Technical Guideline for Material Development with HP 3D Open Materials Platform

This technical guideline is published to help potential material suppliers who are interested in developing suitable materials for HP Multi Jet Fusion (MJF) technology through HP Open Materials Platform. As our knowledge evolves, we will update this guideline. This guideline is to serve only as a general guide for material development.
In this updated guideline, more categories were added with test methods and suggested ranges for various powder attributes that can be helpful for MJF success. The tests have been grouped in these main categories:

- Thermal characteristics of the powder
- Optical absorption properties of the powder
- Particle size distribution (PSD)
- Powder flow
- Powder consolidation and flow during melt
- Powder aging and recyclability
- Powder explosion safety

Melt and Crystallization Temperature

Background: From a Differential Scanning Calorimeter (DSC), information such as the melt and crystallization temperature can be obtained. These temperatures can be used as a baseline to determine the processing parameters of MJF.

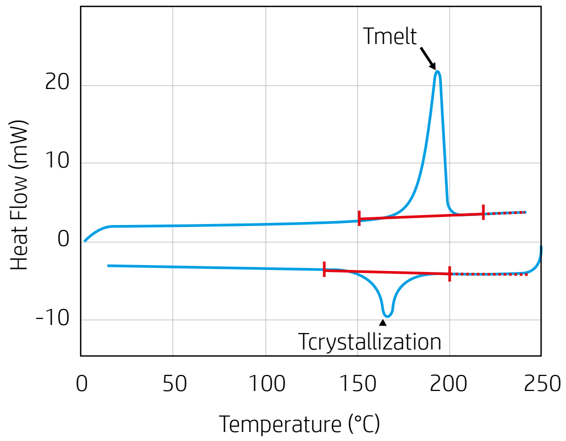

Figure 1: Melt Temperature and Crystallization Temperature

Melt and Crystallization Enthalpy

Background: In an MJF process, a material is melted and crystallized within the operating range of the printer. The melt and crystallization enthalpies can be useful to determine the amount of energy and time associated with these phase transitions and to ensure that the phase transitions are complete at accessible temperatures. The phase transition enthalpies can be determined from a reliable DSC curve of the material of interest. Any good quality commercial DSC instrument is suitable.

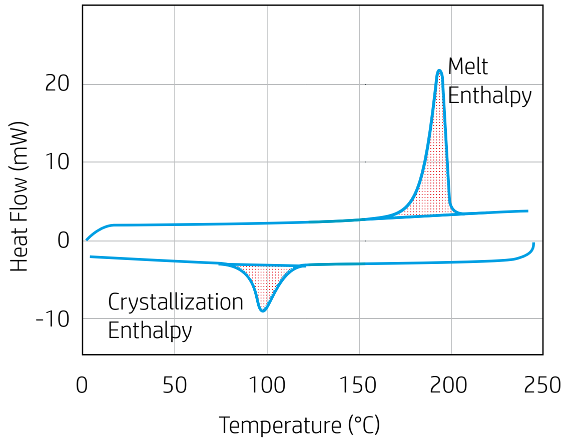

Figure 2: Melt and Crystallization Enthalpy (shaded in red)

Processing Window for MJF

Background: The processing window is a material design parameter used to optimize the thermal window of the material in MJF. In addition to contributing to the MJF printer's temperature set points, the processing window indicates the material's melting behavior which can affect the print mode (or processing parameters) and the likelihood for material outside of the desired print zone to melt.

Determination: The process window can be measured by using a DSC. The processing window can be defined as following:

As seen in Figure 3, the processing window is the difference in temperature of the onset of the crystallization and melt.

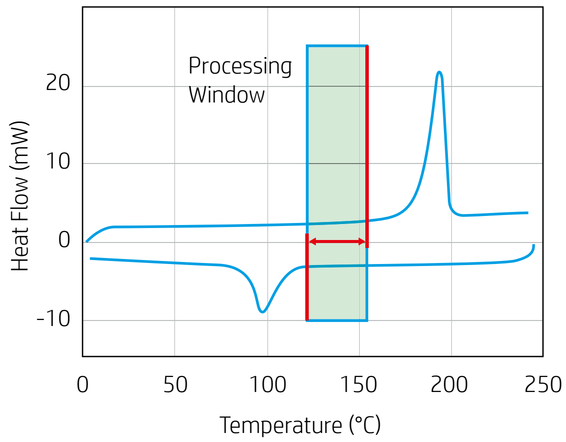

Figure 3. Processing window determined on DSC curve

Design criteria:

Criteria	Suggested Values
Processing window for semi-crystalline materials (ΔT ~ °C)	> 10°C, preferably > 30°C

Powder Absorptivity

Background: The powder spectral absorption should be low throughout the visible and near IR range. A convolution of a Black Body emitter with a filter that cuts out emission that is higher than 2750 nm and the spectral response of the powder should result in a total absorptivity that is less than 20%.

Determination: The spectral absorptivity of a powder sample is measured from 250 to 2750 nm. Powder absorption is measured as a function of wavelength. In addition, the average blackbody emitter is tabulated for the same wavelength range. These values are convolved to determine the powder absorptivity. Said another way, the powder absorptivity is scaled to the emitter spectrum. Next, the scaled absorptivity for each station is summed to determine the Powder Absorptivity.

Suggested metrics:

Criteria	Suggested Values
Total Absorptivity	< 20%

Particle Size Determinations for MJF

Background: The particle size distribution (PSD) is an important powder parameter for the MJF process. Particle size can affect powder flow, the probability of adequate fusing during the print process, reliability of agent print-heads, and the safety of printer operators.

Determination: The particle size distribution of a powder can be measured by using high particle count methods utilizing imaging or diffraction analysis methods capable of accurately and reliably detecting particles in the 3 to 500 um range.
In general, any commercial PSD instrument that can provide a statistically representative sampling method can be used.

Suggested Metrics:

Metric	Suggested Value
D50, Volume distribution	35 - 50 um
D10, Volume distribution	> 20 um
D90, Volume distribution	< 100 um
D90 max	120 um

Particle Shape Determinations for MJF

Background: Particle shape, or aspect ratio, is another powder parameter to consider during the MJF process. In general, spherical particles (AR = 1) tend to flow best while flat or “plate like” particles (AR > 1) tend to flow poorly. The MJF process is tolerant of the presence of some high aspect ratio particles.

Determination: The particle shape or aspect ratio of a powder can be measured using imaging analysis methods capable of accurately and reliably detecting all particles present in the material of interest. Statistically relevant imaging methods such as those integrated into the particle size analysis (non-diffraction methods) are best – but electron microscopy can be used to roughly gauge the distribution of aspect ratios present in the powder. Optical microscopy can also be used providing that the instrumentation is known to be capable for all particle size ranges present. Regardless of method, it’s important to know that a representative sample of material is studied.

Powder Spread Guidelines for MJF

Background: The MJF process works well if a powder spreads consistently and uniformly across the printer build bed at process temperatures for the material of interest.

Determination: It is suggested to use HP's commercially available MJF powder spread assessment tool (MDK tool available from SIGMADesign) for screening of materials. Measurements should be made near the anticipated bed temperature of the material of interest.

Suggested Metrics:

Metric	Suggested Value (% Coverage)
Reasonable spread	70 % < coverage < 100%
Fair spread	50% < coverage < 70%
Poor spread	Coverage < 50%

Apparent Density

Background: Apparent or bulk density is a measure of the volume of the powder that a given mass occupies. The volume includes the material and the voids in the system. Bulk density can change as the powder is handled, so it is helpful to combine this measurement with other methods to characterize the behavior of powder under load.

Determination: Apparent density is a measure of the volume occupied by a given mass of powder according to ISO 60 method and is reported as mass (grams)/volume (L).

Suggested Metrics:

Metric	Suggested Values
Mass / volume	300 - 600 g/L

Copley Flow

Background: Flowability of powders can be measured using several methods. Each method offers a different view at powder characteristics. Copley flowability can be used as a gauge to indicate a change in behavior relative to a given benchmark.

Determination: Copley flow test measures the time it takes for a given mass of powder to flow through a funnel according to DIN EN ISO 6186 method A. Different openings can be used according to the standard, but a 15mm circular opening is suggested

Suggested Metrics:

Metric	Suggested Values
Flow rate	15 - 35 seconds

Powder Melt & Coalescence

Background: A heated stage partnered with a polarized microscope provide helpful information about polymer consolidation and melt behavior. When exposed to a steady heating and cooling ramp, the material exhibits melting and consolidation which can be recorded. The correlation between time / temperature and polymer melt behavior can determine if MJF is applying enough energy to fully melt and consolidate the material.
Coalescence propensity and speed of powders can also be studied and compared.

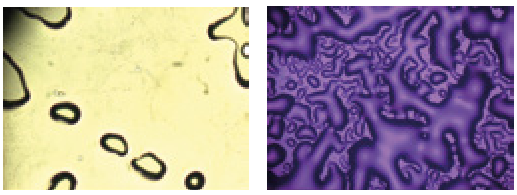

Figure 4: Material that coalesce well (left) and coalesce poorly (right)

Flowability test via Avalanche Angle

Background: Powder flow properties can be helpful in determining the ability of the powder to spread through an MJF system. The flow properties can be measured by various commercially available test tools, one of which is the Revolution Powder Analyzer by Mercury Scientific Inc. Pertinent parameters are the avalanche angle, break energy, avalanche energy, and dynamic density.

Tap Density Guidelines for MJF

Background: The MJF process requires that a powder material is amenable to transport and proper flow both in hoppers, vane paddles, roller spreading, and pneumatic transport. While no single flow metric can completely characterize material behavior under all conditions, the use of a tap density measurements is useful to evaluate the relative flow state of powders using laboratory scale amounts of material.

Determination: While the use of any reputable commercial instrument is possible, the use of a high-quality tap density instrument utilizing Hall Sensor detection is suggested for repeatable, sensitive measurements. The use of the Lumay parameters*, rather than the traditional Hausner Index or Carr compressibility metric, is suggested for most materials.

* Lumay et al.; APPLIED PHYSICS LETTERS 89, 093505 _2006

Suggested Metrics:

Metric	Physical Meaning
$n^{1/2}$	Taps to yield consolidation 5 – 30 taps
Tau	Consolidation Resistance

Melt Flow Index

Background: For a given material, selecting the right molecular weight or melt viscosity is an important consideration. A low melt viscosity material is easy to flow once molten and it consolidates quickly. On the other hand, high melt viscosity materials usually give better part ductility, which can be a desired attribute.

Determination: The Melt Flow Rate is a measure of the ease of flow of melted plastic and represents a typical index for Quality Control of thermoplastics. MFI is intended to provide a simple way of measuring the relative average molecular weight (MW) of the polymer. As MW decreases, MFI increases. MW influences impact performance, fatigue resistance, creep resistance, environmental stress-crack resistance, and barrier properties.

The melt flow index (MFI) of a material is usually measured at 40-50˚C above its melting point per ASTM D1238 or ISO 1133 procedure. The accumulated volume or mass of the polymer during a 10-minute interval under a specified weight is reported (cc/10 min or g/10 min). The weight usually varies from 1.2 kg to 5 kg.

Suggested Metrics:

Metric	Suggested Values
Flow rate	4 - 40 cc/10 min for 5 kg mass

Solution Viscosity for MJF

Background: Solution viscosity is especially useful when molecular weight of a polymer is difficult to measure. Solution viscosity (or sometimes called relative viscosity) is measured according to ISO 307 and is correlated to the mechanical property of a printed part. Direct measurement of molecular weight is performed using Gel Permeation Chromatography (GPC).

Determination: Following the measurement protocol described in International Standard ISO 307, the viscosity is typically measured using a capillary viscometer. The measurement is based on the time it takes for a certain volume of fluid (solvent or solution) to pass through a capillary viscometer under its own weight or gravity compared to the same fluid (solvent or solution) admixed with a small amount of the polymer powder. The higher the viscosity, the longer it takes for the fluid to pass through. Thus, relative viscosity is defined as a ratio that compares the time for a fluid with the polymer powder to pass through the capillary compared to the time it takes for the fluid alone to pass through.

Parameters:

Concentration of sample: 0.5 wt% powder with 99.5 wt% m-cresol
Operating Temperature: 25°C
Preparation:

1. Powder dissolved in m-cresol for 2-3 days
2. Put sample in oven for 1 hour at 95°C
3. Cool to room temperature before running samples.

	Suggested Lower Limit	Suggested Upper Limit
Solution Viscosity	1.0	2.2

Oven Aging / Oxidation Test for MJF

Background: Oxidation and degradation of powder is of concern for the MJF process. Change in molecular weight or color of the powder may affect the mechanical properties or the print parameters for the material. The thermal aging of a powder inherent to the print process can be simulated in the oven. Metrics can be the solution viscosities/MFI and color (b* value) of the powder.

Definitions:
b* value: yellow/ blue coordinate in the L*a*b* color space.
Bed temperature: temperature at which the powder (without fusing agent) is maintained during printing in MJF.

Determination: The material (powder or pellet) is put in small vials or containers, and then aged in the oven at bed temperature for different times. To determine oxidation, measure the b-value of all the aged samples and compare the values with that of the fresh, non-aged samples. To determine degradation, find the solution viscosity using a solution viscometer (ISO 307) and find the time at which the viscosity showed a significant decrease. A significant decrease is defined as a value that is outside of viscometer's accuracy.

Suggested Metrics:

Metric	Suggested Value
b* value - fresh	< 1
b* value after 20 hours	< 3
Relative viscosity	1.0 - 2.2

Injection Molding Guidelines for MJF

Background: The MJF process is a unique fabrication method that is strongly predicated on a material's interaction with the process ecosystem. As such, it is often useful to benchmark the MJF samples to comparable injection molding samples manufactured under conditions known to yield parts of interest.

Determination: Laboratory or manufacturing IM samples may be used, but it is critical to fully understand the conditions of the material and IM process by which the samples are produced. Moisture level, source, grade and molecular weight of the material as well as specific IM process conditions influence the quality of an IM part. It is important to ensure all relevant conditions are known and understood to make a quality comparison of parts.

Recommended Metrics for Comparison:

Metric	Test Method	Comments
Tensile Properties	ASTM D658 or ISO 527	Focus on properties of specific interest for application
Impact Properties	ISO 179 and/or ISO 180, ASTM D256	Focus on properties of specific interest for application
Elastomeric Properties	ASTM or ISO Rebound Energy, Heat Deflection Temp., Shore Hardness	Focus on properties of specific interest for application

Powder Safety Metrics for MJF

Background: The MJF process subjects materials to relatively high temperatures for varying times both from conduction heaters and IR lamps. Electrical devices are also used in MJF equipment. As such, the flammability and explosivity of small particle size polymer powders is of concern to ensure the safe operation of the printer and post printer production units.

Determination: The powder properties useful for safe operation of the MJF printer and post-printer production units are listed below. The determination of these parameters should be conducted by a reliable lab certified to make the measurements according to NFPA Class II test standards.

Suggested Metrics:

Dust Characteristic Test	Standard Test Method	Acronym	Unit	Minimum Acceptance Criteria
Minimum Ignition Energy "dust cloud" w/inductance	EN13821 or ASTM E2019	MIE	mJ	> = 10 mJ
Minimum ignition temperature "dust cloud"	EN50281-2-1 or ASTM 1491	MIT	°C	> = 360°C
Layer Ignition temperature (dust layer)	EN50281-2-1 or ASTM E2021 (till 400°C even if melted before)	LIT	°C	> = 400°C
Auto ignition temp	VDI 2263 ASTM D1929	AIT	°C	> = 400°C

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