minimize the cracking and warpage, improve surface finish of parts the powder beds are preheated using lasers or auxiliary heaters along with careful control of powder size, laser power and scan velocity. SLS involve large number of process parameters: layer thickness, scan velocity scan spacing, scan pattern, powder size, shape, packing density, distribution, laser power, beam size, continuous or pulsed, build chamber atmosphere, temperature, bed preheating, etc. As a result controlling part properties and quality depend on good understanding of process parameter effects and their interaction, which is always challenging. Semi-crystalline polymers are most popular materials for SLS process and do not require support structures for complex parts. For high-quality polymer parts the feedstock must be of high-quality which require precise control of molecular structure, and open chain structure [183]. Particularly in SLS processing of polymers, gradual increase in the melt viscosity during part building due to surrounding hot powder bed result in surface damage (orange peel effect). Similarly, the use of recycled powder can increase molecular weight of the powder, which can enhance interlayer bonding and hence improved mechanical properties [184]. Further, complex thermal behavior of SLS processing of polymers, in terms of molecular diffusion, bonding, solidification, etc., severely limits the choice of polymer suitable for this process [185] and therefore only polyamide (PA), polyethylene (PE), PEEK, PolyEtherKetone (PEK), polycaprolactone (PCL) have been successfully used with and without reinforcements [186–193].

4.1.5. Binder jetting (BJ)

This process is very similar to SLS and is also known as 3D printing (3DP). In this process, an inkjet printer is used to print liquid binder selectively, as per CAD model cross-section, on to powder bed, and immediately the build platform moves under a heat source to remove moisture and dry the binder, Fig. 10e. The drying is very critical to stop

spreading of the binder deeper in to previous layers, which is detrimental to part quality and properties. Each layer build one over the other following these steps and after completing the printing process the loose powder is blow out. The part out of this process is called ‘green part’ and requires careful handling to avoid breakage. The green parts are usually heated in an oven to harden the binder, depending on the binder used. Sometimes UV curable binders may be used and in these cases the final step involves curing in UV oven. Some of the important process parameters include layer thickness, powder size/shape/distribution, feed powder to layer thickness ratio, drop volume, binder saturation, binder viscosity, print head speed, number of printing passes/layer, spearing speed, drying temperature and time, number of foundation layers, etc. [194,195]. All polymers can be processed using BF process as long as they are available in powder form and compatible binders are available. Further, the process is very simple, economical and does not require high temperatures.

4.2. AM of different composite materials

Polymer matrix composites reinforced with different materials in the form of particles (micro and nano-scale) and fibers (short-fiber and continuous fiber) have been fabricated using AM technologies discussed above. Among the two types of reinforcements, particle reinforcements are inexpensive, easy to process and mix with matrices in both solid and liquid forms. Therefore, preparation of feedstock in the form of powder or filament for SLS/BJ and FFF, respectively, is also relatively easy. However, use of nano-scale reinforcements always poses problems in achieving uniform distribution due to agglomeration and some nano-scale materials are also unstable during processing/handling. Table 9 shows variety of matrix and particle reinforcement combinations processed using FFF, SLA, DW and SLS. The resulting composites found to exhibit improved mechanical (tensile strength, modulus, wear resistance), thermal properties (thermal stability, degradation temperature), dielectric and biological properties. Relatively large amount of research has been done in the area of polymer composite processing using FFF compared to other AM technologies. Filaments reinforced with variety of metals and ceramics have been prepared and processed [196,197]. For example, iron particle reinforced nylon matrix filament has been developed and used in FFF to create direct tooling [198]. ABS has been reinforced with Fe and Cu powder (up to 40 vol%) to ABS-based composites using FFF and the composites found to exhibit significant increase in their mechanical and thermal properties [199]. Drummer et al. evaluated PLA-Tri Calcium Phosphate composite scaffolds fabricated using FFF and found that they exhibit desirable mechanical and biological properties for implant applications [200]. Addition of BaTiO₃, up to 70 wt%, to ABS followed by fabrication of structures via FFF resulted in 240% increase in the relative permittivity [201]. Another unique advantage of using AM is its ability to create novel periodic structures with desired variation in composition as shown in Fig. 11a. Inherent and unpredictable expansion of thermoplastics has been addressed by adding metal particles [202], where Fe and Cu particle addition to ABS resulted in considerable increase in their thermal conductivity. As a result, the distortion associated with thermal expansion of ABS has been reduced in large-scale parts. Similarly mixing elastomer with ABS assisted in improving surface of the FFF composites (reinforced with TiO₂ and jute) while decreasing their ductility [203] and strength anisotropy in different directions. FFF fabricated fully dense PLA samples showed high toughness (5 MPa $\sqrt{\text{m}}$) than those prepared using IM processing (3 MPa $\sqrt{\text{m}}$) [204]. Singh et al. [205] developed Nylon-6-Al₂O₃ composite filament and the components made using FFF showed significant improvement in tribological properties [206].

In a recent work [207], acrylate polymer reinforced with 2–4 μm diamond particles (up to 30 w/v.%) were successfully fabricated using SLA. Significant improvement in heat transfer rates have been recorded with 30% composites demonstrating their application potential in electronic thermal management applications. Fig. 11b shows typical

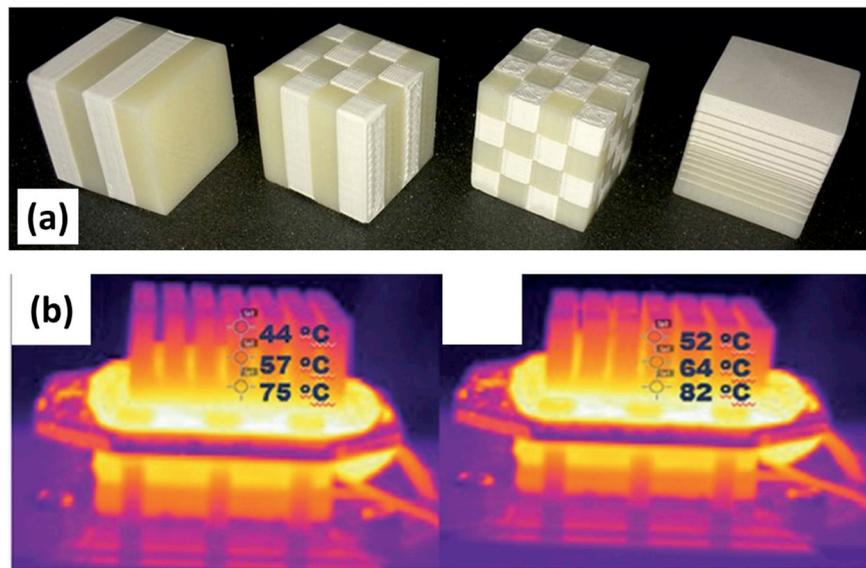


Fig. 11. (a) ABS-BaTiO₃ composite structures with site-specific composition made using FFF [201] (Open access licensed under a Creative Commons Attribution 4.0 International License), (b) Temperature distribution in neat acrylate polymer heat sink (left) and SLA printed acrylate-diamond composite heat sink (right) after heating for 10 min at 100 °C [207].

temperature distribution, recorded using infrared thermal imaging, in polymer heat sinks with and without diamond particles, where superior heat transfer from bottom can be seen in composite heat sink. Thermoelectric composites consisting of photocurable resin and Bi_{0.5}Sb_{1.5}Te₃ with ultra-low thermal conductivity (0.2 W/m.K) in complex shapes have also been fabricated using SLA process [208], which is not possible with conventional manufacturing routes. SLA was also successfully used to fabricate PLA-bioactive glass scaffolds for tissue engineering applications [209]. Uniform distribution of glass in PLA matrix and surface, Fig. 12a, enabled improvement in compressive modulus (from 1.4 MPa to 3.4 MPa with 20 wt% bioactive glass) and in vitro biological properties. Good combination of strength and ductility was also achieved by uniform distribution of graphene oxide (0.2%) in thermoplastic composites prepared using SLA [210]. The strength and ductility was increased by 62.2% and 12.8%, respectively. Multi-scale structures, with tailored site-specific properties in one device, using multi-polymeric materials have also been prepared using SLA [211]. High-quality Polycaprolactone (PCL)-hydroxyapatite (HA) (30 wt%) composite scaffolds were fabricated using optimized SLS process parameters by Eosoly et al. [212]. They reported that the scan strategy and laser parameters (laser power) have strong influence on geometrical accuracy (in different directions) and mechanical properties of PCL-HA scaffolds. SLS has also been used to fabricate functionally graded HDPE-HA composite scaffolds (45–48% porosity and 30–180 μm pore size) for bone and cartilage replacement [213]. These scaffolds exhibited flexural modulus between 36 and 161 MPa.

Now-a-days use of nanomaterials as reinforcements in polymer composites is gaining lot of attention due to their numerous advantages such as superior mechanical, electrical, thermal conductivity, thermal and fire resistance, excellent strength-to-weight ratio and other functional properties compared to their micro-scale counterparts [214–218]. These benefits can be further improved if such nanocomposites are fabricated using AM technologies. Therefore, development and manufacturing of polymer composites reinforced with nanomaterials could offer new opportunities and challenges as well. For example, ABS-graphene nanoplatelets (xGnP) composite filament has been prepared and the composites made using FFF exhibited improvement in tensile modulus and reduction in creep compliance of ABS in all directions [219] compared to CM samples. However, other properties such as tensile strength and elongation showed direction dependency. It

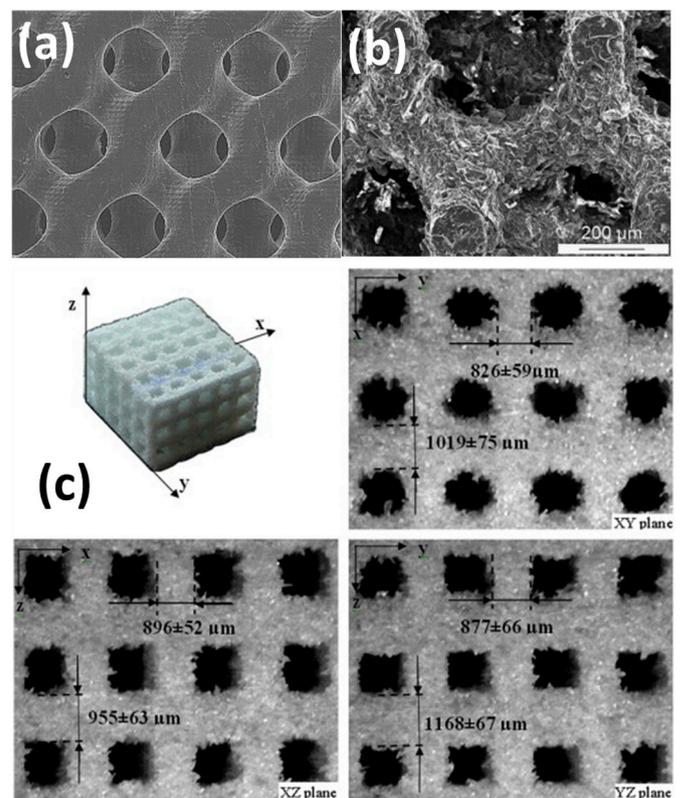


Fig. 12. (a), (b) SEM images showing the morphology of PLA and PLA-bioactive glass composite scaffolds, respectively [209]. (c) Dimensions of SLS fabricated scaffold struts in different directions [212].

appears that FFF of ABS-GnP composites is beneficial in enhancing their elastic modulus but this process had no positive influence on their elongation. Very recently FFF has been utilized to orient graphite flakes along the through-plane direction of parts, which resulted in effective conductive paths with 5.5 W/m.K [220]. It was also observed that printing strategy strongly affects graphite flake orientation and void formation in these parts. Therefore, depending on the orientation of

graphite flakes and voids with respect the through-plane the thermal conductivity increased from 1.6 W/m.K to 2.4 W/m.K and finally to 5.5 W/m.K, as shown in Fig. 13a. Preferred orientation of graphite flakes provide continuity of heat transfer and flux thus improved their performance. Shofner et al. [221] showed that uniform distribution of vapor-grown carbon fibers (VGCFs) in ABS matrix with minimum porosity can be achieved with optimization of mixing, extrusion and FFF process. The composites also exhibited 39% and 60% increase in the tensile strength and modulus due to alignment of VGCFs along the extrusion direction, Fig. 13b. However, addition of VGCFs to ABS changed the fracture mode from ductile to brittle and therefore significant drop in elongation was recorded with these composites. Graphene reinforced ABS composites fabricated using FFF also showed four orders of magnitude improvement in electrical conductivity of ABS [222]. ABS composites reinforced with nano-clay particles (Montmorillonite) showed ~ 15% improvement in tensile strength after FFF compared to IM composites [223]. The composites made using FFF also exhibited improved thermal properties. Significant research has been done using several carbon-based nanomaterials such as nanotubes, nanofibers, graphene, graphite and carbon-black [210,222,224–227], which showed significant improvement in mechanical properties as well as electrical and thermal properties.

Several investigators reported fabrication of polymer composites reinforced with nanoparticles using photocurable resins [228–230], however with considerable shielding and scattering of laser light with high concentration of nanoparticles [231,232]. Therefore, Weng et al. [233] modified the surface of nanofillers (SiO₂, montmorillonite and attapulgite) to improve their stability in SLA resin. Tensile strength and modulus of composites with 5% w/w SiO₂ increased by 20.6% and 65.1%, respectively. Silane coupling agent has been used to modify the surface of nano TiO₂ particles and the influence of TiO₂ concentration on cure depth and viscosity of resin was assessed for SLA processing [234]. The use of modified resin increased the tensile strength of the composites from 25.26 MPa to 47.82 MPa and measurable increase in the ductility and thermal stability was also recorded. The benefits of silane and other couplants in improving properties of composites by transferring the stress between matrix and reinforcement has also been reported by other investigators [216,228,235]. Similar surface modification of nano Al₂O₃ particles with polystyrene (PS) was used to fabricate PS-Al₂O₃ composites using SLS [236]. The laser absorption found to improve with coated particles resulting in well dispersion and reduced voids, as a result impact (50%) and tensile strength (300%) were improved. Therefore, appropriate surface treatment of nanoparticles can help in manufacturing fully dense nanocomposites using AM technologies. Kim et al. [237] reported that functionalization of graphite nanoplatelets improves interfacial bonding and mechanical properties depending on the concentration of reinforcements. Mechanical mixing and ultrasonic dispersion used to disperse MWCNTs in the

SLA resin resulted in limited success [238].

Another form of fabricating polymer composites is to use fibers (short-fiber and continuous fiber) as reinforcing agents, which can also enhance properties of polymer composites [239]. As with particle reinforced composites, the most popular and widely investigated AM technology to fabricated fiber reinforced polymer composites is FFF. Although some reports are available on the use of other AM techniques (DR, SLS and SLA), but are relatively less compared to FFF. Majority of research efforts on FFF are focused on the use of short fibers. The most important characteristic of FFF of fiber reinforced polymer composites is the alignment of fibers along extrusion/material deposition direction. Ferreira et al. [240] reports that preferred alignment of short carbon fiber (15 wt%) in PLA-carbon fiber composites, prepared using FFF, can improve mechanical properties. Short carbon fiber (CF) (0.2–0.4 mm) reinforced ABS composites prepared using FFF exhibited ~ 115% and ~700% increase in the tensile strength and modulus, respectively [241]. FFF resulted in highly preferred fiber orientation (~91.5%) in the material deposition direction, which compensated the detrimental effect of porosity in these composites. More importantly the specific strength of these composites was found to be higher than that of 6061 Al alloy, Fig. 14a. However, composites fabricated via FFF showed relatively high amount of porosity than compression molded samples, Fig. 14b–d. Interestingly the inner-bead and inter-bead voids decreased with fiber concentration and is attributable to the increased thermal conductivity (Fig. 14a). Similar improvements in tensile and flexural properties of thermoplastics reinforced with carbon fibers (CF) has been reported by Ning et al. [242], where longer CFs found to increase tensile strength and modulus, but with decrease in the ductility and toughness of these composites. The influence of different FFF process parameters on mechanical properties of CF reinforced plastic parts has been reported by Ning et al. [243]. Another study used short glass fibers (GF) to improve the strength of ABS filament, which resulted in reduction of filament flexibility and processibility, primarily due to reduction in swelling and increased stiffness of the tape at print head during FFF [244]. However, addition of small amount of plasticizer and compatibilizer found to improve the processibility of ABS-glass fiber composites filament using FFF. Entire polypropylene (PP)-GF composite filament production chain was evaluated by Carneiro et al. [245], where influence of FFF process parameters such as layer thickness, filament orientation, infill degree were assessed. Authors conclude that due to superior mechanical properties of FFF composite parts, compared to compression molding, they can be directly used as functional parts. In FFF processing of polymer composites, the matrix and reinforcing fiber are pre-mixed to make composite filament. However, it is very difficult to make free flowing composite powder, for SLS, using such composites. Further, the quality of SLS parts strongly depends on powder characteristics and uniformity of powder bed. As a result processing short fiber reinforced polymer composites using this process is very challenging [246]. For

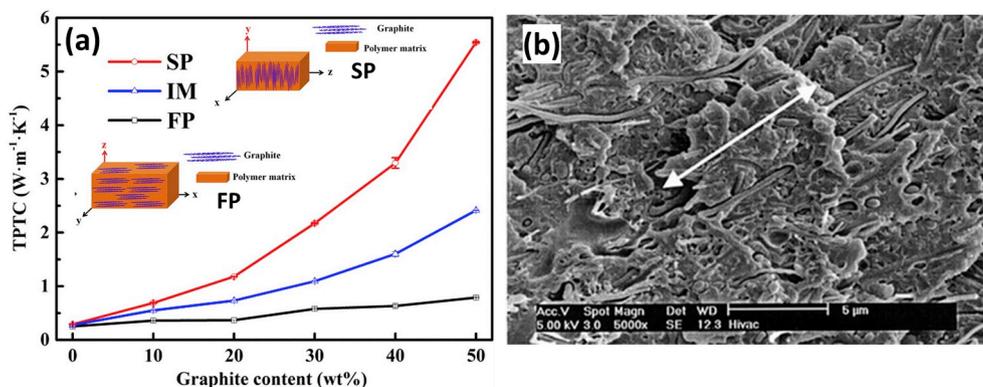


Fig. 13. (a) Through-plane thermal conductivity of polymer-graphite flake composites made by FFF [IM – injection molded samples] Modified/compiled from [220], (b) Alignment of VGCFs along the extrusion direction in VGCF-ABS composites made using FFF [221].

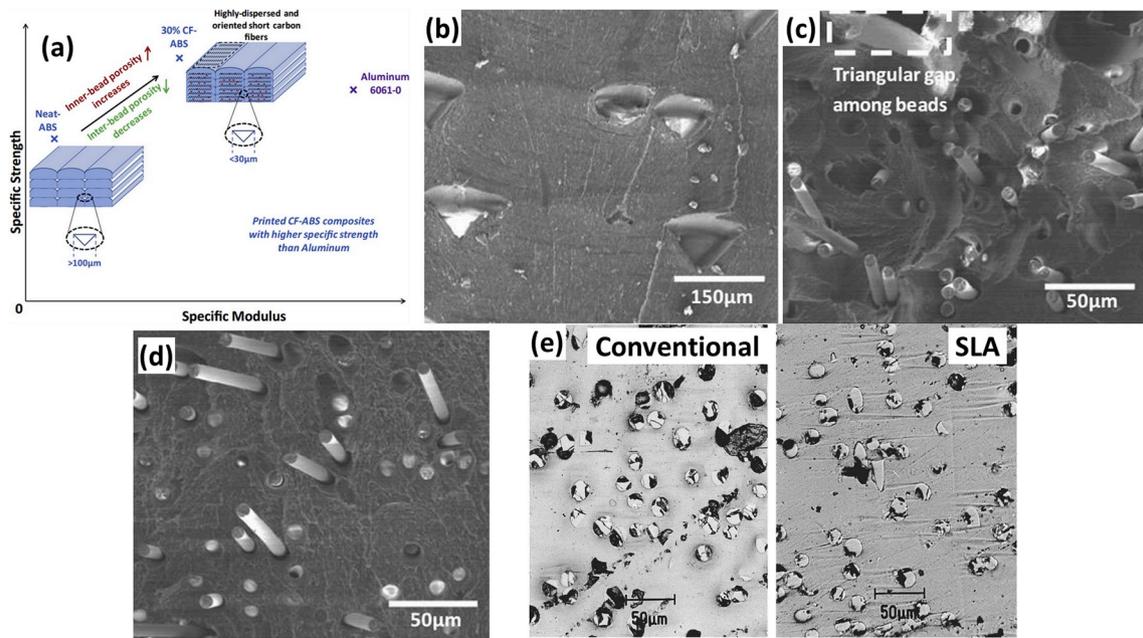


Fig. 14. (a) Influence of CF concentration on specific strength and voids of FFF processed ABS composites (b–d) fractographs showing voids and fibers in (b) pure ABS (c) FFF processed 10 wt% CF-ABS composites, (d) compression molded 10 wt% CF-ABS composites [241], (e) Microstructure showing the distribution of GFs in conventionally and SLA processed composites [250].

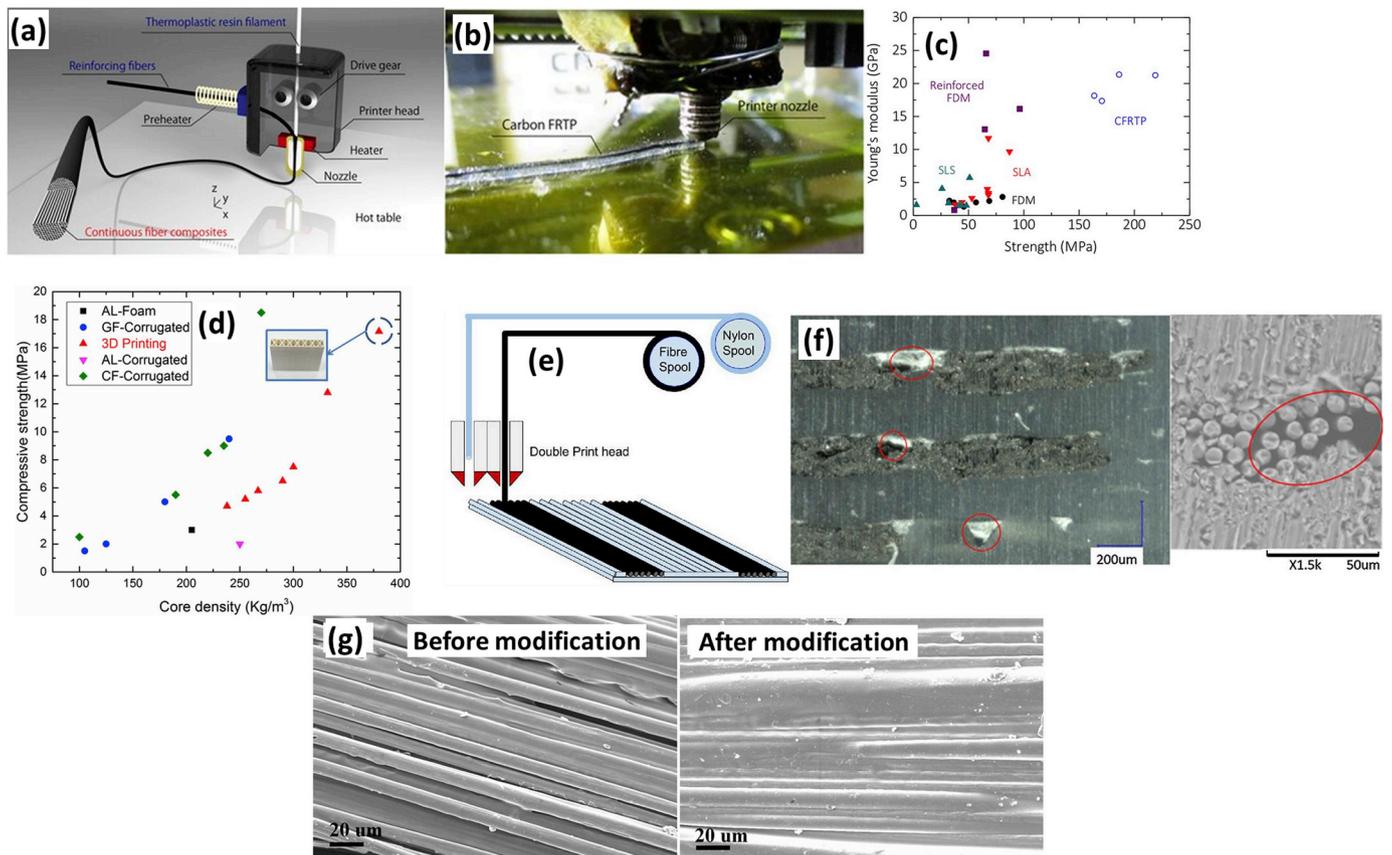


Fig. 15. (a) Schematic of FFF print head to produce continuous fiber reinforced composites, (b) Actual print head during printing, (c) Comparison of continuous fiber reinforced composite properties with the composites prepared using different AM technologies properties [252] (Open access licensed under a Creative Commons Attribution 4.0 International License). (d) Comparison of compression strength of corrugated composite structures made using different technique [259]. (e) Continuous fiber reinforced composite fabrication process in Mark One Composite 3D printer [260] (f) Voids in continuous carbon fiber reinforced composites (glass fibers resulted in less voids and were absent in Kevlar composites) [260]. (g) SEM micrographs showing changes in the carbon fiber-PLA matrix interface due to surface modification of fibers [255].

example, Goodridge et al. [187] attempted to produce polyimide 12 - carbon nanofiber (3 wt%) composite powder using cryogenic fracture method for use in SLS. Although the composite produced using SLS showed acceptable fiber distribution in the matrix with ~22% increase in the storage modulus, the powder morphology appears to be not suitable for this process. Therefore, research efforts may be focused on the composite powder production methods that can achieve desired characteristics suitable for making high strength components using SLS.

Similarly, research activities on SLA of fiber reinforced composites are very scarce [247,248]. For example, the use of CFs in photocurable resins for SLA processing can block UV light leading to uncured regions of resin in the vicinity of CFs. To address this photo-thermal dual curing of resin-CF composites has been proposed by Gupta et al. [249], where after SLA processing the composite parts were thermally treated for 1 h to complete curing (~25% uncured) and improve strength by 95%. Another approach is to replace the CFs with GFs [250], which resulted in significant improvement in mechanical properties and dimensional accuracy. Fig. 14e shows no distinguishable difference in GFs distribution (20 vol%) between conventionally processed and SLA processed composites. Very recently, GFs have been selectively oriented using ultrasonic forces in photocurable resin to create composites for energy applications [251].

Another most important and challenging task is to fabricate continuous fiber reinforced polymer composites using AM technologies [171], as these composites are mechanically superior than short fiber reinforced composites. Recently, a new FFF technique consisting of feeding polymer filament and continuous fiber separately to the print head for in-nozzle impregnation, just before printing, has been developed [252]. Schematic description of the process is presented in Fig. 15a and b. In this work, PLA was used as matrix and continuous carbon fibers (CCF) and jute fibers were used as reinforcements. The PLA-CCF composites exhibited tensile strength of 185.2 MPa and modulus of 19.5 GPa, which are ~6 and 4 times higher than pure PLA. Further, the properties of PLA-CCF composites found to be significantly better than short-fiber reinforced composites, as shown in Fig. 15c. Similar composites of CCF sandwiched between nylon have been prepared using Mark One commercial printer with two different print heads for fiber and matrix [253]. They observed large voids with increased CCFs and decreased the composites' strength. As with standard FFF, process parameters such as print head temperature, layer thickness, printing speed found to have strong influence on mechanical properties of these composites [254]. Other investigator also reported variety of results related to fabrication of continuous fiber reinforced composites using FFF [255–258]. New composites with cross lap and panel-core lap designs were also successfully fabricated with good compressive strength [259]. Specific strength of the composites increased from 18 to 28 kN m/kg with concentration of fibers from 2 to 10%. Further, the with 11.5 vol% fiber the corrugated-core structure showed a compressive strength of 17.17 MPa, Fig. 15d, which is comparable with similar parts made using other techniques. However, additional benefit of using AM is its ability to produce complex structures. Commercial FFF machine (Markforged Mark One) was recently used to understand the effects of fiber orientation, type and volume fraction on mechanical properties of nylon composites reinforced with continuous fibers of carbon, Kevlar and glass [260]. In this process, the reinforcing fiber bundles are stacked between matrix deposits as shown in Fig. 15e. Although carbon fiber reinforcement resulted in highest strength, increasing the fiber concentration found to form large amount of voids, Fig. 15f. Among the fibers, glass fibers appears to provide composites without voids with increasing concentration up to 22.5% [260]. In a similar study, the interlaminar shear strength was maximum with carbon fibers and composites reinforced with Kevlar exhibited lowest properties due to their poor wettability with nylon matrix [261]. However, for high impact strength glass fibers found to be best and the performance of carbon and Kevlar fibers are similar [262]. Li et al. [255] fabricated PLA-continuous carbon fiber composites using FFF and demonstrated that surface modification

of carbon fibers with PLA-methylene dichloride solution can significantly improves fiber-matrix adhesion. Visible improvement in carbon fiber-PLA matrix interface can be seen from Fig. 15g. The modified fiber composites exhibited 13.8% and 164% increase in tensile and flexural strength, respectively. Surface modification of fibers also improved storage modulus of these composites. In another study [263] continuous carbon fibers were modified with polyimide (PA6) to improve the adhesion and thereby enhanced the interlaminar shear strength by 42.2% compared to unmodified fibers.

4.3. NFRCs processing using AM

As discussed above significant research is being undertaken to fabricate polymer composites reinforced with synthetic materials using different AM technologies. However, use of these AM technologies to process NFRCs is extremely rare. In one study twisted yarns of jute fibers were used to reinforce PLA matrix using FFF process, Fig. 16a [252]. These composites exhibited tensile strength and modulus of 57.1 MPa and 5.11 GPa which are 134% and 157% higher than that of pure PLA, respectively. However, the tensile strain was very low between 0.05 and 0.25%. Authors indicated that appropriate pre-tensioning of jute yarn fibers can help in achieving uniform molding and improved mechanical properties. Therefore, very recently Hinchcliffe et al. [264] attempted to fabricate jute and flax fiber (continuous) reinforced PLA composites using AM. They found that pre-stressing the continuous fiber can improve tensile and flexural properties. Le Duigou et al. [265] used commercially available FFF filament consisting of PLA + poly(hydroxyalkanoate) (PHA) matrix reinforced with 15.2 wt% recycled wood fibers to create composite samples. The properties of these composites were found to be comparable with conventionally processed (extrusion and IM) PP-30% wood and HDPE-40% wood composites, but lower than PHA-20% wood composites. Sample size (print width) found to have strong influence on the total porosity of the samples and therefore their mechanical properties. For example, as shown in Fig. 16b, as-received composite filament had ~16.5% porosity, which resulted in similar amount of porosity (14.7–15.5%) in the FFF processed samples (Fig. 16d). However, the porosity increased with sample size (print width) due to loss of deposit temperature during printing large samples with longer deposition paths, Fig. 16e, which reflected in decrease in the properties. The samples with short deposition paths resulted in considerable reduction in porosity (8.4–14%). Thermal consolidation of filament and printed samples resulted in significant drop in porosity of these samples as shown in Fig. 16c. They also found that thermal consolidation can reduce moisture absorption by these composites. From these preliminary studies it can said that research on AM of NFRCs is in its embryonic stage and significant amount of research efforts are required to understand and optimize the process.

5. Challenges and opportunities in AM of natural fiber composites

As discussed above AM of composites shows clear and strong promise towards manufacturing complex parts. However, further growth of its use primarily depends on how fast we can address current issues [170] such as difficulties in preparing composite feedstock filament for FFF, nozzle clogging, void formation, fiber agglomeration and distribution, effect of fiber on curing and resolution, fiber orientation, fiber-matrix adhesion, light reflection from fiber and uncured regions in SLA. Some of the important challenges and opportunities associated with AM processing of NFRCs are discussed here under.

One important consideration in AM of NFRCs is that none of these techniques exerts sufficiently high pressures and shear rates to the material that are experienced during processing of these materials using conventional extrusion or IM. As a result, the composites do not develop strong bonding between the layers or roads in these AM processed parts, which can be seen from relatively poor mechanical properties of these

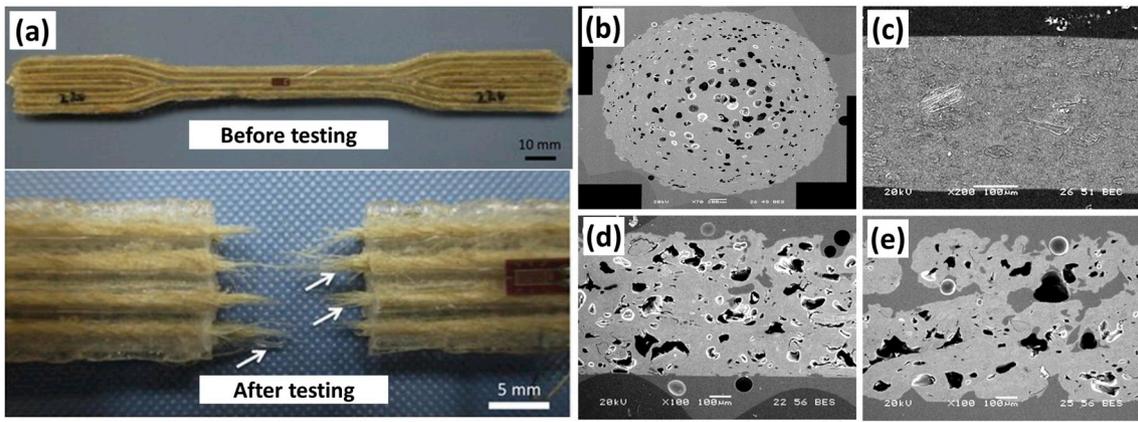


Fig. 16. (a) Typical tensile test specimen of FFF processed jute fiber reinforced PLA composites (top) and fiber pullouts after testing (below) [252] (Open access licensed under a Creative Commons Attribution 4.0 International License). (b–e) Microstructures of PLA-PHA-wood fiber composites (b) as-received filament, (c) consolidated FFF sample, (d) 100% print width, 300% print width [265].

parts especially in transverse direction (loading axis parallel to build direction). The strength of these parts primarily comes from bonding between interlayers and roads by thermal diffusion. Therefore, often the parts manufactured using AM technologies are not mechanically superior than those made using conventional processing such as CM or IM. However, AM offers design flexibility and ability to manufacture complex parts to improve functionality and performance, if appropriate feed

stock materials are developed with high concentration of reinforcements and minimal porosity. At the same time excessively high concentration of fibers can increase composite viscosity and related problems.

There exists several problems in developing composite feed stock filament for FFF [266]. Inherent process steps such as blending, compounding and extrusion that are involved in the preparation of feed stock composite filaments can damage natural fibers due to exposure to

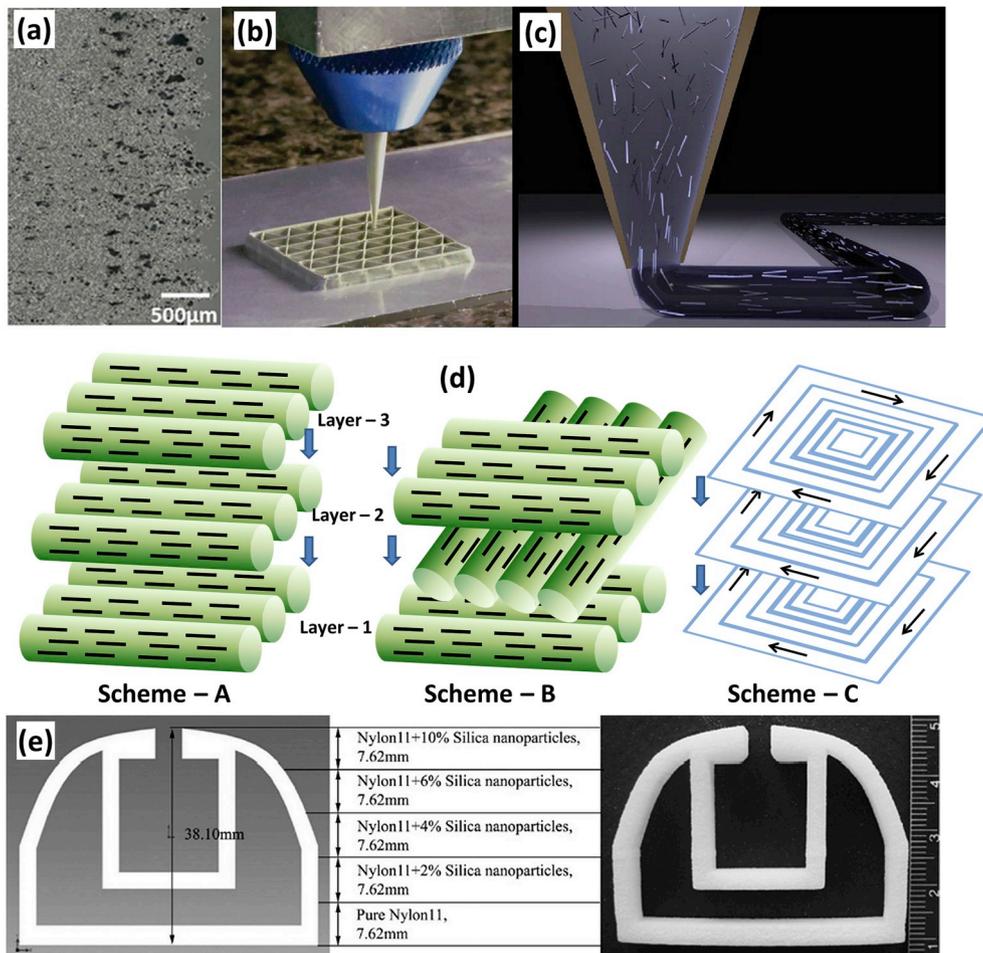


Fig. 17. (a) FFF processed ABS-30 wt% carbon fiber composite showing porosity [241], (b) DW processing of triangular honeycomb composite [267], (c) Schematic showing the alignment of short fibers within the deposit during DW process [267], (d) Schematic illustration of an approach to tailor fiber orientation in each layer by changing the deposition paths during FFF or DW, (e) Typical compositionally graded gripper fabricated using SLS [268].

high temperature and pressures. Further, during FFF processing the fibers are again exposed to high temperature which can further deteriorate their properties/characteristics. Since the viscosity of the polymer increases with fiber concentration the extrusion temperature must be increased to enable easy processing of NFRC filaments and is potentially detrimental to the stability of natural fibers. Use of appropriate plasticizers can address this issue.

Severe clogging of nozzles during FFF of fiber reinforced polymer composites with >40 wt% fibers (synthetic) is another importance challenge to be addressed. Further, it has been observed that feed stock filaments become brittle with high fiber loading [244]. Therefore, improving mechanical properties of fiber reinforced composites beyond certain limit, by increasing fiber loading, would be extremely difficult unless complete understanding of influence of fiber concentration on rheological properties, fiber-matrix interactions during feed stock preparation and AM processing is developed. However, addition of compatibilizers and plasticizers to polymer matrices can aid in improving processability.

Porosity/void formation and fiber orientation with natural fiber reinforcement plays a decisive role in determining mechanical properties of NFRCs. For example, parts made with PLA + PHA- 15.2 wt% recycled wood fibers showed significant amount of porosity [265], as shown in Fig. 16 b,d and e, which must be controlled via proper feed stock preparation and FFF process optimization. Similarly, ABS-carbon fiber composites produced using FFF exhibited large amount of gaps between deposition lines and porosity due to poor fiber-matrix bonding [241], as shown in Fig. 17a. Since the fiber orientation within the matrix have strong influence on composite properties, its control during AM processing assumes significant importance. The detrimental effect of

such porosity can be effectively eliminated by aligning the fibers along the direction of applied load. Although not all AM processes have a capability to tailor fiber orientation during processing, some of them (FFF and DW) provide this flexibility. For example, as shown in Fig. 17b and c, short carbon fibers within the epoxy matrix can be aligned along the deposited road (printing direction) [267] during DW process, which result in direction dependent mechanical and other properties. Moreover, it is plausible to design optimized structures with desired functional and mechanical properties and produce those using AM technologies by tailoring fiber alignment within each deposited road. Further, we also believe that by changing the deposition paths in each layer, fiber orientation in each layer can be changed to achieve design fiber alignment and mechanical performance, in particular site-specific properties in complex 3D parts, as shown in Fig. 17d. AM also offers unique capability to fabricate compositionally and structurally graded composite parts. Such graded composites provide property optimization in complex, net shape 3D parts at desired location to enhance overall performance and functionality. For example, Chung et al. [268] used SLS to produce Nylon-11 reinforced with 15 nm silica nanoparticles (0–10 vol%). A typical functionally graded part produced using SLS is shown in Fig. 17e, which exhibited non-linear and spatially varying mechanical properties.

Although manipulation of fiber orientation is possible with AM technologies, formation of voids during feed stock preparation and part fabrication (Fig. 16 b,d and e) can dramatically decrease mechanical performance of fiber reinforced composites. Recently, Wang et al. [269] demonstrated that by adding thermally expandable microspheres (2 wt %) to polymer matrix followed by appropriate thermal treatment of FFF processed composites can decrease voids in these composites. During

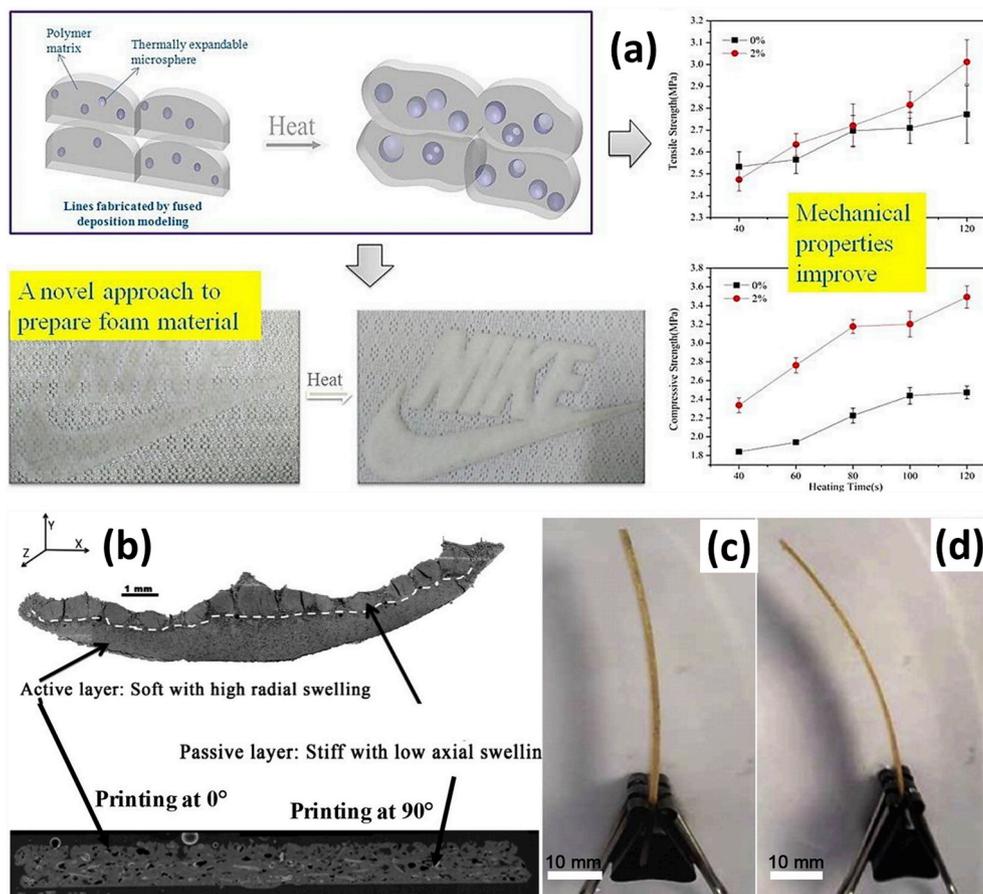


Fig. 18. (a) Schematic representation of thermally expandable microspheres in polymer matrix (left) and expanded deposit (left, below). Improvement in mechanical properties after thermal treatment of microsphere reinforced polymer composites [269]. (b) Design of hygromorph biocomposite. (c) Typical biocomposite (PLA + PHA- 15.2 wt% recycled wood fibers) made using FFF before immersion in water and after immersion (d) [265].

post-fabrication thermal treatment, the microspheres within the matrix expand and create compressive stress on the voids thus close them, Fig. 18a. It was observed that post-FFF heat treatment at 140 °C for short duration of 120 s results in ~25% and 52% improvement in tensile and compressive strength of the samples [269]. Increasing the microsphere concentration to 11 wt% resulted in decrease in the overall porosity from 17% to 7%. Alternatively, the formation of voids during AM of NFRCs can be utilized to manufacture hygromorphic biocomposites, which can be actuated depending on the moisture gradient for smart devices (moisture induced bending). For example, PLA + PHA-15.2 wt% recycled wood fiber composites, manufactured using FFF [265], shows actuation due to swelling when immersed in water, Fig. 18 b-d. The maximum actuation (or curvature) demonstrated to depend on FFF process induced porosity, which control the moisture absorption capacity and swelling of these composites.

From the above discussion, it is understandable that successful processing of NFRCs using AM and conventional processing as well, is limited by inherent characteristics of natural fibers, which depends on their chemical constituents. The dependence of different properties of natural fibers on their constituents, summarized in Fig. 19, shows contradicting compositional requirements to achieve desired properties such as mechanical, thermal, biological and moisture absorption. For example, processing temperature range for most of the polymer matrices is between 180 and 200 °C, where time dependent degradation of natural fibers can occur depending on the type of fiber (Fig. 6). High concentration of hemicellulose in the fiber, Fig. 19, provides high thermal stability to natural fibers, during processing and use. However, high hemicellulose in the natural fiber is detrimental to its mechanical properties and consequently to NFRCs properties as well. Similarly, high crystalline cellulose is beneficial for improved fiber mechanical properties with concomitant decrease in biological degradation and moisture resistance. It is interesting to note that majority of properties can be improved if lignin can be restricted to low concentration. It is believed that fiber treatments such as alkaline treatment (mercerization) are very effective in removing lignin (Fig. 4), which not only improves fiber-matrix interactions/bonding but also enhances other properties depicted in Fig. 19. Therefore, selection of appropriate fiber treatment and processing depends on type of fiber being used and final property requirements in NFRCs.

It has been discussed that addition of natural fibers to thermoplastics and thermoset plastics offer several benefits such a low-cost, eco-friendly, renewable and lower damage to processing equipment compared to synthetic reinforcements. However, NFRCs suffer from low mechanical properties due to fiber-matrix incompatibility and inherently weaker natural fibers than synthetic fibers [57]. These issues can

be effectively addressed by hybridization [271] of NFRCs by adding (i) synthetic fibers to polymer matrices in addition to natural fibers, (ii) more than one type of natural fibers with different mechanical and other characteristics/properties. Addition of synthetic fillers such as glass, talc, etc. along with natural fibers provide benefits of high mechanical and thermal properties from synthetic fillers and low-cost and renewability from natural fibers. Venkateshwaran et al. [272] studied epoxy-banana-sisal fiber hybrid composites with varying volume fractions of banana-to-sisal fiber and it was found that at 0.5–0.5 ratio the tensile strength of hybrid composites is ~50% higher than those of single fiber composites. Similarly, addition of glass fibers to jute-polymer composites significantly enhanced flexural strength of hybrid composites [273]. In another study, addition of sisal fibers reduced the thermal conductivity of composite and hybridization with glass fibers found to increase its conductivity [274]. Relatively small amount of research has been done on hybrid composites containing more than one natural fibers compared to hybridization using natural-synthetic fiber combination. A study by Neto et al. [275] showed interesting observations that chemical treatment of sisal and rami fibers enhanced the mechanical properties of their hybrid composites. However, same treatment found to have no positive influence on jute-curaúá hybrid composites. Combining short and long natural fibers can also provide similar benefits in enhancing properties due to auto-hybridization.

Other considerations for long-term sustainability and market acceptability of NFRCs include (i) continuous and reliable source of natural fibers (ii) energy and cost involved in fiber supply chain, (iii) tax incentives for production, use and recycling of NFRCs. Variations in fiber supply during seasonal and unseasonal times can affect their quantity, cost, quality and characteristics and therefore NFRCs production and properties. As discussed above hybridization of composites using different natural fibers can also address deficiencies in fiber supplies. Establishing processing and storage facilities near the farm land can provide significant cost benefits in the production of NFRCs.

6. Concluding remarks

Based on the studies performed so far, in the area of NFRCs, it can be said that natural fibers are certainly suitable to reinforce several polymers and thus improve their mechanical properties for use in wide variety of industrial sectors such as automotive, infrastructure, housing, packaging. Although, complete replacement of synthetic fibers with current natural fibers would be difficult due to their inherently low mechanical properties, the use of NFRCs expected to grow in future for specific applications in variety of industries. For example, use of light-weight NFRCs in automotive sector can achieve significant weight reductions (up to 25%) and thus result in fuel efficiency while simultaneously reducing CO₂ emissions and the use of crude oil. However, for commercial success of these composites it is imperative that large volume production and sectors such as automotive and packaging accepts and increases the use of NFRCs.

Currently, NFRCs suffer from low thermal stability, moisture resistance and mechanical properties. Although significant research efforts are in progress to address these limitations, newer blending techniques, hybrid polymer matrices, fiber surface modification approaches are required. These approaches enable better interfacial bonding between natural fibers and polymer matrices leading to enhanced processing, balanced mix of strength and stiffness, and thermal properties. Use of appropriate compatibilizers not only improves fiber-matrix bonding but found to have strong influence on final properties of these NFRCs. Since different natural fibers have different mechanical properties, depending on their composition, NFRCs with tailored mechanical properties can be plausibly manufactured by judicious selection of appropriate natural fiber and matrix combination. Further, attempts on multi-fiber (blend of two or more type of natural fibers) reinforced composites appear to be very less and such composites can provide more flexibility in terms of

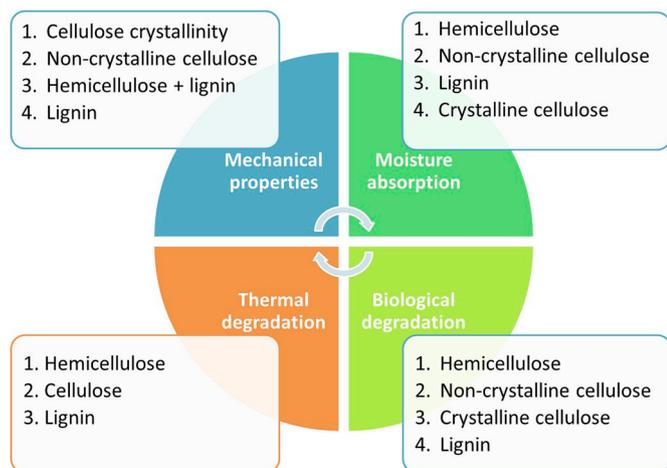


Fig. 19. Influence of constituents of natural fibers on their properties [adapted from Refs. [34,270]].

processing and tailoring properties. Similarly, blend of multiple polymers as matrices is also expected to address some of the inherent limitation of current NFRCs.

As discussed in this review, additive manufacturing (AM) of polymer composites demonstrated its potential in manufacturing net-shape, complex and functional parts for direct use. Further, the unique benefit of using AM to manufacture NFRCs is its ability to manufacture functionally graded composites with site-specific performance and functionality. It is also possible to design and produce structures with tailored fiber alignment by changing the deposition paths in each layer. However, AM of these composites poses significant challenges in terms of composite filament preparation for FFF, inherent agglomeration potential of nature fibers, large amount of moisture and void formation, difficulties in 3DP of NFRCs due to nozzle clogging, fiber degradation/breakage, non-uniform curing, etc. Poor layer-to-layer and fiber-matrix interfacial bonding are two serious issues in AM of NFRCs as the pressures associated with AM are significantly lower than those in conventional processing routes such as compression or injection molding. Therefore, more focus is required to address these issues by modifying the AM process parameters, hardware and feed stock quality. It is known that increasing the fiber concentration in NFRCs is required to achieve maximized mechanical performance. However, excessive fiber content found to clog deposition heads in addition to increased brittleness of feedstock. Therefore, fundamental understanding on the influence of natural fibers, their characteristics and concentration on the rheological properties of polymer matrices, fiber-matrix interactions is essential, which is not yet clear. Such an understanding will enable addressing fiber damage during multi-step feed stock preparation followed by AM of NFRCs. Finally, the success of NFRCs processing is inherently limited by natural fibers' characteristics and their chemical constituents as they found to have contradicting effects on mechanical, thermal, biological and moisture absorption properties. However, decreasing lignin concentration in these fibers can improve majority of properties and therefore, appropriate fiber treatment become very crucial in NFRCs processing. Overall design and processing of NFRCs using AM is very challenging but equally rewarding.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compositesb.2019.106956>.

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