Using Gas Pycnometry to Determine Polymer Crystallinity

Relevant for: polymers, porosity, crystallinity, density, pycnometry

The crystallinity of polymers plays a key role in their properties. Gas pycnometry can be used to assess the skeletal density of polymer materials, which can then be related to the crystallinity. Extremely accurate volume measurements, like those performed with the Ultrapyc 5000, are required when determining relative crystallinity.

1 Introduction

Nylon is a generic designation for a family of synthetic polymers that can be melt-processed into fibers, films, or shapes [1, 2]. Quality control laboratories in nylon manufacturing require that material characterization be performed as quickly and accurately as possible. For many polymer materials, properties such as skeletal density and percent crystallinity are crucial for manufacturers to ensure their materials are consistent across batches.

Crystallinity affects the volume of a material and the degree of crystallinity can be detected using a technique such as gas pycnometry. The mass and measured volume of the sample are used to calculate the skeletal density. This correlates with the crystallinity of a material, where the higher the skeletal density, the more crystalline the material. If skeletal densities of the completely amorphous and completely crystalline formations are known, it is also possible to compute the percent of crystallinity of a given sample.

Often, the skeletal density differences between materials of varying crystallinity can be minute. In order to confidently detect any small changes or differences in crystallinity between samples, the Ultrapyc 5000, with built-in Peltier temperature control was used. Temperature control is crucial when only limited differences in density are expected. To illustrate the use of the Ultrapyc 5000 for this application, a series of commercially available nylon materials (grade 6.6 and 6.10) with differing crystallinity were measured.

2 Percent Crystallinity

The Ultrapyc 5000 was used to measure the skeletal density of commercially available nylon. Deviations from the theoretical density of crystalline nylon 6.6 and 6.10 (1.24 g/cm^3 and 1.19 g/cm^3, respectively) can indicate different impurities are present in the sample. Sample measurement parameters are given in Table 1 and the resulting skeletal densities are shown in Table 2. Excellent repeatability was observed. Crystallinity was calculated using the following equation:

$$P_c = \frac{\frac{1}{D} - \frac{1}{D_a}}{\frac{1}{D_C} - \frac{1}{D_a}} \ x \ 100\%$$

where D is the measured density of the material, D_a is the amorphous density (1.07 g/cm^3 and 1.04 g/cm^3 for nylon 6.6 and 6.10, respectively), and D_c is the crystalline density.

Note that as shown in Table 1, nitrogen gas was used for the polymer density measurement. For most samples, helium is recommended / preferred. However, nitrogen is the gas of choice for polymer samples because helium can diffuse into the solid structure of polymers leading to erroneous results.

Table 1: Ultrapyc 5000 measurement parameters	
Parameter	Setting
Cell size	Medium
Gas type	Nitrogen
Target pressure	18 psig
Flow direction mode	Sample first
Equilibration	Pressure
Preparation mode	Flow, 1 minute
Maximum runs	15
Runs to average	3

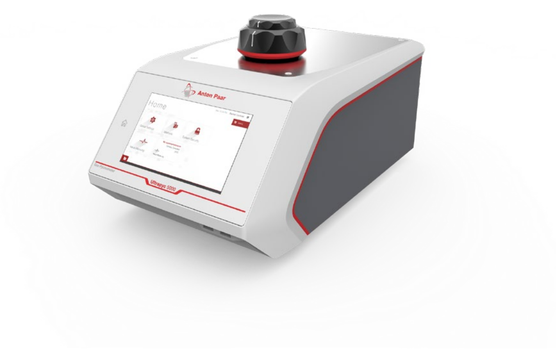
3 Discussion

Table 2: Nylon polymer density measurements					
Sample	Density (g/cm^3)				Repeatability (%)
	Run 1	Run 2	Run 3	Average	
1	1.1195	1.1191	1.1188	1.1191	0.03
2	1.1115	1.1113	1.1112	1.1113	0.01
3	1.0564	1.0558	1.0556	1.0559	0.03

The data in Table 2 shows that density can be measured with excellent repeatability, much less than 1% for all samples. It is known that the increased crystallinity correlates with an increase in skeletal density, so Sample 1 is expected to be the most crystalline of these three samples of nylon. Indeed, this was found to be true. Although both samples 1 and 2 were nylon 6.6, sample 1 was found to be the most crystalline, at 32%. Sample 2 was 27% crystalline, and sample 3, the nylon 6.10, was just 12% crystalline.

4 Conclusions

The Ultrapyc 5000 is ideal for measuring the density of polymers because its highly accurate and repeatable measurements ensure that researchers can measure skeletal densities easily and confidently. The resulting correlation allows researchers to quickly assess skeletal density and screen new materials for crystallinity.



5 References

1. https://en.wikipedia.org/wiki/Nylon
2. Kohan, Melvin (1995). Nylon Plastics Handbook. Munich: Carl Hanser Verlag. ISBN 1569901899.
3. Anton Paar Application Report I17IA001EN-A: Measuring Geometric Density without Mercury

Anton Paar QuantaTec
Tel: +1 561 731-4999
application-sp@anton-paar.com
https://www.anton-paar.com