



A Versatile General-Purpose Water Soluble Formulation for Supporting the Buildup of Three Dimensional Solids. Enhanced Properties, Robust Adhesion, and Critical Application Parameters.

**Nathan W. Ockwig, Gavriel DePrenger-Gottfried,
Brandon Cernohous, Philip J. Brunner, Jeffrey J. Cernohous**

AquaSys® 120 is a general-purpose water-soluble support for additive manufacturing (3D printing) for fused filament fabrication (FFF) and direct extrusion systems. AquaSys 120 offers modest thermal stability and robust adhesion characteristics which make it an ideal material for a wide array of build materials.

The use of support structures in additive manufacturing, commonly referred to as three-dimensional (3D) printing, is a well-understood methodology. Materials used to create these support structures can be separated into two broadly de-fined categories of 'break-away' or soluble. So-called 'break-away' support structures are often constructed from a similar material to the printed object. After printing, removal of the 'break-away' support is accomplished through tedious mechanical breakage, trimming, and abrasion. This tends to be more difficult when working with high-temperature materials. In the case of soluble support materials, after printing, the support material is dissolved either by water or a solvent. Water-soluble supports are the most desirable, but the development of these types of materials is exceptionally challenging. Many water-soluble polymers are quite brittle, thus preventing the conversion to filament. Plasticizing using traditional additives often inhibits thermal stability and adhesion, thus severely limiting utility in 3D printing. Adding to this challenge, there are a limited number of commercially available resins which are

truly water-soluble. Indeed, dissolution of several first generation soluble supports involved harmful chemicals, highly acidic, or highly basic solutions. Although those types of supports are still widely used, advances have been made, and there are now a plethora of products on the commercial market. Presently available soluble support materials are either highly proprietary (Stra-tasys SR35, SR30, SR100, etc.), or based on commonly available polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), cellulose like hydropropyl methylcellulose (HPMC), or the more exotic (currently not commercially available for ad-ditive) polybutenediol vinyl alcohol (BVOH).

AquaSys 120 is an "outside the box" composite material which capitalizes on the unusual thermal stability and outstanding water solubility of a naturally occurring carbohydrate, which has been intimately blended with a flexible and tough, yet water-soluble polymer. What makes this combination so unique is the fact that it is thermally stable, highly water soluble, and yet flexible and tough enough to form filament. This is surprising

because many pure carbohydrates and water-soluble polymers are [usually] far too brittle to form a usable filament. Indeed, many attempts have been made to plasticize water-soluble resins, thereby facilitating their conversion to filament. However, the addition of plasticizers often dramatically reduces base resin thermal stability and may inhibit or interfere with adhesion between materials, thus severely limiting its utility in 3D printing. Our new material, AquaSys 120, has been converted into 1.75 mm and 2.85mm diameter filament, by a highly complex process, for use with a variety of 3D printing platforms and materials.

Advantages and Value

The individual components of AquaSys 120 are widely used in industry for a variety of applications ranging from packaging and drug delivery to cosmetics and personal care products. AquaSys 120 is hydrophilic, biocompatible, biodegradable, non-toxic, and non-carcinogenic composite (based on information available for all the individual components).

AquaSys 120 is compatible with a broad range of materials (including both hydrophilic and hydrophobic polymers), shows excellent thermal stability and is environmentally friendly. AquaSys 120 offers a variety of advantages over traditional PVA in that it: (1) dissolves in water much faster than pure PVA, (2) it can be printed with a wider range of materials, (3) it has enhanced adhesion properties, and (4) it is more quickly biodegraded than PVA, thus making a very versatile, robust, and environmentally friendly soluble support material.

Print Conditions and Thermal Stability

A leading brand of PVA filament prints at 215-225 °C and a maximum build plate temperature of 60 °C whereas AquaSys 120 filament prints at 240-245 °C and a maximum build plate temperature of 130 °C.

Adhesion Characteristics

The ability to build materials to adhere to soluble support, or visa-versa, is of critical importance leading to the success (or failure) of a 3D print. Poor adhesion between adjacent layers of support and build materials causes a sloughing off phenomenon and ultimately print failures. To address this, we have engineered AquaSys 120 with enhanced adhesion properties, so that it is compatible with a wide range of both hydrophobic and hydrophilic materials used in filament driven 3D printing platforms. AquaSys 120 continues to be used with new build materials. To date it, AquaSys 120 has been successfully printed with polylactic acid (PLA), polyamides (Nylon), co-polyester (CPE), acrylonitrile butadiene styrene (ABS), thermoplastic polyurethane (TPU), polycarbonate (PC), and polyolefins like polypropylene (PP). This offers a significant advantage over traditional PVA filament, which has limited adhesion to ABS, CPE, TPU, PC, and PP.

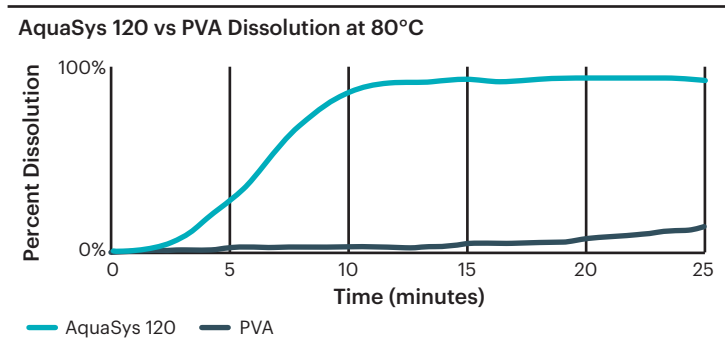
Table 1: Adhesion Characteristics of AquaSys 120 vs. PVA

Build Material	AquaSys 120	PVA
PLA	Yes	Yes
Nylon 6.6	Yes	No
ABS	Yes	Limited
TPU	Yes	Limited
PC	Yes	No
PP	Yes	No

Dissolution

In head-to-head dissolution trials of identically printed parts, AquaSys 120 dissolved twice as fast as a leading brand of PVA at room temperature (22 °C) and over six times faster at elevated temperatures (80 °C). Figure 1 shows the dissolution kinetics of AquaSys 120 vs PVA. Unlike PVA, which can form gels prior to dissolution and especially at elevated temperatures, AquaSys 120 dissolves cleanly with no gelation at temperatures >35 °C.

Figure 1: Dissolution Kinetics of AquaSys 120 and PVA



Disposal and Biodegradability

AquaSys 120 is a composite material which is based, in significant part, on a naturally occurring carbohydrate that is very rapidly mineralized in the environment. Mineralization of this particular [carbohydrate] component occurs in a matter of hours to several days. Whereas the remaining components of AquaSys 120 are biodegraded more slowly, but similar to PVA, are also considered to be ultimately biodegradable based on respirometric mineralization tests using acclimated sludge from wastewater treatment facilities.

Conclusion

AquaSys 120 is a novel soluble support which solves a number of challenging issues in additive manufacturing. This material is an “outside the box” carbohydrate composite. It capitalizes on the unusual thermal stability and outstanding water solubility of a naturally occurring saccharide that has been intimately blended with a flexible and tough water soluble polymer. This unique materials science solution provides advanced adhesion to wide variety of build materials, a broad processing window, and improved aqueous dissolution performance without the use of solvents or harsh chemicals.