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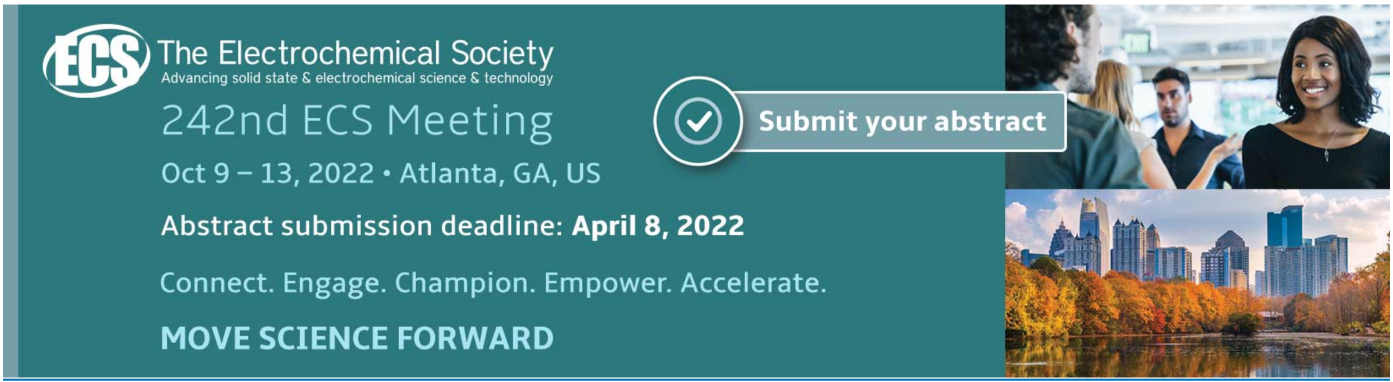

A review on 3D printing bio-based polymer composite

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Abstract. Polymers play a vital role in our daily lives. In various fields such as medical, food industry and automotive applications, the use of biopolymers is commonly used. The most widely used polymers and fillers among biopolymers are polylactic acid (PLA) and cellulose, which are biocompatible and biodegradable due to their eco-friendly properties. Extensive usage of cellulose in various forms has been applied in combination to PLA but there is only a few research that has been done by using the 3D printing method. This paper covers the types of biodegradable biopolymer materials, types of coupling agents and plasticizers, mechanical properties and applications. This paper discusses the types of cellulose ranging from micro to nano, including other types and sources of cellulose that have been researched and are compatible with PLA. In order to generate biocompatible polymers with stronger and better mechanical properties, the findings of these experiments are all tied together. These biopolymers are commonly used in the biomedical industry and are expected to improve their benefits in this field.

Keywords: Biopolymers; Polylactic Acid (PLA); Cellulose; 3D Printing; Mechanical Properties; Applications.

1. Introduction

Additive manufacturing is a technique that applies consecutive content layers to form a 3D model that requires the use of a computer-based 3D model as well as a 3D printer and a process to develop a physical model that is based on the original model concept[1, 2]. In the past years, additive manufacturing (AM) has been frequently utilized as an effective way of prototyping and generating parts with a high level of fracture surface[1]. It offers the facility to create goods at a higher pace and with dimensional precision than most modelling approaches [3]. 3D printing controls the principle of additive manufacturing (AM) which is widely termed as rapid prototyping (RP) and free-form manufacturing that involves a range of methods that uses a layer by layer process to develop parts or items typically of small size, limited quantities and customized design [2]. 3D Printing (3DP) is an extremely versatile fabrication system which can be enforced on various materials, such as ceramics, metals, polymers as well as other materials [1]. FDM is commonly utilized in additive manufacturing processes that produces practical prototypes of many thermoplastics because of its ability to safely build high-quality complex goods. Besides, different additive manufacturing techniques are available, for example, FDM (fused deposition modelling), DMD (direct metal deposition), 3D printing, SLS (selective laser sintering), IJM (inkjet modelling) and SLA (stereo-lithography). Each technique is different in terms of the method and materials that are used for production [3]. While there are many approaches available linked to 3D printing, a technique that is used widely is fused deposition modelling (FDM). This additive manufacturing method allows us to obtain products with better durability, dimensional precision, surface roughness [4]. Materials such as acrylonitrile-butadienestyrene and polylactic acid are frequently used polymer materials for additive processing filament [5].

During the manufacturing phase of a product, the usage of 3D printing has reduced the extra costs encountered. Besides, with comparatively low prices, additive manufacturing can 3D print limited amounts of personalized products [6]. Besides, over the years, the resolution, precision, usability, and repeatability of 3D printed products have increased. The rising number of 3D printers and quick access to applications has resulted in a decrease in the cost of the production process. [7].

3D printing is driving major modernization in a wide variety of fields involving medical equipment, biotechnology and so on [8]. Oprea (2020) suggested that more works need to be done using 3D printing when involving cellulose in order to obtain biomaterials. The FDM process is therefore commonly used in aerospace, automotive manufacturing, bio-medicines, smart houses, stationaries, training aid and artistic gifts [9]. On the other hand, this process has been used for many years to manufacture products for aerospace, medical, mould design and industrial applications from a wide variety of materials, such as plastics, metal powder, ceramics and composites [10]. It is possible to ensure the consistency of FDM 3D printed components that are specially designed by altering printing variables such as the thickness of a layer, orientation of printing and air gap [11].

Graphical description of various biopolymers origin is represented in Figure 1 [12] as polymers play a crucial role in our everyday lives. The assortment of materials are based on the characteristics are defined as the word 'biopolymers'. However, the monomeric units of the biochemical composition and polymers can be classified into two major groups which consist of polymers that are produced biologically and synthetically[12, 13]. Synthetic and natural biopolymers and the subdivision are shown in Table 1 [12]. Therefore, biologically produced polymers are examples of natural polymers derived from animals, microorganisms and plants whereas oils, sugars and amino acids are chemically synthesized polymers that are synthetically processed biopolymers are extracted from biological material. Polyesters, polylactic and polycarbonates are synthetic biodegradable polymers, while polyethylene and polypropylene are some examples of synthetic non-biodegradable [12]. Metabolic processes involving enzyme-catalysis and activated monomers through chain-growth polymerization reactions produce natural bio-degradable polymers[14]. The usage of biopolymers is wide such as they are used in the medical, food industry, which involves additives and packaging materials [12]. This review paper aims to discuss the studies related to bio-based polymer composites which are biodegradable by using 3D printing. Particular focus will be given to Polylactic acid (PLA) reinforced cellulose.

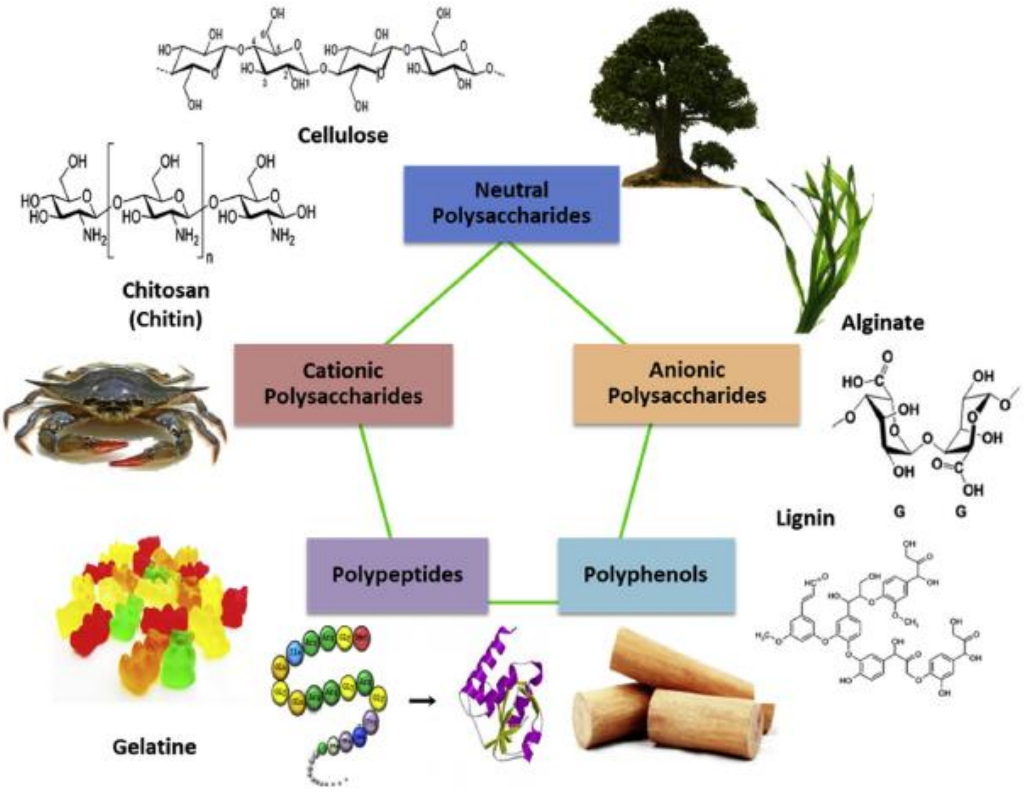

Figure 1. Biopolymers from different sources.

Table 1. Biopolymer categorization.

		Biopolymers	Reference
Natural	Protein	Soy protein, collagen, fibrinogen, silk, gelatin	[13]
	Polysaccharide	Cellulose, starch, chitin, Hyaluronic acid	[5,18]
Synthetic	Biodegradable	Polylactic acid, Polyglycolide, Polycaprolactane, Polyvinyl alcohol, Polyhydroxybutyrate, Polyglutamic acid	[5,7,18,21]
	Non-biodegradable	Polyolefins, Nylon, Polyurethane, Polypropylene, Polyethylene, Polyamides	[7,21]

2. Materials

2.1. Polylactic Acid

PLA has made tremendous strides due to its biodegradability within the 3D printing sector. Generally, for example, corn starch is extracted from biomaterials and is biodegradable in compost, PLA is more renewable and presently in use which has been authorized for numerous biomedical applications [15, 16]. Also, there are hardly have any thermal warping or curling problems with 3D printed PLA parts [16]. Since the PLA is a semi-crystalline structure, thus, the mechanical properties and crystalline structure of PLA are significantly affected by thermal background. Therefore, thermal annealing therapy is a widely used method aimed at removing the impact of the thermal background and rebuilding the crystallinity, crystallite size, and mechanical properties of PLA [16].

In addition, thermal annealing is intended to increase the crystallinity of semi-crystalline polymers by adding thermal heat in between the transition temperature of the polymer (Tg) as well as the melting temperature (Tm). Thermal annealing stimulates the mechanism of polymer nucleation, which further enables existing crystallites to expand [17]. Furthermore, plant-derived fibres like, kenaf, hemp, flax and bamboo fibres were utilized to improve PLA. Micropowders resulting from agricultural by-products have also been packed with PLA. The composite modulus was typically increased, although the elongation at break reduced relative to tidy PLA. A good effect of natural fibres and man-made cellulose fibres on the mechanical properties of roller card-oriented PLA-based composites. [18]. In addition, utilizing nanofillers, nanocomposites can be treated very easily, but the composite's biodegradability was impaired [19].

2.2. Types of fillers (cellulose)

Natural resource-based green polymers are an environmentally sustainable alternative to traditional materials, and its use will minimize the vast amount of non-biodegradable waste created on a daily basis by the pharmaceutical sector. Thus, among these polymers, owing to its unique properties and biocompatibility, cellulose, the key component found in the structure of plant wall and also developed by some microorganisms, is intensively studied in form of aerogels, hydrogels, fillers or films for biomedical application [20]. With its outstanding qualities such as biodegradability low density, toxicological harmlessness, eco-friendliness and robust thermal, cellulose, bio-based polymer, shows tremendous potential uses in automobile, plastics and packaging sectors. In addition to reducing the overall cost of the material from the pure polymer, these cellulosic fibres may also act as composite material reinforcements. It is commonly used for the preparation of (partially) bio-based and biodegradable composites. For instance, using cellulosic fibers, the mechanical characteristics of plastics like PLA, polycaprolactone and polyamide have been modified. Cellulose has an almost ideal inerratic form and robust mechanical properties as an organic raw resource. It was used in composite materials as a fiber improver, and its scale, morphology, and structure governed the enhancing effect [15].

Based on Figure 2, from the studies conducted, many researchers have used nanocellulose as the fillers to be reinforced in PLA compared to microcellulose and other cellulose. Properties of fiber-reinforced composites are highly affected by reactions between the materials. It’s well recognized that the use of nanometer-sized fillers helps one to improve the surface contact of a filler/matrix and change properties at relatively low loading speeds [18]. Therefore, nanocellulose consists of many types of fillers such as nanocrystalline cellulose, cellulose nanofibers (CNF), cellulose nanocrystals (CNC), carbonized cellulose nanofibers (CCNF), man-made cellulose and cellulose nanowhiskers. As strengthening fillers for different natural polymeric matrices, for example, polylactic acid (PLA), polyhydroxyalkanoates (PHAs), poly(vinyl alcohol) (PVA), natural rubber or starch, CNCs, CNFs and BC are often utilized [20]. Majorly from plants or vegetation, cellulose nanofibers (CNFs) are obtained. Due to its exceptional mechanical, physicochemical properties, CNF has been widely used as a filler material for polymer resins. However, when combined with hydrophobic polymers, for example, PLA, the existence of CNF-strong hydrogen bonds typically creates dispersion problems [16].

As for microcellulose, it consists of micro fibrillated cellulose and microcrystalline cellulose. Besides, other cellulose is categorized as natural cellulose, natural fiber, cellulose fiber, man-made cellulose and abaca fibers. A complete "biocomposite "can be produced by using natural fibres only. The 'lightweight capacity' of natural fibres (NF) is one of the key benefits. Venkatarajan (2020) stated that polymer composites strengthened with natural cellulose fibres have recently gained substantial recognition among researchers for their eco-friendliness and strong physical as well as mechanical properties. Due to their desirable advantages, such as renewability, availability, low cost, low density and adequate mechanical properties, natural cellulose fibres are known as a possible alternative to synthetic fibres in polymer matrix composites [21]. Only natural fibres of technological consistency ensure adequate reproducibility of mechanical characteristics [19]. In addition to plant fibres, PLA may be reinforced by man-made fibres dependent on recycled raw materials, for example, viscose, rayon (Cordenka) or Lyocell [22].

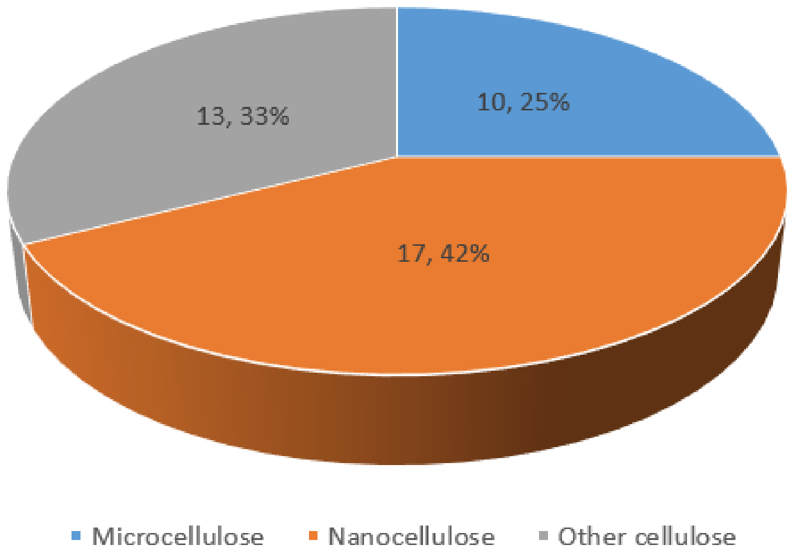

Figure 2. Types of fillers that are suitable for cellulose.

2.3. Types of coupling agent & plasticizer

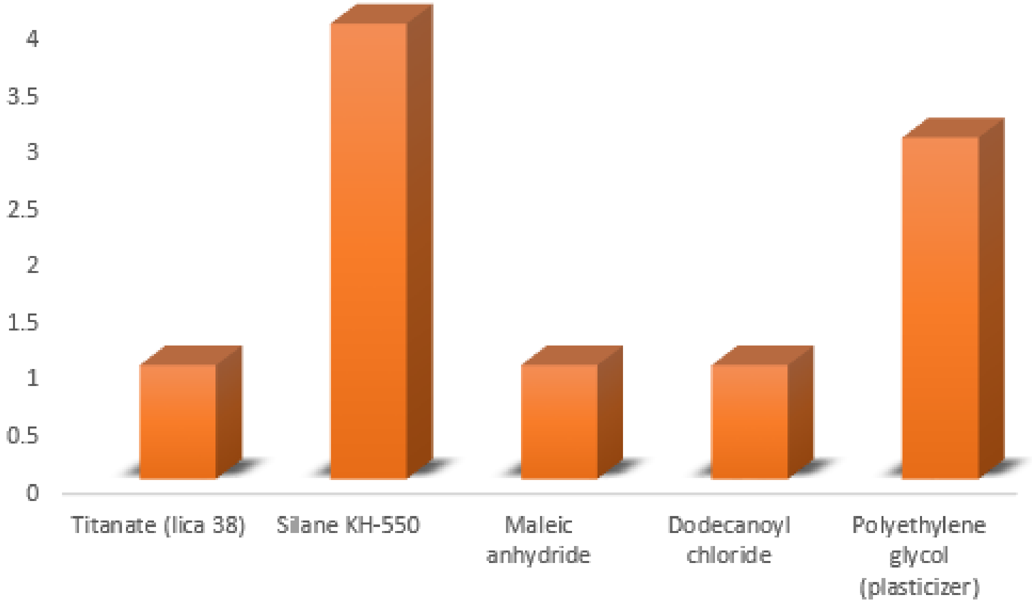

Figure 3. Coupling agent & Plasticizers.

From the studies conducted based on Figure 3, the commonly used coupling agent is silane KH-550 and followed by Polyethylene glycol, which is used as a plasticizer. Likewise, as a plasticizer, silane-coupling agent (KH-550) as well as polyethylene glycol (PEG) has been reported to work with each other to increase the sustainability and printability of 3D-based composite filaments [16]. Two techniques are primarily known in order to preserve the proper viscosity of the PLA-printing ink which are raising the manufacturing temperature or by using a plasticizer. It is more effective to use a suitable plasticizer because it helps the material to survive at low temperatures without triggering any thermal deterioration. In general, low molecular weight polyethylene glycol has been commonly accepted as an effective plasticizer for PLA. It is, therefore anticipated that the use of PLA/PEG blends could enhance the manufacturing process of 3D structures for tissue engineering [23].

PEG with strong interfacial compatibility was commonly used in industrial processing technology as an essential plasticizer [15]. In addition, PEG is a biocompatible hydrophilic, polymer utilized in many applications, ranging from industrial processing to biotechnology [23]. Cellulose micro/nanomaterials could be added to reinforced PLA based bio-composites only with modification. To improve its stability with the PLA matrix and microcrystalline cellulose, and to increase the crystallinity and storage modulus of the resulting bio-composites, the titanate coupling agent (Lica38) has been published [16].

3. Mechanical properties of PLA reinforced cellulose

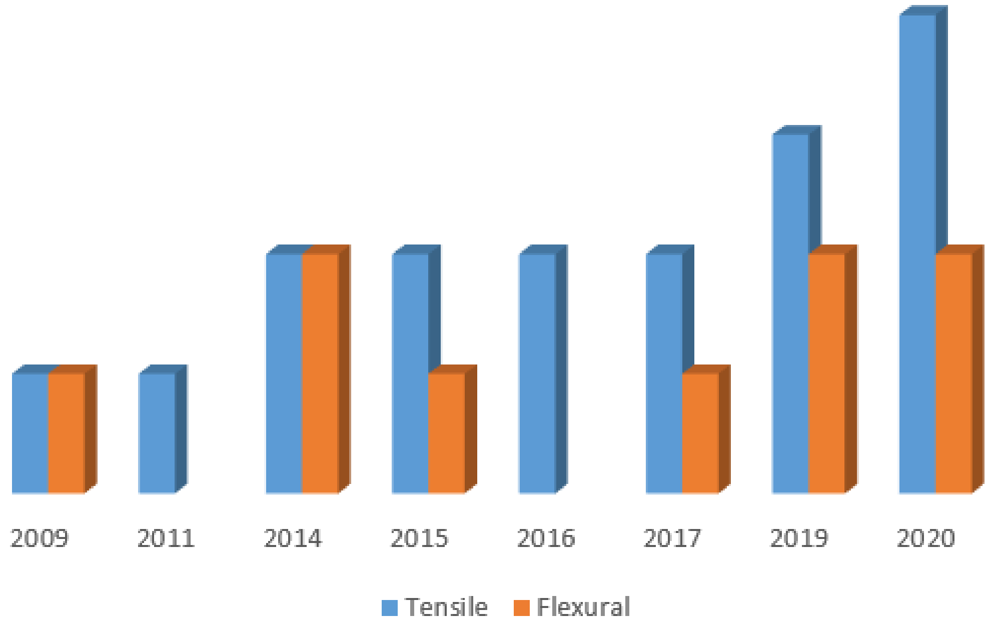

Figure 4. Types of mechanical properties to study PLA reinforced cellulose.

The evaluation of mechanical properties aids in the analysis and development of more effective and less expensive components and goods as they last longer. Thus, by determining the mechanical properties, it helps to develop and design items that are needed. Various mechanical testing experiments were undertaken to research the polymer composite mechanical properties, for example, tensile test, impact test and flexural test. Based on Figure 4, the tensile strength test is the most common test that is preferred by researchers when compared to other tests which are flexural, impact (Izod) and impact (Charpy) test. Awal (2015) reported that, with the addition of fibres and fillers, the mechanical properties of PLA bio-based composites might be strengthened. As an example, Awal (2015) stated that initially, the tensile strength of PLA was 62.7 MPa. However, the tensile strength was improved due to the fibre reinforcements as wood fibres were integrated into the bio-composites [24]. In addition, Bledzki (2009) stated that a boost in tensile strength by factor 1.45 could be accomplished with the addition of 30 % wt of man-made cellulose fibres [19].

4. Applications of cellulose in biomedical fields

The application of cellulose can be implemented in various medical fields such as pharmaceutical, dental and medical fields [25]. Therefore, the most significant fact, however is that cellulose is a polymer of natural origin and has a highly biocompatible character. These characteristics are one of the potential prospects relevant to the applications of cellulose derivatives in the biomedical field [20]. Recently, with many developments in the biomedical field, nanocellulose has been identified as an essential biomaterial. This application includes the growth of blood vessels, nerves, skin substitutes for burns and wounds, the mechanism of drug release, regeneration of gums, tissue engineering scaffolds and bone reconstruction. Nanocellulose mats were known to be very skilled in facilitating pain relief and accelerating granulation for successful wound healing. The structure and scale of such membranes could be manipulated to make them adequately efficient for the treatment of large and diverse body regions. Thus, with the help of nanocellulose, dental tissue reconstruction is being carried out. Crystalline nanocellulose is known to have several significant benefits as a drug delivery excipient. The advantage of having a considerably larger nanocrystalline cellulose surface area makes it possible to bind vast amounts of drugs to the surface of this cellulosic material with the promise of high payloads and optimal dosing power [25]. In many industries such as automotive, aerospace, maritime, electronic, packaging, and building, natural fibre reinforced polymer composites have been used due to its outstanding properties and benefits found over synthetic fiber reinforced polymer composites [21]. Table 2 summarizes the application of cellulose in the biomedical field.

Table 2. Application of cellulose in biomedical field.

Field	Applications	References
Medical	Growth of blood vessels, nerves, skin substitutes for burns and wounds, bone reconstruction, tissue engineering scaffolds	[21,26]
Dental	Dental tissue reconstruction, regeneration of gums	[26]
Pharmaceutical	Drug delivery	[26]

5. Conclusion

The types of commonly used biopolymers consisting in the group of biodegradable have been analysed in this article. Extensive usage of cellulose in various forms and sizes have been used as fillers. In order to improve the printability and sustainability of composite filament based on 3D printing, silane-coupling agent (KH-550) and polyethylene glycol are used as plasticizer. In general, based on the research that has been performed, the most widely used mechanical properties to measure the PLA/cellulose specimens are tensile strength compared to others. As PLA is a semi-crystalline polymer, the thermal annealing process is highly recommended to increase its crystallinity. Thus, due to its highly bio-compatible characteristics different forms of cellulose are being used in the biomedical while PLA are being incorporated in automotive, aerospace and packaging industry. Some research studies suggested that in order to obtain biomaterials, more work needs to be done using 3D printing when cellulose is involved.

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