

## A High-Temperature, Water-Soluble Formulation for Supporting the Buildup of Three-Dimensional Solids Derived from Engineering Thermoplastics

Nathan W. Ockwig, Gavriel DePrenger-Gottfried, Brandon Cernohous, Samantha Dickenson, Jordan Egner-Schnitzler, Jonathan Farren, Jeffrey J. Cernohous

AquaSys<sup>®</sup> 180 is a general purpose water-soluble support material for additive manufacturing (3D printing), designed for use in fused filament fabrication (FFF) and direct pellet extrusion systems. AquaSys 180 offers excellent thermal stability, functionality at high chamber temperatures, and robust adhesion characteristics. These attributes make it an ideal material for a wide array of engineering thermoplastics, including polyetheretherketone (PEEK), polyetherketoneketone (PEKK), polyetherimide (PEI).

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 defined categories: 'break-away' and soluble.

So-called 'break-away' support structures are often printed from a similar or identical material to the printed object. After printing, removal is accomplished through tedious mechanical breakage, trimming, and abrasion. In the case of soluble support materials, however, the support material is dissolved away after printing.

### Development Challenges for Soluble Support

While soluble support material may add simplicity to the 3D printing process, development of the material itself is exceptionally challenging and complex. Since many water-soluble polymers are

quite brittle, for example, using them to produce a filament is extremely difficult. Even if the material can be shaped into a filament, the traditional plasticizing techniques involved can inhibit thermal stability and adhesion, thus severely limiting utility in 3D printing.

Adding to this challenge is the simple fact that there is a limiting number of commercially available resins which are truly water soluble. As a result, dissolution of several first-generation soluble supports required 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 support materials are either highly proprietary (e.g. SR30, SR 100, etc.), or based on commonly available polyvinyl alcohol (PVA) materials that lack desired functionality.

Specifically, the market desires support materials that are:

- Tap water-soluble
- Able to adhere to a wide range of build materials
- Eco-friendly
- Compatible with a wide variety of printing platforms

One of the key gaps in current support material technology is temperature resistance. This is especially crucial when it comes to printing high-temperature engineering thermoplastics. Many of these build materials are extruded at very high temperatures (>300°C) and require elevated chamber temperatures to reduce warpage and improve z-axis adhesion.

AquaSys 180 is exactly what the market has been waiting for. This material has outstanding thermal stability, can be printed at chamber temperatures up to 180°C, dissolves in warm tap water and has excellent compatibility and adhesion to a variety of high temperature engineering thermoplastic materials. We have achieved this through a patented formulation that relies on the combination of a water-soluble polymer, a compatible disaccharide (Trehalose) and a reinforcing additive. Our new material, AquaSys 180 is available in 1.75mm and 2.85mm diameter filaments and will function on a variety of 3D printing platforms. It has been especially designed to print with high-temperature engineering thermoplastics like PEEK, PEKK, PEI, and PPSU.

### AquaSys 180 Advantages and Value

The individual components of AquaSys 180 are widely used in industry for a variety of applications ranging from packaging and drug delivery to cosmetics and personal care products. AquaSys 180 is a hydrophilic, non-toxic and non-carcinogenic composite (based

on information available for all the individual components). AquaSys 180 is compatible with a broad range of materials (including both hydrophilic and hydrophobic polymers), shows excellent thermal stability and is environmentally friendly. AquaSys 180 offers a variety of advantages over other support materials:

- It has faster dissolution kinetics
- It can be printed with a wide range of materials, including high temperature engineering thermoplastics
- It has enhanced adhesion properties
- It has best-in-class thermal stability (up to 300°C)
- It can be printed at chamber temperatures up to 180°C

### Print Conditions and Thermal Stability

AquaSys 180 filament prints at 230-300°C (240-260°C recommended), with a build temperature range of 60-180°C and a maximum chamber temperature of 180°C. This exceptional thermal stability and temperature resistance enables users to print with materials that previously had no compatible support material that could be dissolved, rather than removed manually.

### Adhesion Characteristics

A build material's ability to adhere to a soluble support, or vice versa, is of critical importance—it can lead to the success or failure of a 3D print. Poor adhesion between adjacent layers of support and build materials causes a sloughing off phenomenon which ultimately results in print failures. To address this, we engineered both AquaSys 180 and AquaSys® 120, our other grade of water-soluble support filament, to have enhanced adhesion properties. This ensures that they are compatible with a wide range of both hydrophobic and hydrophilic materials used in filament driven 3D printing platforms. Table 1 provides the compatibility with different build materials for AquaSys 120, AquaSys 180 and PVA (Ultimaker Brand). As the table indicates,

AquaSys 120 has been successfully printed with polylactic acid (PLA), polyamides (Nylon), co-polyesters (CPE), acrylonitrile butadiene styrene (ABS), thermoplastic polyurethane (TPU), polycarbonate (PC), polyvinylidene fluoride (PVDF), and polyolefins like polypropylene (PP). AquaSys 180 prints with many of the same grades as AquaSys 120, but also functions with PEEK, PEI, PEKK and PPSU. We believe that together these grades offer best in class performance attributes for the additive manufacturing market and are highly differentiated when compared to the competition.

### Dissolution

In head-to-head dissolution trials of identically printed parts, both AquaSys 120 and the soluble components of AquaSys 180 dissolved approximately twice as fast as a leading brand of PVA at room temperature (22°C) and over six times faster at elevated temperatures (80°C). Unlike PVA, which can form gels prior to dissolution and especially at elevated temperatures, AquaSys 120 and AquaSys 180 dissolve cleanly with no gelation at temperatures >35 °C. This is demonstrated in Figure 1.

Figure 1: Percent Dissolution versus Time at 80 Celcius

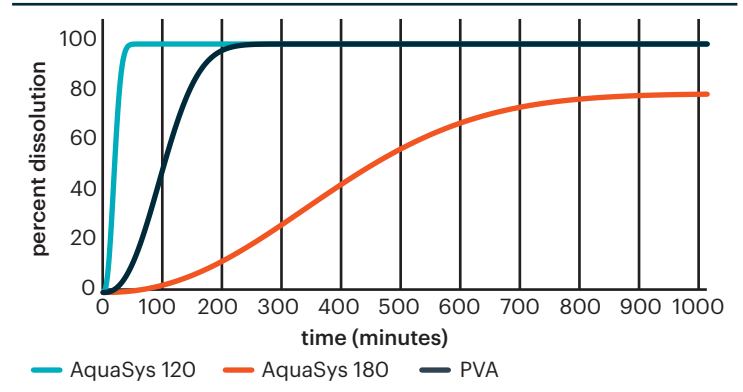


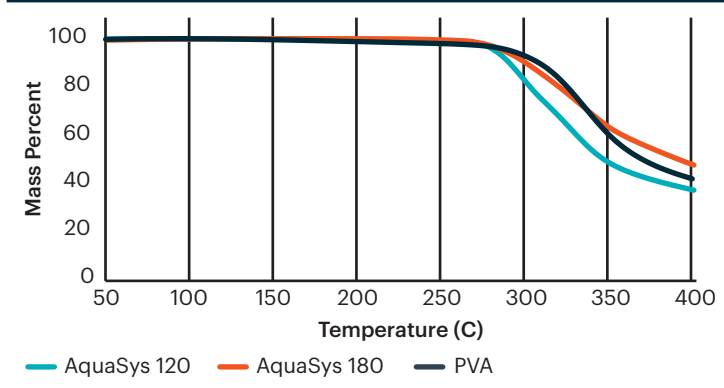
Table 1: Adhesion of AquaSys 120, AquaSys 180, and PVA

Build Material	AquaSys 120	AquaSys 180	PVA (Ultimaker)
PLA	Yes*	—	Yes
Polyamide (Nylon 6, 6.6, 11, 12)	Yes	Not recommended	Yes
Carbon Fiber Filled Polyamide	Yes	Not recommended	—
ABS	Yes	—	Yes
TPU	Yes	Not recommended	Limited
PC	Yes	—	No
PP	Yes	—	No
Glass Filled PP	Yes	—	No
PVDF	Yes	—	No
PEI (ULTEM 9085)	No	Yes	No
PEEK	No	Yes	No
PEKK	No	Yes	No
PPSU	No	Yes	—

### Thermal Stability

The thermal stability of PVA, AquaSys 120 and AquaSys 180 was determined by thermogravimetric analysis (TGA). The results are summarized in Figure 2. As the figure indicates, both AquaSys 120 and AquaSys 180 have enhanced thermal stability when compared to PVA. AquaSys 180 is stable, in air, at temperatures approaching 300°C.

Figure 2: TGA of AquaSys 120, AquaSys 180, and PVA



### Disposal and Biodegradability

AquaSys 180 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. AquaSys 180 has two remaining components, one of which is biodegraded more slowly. Similar to PVA, however, these components are also considered to be ultimately biodegradable based on respirometric mineralization tests using acclimated sludge from wastewater treatment facilities. There is approximately 20 wt % of an inert, non-hazardous, non-biodegradable component in AquaSys 180 that should be collected and disposed of after dissolution.

### Rheology

The storage ( $G'$ ) and loss modulus ( $G''$ ) of PVA, AquaSys 120 and AquaSys 180 were determined by parallel plate rheological measurements. The results are summarized in Figure 3. As the figure indicates, both AquaSys 120 and AquaSys 180 have enhanced modulus at elevated temperatures when compared to PVA. AquaSys 180 has modulus that enables it function as a support material at temperatures up to 180°C.

Figure 3: Rheology of AquaSys 120, AquaSys 180, and PVA

