

MICROWAVE MEASUREMENTS OF NYLON-12 POWDER AGEING FOR ADDITIVE MANUFACTURING

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Abstract

With repeated recycling, nylon powders used in Selective Laser Sintering are known to degrade and ultimately cause mechanical performance and surface finish deterioration in produced parts. In order to maintain consistent production and to reduce cost by minimising waste powder, it is desirable to monitor this degradation. However, any techniques used must be inexpensive, quick and simple in order to maintain industrial relevance; dielectric measurements by microwave cavity perturbation can offer these advantages. Here, samples are taken from a working SLS machine and their permittivity measured using microwave cavity perturbation operating around 2.5 GHz. A 2% reduction in effective dielectric constant and an 8% reduction in effective dielectric loss is observed between new powder and recycled feedstock. Furthermore, in-situ measurements simulating build chamber conditions show a similar trend.

Keywords- Microwave, Nylon, Perturbation, Permittivity, Powder, Polyamide, Laser Sintering

Introduction

Selective Laser Sintering (SLS) is a popular and widely used additive manufacturing technique. Typically, a CO₂ laser is used to iteratively heat and fuse a powder bed in order to create a solid object. Since the majority of the powder bed is left unfused, in order to reduce costs, it is important that this powder is collected and recycled back through the process.

Polyamide 12 (PA12), also known as nylon, is the most commonly used material in SLS. Extensive previous studies have been conducted into the recycling of PA12 powders [1], [2]. It is well understood that the processing conditions, namely repeated and extended thermal cycling close to the melting temperature, cause gradual changes to the powder which result in deterioration of its mechanical and thermal properties, as well as changing the visual appearance of parts made from SLS. Common practice is to mix a constant proportion of fresh powder to previously used powder in order to maintain build quality. However, this mixing regime is not sufficient to re-use the powder fully and substantial powder waste is generated. Furthermore, the SLS build duration and density of parts inside a build will affect how long the powder is heated for, as well as the temperature it is exposed to. For this reason, mixing used and fresh powders at fixed ratio does not guarantee full powder consistency and can sometimes result in parts needing to be scrapped, the obvious external sign being an ‘orange peel’ surface effect as described in [1] (Fig. 1).



Fig. 1. SLS vertical wall surface finish. Side by side samples: standard finish (left) and orange peel (right).

PA12 powder deterioration occurs because the powder in the SLS machine's build chamber must be kept between its crystallization and melting temperature in order to prevent shrinkage and thus part distortion during the build as shown in Fig. 2 [3].

At these elevated temperatures, the polymer molecules become relatively mobile. Firstly, amorphous regions will undergo nucleation whereby ordered crystalline regions form and grow. In nylon, these regions take the form of chain-folded Lamellae. Given time, these lamellae further organize into spherulites. Furthermore, elevated temperature will cause an increase in the average molecular weight [4].

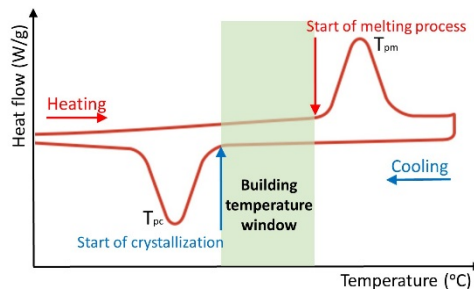


Fig. 2. differential scanning calorimetry curve for melting and crystallization of PA12 (Adapted from [3])

Unsurprisingly, these molecular changes have significant impact on the melting characteristics of the polymer, which can adversely affect build performance. It has also been previously reported that annealing at high temperatures effects the electrical properties of nylon. For instance, [5] reports an increase in DC conductivity and decrease in polarization (at relatively low frequencies). This paper demonstrates the observable effect in changing dielectric properties of aged nylon powder at microwave frequencies, measured in a contactless (i.e. noninvasive way).

Some SLS manufacturers offer solutions for material traceability, however, a more advanced controlled recycling system, which actively grades powder quality and determines mixing proportions, is desirable but, in order to be feasible, requires a cheap and easy testing method.

The common methods for characterizing powder are typically cumbersome and slow often requiring expensive equipment. Examples include; Differential Scanning Calorimetry (DSC) to measure thermal properties such as the melting and glass transition temperatures, Melt Flow Indexing to measure the molten viscosity and Gel Permeation Chromatography to measure average

molecular weight [6]. The testing of dielectric properties by microwave cavity perturbation offers a potential solution requiring minimal sample preparation, quick testing times and inexpensive hardware.

Microwave Cavity Perturbation

As described by perturbation theory [7], the complex dielectric constant ($\epsilon_1 - j\epsilon_2$) describing the sample dielectric constant and losses can be measured by observing the shift, from the unperturbed state, in resonant frequency and quality factor (Q), respectively, on the insertion of a sample into a cavity resonator. For measurement of powders, these measurements are usually termed ‘effective’ due to local field modifications caused by the shape and packing of particles.

Furthermore, since the error in resonator measurement parameters (frequency and Q) is typically very small, samples can be compared with very high sensitivity. However, since the measurement is volumetric, the samples must be weighed and a correction factor applied to the sample volume in order to eliminate any density variation between samples. The majority of measurement uncertainty encountered here (~1%) can be attributed to uncertainty in the sample volume.

The measurement setup comprises a cylindrical cavity resonator operating in the TM_{010} mode. Coupling is provided by two extended co-axial probes along the flat cavity surface. Machined in two parts from aluminium to eliminate the effect of contact currents across the join, the internal radius is 4.6cm and the internal height is 4cm which places TM_{010} at 2.5 GHz. The electric field distribution and a photograph of the constructed cavity can be seen in Fig. 3.

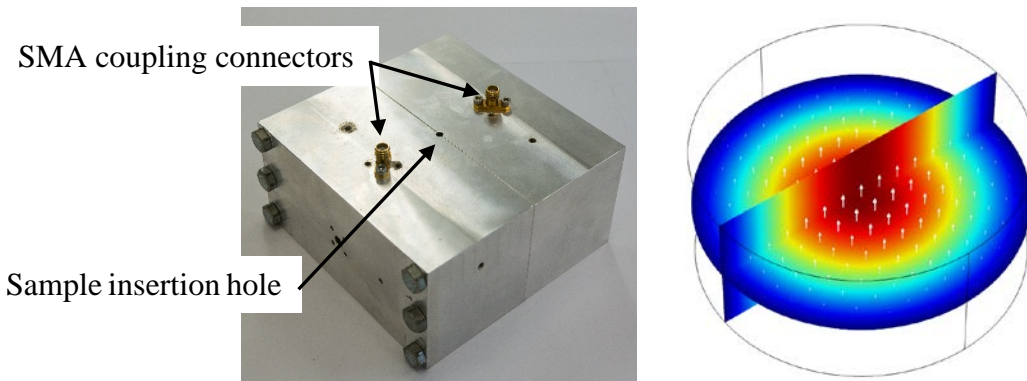


Fig. 3. Cylindrical cavity used in the experimentation and the TM_{010} electric field distribution showing high field intensity in the center region.

Here, the measurement of the resonator parameters was done by fitting a Lorentzian curve to the power transmission coefficient, $|S_{21}|$, measured by an Agilent PNA-L (N5232A) network analyser, in a small span around the resonant frequency as described elsewhere [8].

Samples were filled into quartz tubes (ID: 2mm OD: 2.4mm) and sealed with a silicone adhesive. To ensure a uniform powder density, the samples were placed on a simple vibration platform (1kHz) for 10 seconds before insertion axially into the cavity.

Results

Initially, samples were taken from a machine setup in constant current use, in this instance an EOS P700 using EOS PA2200 powder. Alongside new ‘virgin’ powder, a sample, labelled ‘recycled’, was taken from the in-use feed which contained a mixture of new and powder which had been previously cycled through the machine. It can be seen in Fig. 4 that the recycled powder exhibits reductions in both real and imaginary parts of the complex permittivity, more prominent in the latter.

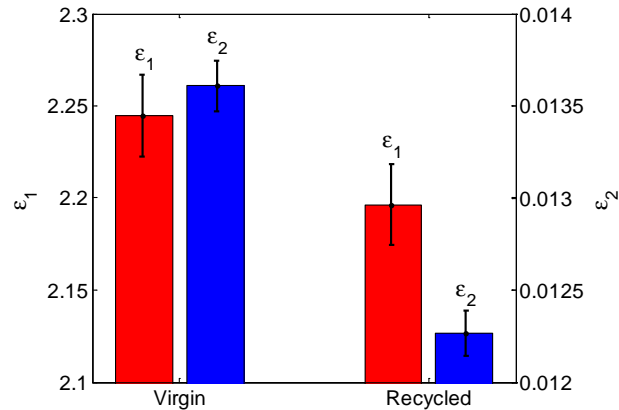


Fig. 4. Measured real and imaginary effective permittivity of a sample of virgin and recycled virgin powder. The error bars consider the random error in resonator measurement parameters and sample volume only and not the cavity calibration, which can add an additional ~1% systematic error.

The effect was further explored by the undertaking of an in-situ aging experiment. In order to simulate the conditions in the build chamber, a sample of virgin powder was measured continuously over 15 hours whilst at 170°C within an oven (Mettler UF30Plus). Modifications in the resonator parameters themselves, due to the increased temperature, were corrected for by measurement of a second mode as described elsewhere [9]. The inert atmosphere of the build chamber was also replicated by filling and sealing the quartz tubes within an Argon filled glove box. Whilst Nitrogen is typically used in commercial SLS, the Argon is expected to perform the same function by eliminating the polymer reaction with atmospheric oxygen. This technique does not allow accurate comparison of the sample before and after heat treatment as thermal expansion in the tube changes the relative density of the powder and therefore the perturbation measurements. However, at a steady temperature, density changes are not occurring and so any changes can be attributed to the powder itself.

By examination of the resulting plots in Fig. 5, it is firstly observed that a dramatic increase in permittivity occurs as the temperature is initially increased. This change is largely reversible, as seen when the sample is allowed to cool, and can be attributed to a significant rise in bulk conductivity with temperature. However, in addition, once at a steady temperature, both components of permittivity show a gradual reduction congruent with the earlier result. The rate of change slows after ~6 hours but it has not plateaued after 12+ hours.

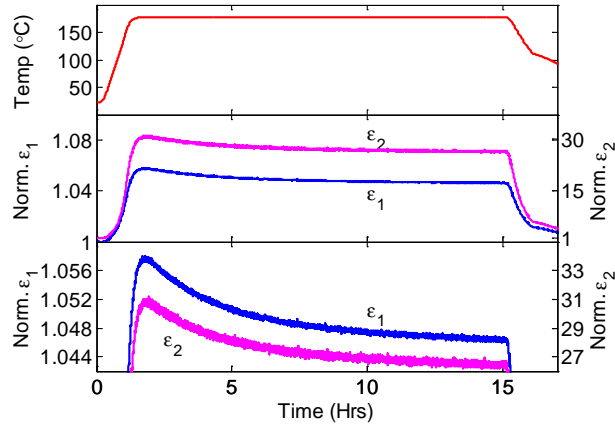


Fig. 5. Normalized change in real and imaginary effective permittivity of virgin powder as it is heat treated at 170°C. Once at a steady temperature, a gradual reduction can be seen.

The next step involves the heat treatment of argon sealed samples and subsequent filling of quartz samples before measurement at room temperature. This more closely mirrors the potential measurements which could be undertaken to assess powder quality in the context of SLS. The results in Fig. 6 show a two-stage response whereby the permittivity is seen to rise initially before showing the decrease shown in previous measurements.

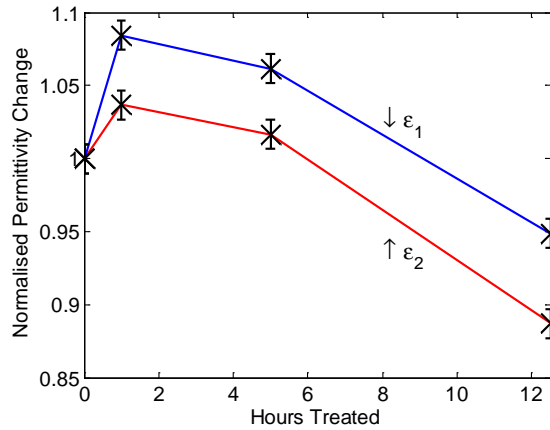


Fig. 6. Normalized change in real and imaginary effective permittivity after treatment at 150°C in sealed, argon filled, containers.

Some indication of the cause of this response can be given by examination of the X-Ray diffraction spectra of these samples. Fig. 7 shows the increasing γ phase where the crystalline transformation occurs between 0-5 hours. Since no further change is seen between the 5 and 12 hour treated samples, no comment can be made of the cause of permittivity reduction after extended treatment.

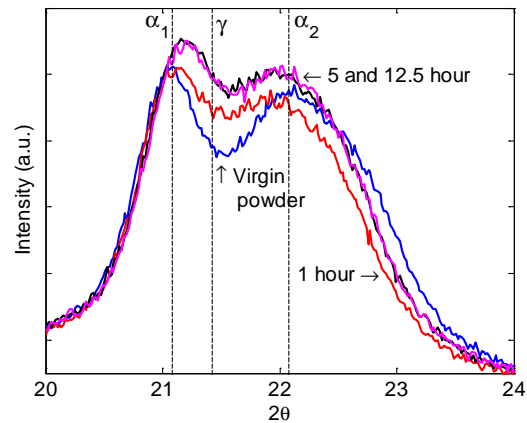


Fig. 7. XRD spectra of nylon samples after heat treatment at 150°C in sealed argon containers. Location of α and γ peaks taken from [10]. The rise in intensity around $2\theta \approx 21.5^\circ$ is attributed to the increase in γ phase content.

Conclusions

The measurements here have demonstrated the potential for the microwave cavity perturbation technique to measure the gradual deterioration of Nylon-12 powders as they are repeatedly recycled in the SLS process. Experimental evidence has shown a reduction in permittivity as the powders are subjected to extended heat treatment (> 5 hours) as encountered in the SLS build chamber. Short heating times have shown to increase permittivity and this can be linked to changing crystalline structure as shown in XRD measurements.

This result is of significant value since it is known that powder deterioration has an impact on SLS performance and the method presented here can be implemented cheaply and easily. Furthermore, since it is a non-destructive technique, it is conceivable to place such a sensor within powder processing loop itself.

In order to properly assess the value of this technique, further work needs to be undertaken to experimentally quantify the rate at which permittivity is effected by deterioration and discover the limits before sufficient deterioration has occurred as to effect part performance. Whilst previous studies have examined a number of mechanisms by which the powder changes during heat treatment, further work could be done to directly correlate these mechanisms to electrical effects.

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