Thermal Properties of Powders

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Abstract

This paper presents measurements of the specific heats of various powders, including nylon, ABS, PVC, and two kinds of wax. An unsteady-state conduction technique is also presented for measuring the thermal conductivities of these powders at temperatures below those where sintering occurs. Both specific heats and thermal conductivities are found to be functions of temperature.

Introduction

The specific heats and thermal conductivities of powder beds are important parameters for the description of unsteady state heat transfer by conduction in the powder. While these parameters do not drastically change with polymer type, differences do occur within this class which could relate to observed differences in sintering behavior. In this paper we explore methods for obtaining these parameters for powder beds at temperatures below those needed for sintering. Differential Scanning Calorimetry is used to obtain the specific heats, and an unsteady heat transfer technique is developed for measuring bed thermal conductivity.

The authors have investigated the specific heats of various powders and found them to be quite the same as those of the corresponding solids. The specific heats show increase with the increase of temperature. The thermal conductivities of powders are measured at different temperatures by an unsteady state method which uses small temperature differences. Owing to the gas contained in the powders, the thermal conductivities of powders are found to be smaller than those of the solids, and show an increase when the testing temperature is increased.

Experimental Methods

The Materials of Study

All of the materials used in this study are somewhat proprietary. Consequently, a complete description of their properties is not available. Most of the powders which we used (e.g. the PVC powders and the wax materials) were supplied by BFGoodrich Company. The nylon powder which we used is a commercial powder coating material. The ABS used in this study is the original high melt flow (M. I. = 20) material used to make parts in our SLS machine.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) has been used to measure the specific heats at various temperatures between 0°C and 100°C for the following powders: nylon, ABS (acrylonitrile-butadiene-styrene), four kinds of PVC, and two kinds of wax. Each time a sapphire sample was used as a standard after the baseline had been run. The tested standard and samples were held at two limiting temperatures (between these two limits, the samples were tested for the specific heats) for several minutes during every run. Each time, a line is drawn at the bases of the held temperature readings. The heights of the curves above this line at various temperatures were proportioned to the specific heats of the sapphire and the samples at the temperatures. The readings of the curves obtained were read directly from the screen at the different temperatures in the "calculation" mode of the DSC machine, so the readings might be more accurate than by just reading from the graphs. The specific heats were found to be function of temperature for the polymers studied.

Unsteady State Conduction Measurements

An unsteady state method for measuring the thermal conductivities of powders has been developed to permit the assumption of constant properties to be made.[1] We used a cylindrically symmetric tube, open at one end. The tube was a thin-walled aluminium tube with an inner diameter of 1.9 cm and 15 cm in length. It was packed with the sample powder. A thermocouple was placed at the center of the tube from the opening above. This filled tube was brought to a constant temperature in a thermostat. Subsequently, the tube was placed in a bath which was held constantly at a higher temperature, and the temperature development at the middle of the measuring tube was recorded by a computer. This process of measurement can be reversed; that is,the tube can be cooled instead of being heated. Typically the temperature changes are about 10°C. These small changes permit the assumption of constant physical properties to be employed in the analysis. The temperature changes may be mathematically expressed through the solution of the heat conduction equation for a cylindrically symmetric boundary. The solution, in detail, for this case may be found elsewhere.[2]

If we limit the discussion of temperature profile to that at the tube axis, then the solution simplifies to the infinite series of exponential functions:

$$U(r = 0\,;t) = 1.6\, e^{-5.8at/R^2} - 1.06\, e^{-30.5at/R^2} + 0.84\, e\text{-}75^{-75at/R^2} - 0.74\, e^{-140at/R^2} + .. (1)$$

In the above equation:

r	Tube radius coordinate
R	Inner radius of tube
t	Time
a	Thermal diffusivity
U	$[T(t) - T_{bath}] / (T_0 - T_{bath})$
$T(t)$	Momentary axial temperature
T_o	Initial powder temperature
T_{bath}	Bath temperature

If the time is long enough ($t > 0.15R^2/a$), the temperature T(t) of the measuring tube axis approaches the bath temperature T_{bath} asymptotically according to the simple exponential function:

$$T(t) = Tbath - (Tbath - T0)\ 1.6\ e^{-5.8\alpha t/R^2} \qquad (2)$$

To determine the thermal diffusivity, we arrange the equation as follows:

$$\alpha = \frac{R^2}{5.8\,t} \ln[1.6 \frac{T_{bath} - T_0}{T_{bath} - T(t)}] \qquad (3)$$

If we name another function y as

$$y = \frac{R^2}{5.8} \ln[1.6 \frac{T_{bath} - T_0}{T_{bath} - T(t)}] \qquad (4)$$

and get the plot of y versus t for the data, assuming the thermal conductivity of the powder to be constant in a short temperature interval, we get the slope of the line on the y-t graph as the thermal diffusivity of the powder in this temperature interval.

A sample diagram of a run of heating up a tube of nylon powder is shown in Figure 1. The temperature data appeared to be uncertain to about ± 0.2 °C.

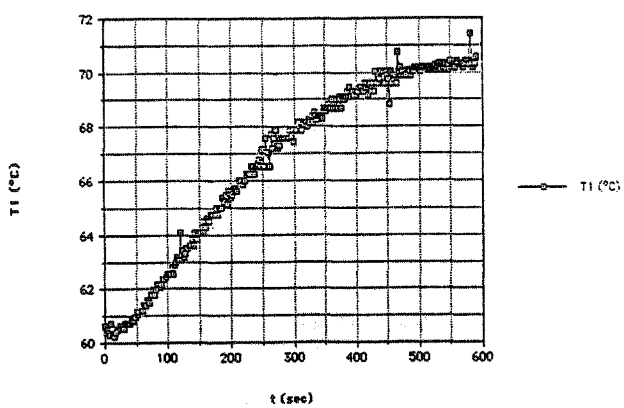

Figure 1. The heating curve of nylon powder (60-70°C)

A sample y-t graph is shown in Figure 2. This figure clearly shows the construction mentioned in equations (3) and (4). Good straight lines of y vs. t result, from which the thermal diffusivity of the powder can be obtained.

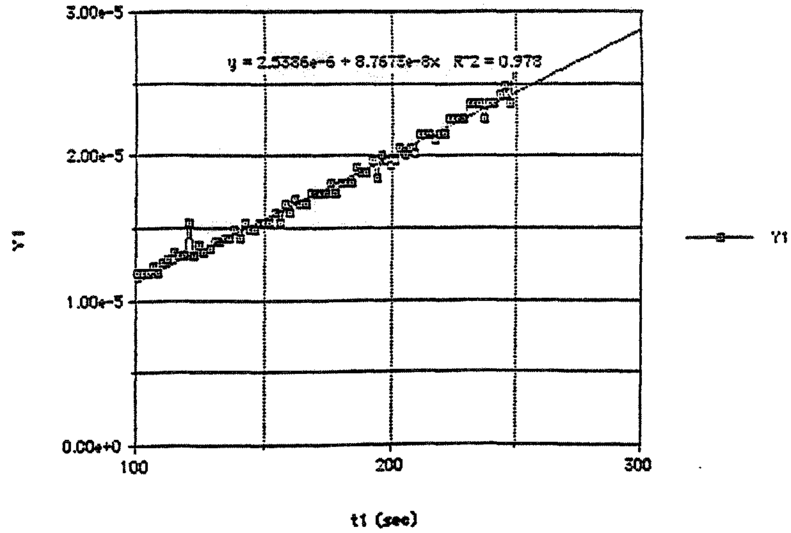

Figure 2. y-t graph of heating nylon powder (60-70°C)

The thermal conductivity of the powder is obtained from the following equation:

$$k = \alpha \rho C_p$$

In the above equation:

k	Thermal conductivity
a	Thermal diffusivity
r	Bulk density of powder
Cp	Specific heat of powder

Results and Discussion

Specific Heats of Powder Beds

The specific heats of all the powders found by this method are quite the same as those of the corresponding solids. This is because of the mass of gas relative to that of the solid phase. The specific heats of all the powders investigated increase as the testing temperature is raised, as shown in Figures 3-6, below

Figure 3 shows a typical specific heat versus temperature graph for nylon powder. As shown, Cp increases by approximately 40% as temperature increases 100°C. All specific heats do not increase in a simple linear function with increasing temperature. For example, the ABS powder, Figure 4, shows some downward concavity to its Cp vs. T behavior, and PVC powders, Figure 5, show even more complex behavior. The general trend for these materials is the same, however; the specific heat generally increases with increasing temperature.

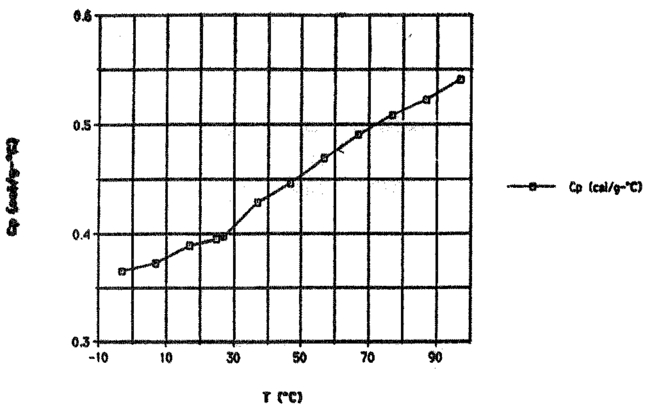

Figure 3. Cp (cal/g-°C) vs. temperature graph of nylon powder

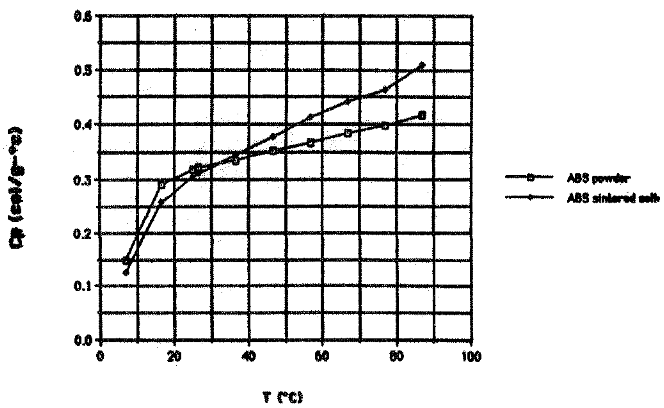

Figure 4. Cp (cal/g-°C) vs. temperature graph of ABS powder and the sintered solid obtained from ABS powder

Figure 4 also compares the specific heats of sintered (solid) and powdered materials. As expected from the low mass of air in the powder relative to that of the solid, the specific heat of the powder is the same as that of the sintered solid, to within 10% relative error.

Little is known about the difference in formulations of the PVC materials shown in Figure 5. Apparently these differences do not drastically affect the specific heat. All materials appear to have the same specific heat to within the error of the experiment, ± 10%.

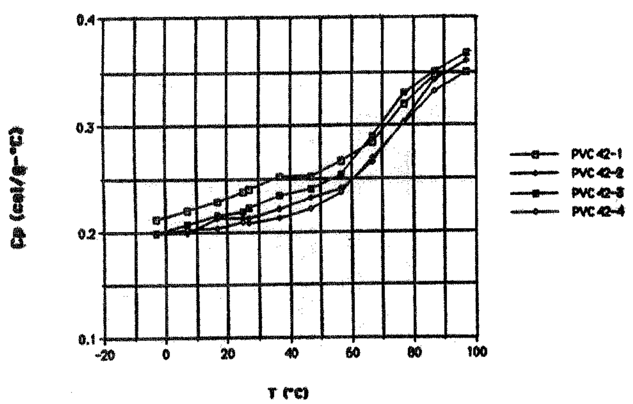

Figure 5. Cp (cal/g-°C) vs temperature graph of four different kinds of PVC Powder

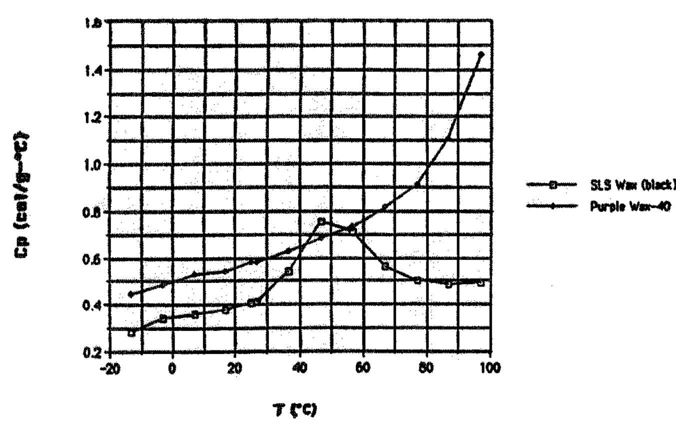

Figure 6. Cp (cal/g-°C) vs. temperature graph of Purple Wax-40 powder and SLS Wax (black) powders

Specific heats of wax powders are presented in Figure 6. The purple wax powder shows a smooth concave upward increase in Cp with increasing temperature. This wax was prepared by our laboratories by adding gentian violet dye to a standard investment wax. The SLS black powder is probably a filled wax. This material shows the peak in Cp characteristic of a melting transition at about 50°C.

Thermal Conductivities of Powder Beds

Because Cp is generally a function of temperature, for the polymer powders examined,the unsteady state method, described above, which assumes constant physical properties, must be applied only over narrow ranges of temperature change. Increments of 10C° have been used by the authors when measuring thermal conductivities by the unsteady state method.

Typical results are shown in Figure 7 and 8 below. The thermal conductivity is found to generally increase with increasing temperature, however the general shapes of the k versus t curves can be quite different for different materials, as reflected in the numerical parameters obtained from power series curve fits of the data:

Nylon

$$k = -2.2139 + 0.020569T - 0.000062289T^2 + 0.000000063221T^3 \quad \text{(W/m-K)} \qquad (5)$$

where T is the absolute temperature K, in the range of 280-360 K.

The values of thermal conductivity of nylon powder at different temperatures are shown in Figure 7 below.

ABS

$$k = 0.18728 - 0.000863T + 0.0000014755T^2 \quad \text{(W/m-K)} \qquad (6)$$

where T is the absolute temperature K, in the range of 280-360 K.

The values of thermal conductivity of ABS powder at different temperatures are shown in Figure 8 below.

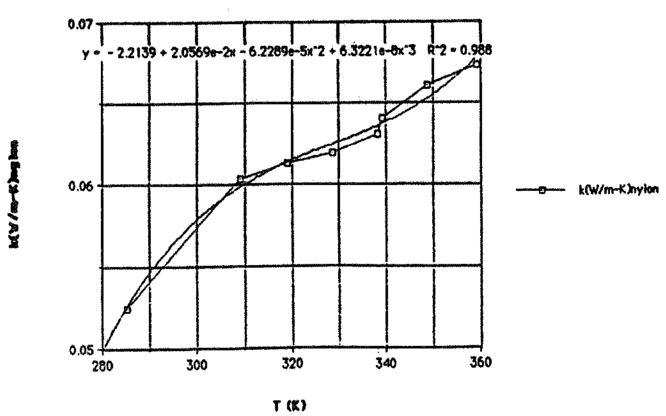

Figure 7. Thermal conductivities of nylon powder at different temperatures

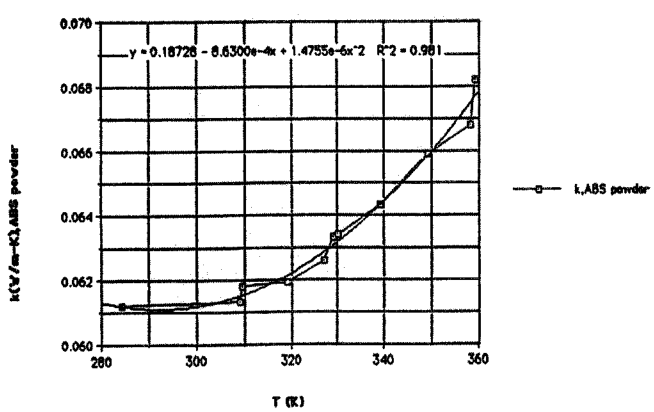

Figure 8. The thermal conductivities of ABS powder at different temperatures

Conclusion

For specific heats, all powders show an increase as the temperature is raised. The specific heats of powders are quite the same as those of their corresponding solids. The thermal conductivities of powders are smaller than those of their corresponding solids.The thermal conductivities of polymer powders show an increase as the temperature is raised.

References

1. Dieter Naumann and Klaus-Jürgen Seydel, "Messung der Wärmeleitfähigkeit von Pulvern," Plaste und Kautschuk, vol. 30, no.4 (1983).

2. B. Baule, Die Mathematik des Naturforschers und Ingenieurs, vol. VI: Partielle Differentialgleichungen, Leipzig, Hirzel-Verlag.