Thermal Conductivity Measurements of Polyamide 12

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Abstract

An important component in understanding the laser sintering process is knowledge of the thermal properties of the processed material. Thermal conductivity measurements of pure polyamide 12 were conducted based on transient plane source technology using a Hot Disk® TPS500 conductivity measurement device. Polyamide samples were packed to three different densities in nitrogen at steady state. Thermal diffusivity and conductivity were measured from 40°C to 170°C for both fresh powder and previously heated ("recycled") powder. The fresh powder tests revealed that thermal conductivity increased linearly with temperature while for previously heated powder, more constant and higher thermal conductivity was observed as it formed a powder cake. Tests were also performed on fully dense polyamide 12 to establish a baseline. Polyamide 12 powder had a room-temperature thermal conductivity of approximately 0.1 W/mK which increased with temperature, whereas the bulk laser sintered polyamide 12 room-temperature value was 0.26 W/mK and generally decreased with increasing temperature.

Introduction

Laser sintering is an additive manufacturing technology that uses a high power laser to fuse polymer powder into a mass that has a desired 3-dimensional shape. The laser selectively scans and fuses powder material on the surface of the powder bed based on the previously generated CAD file. After one layer is scanned, the powder bed is lowered by one layer thickness, creating a new layer that is scanned. The process is repeated until the part is completed.

Polyamide 12, also known as Nylon 12, is a thermoplastic material that widely is used in laser sintering. It has high elongation, good abrasion resistance, good specific strength, and melts at a temperature around 180°C. Thermal conductivity measurement of polyamide 12 is essential to assessing the material performance during heating and cooling in laser sintering. Based on the material performance observed and samples produced, a more effective and accurate process control may be maintained.

To understand the material behavior during the laser sintering process, there is a basic relation that combines a material physical property with thermal properties:

$$\alpha = \frac{k}{\rho c} \tag{1}$$

where α is thermal diffusivity, k is thermal conductivity, ρ is the sample density, and c is the specific heat.

There are limited experimental results for thermal conductivity of polyamide powder, but some exist for other powders, including metal and ceramic powder. Samuel Xue and J. W Barlow [1] made measurements on several powders, including ABS, PVC, nylon, and wax. They found that the thermal conductivity of powder generally increased with increasing temperature. However, the shape of the thermal conductivity versus time curves can be quite different for the varying materials. For an unspecified nylon powder, they found the following relationship for the thermal conductivity of polyamide:

$$k = -2.2139 + 0.020569T - 0.000062289T^2 + 0.000000063221T^3 \qquad (2)$$

where k is in W/mK, T is the absolute temperature in K from 280-360 K. It gives a thermal conductivity around 0.0604 ~0.0679 W/mK from 40°C to 87°C. The value of this prediction is limited due to the limited temperature range, lack of information relating to material and experimental conditions, and sample preparation.

Deissler and Boegli [2] described the condition of the maximum and minimum effective thermal conductivity k_{ef} of a two phase system (gas and solid): the maximum k_{ef} occurs when the material is arranged in alternating layers parallel to the flow of thermal energy, which means the contact resistance is ignored; while the minimum k_{ef} occurs when the material is arranged in alternating layers perpendicular to the flow of thermal energy, which means the contact resistance reaches the maximum. Equation (7) and (8) indicate these two conditions separately:

$$\frac{k_{ef}}{k_g} = \varepsilon + \frac{k_s}{k_g}(1-\varepsilon) \qquad \text{[maximum]} \qquad (3)$$

$$\frac{k_{ef}}{k_g} = \frac{1}{\varepsilon + \frac{1-\varepsilon}{k_s/k_g}} \qquad \text{[minimum]} \qquad (4)$$

where k_s is the thermal conductivity of the solid, k_g is the thermal conductivity of the gas, ε is the relative porosity, k_{ef} is the maximum or minimum effective thermal conductivity. The porosity-based method is appropriate for powder beds in that the thermal conductivity varies with porosity which would influence the laser sintering process and the bulk material produced. However, this approach assumes good thermal contact and is not suitable for unsintered powders.

Polyamide is an essential material in the laser sintering process. However, limited experimental data for thermal conductivity of polyamide powder exists in the published literature. Therefore, thermal conductivity measurements of polyamide and polyamide nanocomposites were conducted and analyzed in this paper.

Experiment Procedure

1. Thermal conductivity measurement

Apparatus A plane-source transient thermal conductivity measurement machine (HotDisk® TPS 500) and a temperature control oven were acquired, which are shown in Fig. 1. A powder holder was fabricated, allowing the conductivity probe to be sandwiched between the two sections of powder. The interstitial gas was heated through the copper tubes that were hung on the inside wall.

The powder (Duraform® PA, a 50 µm polyamide 12 powder) was loaded into the sample holder and tapped to settle it before the measurement. The apparatus output the thermal diffusivity which was converted to thermal conductivity using Equation 1 with the measured relative density and the specific heat calculated from Equations 5 and 6.

Figure 1: Experimental apparatus for measuring the thermal conductivity of polyamide-12 powder. The view is inside the temperature control oven, which includes the sample holder, rack, copper tubes and sensor.

Procedure According to Mark's Handbook [3], polyamide 12 powder has a melting temperature approximately 180°C. For this reason, 170°C was selected as the highest test temperature. During experimental runs, a 10°C increment was selected. Interstitial gas-N_2 (purity 99.95%) was purged by adding an inlet port at the bottom, and a diffuser port at the top was constructed to prevent oxidation and to boost the heating process.

In each experiment, a direct current that was large enough to increase the sensor temperature by 1-2K, passed through the sensor. The sensor resistance changed which resulted in a voltage drop. A precise relation of the heat flow between the sensor and the test specimen was obtained. According to the heat flow and the geometric information, specific heat and thermal diffusivity were calculated. According to the basic relation $k=\alpha\rho c$, the thermal conductivity could be obtained [4]. Here α is the thermal diffusivity, ρ is the density and c is the specific heat,

The specific heats at three typical temperatures, 300 K, 400 K and 600 K, were obtained from Mark's Handbook [12]. Xue's paper established a linear relation on specific heat of polyamide and temperature [5], so a relation was built:

$$C_p = (T-300)*\frac{(2.4709-1.6952)}{(100)} + 1.6952 \qquad [313\ K \le T \le 400\ K] \qquad (5)$$

$$C_p = (T-400)*\frac{(3.2786-2.4709)}{(200)} + 2.4709 \qquad [401\ K \le T \le 443\ K] \qquad (6)$$

To convert the standard C_p mass units (KJ/kg K) into volumetric units (MJ/m^3 K) that the TPS500 used for the thermal diffusivity calculation, calculated values of the specific heat were multiplied by the sample relative density.

The powder density was obtained from dividing the powder mass by the measured interior volume of the sample holder, which was 21,097 mm^3. Powder mass was obtained by measuring the difference from an empty beaker and the beaker with a sample after the experiment.

At each temperature, eight individual measurements were made, each of which lasted 80 seconds. Fifteen minutes separated each measurement, allowing the sample to reach a steady state. It took 2~3 hours to reach an equilibrium state at each temperature. The heating power was 60 mW with a electrical frequency of 60 Hz. The sensor material was Kapton, with a radius of 6.403 mm. The available probing depth was 12.00 mm.

The 80-second experiment time included a 40 s drift time and 40 s testing time. The measured sensor temperature before heating showed small variations, which indicated the equilibrium state. The transient graph shows the temperature increases 1-3K. The first 50 points are ignored in that the temperature increases too quickly in a short time, while 51-200 points are selected, which perform a smoothly increasing straight line.

In terms of analyzing the effect of previously heated powder, the experiments were conducted in the same manner from 40°C to 170°C after fresh powder was heated to 170°C and cooled down to room temperature.

To assess the effect of powder cake morphology in thermal conductivity measurement, fresh polyamide 12 powder was heated to 170°C and cooled down to 40°C at which point it became caked. Powder cake was crushed back into powder, packed into the sample holder, and the experiment was repeated.

To analyze the temperature effect of powder caking on the thermal properties, a repeated experiment containing five runs was first performed at 40°C, 90°C and 140°C; second performed at 40°C, 90°C, 140°C, and 150°C; third performed at 40°C, 90°C, 140°C, 150°C, and 160°C; fourth performed at 40°C, 90°C, 140°C, 150°C, 160°C and 170°C; the last run repeated the forth run again.

2. Bulk sample density measurement

A Quantachrome INSTRUMENTS® ULTRAPYC 1200e helium pycnometer were used to measure the density of a fully dense polyamide 12 bulk cylinder that was produced by laser sintering. Helium was chosen as a probe gas in that it features a very small atomic size and can permeate the narrow pores in a solid, permitting the determination of the real volume occupied by the sample [5]. An accurate polyamide 12 cylinder volume was obtained from the well known ideal gas law:

$$PV = NRT \tag{7}$$

The mass was measured by a Denver INSTRUMENT® weightometer APX-200. The density of the polyamide 12 solid cylinder was calculated from $\rho = m/V$.

Results and Discussion

1. Effect of powder behavior at different density

The effect of powder packing density for fresh polyamide 12 powder is shown in Figure 2. Also shown is Xue's data for unspecified polyamide powder [1].

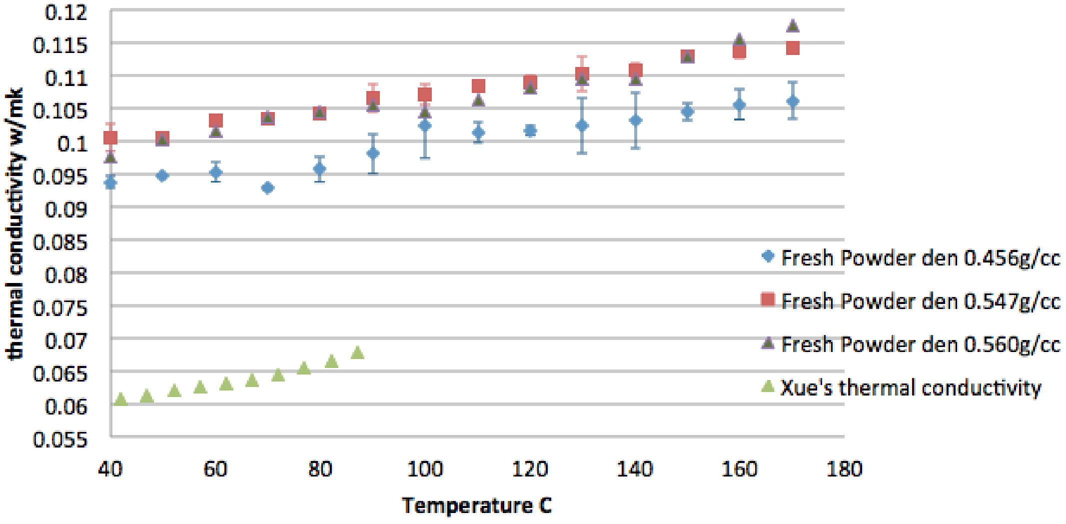

Figure 2: Temperature dependent thermal conductivity of fresh polyamide 12, initially packed at three densities: 0.456g/cc, 0.547g/cc, and 0.560g/cc. Each point on the graph is the mean value of five individual measurements. Figure 2 also includes a comparison with Xue's data [1].

It is observed that at the same temperature, the thermal conductivity of fresh polyamide 12 increased with the increasing density. Three linearized equations were obtained by fitting the data from the graph:

$$k = (T\text{-}273)/10{,}000 + 0.0888 \qquad [\rho = 0.456\ \text{g/cc}] \tag{8}$$

$$k = \backslash(T\text{-}273)/10{,}000 + 0.0938 \qquad [\rho = 0.547\ \text{g/cc}] \tag{9}$$

$$k = (T\text{-}273)/10{,}000 + 0.0962 \qquad [\rho = 0.560\ \text{g/cc}] \tag{10}$$

where k is in units of W/mK and T is in a units of degree K.

The slopes of three equations are the same, which indicates that the fresh powder temperature dependent property is constant with density change. However, the starting point (thermal conductivity at 40°°C) increased with increasing density, which may be a result of the geometry and the sample packing condition: larger density means more particles in a constant volume.

Figure 2 also includes a comparison of thermal conductivity results from the TPS 500 to Xue's experimental data [1]. It reveals that the thermal conductivity results were larger than the results in Xue's work. However, Xue did not mention the sample density and chemical makeup, and the temperature range was narrow.

Figures 3 and 4 show a comparison with Deissler and Boegli's maximum and minimum thermal conductivity model [2], Equations 3 and 4, respectively, with experimental measurements of the thermal conductivity of fresh polyamide 12 powder. Shown are the low and high packing density levels, 0.456 g/cc (Fig. 3) and 0.560 g/cc (Fig. 4). The results of the intermediate density, 0.547 g/cc, were similar to the values shown in Fig. 4.

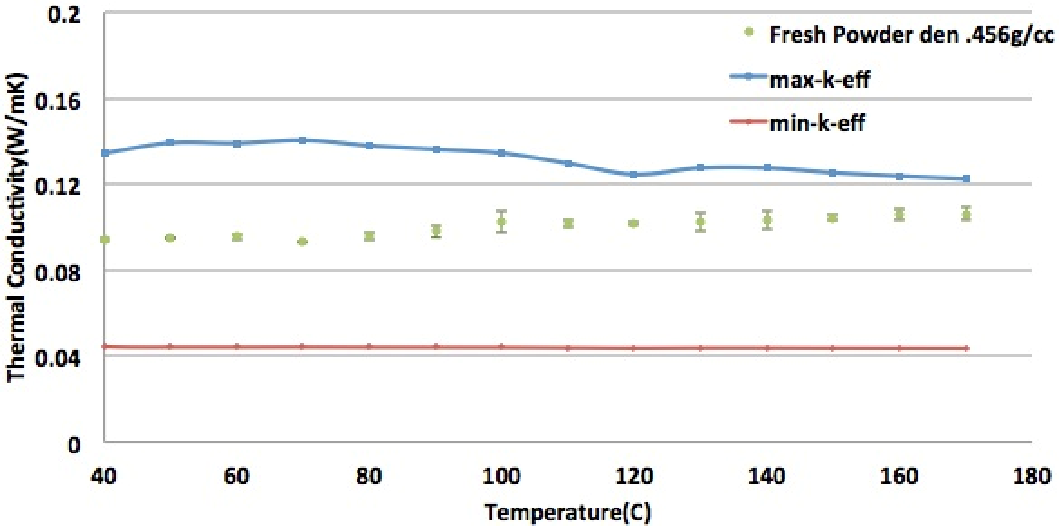

Figure 3: Comparison of thermal conductivity experiment results of polyamide 12 packed at 0.456 g/cc and Deissler and Boegli's theoretical model [2] that estimates the maximum and minimum effective thermal conductivity.

It is clearly seen that the experiment results fit well between the upper and lower limits. The thermal conductivity of nitrogen was obtained from E.W. Lemmon and R.T. Jacobsen's work [6].

Figure 5 indicates that the bulk laser sintered polyamide 12 cylinder had much higher thermal conductivity than loose powder. Thermal conductivity is dependent on the nature of inter-particle bonding, in that heat is conducted more easily through a polymer powder mass that is strongly bonded [7]. The solid sample had a more packed interior structure than the loose powder, so the thermal conductivity is significantly higher than that of the loose powder. Similarly, the thermal conductivity is higher for larger density samples.

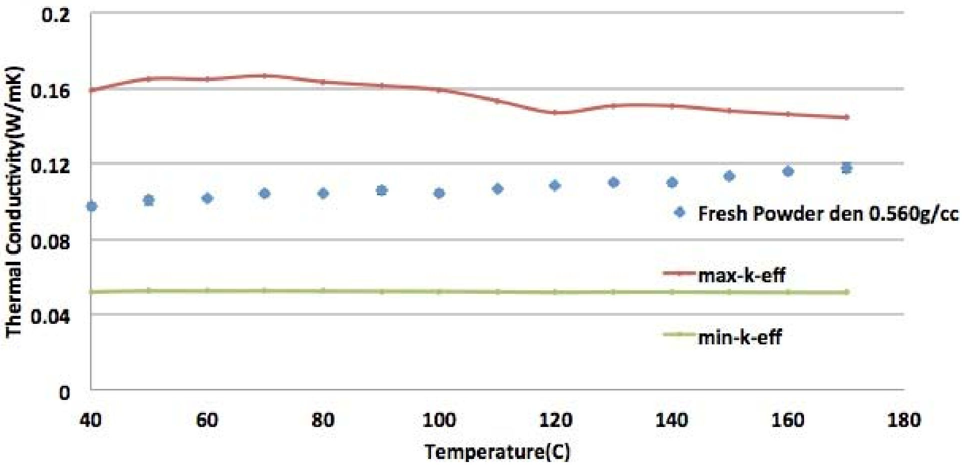

Figure 4: Comparison of thermal conductivity experiment results of polyamide 12 packed at 0.560 g/cc and Deissler and Boegli's theoretical model [2] that estimates the maximum and minimum effective thermal conductivity. The comparison of polyamide 12 packed at 0.547 g/cc with the theoretical model is similar with Figure 4.

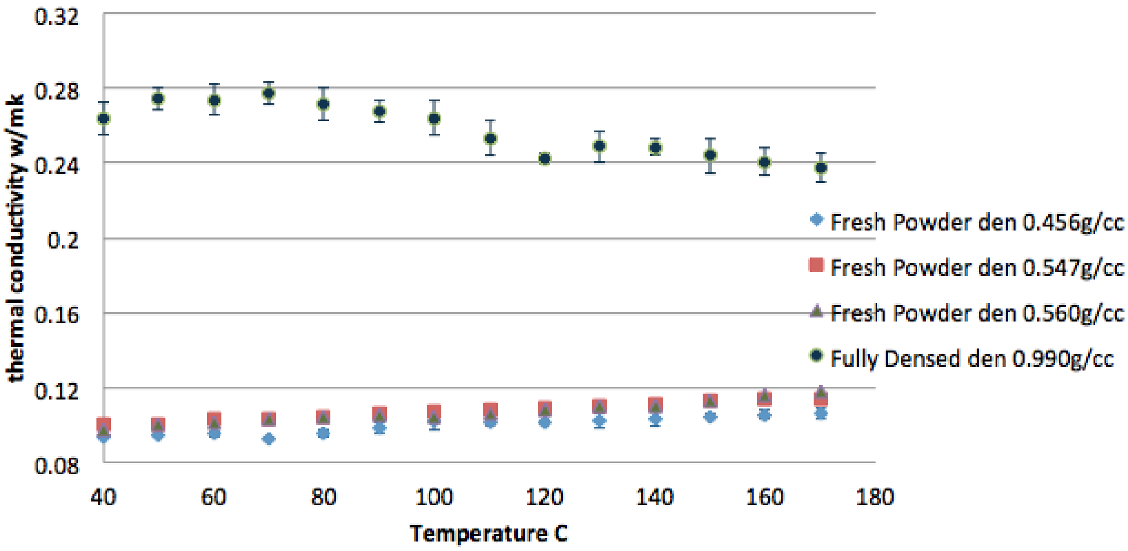

Figure 5: Temperature dependent thermal conductivity of loose polyamide 12 powder at three densities as compared to bulk laser sintered polyamide 12 .

However, the bulk polyamide showed a different trend compared to the loose powder. It reached a peak between 60°°C and 80°°C and then decreased constantly with increasing temperature. It is suggested thatthe polyamide molecular bonds were slightly weakened by increasing temperature, which reduced the effectiveness of the lattice to transmit phonons, the primary mechanism for thermal transport in polyamide. The thermal conductivity would thereby be lowered.

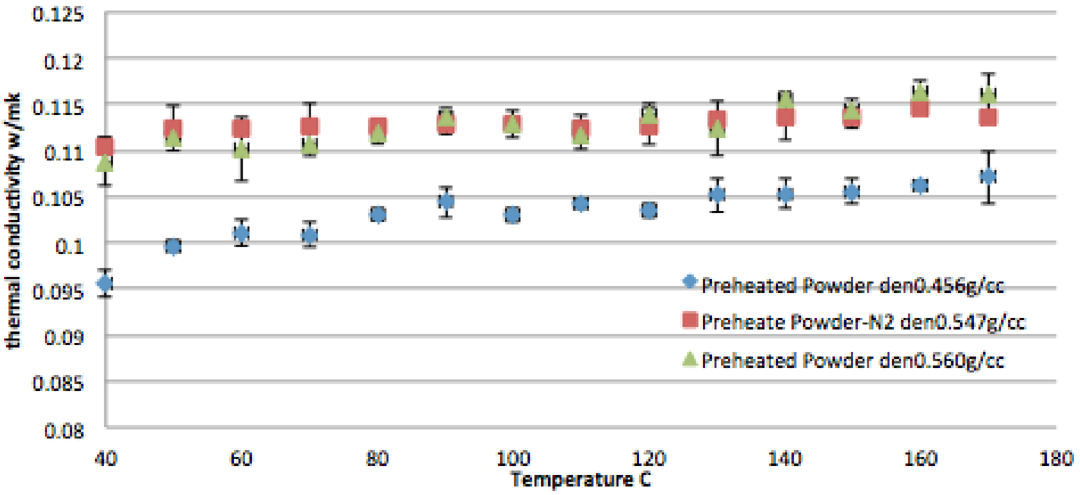

Figure 6 : Temperature dependent thermal conductivity of polyamide 12 powder that was packed at three densities: 0.456g/cc, 0.547g/cc, and 0.560g/cc and heated to 170°C cooled and then tested. Each point on the graph is the mean value of five individual measurements.

Regarding to Figure 6, thermal conductivity of previously heated powder (mimicking laser sintered “powder cake”) shows the same trend as the fresh powder: the curve for 0.547 g/ cc preheated polyamide 12 was close to that of 0.560 g/cc. Both curves showed constant higher values than the 0.456 g/cc specimen, but all maintained the same increasing trend. Mechanical bonds between individual contacting particles were strengthened during the initial heating process., This results in increased heat conduction through the polyamide powder mass on reheating.

2. Effect of preheated powder

Figures 7-9 compare the thermal conductivity of fresh powder to powder previously heated to 170°C as functions of the three powder packing densities.

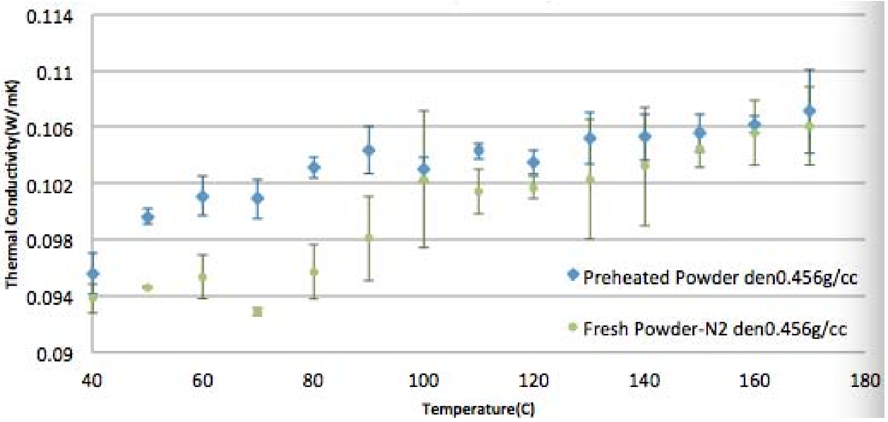

Figure 7 : Thermal conductivity comparison between fresh polyamide 12 powder and polyamide 12 powder that previously heated to 170°C. The initial packing density was 0.456 g/cc.

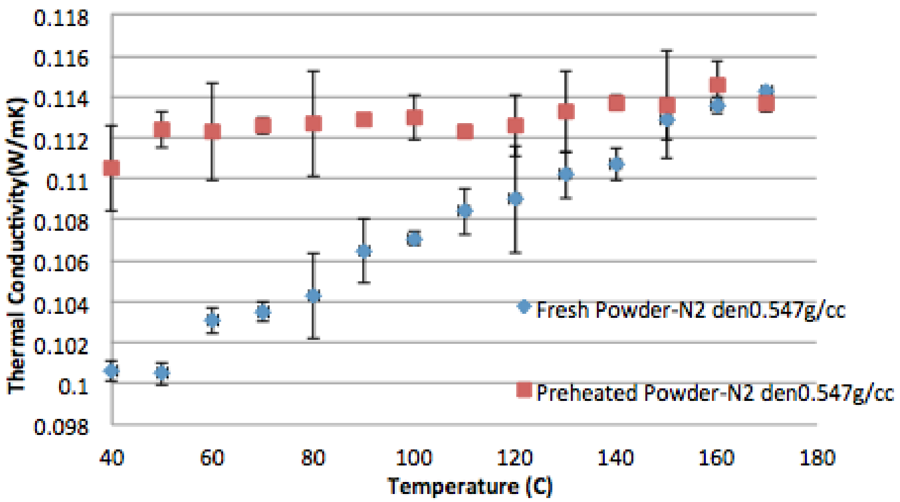

Figure 8: Thermal conductivity comparison between fresh polyamide 12 powder and polyamide 12 powder that previously heated to 170°C. The initial packing density was 0.547g/cc. The comparison at a density of 0.560 g/cc is similar with that at 0.547g/cc.

Figures 7 and 8 illustrate that at same temperature, for different densities 0.456 g/cc and 0.547 g/cc, preheated powder shows higher thermal conductivity than fresh powder, especially from 40°°C to 150°°C. This could be explained as due to interparticle bonding as the polyamide 12 powder cake was formed after reaching 170°°C. Adjacent powder particles adhere to each other, so the preheated powder had a higher thermal conductivity compared to fresh powder. The thermal conductivities for both are similar above 160°°C.°°This may be explained that at high temperature close to the melting point, both forms of polyamide 12 are closely bonded.

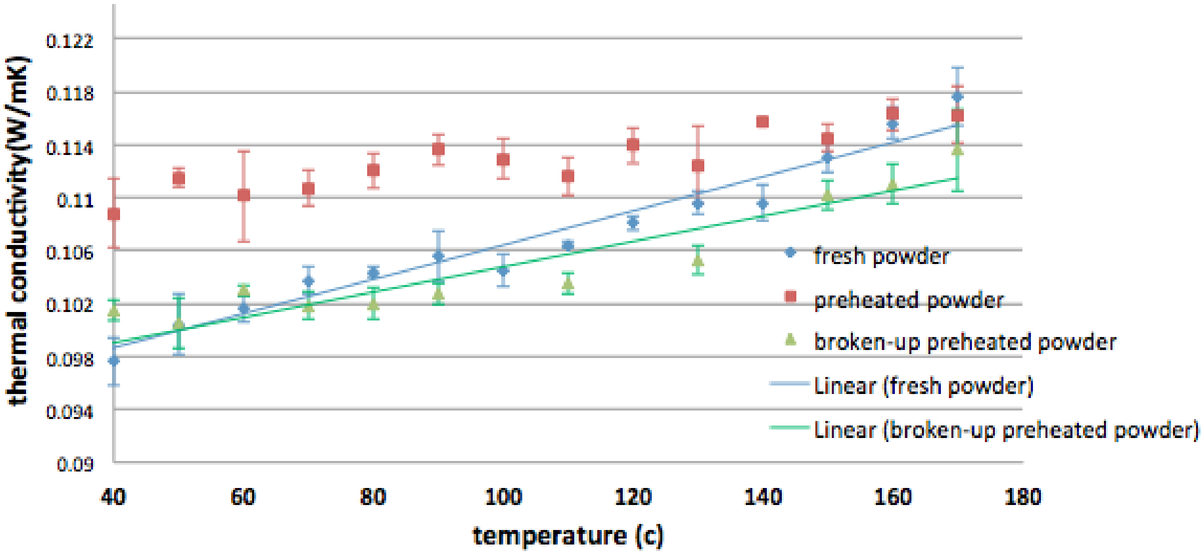

Figure 9: Thermal conductivity comparison between fresh polyamide 12 powder and polyamide 12 powder that previously heated to 170°C. The initial packing density was 0.566g/cc. Also shown is the change in thermal conductivity that occurs when the previously heated ("part cake") powder was mechanically crushed back into loose powder.

Figure 9 illustrates the effect of preheat treatment on thermal conductivity of polyamide 12 at a density of 0.566 g/cc. The sample was removed from the powder holder after heating to 170°°C twice, crushed back to loose powder, packed in the sample holder and retested.

The broken-up preheated powder line is similar with the fresh powder line, which shows a significantly different trend compared to the preheated powder line. From this, it is concluded that the increase in thermal conductivity is solely due to mechanical bonding of the particulate.

Two linearized relations were produced by regressing the data in Fig. 9 for the fresh powder and “part cake”:

$$k = (T-273)/7{,}800 + 0.0935 \qquad \text{[fresh powder]} \qquad (15)$$

$$k = (T-273)/10{,}000 + 0.0952 \qquad \text{[”part cake”]} \qquad (16)$$

where k is the thermal conductivity in W/mK and T is absolute temperature (K). The slight decrease in thermal conductivity of the crushed “part cake” is attributed to a lower relative density of the powder mass due to incomplete break-up of the bonded particulate.

3. Effect of temperature on powder caking

The effect of temperature on powder caking was analyzed by measuring the thermal conductivity from 140°°C to incrementally higher temperatures and assessing the point at which the thermal conductivity increased upon cooling to room temperature. °°°°°°°°°°°°°°°°°°

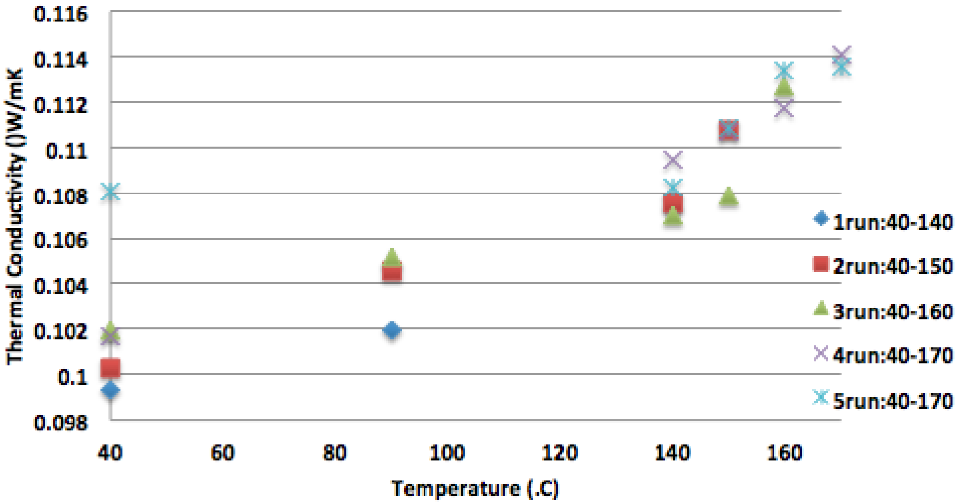

Figure 10: Polyamide 12 powder heated from 40°C to increasingly higher maximum temperatures before cooling. The powder initial relative density was 0.566 g/cc. Based on a deviation from linearity on cooling, it is concluded that the powder begins to cake at ~170°C.

Figure 10 indicates that the polyamide 12 powder caked at a temperature between 160°C and 170°C. In the first four runs, thermal conductivity was linear with increasing temperature. However the fifth run presented 6 % higher thermal conductivity at 40°C, which is associated with the formation of powder cake.

Summary and Conclusion

Thermal conductivity of polyamide 12 was analyzed in this paper. There are several factors that attributed to the thermal conductivity change according to this research. First, thermal conductivity increased with increasing temperature in the loose powder form; however, it increased and then decreased with increasing temperature in the bulk form. Second, the thermal conductivity was proportional with the loose powder tapped density. The closer packed the sample is, the more particulate surfaces contacted other particles, which resulted in more hear transfer and a larger thermal conductivity. Third, previously heated to 170°C polyamide powder shows constantly higher thermal conductivity than fresh powder, especially from temperatures ranging between 40°C to 150°C. Moreover, the crushed, preheated powder (“part cake”) performed similarly to fresh powder. The experiment shows the powder caking temperature was approximately 170°C.

Acknowledgments

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