

Caverna™: A Microporous Build Material Derived from a Co-Continuous Blend Morphology Including a Water-Soluble Polymer

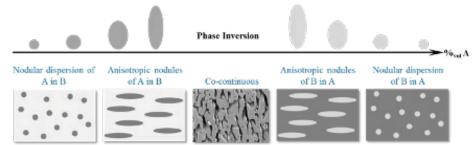
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Caverna™ is a novel, microporous build material. It is derived from a co-continuous polymer blend morphology that includes a water-soluble polymer that is specifically designed for thermoplastic based additive manufacturing platforms, including fused filament fabrication (FFF) and direct pellet extrusion systems. The methology to produce Caverna microporous build materials can be applied to nearly any thermoplastic polymer system. Caverna has utility in many fields and enables many applications including the printing of lightweight components, gas and liquid filters, tissue scaffolds, porous tooling, and consumer goods. Caverna has been designed to perfectly pair with Aquasys® water-soluble support materials.

Introduction

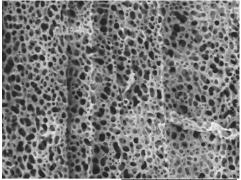
There has been extensive research relating to the alloying of immiscible polymer blends to create materials with unique performance attributes. When two immiscible polymers are melt processed, they are known to assemble into a blend morphology wherein one of the phases is dispersed into the other depending on their specific volume fractions. This phenomenon is depicted in Figure 1. As you can see from the figure as the volume fraction of polymer A is in increased relative to polymer B, the system transitions from discreet domain of polymer A dispersed in polymer B to discrete phases of polymer B in polymer A. This is called a phase inversion. At or near the point where the volume fractions of polymer A and B are equivalent, the polymer blend can become cocontinuous in nature. In this instance, there are interconnected, continuous "channels" of both polymers intermeshed in one another as depicted in Figure 1.

Figure 1. Multiphasic morphologies of immiscible polymer blends



In order to achieve this morphology, it is critical to understand and engineer certain attributes of polymers A and B, including their respective melt viscosity and compatibility/interfacial tension. It is also critical to design a melt processing method to create and retain this morphology such that it survives subsequent melt processing. Caverna has been developed by including a watersoluble polymer in the immiscible polymer blend and subsequently removing it after printing to create a microporous cocontinuous build material (Figure 2).

Figure 2. SEM Micrograph of Caverna Nylon 6.6 after removal of the watersoluble polymer phase (800x)



IFC4848 2019/10/11 09:46 NL MD3.8 x800 100 μm

A key aspect of Caverna is that Infinite™ has engineered this material to maintain this morphology even when it is processed using a variety of additive manufacturing platforms that markedly vary in shear rates, liquefier designs, tip sizes and processing conditions. Caverna® PP (polypropylene), our first product offering has also been designed to perfectly pair with Aguasys® 120 water-soluble support. Figure 3 shows Caverna PP printed with Aguasys 120 and the part after removal of the support material and water-soluble phase in Caverna PP. Available in 1.75 mm and 2.85 mm diameter filament, Caverna PP will function on a variety of 3D printing platforms.

Figure 3. Caverna PP printed with Aquasys 120 before and after dissolution/removal of the soluble support and water-soluble polymer phase.





Advantages and Value

Infinite believes that our Caverna products offer additive manufacturing engineers new-to-the-world, unparalled design freedom. Specifically, we believe that the ability to 3D print articles and devices having this type of ultrafine, highly controlled morphology opens up previously impossible applications. Infinite's motto is "Disruptive Materials, by Design" and Caverna embodies this ethos. We expect this new to the world class of materials to enable concepts like the distributive production of air and water filters, 3D printed tissue scaffolds, high performance chromatographic filters, temporal composite microporous articles/devices, breathable printed wearables and many, many other disruptive product concepts. We look forward to working with all of you to help us unlock these possibilities.

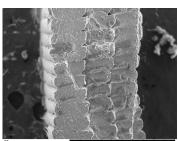
Print Conditions and Thermal Stability

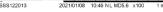
Caverna PP filament prints at 190–240°C, with a build chamber temperature range of 20-50°C, and a build plate temperature of 95–125°C.

Morphology and Properties of Caverna PP

As previously mentioned, Caverna is unique in that it has a highly uniform microporous morphology that can be created and maintained using a wide variety of additive manufacturing printer platforms. Figure 4 shows an electron micrograph of three layers of Caverna PP after 3D printing and dissolution of the water soluble phase. Figure 5 shows this same print at even higher magnification. As can be seen from Figure 5, the Caverna PP has extremely uniform channels that approximately 2-3 microns in diameter throughout the entire print.

Figure 4. SEM micrograph showing morphology of Caverna PP after 3D printing and dissolution. (left, 100x), (right, 1000x)





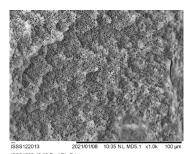
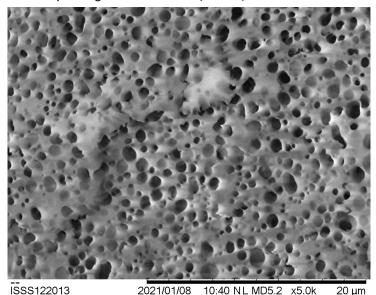


Figure 5. SEM micrograph showing morphology of Caverna PP after 3D printing and dissolution. (5000x)



ISSS1220-13 #9 Post Dis Print

The properties of printed Caverna PP are given in Table 1. As evidenced in the table, the differences in properties between the printed Caverna PP part pre-dissolution and post-dissolution are striking. More than 45% of the mass is lost, the hardness of the material is over 250% lower, the tensile elongation increases over 400%, the tensile modulus is reduced nearly 1000%, and most notably, the material transforms from a material with an incredibly high moisture vapor barrier to one that is a highly breathable material with an incredible moisture vapor transmission.

Table 1. Properties of Caverna PP

Property	Printed Part Pre-dissolution	Printed Part Post Dissolution
Tensile Strength (ksi)	3.8	1.0
Tensile Modulus (ksi)	370	33
Elongation (%)	9.5	39.5
Flexural Strength (ksi)	6.7	1.2
Flexural Modulus (ksi)	305	40
Izod Impact (ft-lbs/in)	15.8	7.6
CLTE (cm/cm°C)	5.8 x 10-5	9.5 x 10-5
Hardness (Shore D)	74	28
Hardness (Shore A)	>98	94
MVTR 2-layer print (g/m2/24 hours)	0	2800
Specific Gravity	1.10	0.63



Disposal and Biodegradability

Caverna PP, like Infinite's AquaSys product line, is based in significant part on a naturally occurring carbohydrate that is very rapidly mineralized in the environment. Mineralization of this particular component occurs in a matter of hours to several days. AquaSys has two remaining components, one of which is biodegraded more slowly. But similar to PVA, these components are also considered to be ultimately biodegradable based on respirometric mineralization tests using acclimated sludge from wastewater treatment facilities. The resulting Caverna PP microporous build material is non-hazardous and can be disposed of in standard municipal waste streams, similar to articles and components derived from polypropylene (PP).

