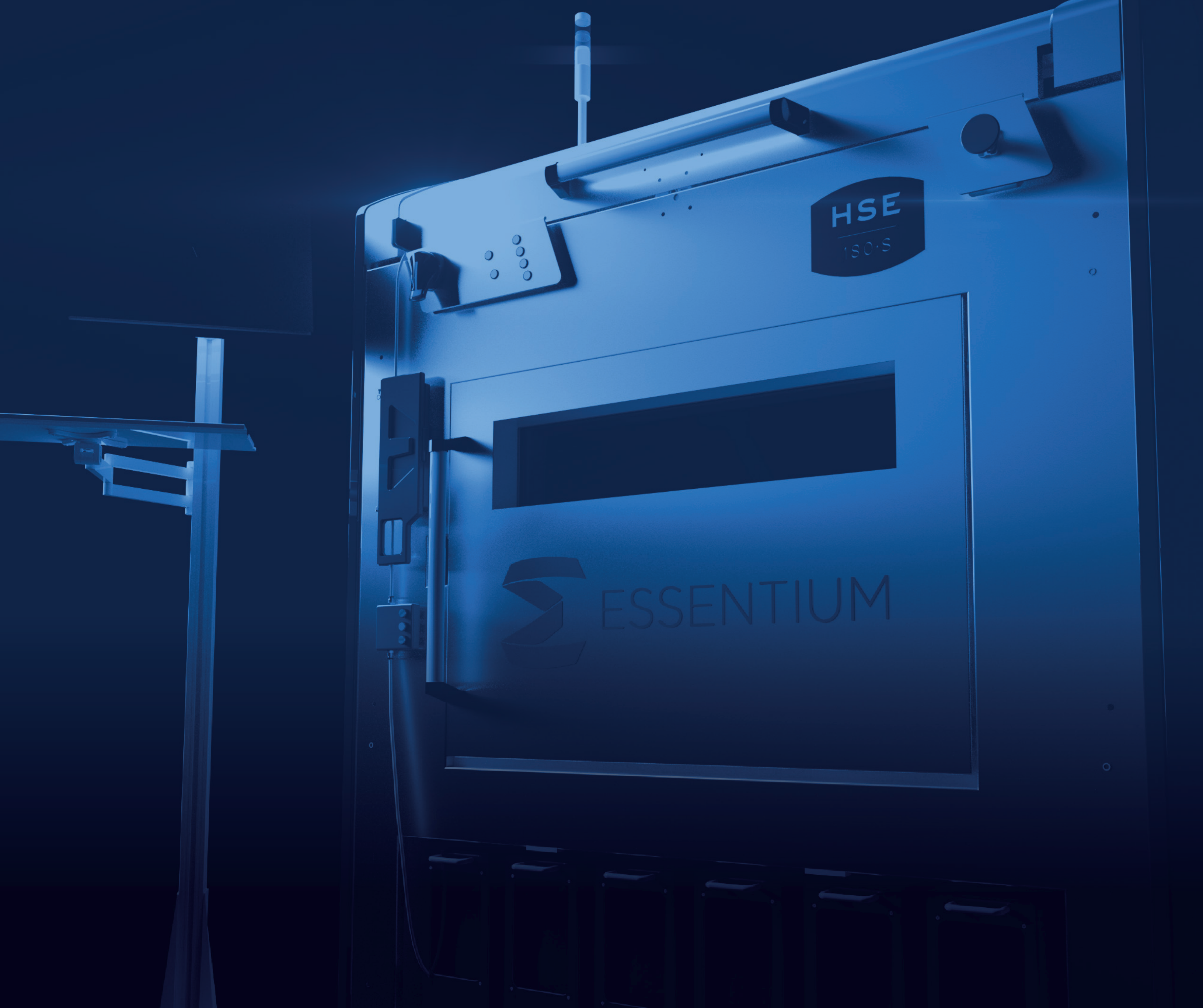
ESSENTIUM MATERIALS HANDLING GUIDE

ESSENTIUM™

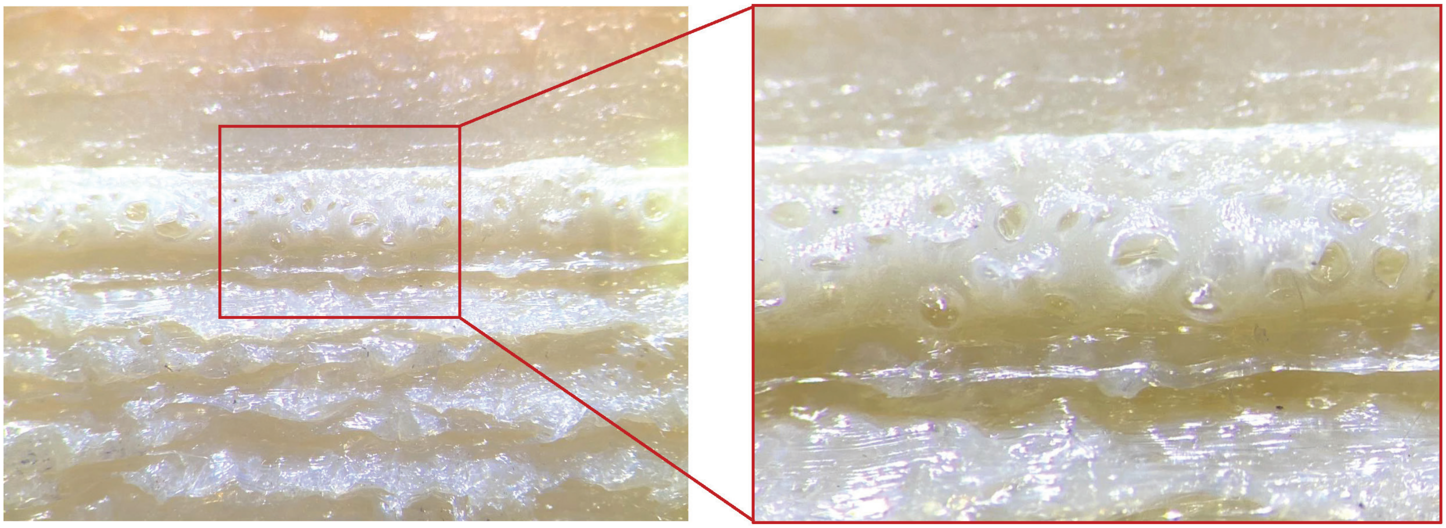


High performance industrial 3D printers have evolved tremendously over the past decade. Open platform systems that enable users to purchase and print any filament available on the market are becoming the new standard. Today's industrial 3D printer operators demand the freedom and flexibility to operate their additive manufacturing equipment the same way they operate their injection molding and CNC machining equipment. With that freedom however come the challenges of proper material handling that is paramount for consistent results from printed parts. This challenge stems from a lack of education and knowledge transfer from the plastic processing community to the 3D printing community, as well as the lack of specialized equipment that specifically addresses the material handling needs of filament-based material extrusion 3D printers. In this guide, we aim to educate users on best practices for material handling and point users to the proper equipment to implement a material handling workflow at their facility.

The moisture content in thermoplastic filaments is a major driver of part quality and consistency. Some polymers are more susceptible than others, but most engineering-grade thermoplastics should be dried appropriately for best results. If a spool of filament does pick up moisture, it can cause both visible and invisible defects in the material and part. Bubbles and foaming are the most readily identifiable moisture-related defects. As filament is heated in the nozzle, any moisture present in the material expands rapidly and can form millions of microscopic bubbles (foam) or larger, macroscopic bubbles (Figure 1).

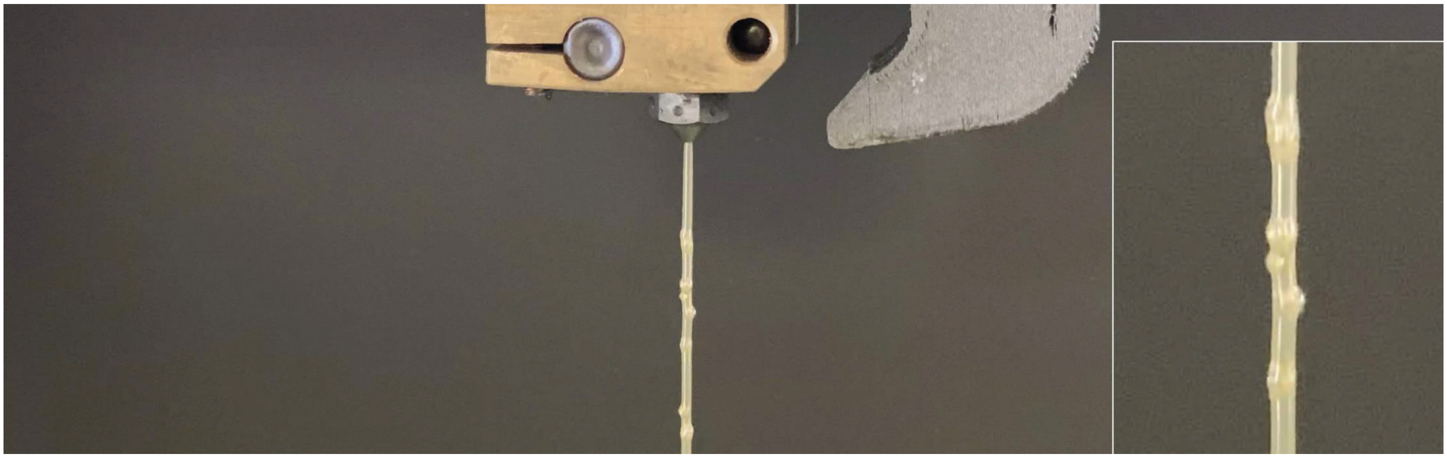
Figure 1

Visible defects in ULTEM™ 9085



While foamed polymer systems are a compelling class of materials for light-weighting applications, uncontrolled voids in thermoplastics are considered defects that lead to unpredictable failure in finished parts. Even though high temperature thermoplastics like PEEK and PEI absorb little moisture compared to polyamides, the higher melt processing temperature results in a much greater expansion of the absorbed moisture into steam (Figure 2).

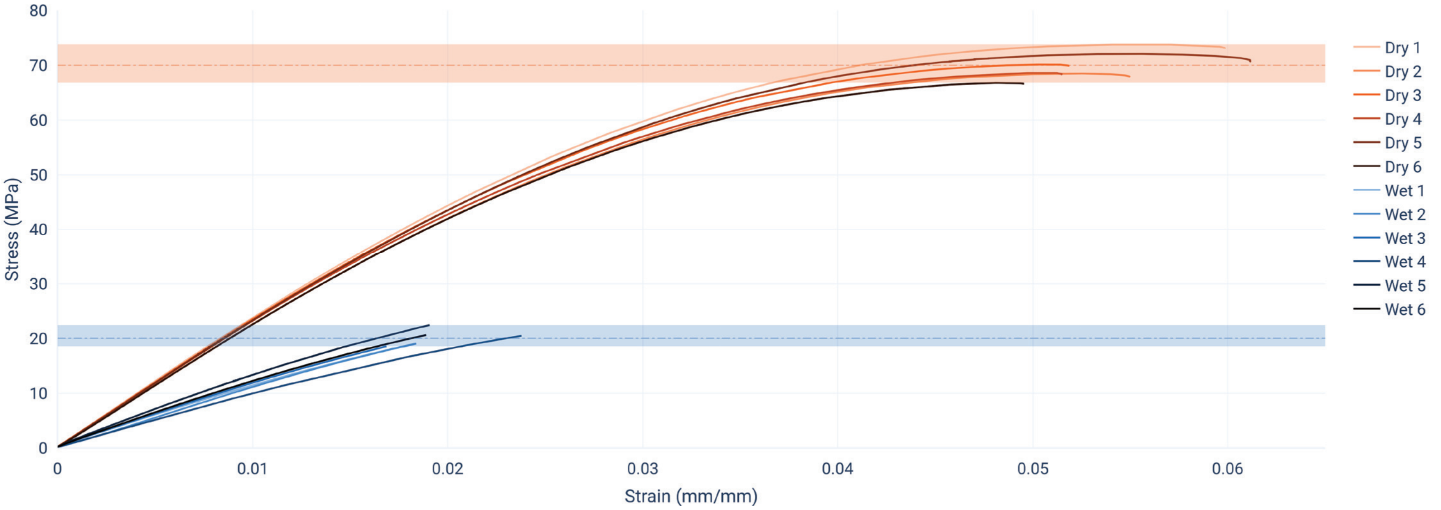
Figure 2



Common indicators of wet filament are excessive stringing or a rough surface finish due to dramatic changes in the polymer viscosity (water can act as a plasticizer for certain polymers). Other changes caused by the presence of moisture are invisible. Polycondensation polymers including polyester (PETG, PCTG, PLA), polyamide (nylons), polyether (POM), and polycarbonate are susceptible to hydrolytic degradation. If the material is heated (especially during melt processing) in the presence of excess moisture, the polymer chains are physically chopped (chain scission) into lower molecular weight segments. This has a dramatic negative effect on impact resistance, elongation at break, toughness, and strength To demonstrate the combined effects of moisture on the mechanical properties of 3D printed parts, we prepared two sets of tensile dogbones printed from Essentium 9085 (made with ULTEM™ 9085 resin), one set with properly dried material, and another set printed from material that was left out in ambient conditions to absorb moisture from the air. The specimens were printed according to ISO 527-2/1A with one outline and 45/45 infill. The results of the tensile tests are shown in Figure 3; the dry specimens had an average ultimate strength of 70 MPa and elongation at break of 5.5%, whereas the wet specimens had an ultimate tensile strength of 20 MPa and elongation at break of 1.9%. These results demonstrate how important it is to keep materials dry during storage and while feeding material to a printer.

Figure 3

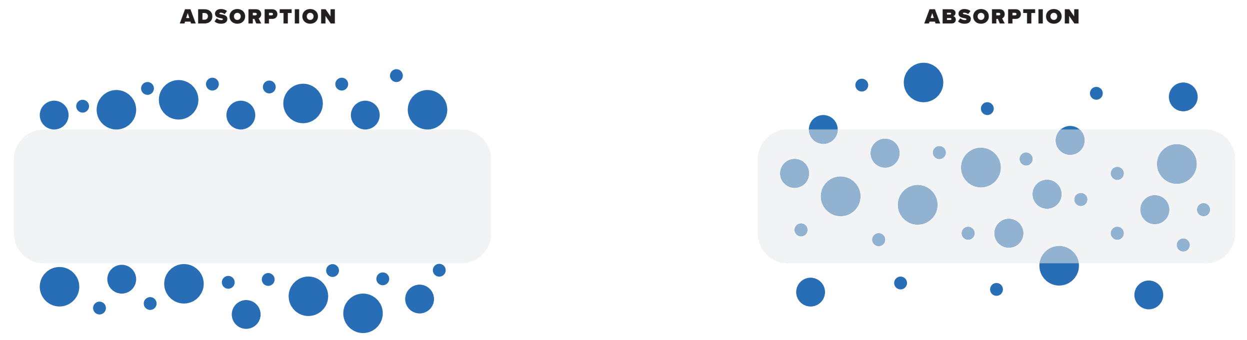
Wet vs. Dry Essentium 9085 Tensile Stress-Strain Cruve



On the other hand, properly drying material is often a balancing act. The same polymers that hydrolytically degrade in the presence of excess moisture can also be overdried, which negatively influences processing and final properties. Trace amounts of moisture in polyamides can act as a plasticizer and effectively reduce the melt viscosity of the resin to yield better part quality. Other resins like polyester often have lower molecular weight plasticizers or processing aids that can be driven off by excessive drying. It is very important to dry each polymer type at the appropriate temperature and time recommended by the manufacturer. The best way to avoid overdrying material is to have a material handling procedure that minimizes the introduction of moisture into the resin in the first place. This is especially true for extremely hygroscopic polymers used for water soluble support materials like PVA, HPMC, and BVOH. With these materials, sustained exposure to high levels of humidity or moisture can cause irreversible swelling in the filament with permeant negative impacts on melt processing.

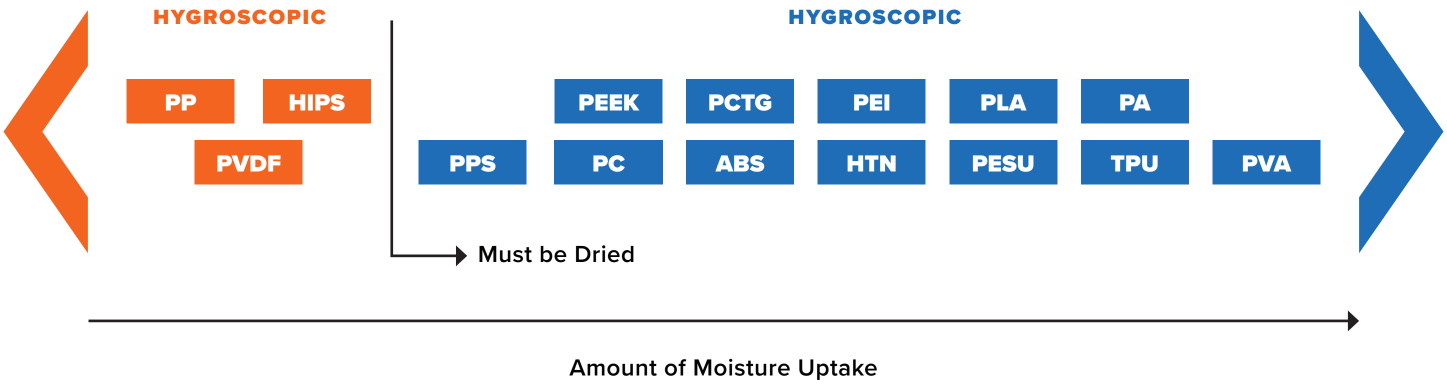
Moisture is introduced to polymers in two primary ways: absorption and adsorption. Absorption is the diffusion of water molecules into the volume of polar polymers. Adsorption is the adhesion of water molecules to the surface of a polymer and can affect both polar and non-polar polymers (figure 4).

Figure 4



The vast majority of thermoplastic polymers used in material extrusion 3D printing are polar and hygroscopic – that is, they both absorb and adsorb moisture from ambient air. The exception to this is hydrophobic polymers which are non-polar based on their chemical structure. PVC, PVDF, and polystyrene as well as most polyolefins including polyethylene, polypropylene, and olefin copolymers are non-polar and therefore do not absorb moisture (figure 5). In most cases, these hydrophobic polymers do not require drying unless excessively high humidity or fluctuating temperatures cause significant surface moisture adsorption.

Figure 5



For hygroscopic polymers, the moisture present in the material is based on three primary factors: polymer chemistry, ambient conditions, and time. Moisture absorption into hygroscopic materials is a Fickian diffusion process with the diffusion rate governed by the concentration gradient and the diffusion coefficient, which is dependent on the material properties and temperature. At infinite times, or equilibrium, a polymer will absorb a specific amount of water per unit mass (measured in parts per million – ppm) based on its chemical structure. Polymers based on polyamide chemistry (nylons) or water-soluble support materials based on PVA or BVOH can absorb vast amounts of moisture at equilibrium. The equilibrium moisture content in the polymer is also dependent on the moisture content in the air around it; higher ambient humidity leads to higher equilibrium moisture levels in the polymer. When a polymer is not at equilibrium, such as when it is first removed from its vacuum packaging, the most important factors are time and temperature. For simple Fickian diffusion of water vapor into a solid, the diffusion coefficients are correlated to temperature by an Arrhenius relationship: the higher the temperature, the faster water diffuses into the polymer. Thermoplastic 3D printer filaments can take anywhere from days to weeks to reach equilibrium moisture values. However, even trace amounts of moisture can cause serious problems when melt processing the polymer in a 3D printer. Highly hygroscopic resins like nylon and TPU can show visible signs of moisture in printed parts after being left out in a humid room for only 30 minutes.

The same mechanism by which moisture makes its way into a polymer is the way to get it back out and dry it. Moisture originally diffused into the polymer because the concentration gradient was high for humid ambient air to diffuse into the dry polymer. To drive the diffusion process backward, you must reverse the concentration gradient: place the moisture-laden polymer into a dry ambient environment. This is typically accomplished in one of three ways: hot air drying, desiccant air drying, or vacuum drying. All methods share one commonality: heat. Remember that diffusion is governed by an Arrhenius relationship, so the higher the drying temperature, the faster the drying. The upper limit for temperature and drying times is based on the degradation temperature of the polymer, the glass transition temperature for amorphous polymers (so the spool doesn't sinter into a solid chunk), or the temperature at which an additive in the material will be degraded. A secondary reason for drying at elevated temperatures is that some polymers like nylon form a chemical bond with water (hydrogen bonding) that cannot be broken at ambient temperatures no matter how dry the air is. This means wet nylon can never be dried by placing it in a desiccant or vacuum chamber at room temperature. A circulating hot air dryer is sufficient for hydrophobic resins where adsorbed surface moisture is the only concern. Hygroscopic resins however require hot and dry conditions to properly dry. If a spool of saturated nylon is placed in a sealed convection oven, moisture will be driven out of the spool and into the air in the oven until the concentration gradient of the air and spool are equal. If the moisture from the hot air is not removed, the material will not be able to dry to sufficiently low levels. The most common method for removing moisture from a dryer is with a desiccant. With this technique, the hot humid air from the dryer output is fed over a bed or membrane containing a silica, clay, or molecular sieve type desiccant. The desiccant has a very high affinity for the moisture and pulls it out of the air, allowing very dry air with a dew point typically below -40˚C to be heated and fed back to the hopper. Once the desiccant is saturated with moisture it is removed from the drying airflow (with a rotating wheel, diverted to another canister, or mechanically isolated) and regenerated by heating it at high enough temperatures, typically between 190˚C and 215˚C, to drive off the moisture. Desiccant dryers are the industry standard for drying thermoplastic pellets prior to melt processing. They are simple, economical, relatively energy efficient and very low maintenance.

SPOOL MATERIAL AND DRYING TEMPERATURES

Not all spools are created equally. The most common spools are made by injection molding polystyrene (PS), which has a heat deflection temperature around 80 °C. This amorphous material can deform when heated to near that temperature due to the residual stresses left from the injection molding process. Depending on your system, this can make the spool unusable due to unstable feeding. We don't recommend putting PS spools in an oven any hotter than 70 °C.

The properties of the filament material deserve some consideration as well. Above 70 °C, the PCTG and PETG filament can fuse to itself, causing anything from an annoying 'stickiness' to a solid, unusable donut of filament.

For high performance materials, such as high temperature nylon (HTN), PEI, PEEK, and others, the dryer temps need to be significantly higher. These materials should come on PC/ABS, PC, or metal spools, which can withstand 110 °C and 130 °C, respectively, or a little higher.

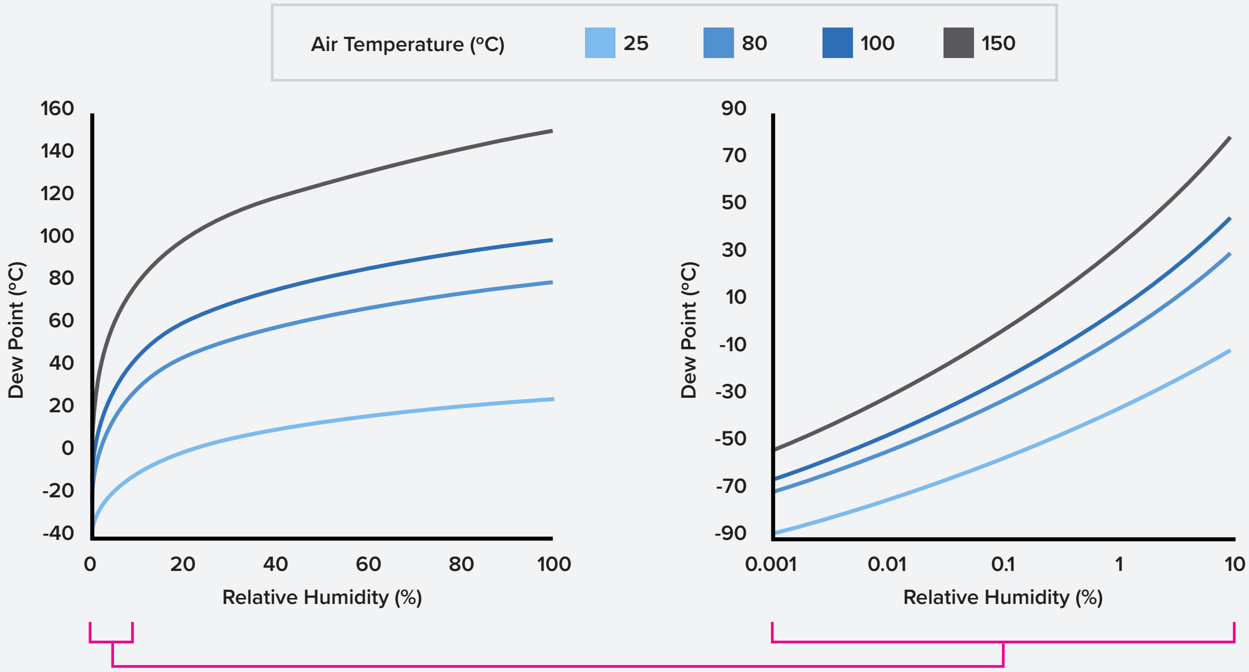
DEW POINT, RELATIVE HUMIDITY, ABSOLUTE HUMIDITY

There are many ways to describe the amount of water vapor in air, which is what humidity refers to. The most common is relative humidity (RH), which is expressed as a percentage of the total capacity in the air. For example, 90% humidity is Houston, Texas in the summer, which feels like walking in a sauna. The air contains almost as much water vapor as it can hold at that temperature.

The dew point refers to the temperature at which water vapor will condense, which is the same as the temperature at which the RH would be 100%. At 98°F (37°C) and 90% RH, the dew point is 95°F (35°C). A cold glass or can is quickly covered in condensation, since the cool temperature lowers the local air temperature below the dew point. The absolute humidity, or mass of water per mass of dry air, is 38.8 g/m3.

On the other hand, a San Francisco, California summer morning may easily be 55°F (13°C). At a RH of 90%, the dew point is 52°F (11°C). At the same RH, the absolute humidity is only 10.1 g/m3. That's less than one third of the Houston scenario. This is because cooler air has less capacity to absorb water vapor.

Dew point and absolute humidity both express the absolute amount of water vapor in the air, independent of the air temperature. Dew point is more commonly used for drying equipment since it's a little easier to relate to and conceptualize. Good quality drying equipment will have a dew point below 0°F, commonly at –40°F. This is about the same as 0.7% RH at room temperature (73°F, 23°C). The other reason dew point is preferred over relative humidity in drying equipment is the sensitivity of the measurement at high temperatures and low moisture values. For a drying temperature of 100˚C, a change from -30˚C to -40˚C is equivalent to measuring a change in relative humidity of 0.049% to 0.018%; most sensors designed to measure relative humidity are not tuned to report these values and remembering them would be cumbersome.



This is to indicate that these are the same graph, the graph on the right is a zoomed in view plotted on a log scale

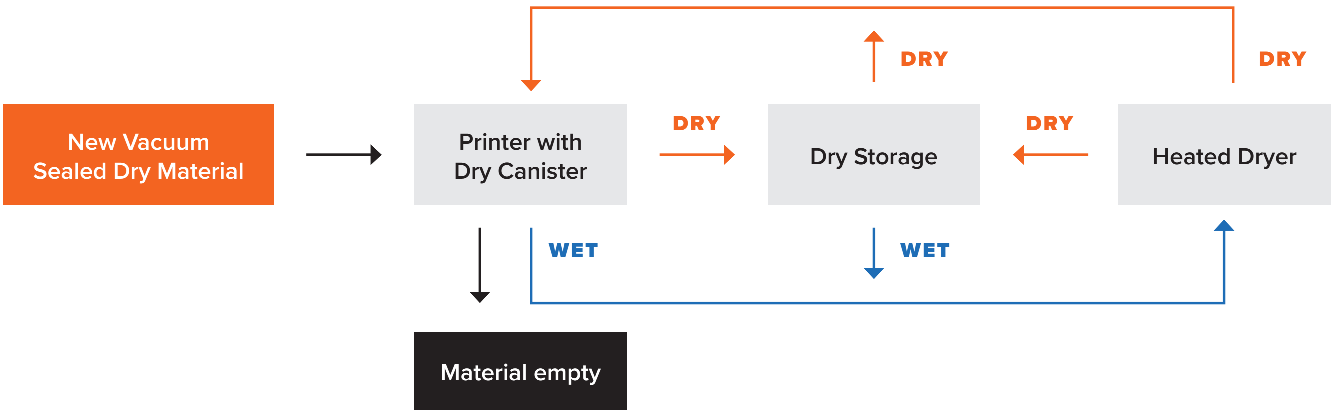
Desiccant based systems are not the only method for pulling moisture out of the process air. If a compressed air source is available, membrane type dryers can be very cost effective with little to no maintenance. Membrane dryers operate like a reverse osmosis membrane for purifying water, but instead of blocking salts and impurities in water, compressed air membranes block water molecules, while allowing dry air to pass through. These compact systems are able to supply a consistent source of -40˚C dew point process air to resin dryers with no moving parts, and no contamination from desiccant bead dust.

Another method for creating a diffusion gradient that drives moisture out of wet thermoplastics is pulling a vacuum on the material. By evacuating the ambient air and evolved moisture from a spool of filament, the driving force for pulling moisture out of the material is maintained throughout the drying process. This method is far more effective than any circulating dry air environment at equivalent drying temperatures. Vacuum drying of thermoplastics is the most effective method for quickly and gently removing moisture from the feedstock. The main drawback is that vacuum drying requires an appropriate oven and vacuum pump combination that is typically more expensive than a desiccant drying counterpart, especially for large drying operations encountered in thermoplastic melt processing. For higher drying temperatures above 100˚C, desiccant type dryers require extra air handling equipment for cooling the incoming hot and moist air. Because of this, for smaller scale drying needs, a vacuum drying oven can be the more efficient and economical choice for drying engineering-grade 3D printing materials.

As with most resource constrained processes, a proper material handling procedure for your facility starts with identifying the degree of quality control required for your application. The quality control measures for printing a fit checking prototype versus an avionics cooling duct are vastly different. We have seen spools of PLA and ABS hang off the back of desktop printers without any consideration for material dryness for the past decade, with plenty of satisfied hobbyists and functional industrial prototypes. Then again, we have also observed plenty of industrial users print jigs and fixtures with engineering grade materials, without drying the material, and declare 3D printing “isn’t ready yet” when the machine cranks out junk. Fortunately, if you are just getting into 3D printing, there are ways to implement proper material handling procedures for your facility on a budget. As you start to scale up and invest in more industrial equipment, you can similarly invest in more sophisticated and reliable material handling equipment to meet your needs.

The basic workflow that covers most industrial manufacturing operations consists of a sealed dry container to feed filament into a printer, a dryer to re-dry material that has picked up moisture, and an offline container to store dry material before it is fed to a printer (figure 6). New spools of material received from the manufacturer should be vacuum sealed in a bag with a desiccant pouch inside to scavenge residual moisture not removed by the vacuum sealer. If you notice issues with new spools that indicate the material is wet, the manufacturer may not have completely dried the material prior to packaging. In this case you should pre-dry the material as a first step, notify the material manufacturer of the issue, and consider another filament manufacturer who has a proper quality control process in place.

Figure 6



ESSENTIUM DRYING PRACTICES

Essentium dries pellets prior to filament extrusion according to the resin manufacturer’s recommendations and our own best practices to achieve tight control over filament quality, including monitoring of filament diameter and ovality. Since cooling the filament involves quenching in water, spools are placed in an oven for an additional drying cycle prior to packaging. Every Essentium spool will arrive to our customers dry and ready to print.

When you receive new material, you should keep the spool sealed until the moment you are ready to load it into a dry canister for printing. When you are ready to print, the material should be transferred from the vacuum sealed packing to the canister as fast as possible in a dry, air-conditioned area, under one minute is ideal. Always avoid situations where a spool at a lower temperature is opened or transferred in a hotter and more humid environment to avoid condensation of moisture onto the filament.

A very economical solution for feeding dry material into desktop printers is modifying a Pelican® case with a push fit connector and Bowden tube, adding a pouch of indicating molecular sieve desiccant, some roller wheels for the spool to sit on, and if you want to monitor the environment, a SensorPush® temperature and humidity sensor is very handy. For very moisture sensitive materials like PA, TPU, and water-soluble support materials, we recommend adding a push fit ball valve that allows you to purge the canister with dry nitrogen purchased from a welding supply store. The Essentium HSE printer addresses this need by having sealable roller carts which are plugged into a manifold in the front of the machine; dry air is then continuously circulated though the canisters by a manifold with actively regenerated desiccant dryers (figure 7).

Figure 7

If a spool of material is used quickly enough after being loaded into a dry container, then the process ends there. This is a sufficient quality control process for keeping material dry and will yield more consistent quality in prints. If the material needs to be exchanged for another material type or a spool with more material to complete another print, it is best to either leave the material in the dry container (necessitating multiple dry containers for a regular workflow) or to transfer it to a larger dry storage container like the Essentium DryBox™. If a material is left in a "dry" container for a period of weeks or months, it still may slowly pick up moisture that diffuses into the container, and for highly hygroscopic resins it may be best to re-dry the spool in an oven prior to use. The only way to truly know the state of the spool is to test moisture content with a loss of mass (LOM), moisture-specific, or Karl Fisher titration moisture analyzer.

ESSENTIUM DRYBOX

Essentium has partnered with industry-leading dry cabinet maker: Electronic Controls Design Inc. to release the next generation of DryBox™ filament storage technology. The all new humidity-controlled cabinet is designed to have a humidity recovery time less than 5 minutes and can maintain relative humidity values under 1% (dew point under -40˚C). This means spools stored in the cabinet will stay dry longer than ever giving users the flexibility to swap materials as often as their workflow requires. Available in two sizes the DB90 cabinet can accommodate up to 24 - 750 g spools, 8 - 2.5 kg spools or 6 - 15kg spools, and the DB270 cabinet can accommodate up to 72 - 750 g spools, 24 - 2.5 kg spools or 18 - 15kg spools. The Essentium DryBox™ is Industry 4.0 ready with a dedicated digital touch screen interface for setting desired dry storage parameters, intelligent LED interior status lighting, onboard data logging and network connectivity.

If a spool does go above the recommended moisture limits for the material, it should be dried with proper equipment. For low criticality materials where only cosmetic concerns apply, a convection oven may be sufficient to re-dry the filament; however, this is not best practice and may very well lead to degradation of the polymer, especially for long drying times. Unfortunately, small-scale desiccant dryers that meet the needs of additive manufacturing are difficult to find and can easily be ten times the price of an equivalent convection oven. We have seen some dryers come on the market that address this need, but their performance needs to be evaluated. For high performance thermoplastics that need to be dried above 100 ˚C, a vacuum oven can be the best solution for reduced drying times, gentler temperatures, and the lowest price point. Small lab ovens with a decent rotary vane pump that would fit a one kg spool can be purchased for under $1,000 (US). Large ovens that can fit multiple 15 kg spools with a high-performance scroll pump run closer to $10,000.

It is important to dry the material only for the recommended time and temperature provided by the material manufacturer. An oven is not an acceptable storage solution for material. Ovens with programmable time and temperature settings are preferable so that material is dried precisely the same way from batch to batch. Once a material is dry, it should be transferred back to the dry canister for feeding into the printer or placed in an appropriate dry holding container for later use.

MATERIALS	DRYING TEMP*	DRYING TIME†	MAX MOISTURE CONTENT
PLA	65-90˚C	4-12 hrs	250 ppm
ABS	80-90˚C	2-4 hrs	200 ppm
PCTG	65-70˚C	4-8 hrs	600 ppm
TPU A	80-90˚C	2-3 hrs	200 ppm
TPU D	90-120˚C	2-3 hrs	200 ppm
HTN	130˚C	6-8 hrs	400 ppm
PA 12	80˚C	4 hrs	1000 ppm
PACF	100-120˚C	4-8 hrs	500 ppm
PC	120˚C	3-5 hrs	200 ppm
Ultem 9085	120-130˚C	4-6 hrs	200 ppm
PEEK	120-150˚C	3-6 hrs	200 ppm
PEKK	120-150˚C	3-8 hrs	200 ppm
PPS	135-150˚C	2-4 hrs	100 ppm
PESU	130-150˚C	3-4 hrs	200 ppm

*Temperature for a desiccated hot air dryer with <-40˚C dew point air

†The times indicated in this table are approximations based on typical industry workflows for these materials. Spools that have picked up very little moisture can be dried on the shorter end of the time ranges indicated, whereas higher levels of moisture exposure will require longer times and higher temperatures for effective drying. Very hygroscopic resins including polyamides, polysulfones, TPU, PEI, and PVA may require even longer drying times if they are allowed to absorb moisture up to their equilibrium moisture content; we strongly recommend that these resins be kept dry and not allowed to absorb large amounts of moisture.

ACKNOWLEDGEMENT

We would like to thank Steve Gillmeister and Mark Haynie at Novatec for reviewing and contributing to this white paper.

REFERENCES

- https://polymerdatabase.com/polymer%20chemistry/Hydrolysis.html
- https://knowledge.ulprospector.com/1210/pe-overdrying-resins/
- https://www.plasticstoday.com/content/materials-analyst-part-89-myth-overdrying-part-1/6917703313643
- Duncan, B. C., and W. R. Broughton. "Absorption and diffusion of moisture in polymeric materials." (2007). http://eprintspublications.npl.co.uk/3865/1/mgpg102.pdf
- Srubar III, Wil V., Curtis W. Frank, and Sarah L. Billington. "Modeling the kinetics of water transport and hydroexpansion in a lignocellulose-reinforced bacterial copolyester." Polymer 53.11 (2012): 2152-2161.
- Michael Sepe, "Drying done right: Practical Ideas, Technology & Solutions to Plastics Drying", Drying Technology, Knowledge Center Supplement, Feb 2015, https://www.novatec.com/wp-content/uploads/2016/03/Drying-Supplement-2-14.pdf
- Alduchov, Oleg A., and Robert E. Eskridge. "Improved Magnus form approximation of saturation vapor pressure." Journal of applied meteorology 35.4 (1996): 601-609.

If these controls and procedures are put into practice at your facility, we guarantee that you will see more consistent print results with better part quality. For more demanding applications it is essential that each facility adopt their own material handling procedures that are followed and documented. Essentium is here to help and our team of materials scientists and polymer experts are available to discuss your individual needs. For more information please contact us at Info@Essentium3D.com or visit our website at Essentium3D.com/Drying.