Energy-Efficient Biodegradable Foams for Structural Insulated Panels

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Introduction

Residential and commercial buildings are responsible for roughly 40 percent of U.S. energy consumption [1]. Within these types of buildings, space heating and cooling was responsible for roughly 36% of the energy consumption in 2005 [2]. Moreover, attributes of the building envelope have a large impact on this energy consumption, namely how much energy is needed to maintain comfortable room temperatures. For instance, heat loss can occur through walls, windows, ceilings, floors, doors, and infiltration (e.g. leaks out of cracks and holes). One area in particular where advancements have been made for homes is in the use of structural insulated panels (SIPs).

SIPs consist of two outer skins sandwiching an inner core made of an insulating material (Figure 1). Together they form a monolithic structural element that can be used as the structure of a building, i.e. no structural frame is needed. For energy efficiency, this is an advantage as it has been shown that frames and studs are thermal bridges that lower the effectiveness of any insulation material around them by serving as "leaks". Furthermore, as the SIPs are compressed together, there is less possibility for voids to exist in the insulation, which would lower the R-value of the wall. Infiltration is also less likely in a building that uses SIPs as there are fewer gaps to be sealed during construction.
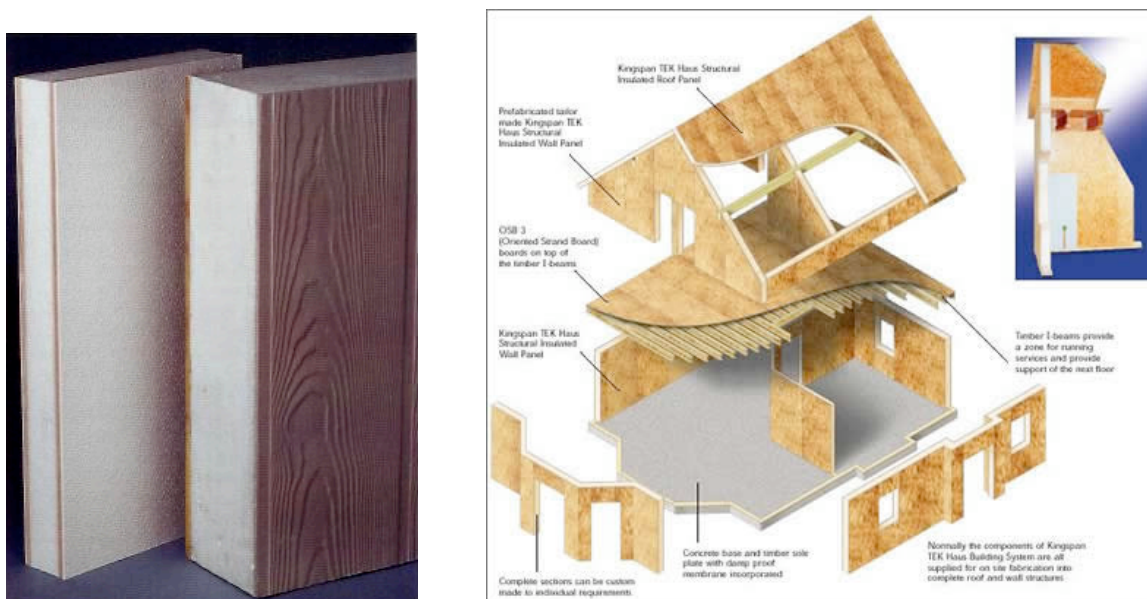

Figure 1. Sample SIPs with EPS cores (left, [3]) and a schematic of a house built with SIPs (Kingspan TEK Building System)

Current common materials used in manufacturing SIPs are plywood or oriented strand board (OSB) for the outer skins and petrochemical-based molded expanded polystyrene (EPS) and extruded polystyrene

(XPS). Polyurethane foams are also used but in only ~5% of SIPs produced today; limited use of polyisocyanurate foams also occurs. Recent research at Stanford by Prof. Billington and Prof. Criddle (CEE) has led to the development of composite materials made entirely from renewable resources that have properties capable of serving as replacement materials for engineered wood such as OSB and petrochemical plastics. We now believe there is also strong potential for these materials, in particular those based on polyhydroxyalkanoates (PHAs), to be used as insulating foams to produce a truly "green" and more energy-efficient wall material for residential and commercial buildings.

Polymer foam is a large and diverse industry that touches almost every aspect of daily life. In addition to the expanded polystyrene and polyurethane foams, other polymers that have been fabricated into foamed products include high-density and low-density polyethylene (HDPE, LDPE), polypropylene (PP), polyvinyl chloride (PVC), and poly(ethylene terephthalate) (PET) [4]. Along with the obvious reduction in material costs compared to the unfoamed case, the cellular structure of the foam produces very low thermal conductivity materials, making them excellent thermal insulators [5].

Recently, concerns about the potentially harmful effects that non-degradable plastics may have on the environment and about the depletion of petrochemical feedstocks has raised new challenges for the polymer foam industry. In response, interest is growing in a new generation of foamed polymers made from sustainable and biodegradable materials. None of the current petrochemical-based foams fabricated from polystyrene, polyurethane, polyethylene, polypropylene, poly(vinyl chloride) and poly(ethylene terephthalate) are biodegradable. Several research groups have carried out studies on the extrusion foaming of well-known biodegradable aliphatic polyesters, such as poly(lactic acid) (PLA) [6, 7] and poly(caprolactone) (PCL) [8] and their blends with starch [9]. Successful development of biodegradable foams would entail a critical step in the development of energy-efficient "green" buildings and completely biodegradable packaging systems.

The objective of the proposed research is to develop a biodegradable polymer foam based on a microbial-produced polyester that will compete successfully with expanded polystyrene, which is the industry standard, for energy-efficient construction. In particular, we propose that a new class of biodegradable polymer foams can be made from another member in the aliphatic polyester family, poly(hydroxyalkanoates) (PHAs), whose structure is shown in the following:
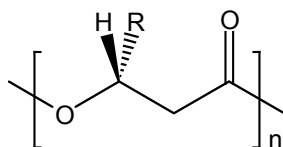

Fig. 2. Structure of poly(hydroxylalkanoates) (PHAs). R refers to an alkyl group; if R is CH_3, the compound is poly(hydroxybutyrate) or PHB; if R is CH_2CH_3, the compound is poly(hydroxyvalerate) or PHV; Poly(HB-co-HV) copolymers are also possible.

PHAs are produced as intracellular energy storage materials by bacteria under growth conditions when a critical nutrient is missing [10]. Besides being enzymatically degradable, PHAs possess good mechanical properties that are often compared favorably to petroleum–based foamed thermoplastics. For instance, poly (3-hydroxybutyrate) (PHB), the most widely investigated member of the PHA family, has similar degree of crystallinity, glass transition temperature, melting temperature, Young's modulus, and tensile strength as polypropylene (PP), a very tough, robust material [11]. Studies have shown that PHB, which has been used mainly in medical applications [12, 13], may be processed by melt spinning and compression molding [14, 15], but little work has been performed on its extrusion or foaming. At present, PHB is expensive, but separate research by Professor Criddle on the use of landfill-produced methane or waste treatment plant volatile fatty acids as feed stocks is expected to lower the cost significantly (see discussion of Precourt Institute Criterion #2), as will the fact that the building materials will be recyclable.

Precourt Institute Evaluation Criterion #1: Research Plan

Preparation of polystyrene foam – a reference point for comparison
In order to allow comparison between the industry standard PS foam and our proposed PHA foam, we first offer a brief description of the PS foaming process. In fact, two approaches are taken. In the first, expanded PS (EPS) is typically prepared by a multiple-step process: (1) PS is synthesized by suspension polymerization in which styrene monomer is dispersed in water as droplets that are stabilized by a colloidal additive and a monomer-soluble free-radical initiator is added to initiate the polymerization process, (2) the resulting PS particles (0.2-3.0 mm diameter) are washed, separated by size, and dried, (3) particles are exposed to a physical blowing agent consisting of a volatile hydrocarbon (e.g. n-butane, n-pentane, isopentane), chlorinated hydrocarbon (e.g methylene chloride), or chlorofluorocarbon (e.g. HCFC-22), (4) PS particles are pre-expanded to a density very close to their final value by heating, (5) pre-expanded PS particles are poured into a mold and fused by heat and pressure into the final shape.

In the second process, extruded, expanded PS foam (XPS) is prepared by melt foam extrusion. In a typical XPS foam extrusion process, PS pellets along with stabilizers and a physical blowing agent (e.g. HCFC-22) are fed into an extruder, where they are melted and mixed under elevated temperature and pressure. Gases generated by the blowing agent dissolve in and plasticize the PS matrix, enhancing phase homogeneity. Upon leaving the die, the pressure gradient will cause the dissolved gases to expand and diffuse from the bulk interior to the surface. At the same time, solidification of the PS melt due to cooling will constrain the release, and the balance of these two effects leads to foaming. To obtain a low-density foam, the PS melt undergoes high biaxial extension to form cell faces. For this melt inflation process to succeed, the melt must sustain high tensile stresses without cell face fracture, which would cause neighboring cells to merge. A melt with low viscosity and low melt elasticity often lacks sufficient tensile strength, causing cell faces to fracture, even coalesce, leading to foam collapse [4].

While the EPS and XPS processes yield low-density foams, both processes have the potential for significant environmental pollution by volatile organic compounds that either contribute to greenhouse gases or are deleterious to the ozone layer. Choice of physical blowing agents has fluctuated between initial use of highly volatile hydrocarbons, then to the chlorofluorocarbons and, with the growing concern about the ozone layer, back to the volatile hydrocarbons. The Montreal Protocol gives industry until 2030 to eliminate HCFCs entirely, but these are the only types of blowing agents currently used for XPS as well as for polyisocyanurate foams. Research is currently underway to develop super-critical carbon dioxide as a blowing agent.

Poly(hydroxyalkanoates) – an alternative material approach
To be successful, the proposed research on bidegradable foam insulation for energy-efficient construction must address two limitations of the PHB homopolymer produced by the microbial route: (1) low melt elasticity, and (2) a narrow thermal processing window [10]. The low melt elasticity inherently stems from the lack of long chain branching and the relatively narrow molecular weight distribution produced by the microbial synthesis. In addition, since PHB is highly crystalline, a high processing temperature (close to or above T_m) is needed. At this temperature, the thermal degradation of PHB is significant; random chain scission occurs at ester groups through a six-member ring ester decomposition reaction within the time scale of the melt extrusion process [16-18]. The degradation causes the molecular weight to decrease and thus further weakens the melt strength. Therefore, finding methods to decrease the melting temperature of PHB (or the derivative materials) and, hence, the processing temperature and improve the melt rheological properties is critical to being able to replace EPS and XPS as the foam core material of SIPs.

Although we have found no published information on processing details for fabrication of PHB foams, we believe that there is a strong analogy to polypropylene, which may be fabricated both by a bead

foaming process (like EPS) and by melt extrusion (like XPS). PHB and PP have very similar thermal and mechanical characteristics as well as degree of crystallinity. Considerable information exists on the microstructure and processing of polyolefin foams, which include low-density polyethylene (LDPE) and polypropylene (PP). The key to achieving good foam stability is to have high melt modulus and elasticity, which is normally accomplished by having a small percentage of long-chain branches attached to the main polymer chain. This is intrinsic to the LDPE structure, but processing conditions for PP needs to be manipulated to achieve the same result. A simple solution is to add a small amount of cross-linked gel to the melt; resulting chain entanglements effectively increase the melt elasticity to achieve good foaming behavior. We intend to include the same approach as one of the protocols for PHB modification, to be described shortly.

Once we have developed a suitable foaming protocol, we will work on optimizing it to achieve the highest possible insulating characteristics for SIP fabrication. The bulk foam density is critical to this, with the thermal conductivity decreasing as the density decreases. In addition, the nature of the cellular structure is important, and a detailed analysis of the contributions of conduction through the polymer struts and cell walls, convection of the gas trapped in the closed cells, and radiation from the cell walls exists. This analysis explicitly incorporates cell size, bulk density, and polymer material characteristics, so we will have a strong analytical tool to use to systematically evaluate the relationship between chemical composition and structure, processing protocol, foam morphology, and the mechanical and thermal characteristics of the model SIP structures

Facing these challenges, our work aims to achieve low-density PHB-based biodegradable foams by properly tuning the melt rheology and optimizing various foaming process conditions. We would like to achieve better understanding of how the enhancement of viscoelastic properties of the PHB melt could lead to improved processability and foamability. To achieve these goals, we will consider three methods as described below and their combinations:

PHB copolymers or blends: Our first approach will be to use copolymers of PHB or PHB/PHB copolymer blends. A general formula for PHB copolymers is shown in Fig. 3.

Fig. 3. Structure of PHB copolymers
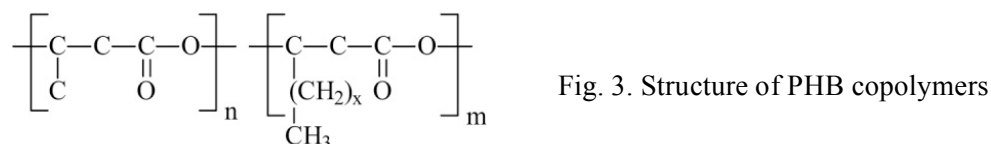
By incorporating other type of monomers with bulky side branches (x=1-18 in Fig. 3) into the main chain, the long-range packing of PHB is disrupted, resulting in a lower degree of crystallinity and a reduced melting temperature. As a result, the degradation rate will decrease and the melt processing window will become broader [19-21].   Research has shown that copolymerization of 3-hydroxybutyrate with monomers such as 3-hydroxyvalerate, 4-hydroxybutyrate, or 3-hydroxyhexanoate can be realized by feeding different molecules to the fermenter or by using different bacterial lines [10, 22].

While the use of microbial fermentation with variable feedstock is an ultimate goal for the production of PHB copolymers, this work, which is being carried out in the Criddle laboratory, is outside the scope of this proposal. However, commercially available materials will allow us to develop the necessary understanding of how molecular structure affects rheological processing, how this subsequently determines cellular morphology, and what the consequences are with regard to the thermal insulating

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characteristics. The PHB homopolymer and several copolymers of hydroxybutyrate (HB) and hydroxyvalerate (HV), commercially named Biopol, with HV contents of 5, 8 or 12 wt. %, are available from Aldrich Chemicals. This microbial copolymer has been produced by *A. eutrophus* from propionic acid or pentanoic acid [22] and has been the subject of extensive and ongoing research for biomedical applications [14, 19, 20]. Depending on HV content, the melting temperature can be reduced by between 50 and 180°C. Moreover, the mechanical properties of these copolymers are also improved over those of the PHB homopolymer [23]. Another series of such copolymers (named Nodax) developed by Procter & Gamble have longer alkyl branches (x=2-18 in Fig. 3) compared to Biopol (x=1). It is quite conceivable that these PHAs will have high melt elasticity and provide increased foam stability.

<u>Chain extension in the melt:</u> Our second approach to achieve the desired material properties will be to chemically modify the molecular composition by chain extension or branching during the melting process and thus to tune the melt rheology. Macromolecular architecture modification has been shown to strongly influence the viscoelastic properties of the polymer [20]. There are two ways to accomplish this: (1) to optimize the molecular weight and molecular weight distribution, and (2) to induce branching of the macromolecules. Both methods will increase the melt modulus, which prevents the cell walls from rupture and collapse during foaming, allowing cell density to increase and foam density to decrease [4]. A combination of diol and diisocyanate will be used as chain extension and branching reagents, respectively; this technique has been used previously on polyester-based polyurethanes. The most popular isocyanates are toluene diisocyanate (TDI), 4,4-diphenylmethane-diisocyanate (MDI), and their derivatives. Here the diol serves as the first coupling agent and acid value reducer to link the carboxyl groups of PHB, whereas the diisocyanate comes in next and reacts with hydroxyl end groups of PHB to achieve chain extension. As proof of concept, Di et al. (2005) reported realizing chain branching of PLA using this method, where they reacted small amount of a 1,4-butanediol with the PLA chain and then added 1,4-butane diisocyanate to link the chains together through the cyanate-hydroxy bonds [24]. The modified PLA showed an enhanced melt viscosity and elasticity, producing PLA foams with a two-fold density reduction. Furthermore, both the diisocyanates and diol components could be varied to produce foams with a wide range of properties. To go one step further, if the diol is mixed with some triols or polyols, based on glycerine and polyproylene oxide (PPO), the PHB would become crosslinked.

<u>Blends and particulate additives:</u> Our third approach will be to blend PHB with other components, such as starch, polymers, nucleation reagents and plasticizers. Such techniques have been widely applied to improve the foamability of semicrystalline polyolefins, e.g. polypropylene and polyethylene are often blended together to make better foams. It has been shown that adding other polymers as blending modifications can increase the polymer melt strength effectively and decrease the sensitive dependence of melt viscosity on the temperature [25]. Moreover, incorporating nanoparticles, such as clay, $CaCO_3$ or nucleation reagents like talc, has also been shown to improve nucleation and retard the growth of bubbles, thus reducing the cell diameter and the corresponding tension on polymer melt [26]. Blends of PHB and the copolymers with other polymers have been widely studied [27-42]. Some of these methods have been shown to effectively improve melt viscoelastic properties, e.g. Yamaguchi and Miyata reported that blends of PHB-HV and a small amount of lightly crosslinked gel greatly enhances the melt elasticity [43].

Material characterization
First, we will characterize bulk material properties, such that we can identify those suitable for the foaming process.
- Molecular weight of the commercially available PHB and copolymers will be evaluated with gel permeation chromatography in the Department of Chemical Engineering.
- A TA Instruments Q100 differential scanning calorimeter in the Shared Experimental Facility (SEF) of the Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA) will be used to determine melting, crystallization, and glass transition temperatures and the degree of crystallinity.

- A TA Instruments AR2000 Rheometer in the CPIMA SEF will be used for the determination of the polymer melt viscosity, elasticity, and other rheological properties
- An FEI XL30 Sirion scanning electron microscope in the Stanford Nanocharacterization Laboratory will be used to study the morphology of the PHB-based foam, including cell size, shape, and cell distribution in the foamed structure.

Second, we will characterize foam properties, such that we can identify how best to apply them in SIPs and other insulation systems in buildings.
- An Instron 5844 mechanical tester in the CPIMA SEF and/or a Model 858 MTS test system in the Blume Earthquake Engineering Research Center will be used for measuring the mechanical properties of the final foam materials. The tensile and compressive stress-strain relationship, Young's modulus, flexural, and shear strength as well as shear modulus will be determined (all fixtures needed are available).
- A heat flow meter apparatus will be fabricated and used to determine thermal conductivity as per ASTM C518, and R-values for the foam will be calculated and verified by testing samples of different thickness. We will also monitor the loss of insulating capacity over time.
- Resistance to moisture will be measured in terms of water absorption and water vapor permeance as well as dimensional stability using a new ATLAS Weatherometer on order for the Sustainable Construction Materials lab in the new Yang & Yamazaki Environment & Energy Building.

SIP fabrication and testing

The key components of a SIP are the facing sheets (e.g. plywood. oriented strand board), a rigid foam core, and an adhesive joining the sheets to the core. The face sheets are pressure-laminated to the core with the adhesive and allowed to cure. The face sheets primarily carry the tension and compression in the panels whether under flexural or axial load. The core provides resistance to shear as well as prevents buckling of the face sheets and panel as a whole. To act as a monolith and prevent delamination and eventual buckling, the adhesive must have both sufficient shear and tensile strength.

SIPs used in construction are typically 8 ft. x 24 ft. panels. For our pilot testing, we will study small-scale samples and focus primarily on mechanical performance as we do not yet have the capabilities to perform structural scale thermal analyses. However, the thermal properties of the individual components will be known from our testing. Our mechanical testing will focus on the ability of our foams to adhere well to face sheets as well as overall SIP performance under tension, compression, and flexure/shear. We will evaluate existing and possibly PHB-based adhesives in terms of their ability to transfer shear and tensile loads between the foam and face sheets (e.g. pull-off tests). We will use both thin plywood and PHB-based fiber-reinforced polymer composites as face sheets. For small-scale panel testing, we will manufacture panels of 6"x18" that have a 1.25" core and 0.125" face sheets. We will make the foam by oven molding using a new large oven currently on order for the Y2E2 lab, and pressure laminate the panels using the hot press available in the Structure & Materials Lab in the Durand Building. Panel testing will focus on compression and flexure testing.

Ideally, the foams we create will have similar or better adhesive and mechanical properties than existing EPS cores. However, should we find weaker properties in some dimensions, we will evaluate alternate SIP designs primarily analytically (by hand and with finite element analyses where necessary). Design alternatives could include stiffening of the foam with fibers or vertical elements through the core. Trade-offs between stiffening and strengthening the core and potentially reduced R-values (the stiffeners may serve as thermal bridges) will be evaluated.

Precourt Institute Evaluation Criterion #2: Economic Viability & Social Benefits

The current price of PS, used to make expanded PS (for ~85% of all SIPs) is roughly $2.10/kg [44]. The current cost of PHA polymers, which are produced from sugars, is between $5.2 and $5.8/kg [45]. However, at Stanford research led by Prof. Craig Criddle in collaboration with Prof. Billington and Prof. Frank is being conducted to produce PHA biopolymers with a cost target of roughly $2/kg through a change in commonly used feedstock and extraction processes. New feedstocks include, for example, using anaerobic fermentation products, which is essentially $0/kg as opposed to the currently used sucrose ($0.34/kg) or starch ($0.80/kg). Additionally, developments in the area of PHA polymer extraction, which is estimated to be 20-50% of total production cost [46,47], have recently been reported to decrease PHA extraction costs by up to 90% [47]. Therefore, on a direct cost basis of the raw material, we believe PHA-based foam can become directly competitive with PS-based foams in the near future. Our research will strive to develop PHA-based foams that will have better insulation properties and at least equal mechanical and moisture- and degradation-resistant properties.

Additional economic and social benefits of PHA-based insulating materials are derived from the ability of these polymers to rapidly degrade to methane in an anaerobic environment. Construction & Demolition debris makes up roughly 40% of all U.S. landfill volume [48]. Populating these landfills with more rapidly degrading materials would provide strong incentive for methane capture as a fuel source, thus reducing "fugitive" methane emissions from landfills and digesters. We expect that the use of PHA-based foams proposed herein combined with related developments in PHA-based composites that can replace wood and plastics in construction will create economic incentives for efficient methane capture, extending landfill life and increasing the value of methane recovery efforts.

Precourt Institute Evaluation Criterion #3: Potential for Energy Use Reduction

As presented in the Introduction, residential and commercial buildings are responsible for roughly 40 percent of U.S. energy consumption with roughly 36% of this consumption going to space heating and cooling. Improved thermal performance of the building envelope and, in particular, insulation through walls, ceilings, floors and doors as well as lowering infiltration can significantly lower heating and cooling demands. A case study of two houses built in Kentucky demonstrated a 15-17% energy savings over a 24-hour period and annual heating-season savings of 14-20% for a SIP house (used for walls and second-floor ceilings) compared to a traditional stick-built house with 2x4 studs and R-13 fiberglass batts [3]. In addition to more energy-efficient building operations, we believe the PHA-based foam will have less embodied energy.   PHA polymers produced from glucose and soybean oil require 55 MJ/kg plastic [49] whereas expanded polystyrene requires 88.6 MJ/kg [50]. By using waste (anaerobic fermentation products) as the substrate (on-going Stanford research), the energy input for PHA biopolymers should decrease further.

Precourt Institute Evaluation Criterion #4: Potential Diffusion of Proposed Technology in the U.S. and Abroad

There are several companies producing PHAs globally (US, China, Brazil). Many are developing novel applications and are just beginning to explore the construction industry. There is no reported work that we could find on PHA foams. Foaming of low-environmental impact polymers (e.g. bio-based polymers such as PHB) has been identified as a possibility [51]. For lower-cost PHA production, much of the technology required has already been demonstrated at a small scale by other researchers and production in this way would be possibly essentially everywhere there was a waste stream (i.e. any waste water treatment plant). In addition, the use of physical blowing agents is a simple technology, particularly if coupled with an oven foaming process. Even if foam extrusion is the preferred route, such equipment is

available worldwide. In addition, the SIP technology itself is also not difficult to translate to other parts of the world where it is not yet used due to the simplicity of fabrication. We do not foresee any technical barriers to implementing these structural elements abroad.   Testing as per various international code specifications will ensure potential early adoption. Should specifications for SIPs be unique in some parts of the world, an International Code Council Evaluation Service Report would be one approach to take to facilitate adoption in the local construction industry.

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