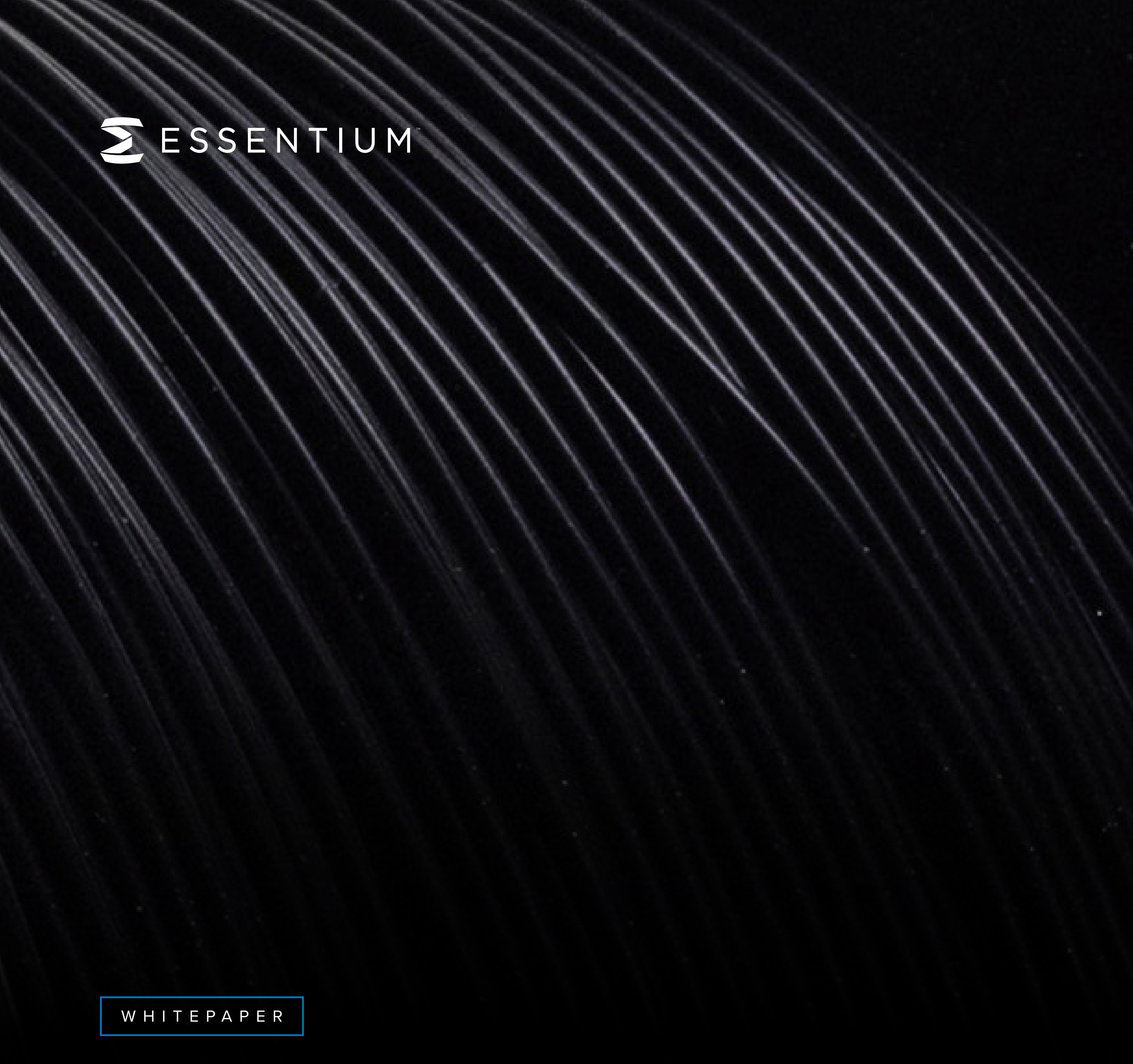

ESSENTIUM

WHITEPAPER

Carbon Fiber Reinforced Composites for Additive Manufacturing Applications

A look into the material science, formulation, and applications for fiber-reinforced thermoplastics.

WRITTEN BY RAVI SADANALA

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Essentium Carbon Fiber Materials

Fiber-reinforced composites are mixtures of thermoplastic polymers and various fillers. The benefit of these composite materials is the combination of material classes that each yield unique properties not achievable with either material individually. Composites tend to be high-performance materials with higher strength and stiffness at a lower density, but they also solve problems like wear, heat, chemical resistance, and creep. Composite materials in additive manufacturing typically use glass or carbon fiber filler embedded in a polymer matrix. Relative to glass filled composites, carbon fiber reinforced composites are more attractive for many applications because they are less abrasive and have higher thermal conductivity, which helps suppress warping and shrinkage in printed parts.

Carbon fiber is readily used in industrial applications in the aerospace, automotive, electronic manufacturing, medical devices, and battery segments. The potential applications for fiber reinforced composites continue to increase as industry experts recognize the benefits of this material class. The primary reason for this increase is the proven advantages this material class can offer when carbon fiber is embedded into matrices that normally have underperforming properties. These advantages include:

- Low density, low Coefficient of Thermal Expansion (CTE,) high stiffness, and strength-to-weight ratio
- Resistance to corrosion and fatigue
- Increased electrical and thermal conductivity
- Reduction in shrinkage during processing
- Reduction in thermal stresses caused while printing
- Improvement in dimensional accuracy of the printed parts
- Minimized temperature gradient between the layers
- Increased stiffness and creep resistance
- Wear and chemical resistance improvement

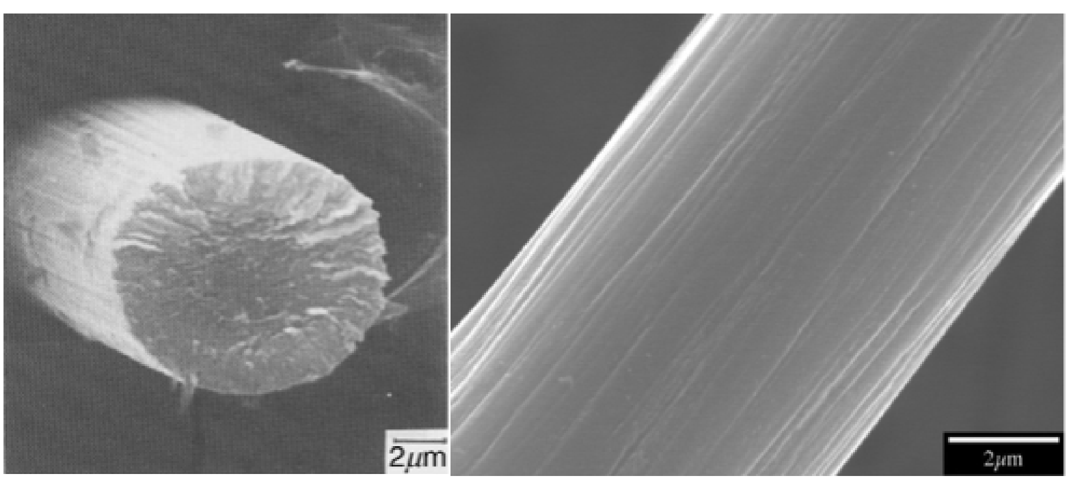


Figure 1: *Microscopic image of a carbon fiber [1]*

The Different Types of Fibers

The different types of fibers implemented in polymer composites (carbon, glass, Kevlar, PAN) and their associated properties **Figure 2**. Generally, carbon fiber is a folded structure that has a diameter in the range of 7-10 µm. When compared to glass, carbon fiber is less dense, stiffer, and has a lower CTE. As seen in **Figure 3,** carbon fibers can be PAN or pitch-based. PAN (polyacrylonitrile) based carbon fiber is made from thermoplastic polymers that are generated from oil and later turned into carbon fiber. Pitch based carbon fiber is made from distilling oil and using the pitch that forms in the bottom of the distillation column that is rich in aromatic hydrocarbons. As a result, pitch-based carbon fiber is more thermally and electrically conductive, stiffer, and more expensive compared to PAN-based fibers. Because of high processing times and fewer oil refineries, it is more difficult to make pitch-based carbon fiber than PAN-based carbon fiber. PAN-based fibers are often readily available as they are processed from thermoplastics.

Property	Carbon Fiber (T300)	Glass Fiber (S-2)	Kevlar Fiber (49)	Carbon Steel (Not Fiber)
Density (g/cm^3)	1.76	2.46	1.45	7.85
Tensile modulus (GPa)	230	86.9	112	190–210
Specific tensile modulus (GPa)	131	35.3	77.2	24.2–26.8
Tensile strength (GPa)	3.53	4.89	3.00	0.276–1.882
Specific tensile strength (GPa)	2.010	1.990	2.070	0.035–0.24
Tensile strain (ductility)	1.5%	5.7%	2.4%	10–32%
Compressive strength (GPa)	0.87[a]	1.60	/	/
CTE (axial, 10^{-6} K^{-1})	−0.41	2.9	−6	11.0–16.6

There are various grades of each type of fiber. A commonly used grade is chosen to represent each type of fiber. The data are from the manufacturers' datasheets, unless stated otherwise. CTE, Coefficient of thermal expansion.
[a]Calculated value (Kumar et al., 2013).

Figure 2: *Different types of fibers [1]*

	PAN-Based		Pitch-Based	
Property	Toray T300	Toray T1000GB	Mitsubishi K13D	Nippon XN-05
Diameter (µm)	7.7	5.1	11.5	9.3
Density (g/cm^3)	1.76	1.80	2.20	1.65
Tensile modulus (GPa)	220	290	940	41
Tensile strength (GPa)	3.2	5.7	3.2	1.1
Failure strain (%)	1.5	2.1	0.4	2.8
Flexural strength (GPa)	5.2	8.2	2.1	3.0
Flexural modulus (GPa)	220	260	1000	55

PAN, Polyacrylonitrile.

Figure 3: *Mechanical properties of PAN and pitch-based carbon fibers [1]*

Coefficient of Thermal Expansion (CTE)

Improving the dimensional accuracy of a part by mitigating shrinkage or expansion is a pivotal piece of any manufacturing process. The amount of shrinkage of the polymer depends on operating temperature, fiber aspect ratio, fiber type, and the interfacial bonding between the polymer matrix and the fiber. By reinforcing polymer matrices with fiber, this reduces the CTE of the plastic along the fiber direction. **Figure 4** shows different types of fillers based on their aspect ratio inside a polymer matrix. Case (i) shows the fillers with an aspect ratio (l/d) >1, where the shrinkage and CTE of the polymer is less in the X-direction compared to the Z-direction due to the fiber orientation. However, the orientation of the fibers will drastically improve the strength of the composite in the X-direction. Conversely, Case (ii) shows the fillers in a spherical shape with an aspect ratio of one. In this case, the shrinkage is essentially equal in both the X and Z-directions because the CTE is the same regardless of direction. Case (iii) shows the combination of both Cases (i) and (ii), which provides a balance of strength, shrinkage, and warpage. Therefore, the type of fiber that is used to make the composite can have a substantial effect on the material properties.

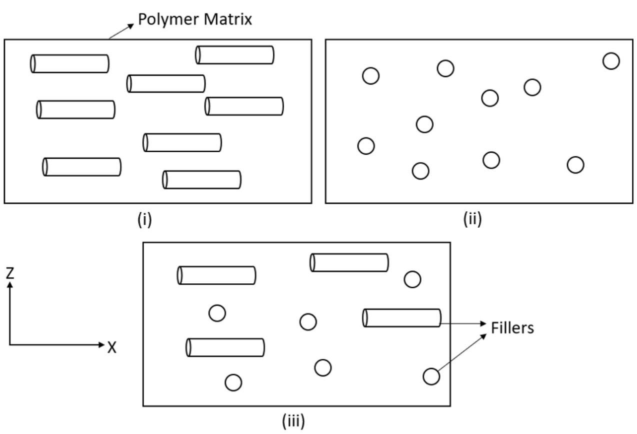


Figure 4: *Shrink and warp control with filler type*

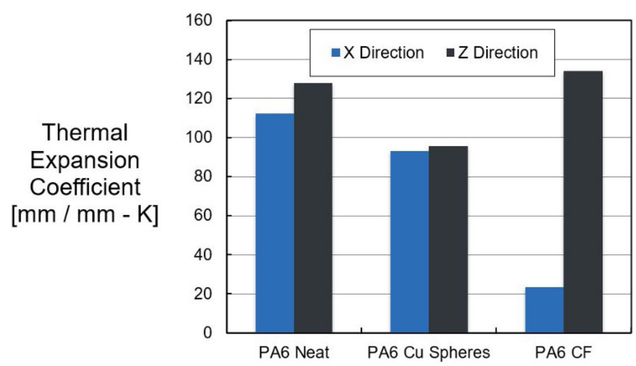


Figure 5: *CTE comparison with filler type and load direction in PA6 [2]*

Figure 5 shows the effect of different types of fillers on the CTE of a PA6 polymer. Adding Copper spheres in PA6 reduced the CTE in the X and Z-direction by almost 20%, whereas the carbon fiber filler reduced the CTE by nearly 85% in the fiber direction. In this case, the CTE in the Z-direction was unaffected due to the orientation of the fiber in the X-direction. This result is caused by the filler aspect ratio and fiber orientation, which affects the CTE and resulting shrinkage rate.

Temperature Gradient and Warpage Control

In the context of additive manufacturing, temperature gradients present in the part during manufacturing can lead to the buildup of residual stresses and warping. Temperature gradients can be decreased with the addition of carbon fiber to combat these residual stresses. In **Figure 6** and **Figure 7**, temperature maps of Essentium HTN compared to Essentium HTN-CF25 parts are illustrated. In these plots, data was recorded using an infrared camera system while the part was actively printing. In the HTN-CF25 printed part, the temperature of the printed bead is higher because the extruded material retains more heat over time due its higher thermal conductivity compared to HTN. By increasing time at elevated temperature, this allows the polymer chains to relax and thus reduce residual stresses caused by the temperature gradient between the printed beads along the Z-direction. This time at temperature relationship between both materials is shown in **Figure 8**, where HTN-CF25 has a higher temperature at a given height and time compared to HTN.

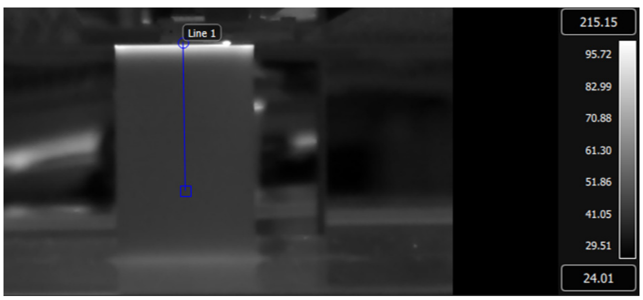


Figure 6: *Temperature gradient in a section of an HTN plaque along the Z-direction. The image was recorded using an infrared camera system during the printing process. Line 1 shown here denotes where data is collected. The temperature scale is shown to the right, with a maximum temperature of 215.15 °C and a minimum temperature of 24.01 °C.*

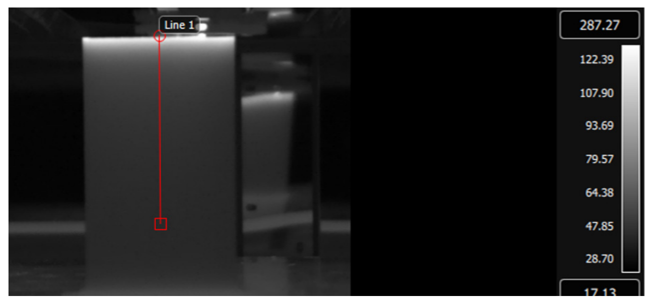


Figure 7: *Temperature gradient in a section of HTN-CF25 plaque along the Z-direction. The image was recorded using an infrared camera system during the printing process. Line 1 shown here denotes where data is collected. The temperature scale is shown to the right, with a maximum temperature of 287.27° C and a minimum temperature of 17.13 °C.*

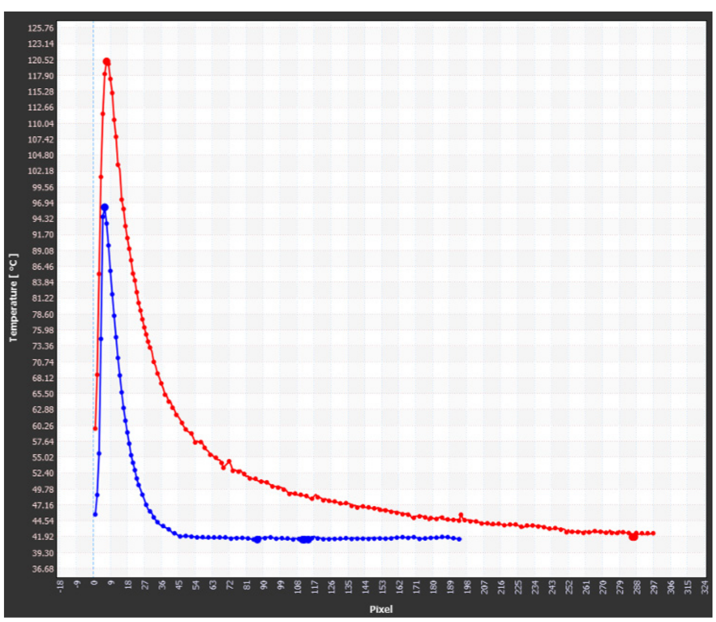


Figure 8: *Temperature difference in Z direction across the layers in HTN-CF25 (red) vs. HTN (Blue) printed parts*

As mentioned previously, carbon fiber can help with warpage control in 3D printed parts. **Figure 9** shows the warpage behavior in PP compared to PP-CF10. Adding carbon fiber into PP reduced the overall CTE and shrinkage along the bead direction, which is reflected in the amount of curling in the part. Carbon fiber reduces curling by decreasing the temperature gradient across the layers resulting from an increase in thermal conductivity of the material.

Figure 9: *Warpage/Curling behavior in PP vs PP-CF 10 [3]*

Anisotropy

In the context of 3D printing, fiber reinforced thermoplastics are stiffest and strongest along the printed bead direction, where fiber alignment is highest. The process of extruding composites from a heated nozzle causes the fibers to align in the direction of the extrudate. Therefore, some print orientations will exhibit different material properties relative to others. **Figure 10** shows different build orientations (XY, 45/45, YX, and ZX) of a 3D printed part. The XY plane is the build orientation along the direction of the printed bead, where fiber orientation is highest. While using fillers inside the polymer matrix improves the stiffness of the overall polymer along the XY direction, it also reduces the interlayer bonding or wetting across the layers in ZX direction. This is due to the formation of nucleates on the fiber surface via transcrystallization as depicted in **Figure 11**. This increases the crystallinity and inhibits polymer chain entanglement between the layers, which makes the overall part anisotropic. **Figure 12** and **Figure 13** shows the effect of carbon fiber on mechanical properties of different polymers in XY and ZX directions. It can be seen clearly that XY properties are impacted more than ZX properties due to carbon fiber orientation along the bead direction and its aspect ratio.

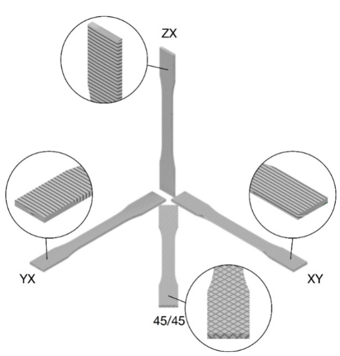


Figure 10: *This graphic depicts different build orientations*

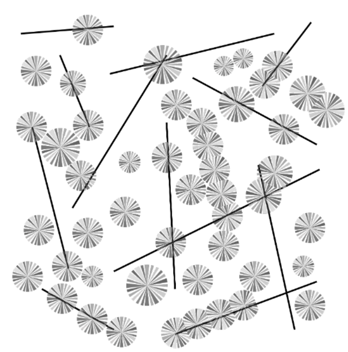


Figure 11: *Transcrystallization causes nucleation sites for spherulites on the carbon fiber surface.*

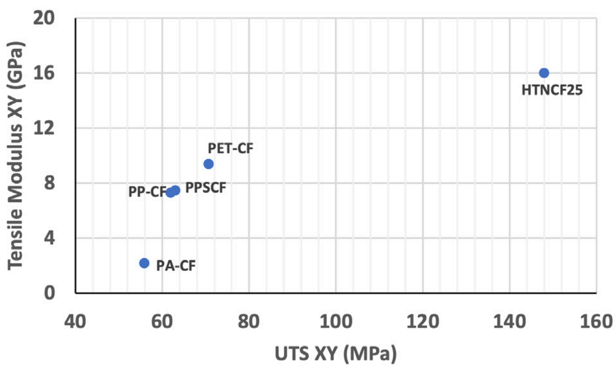


Figure 12: *Ultimate tensile strength (UTS) versus tensile modulus (XY)*

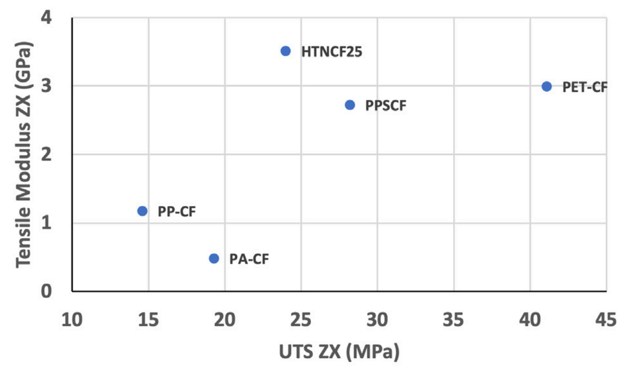


Figure 13: *Ultimate tensile strength (UTS) versus tensile modulus (ZX)*

Increased Stiffness Over Temperature

Adding carbon fiber into neat polymer improves the mechanical performance of the material at elevated temperatures. **Figure 14** shows the storage modulus at a load frequency of 1 rad/sec for Essentium HTN and Essentium HTN-CF25 as a function of increasing temperature. The addition of carbon fiber drastically improves the performance of HTN at elevated temperatures. It is important to note that stiffness drops significantly above the Tg of the polymer (76 °C), but the addition of fiber helps mitigate the loss in performance. In this test, storage modulus of HTN-CF25 briefly drops below HTN, but this could be caused by moisture in the test sample. It is well understood that moisture acts as a plasticizer in nylons and reduces stiffness. Once the moisture is baked out from the polymer, the storage modulus improves.

Materials loaded with carbon fiber will typically have a higher Heat Deflection Temperature (HDT) when compared to the neat material. The HDT of a polymer is the measured temperature at which the test sample deflects up to 0.25mm under a constant stress/load. **Figure 15** shows the HDT of Essentium carbon fiber materials at 0.45MPa. This test metric is a good universal gauge for quantifying the heat resistance of a thermoplastic. HDT data may also be found on the Essentium website for many materials that Essentium offers.

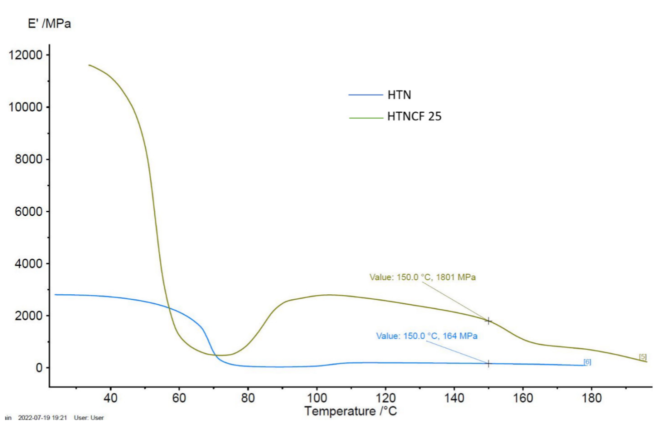


Figure 14: *Storage modulus of HTN versus. HTN-CF25 as a function of temperature*

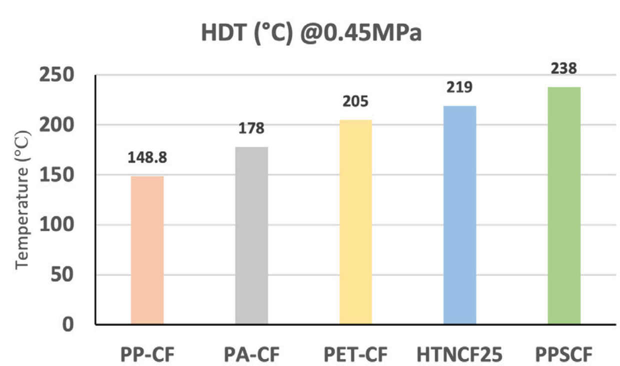


Figure 15: *HDT of Essentium carbon fiber materials at 0.45 MPa*

Essentium Carbon Fiber Materials

Essentium offers a few different materials that are reinforced with chopped carbon fiber fillers and is actively developing glass fiber reinforced composites. These fillers enhance strength, stiffness, temperature resistance, suppress warping and can offer matte surface finishes. Below, a brief description of each fiber loaded material from Essentium is provided.

HIGHLIGHTS

- Strength up to 150 MPa
- Modulus up to 16 GPa
- Good wear and creep resistance

Essentium PA-CF

DESCRIPTION

Essentium PA-CF is a carbon fiber-infused polyamide filament specially formulated for additive manufacturing. Essentium PA-CF provides exceptional strength, durability, thermal stability, and stiffness that is customary of carbon fiber materials, and is readily printable with a wide processing window, providing a highly accessible engineering-grade solution or open platform and even open-air printers.

KEY FEATURES

- Exceptional strength
- Perfect for industrial-grade parts
- High impact resistance
- HDT of 178 degrees Celsius
- Optimized for low moisture absorption

Essentium PET-CF

DESCRIPTION

Essentium PET-CF is a 15% carbon fiber reinforced polyester filament made with Luvocom® 3F resin from Lehvoss. Polyethylene terephthalate (PET) is a semicrystalline polyester commonly used in soda bottles and automotive parts when reinforced with a fiber-filler. This material is one of the easiest filaments in our portfolio to print and has an outstanding price-to-performance ratio. PET-CF has a good balance of stiffness and strength, and when annealed it has temperature resistance of over 155˚C, and good chemical resistance for common solvents.

KEY FEATURES

- Excellent price-to-performance ratio
- Good stiffness and strength
- Minimal warping
- Low moisture absorption
- Easy to print
- Good chemical and wear resistance

Essentium PP-CF

DESCRIPTION

Essentium PP-CF is a 20% carbon fiber reinforced polypropylene filament made with Luvocom® 3F resin from Lehvoss. Polypropylene (PP) is a semicrystalline polymer commonly used in consumer goods and automotive parts when reinforced with a fiber filler. This material has excellent chemical resistance and low surface energy which makes it useful for silicone and urethane low pressure molding applications.

KEY FEATURES

- Low surface energy
- Excellent mold release property
- Excellent chemical resistance
- Low density
- Less abrasive than glass filled PP

Essentium PPS-CF

DESCRIPTION

Essentium PPS-CF is a 15% carbon fiber reinforced polyphenylene sulfide (PPS) filament made with LUVOCOM® 3F resin from LEHVOSS Group. PPS is a semicrystalline, high-performance polymer used in numerous challenging applications in various industries. This material has an outstanding price-to-performance ratio with exceptional strength, stiffness, temperature, chemical and wear resistance. PPS is suitable in many cases instead of higher priced super polymers such as PAEKs (PEEK, PEKK).

KEY FEATURES

- Excellent heat resistance
- Excellent chemical resistance
- Lower cost compared to PEEK
- Inherently flame retardant

Essentium HTN-CF25

DESCRIPTION

Essentium HTN-CF25 (high-temperature nylon) is a polyamide-based chemistry with a 25% carbon fiber reinforced core. HTN-CF25 is the highest strength and stiffness material in the Essentium portfolio. This material also boasts easy processing and excellent thermal resistance. This material is designed for tooling applications, high-strength/stiffness jigs and fixtures, and as a replacement for light-duty aluminum parts.

KEY FEATURES

- High strength
- Good chemical resistance
- Good heat resistance
- Easy to print
- Solvent resistance

Price-Performance Ratio Comparison

Property	HTN-CF25	PP-CF	PET-CF	PA-CF	PPSCF	Competitor 1	Competitor 2
Tensile Modulus, Gpa	16	7.28	9.38	2.16	7.46	2.4	8.2
Tensile Strength at Yield, Mpa	148	62	70.7	55.9	63	40	87*
HDT @ 0.45MPa	219	148.8	205	178	238	145	240
Price ($/cc)	0.27	0.09	0.13	0.16	0.26	0.24	0.27

** Tensile strength at Break*

Table 1: *Price to performance ratio comparison for different materials*

Applications

Essentium PP-CF

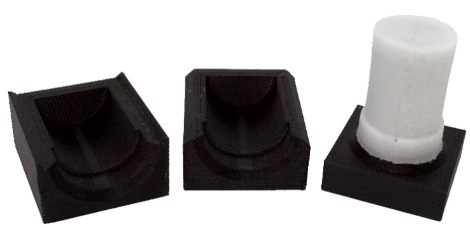
It is semicrystalline material processed with milled carbon fiber. Having carbon fiber in it helps it to limit warping and also helps to improve its overall mechanical properties. Due to its non-polar nature, it can be used for low temperature casting applications without any adhesion issues with the mold.

For more information, please visit **https://www.essentium.com/product/fil0048_parent/**

USE CASE ONE: RESIN FOAM CASTING

The three-part mold was printed for packaging the extruder die with foam. The foam material used for this application is from Smooth-On and can be casted easily using PP-CF with smooth surface finish.

Extruder Die



Three Part Mold

Foam Casted Die

Table 16: *Resin Casting*

USE CASE TWO: OVERMOLDING METAL HANDLE

Metal handles can be overmolded easily with silicone rubbers by casting them into PP-CF molds. Below figure shows the pressure cooker handle which can be overmolded with rubber by casting into PP-CF molds.

Table 17: *Mold for over molding the pressure cooker handle*

USE CASE THREE: HIGH TEMPERATURE RESIN TOOL CASTING FOR INJECTION MOLDING

The below part was printed with Essentium PP-CF on Essentium HSE 180 HT machine. One easy way to make injection molds is casting high temperature tooling epoxy. The steps for this casting process are as follows:

- Printing a thin shell of 1mm thickness using PP-CF.
- Casting tooling epoxy into the mold
- Waiting until the resin gets cured
- Annealing the part for improving the thermo-mechanical properties prior to injection molding

Table 18: *PP-CF shell used for tooling epoxy casting for Injection Molding applications*

Essentium PPS-CF

PPS-CF can be used for high pressure and temperature tooling applications due to its high crystallinity and high deflection temperature of 240°C. It can be easily machined after printing and prior to injection molding for getting smoother surface finish on the molds. Below images shows the PPS-CF printed molds using ASTM Type V specimen type and Essentium logo. The molds were used to make polypropylene parts.

For more information, please visit **https://www.essentium.com/product/essentium-pps-cf/**

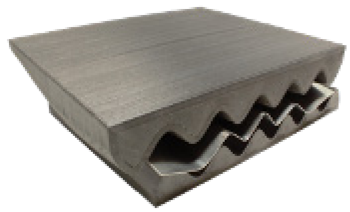
Table 19: *Injection Molding*

Essentium HTN-CF25

Due to its stiffness and high heat deflection temperature, it can be used to make jigs and fixtures, high temperature and low pressure applications, forming tools etc. Below images shows different applications which include Blow molding, Sheet Metal Forming, and Vacuum forming.

For more information, please visit **https://www.essentium.com/product/essentium-htn-cf25/**

Blow Molding



Sheet Metal Forming

Vacuum Forming

Table 20: *Tooling Applications*

Essentium PA-CF

PA-CF is one of our bio-compatible materials among PCTG, PET-CF, and TPU 74D. It is durable, flexible and have great surface finish which can be used for foot orthotics applications for patients. This material passed all the requirements like cytotoxicity, sensitization, and irritation to be on skin. Below image shows the different O&P applications with PA-CF.

For more information, please visit **https://www.essentium.com/product/essentium-specialty-pa-cf-nylon/**

Table 21: *Orthotics and Prosthetics*

Essentium PET-CF

PET-CF is a stiff material which can be used for manufacturing low temperature jigs and fixtures. This material is also a biocompatible material which can be used for other biocompatible applications.

For more information, please visit **https://www.essentium.com/product/essentium-pet-cf/**

Table 22: *Jigs and Fixtures*

References

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3. Spoerk, Martin, Clemens Holzer, and Joamin Gonzalez-Gutierrez. “Material extrusion-based additive manufacturing of polypropylene: A review on how to improve dimensional inaccuracy and warpage.” Journal of Applied Polymer Science 137.12 (2020): 48545.