Short Note No. 125/2013

Melting range determination of semi-crystalline polymers according to EN ISO 3146

Melting Point M-565, Sample Loader M-569 and Melting Point Monitor 1.2: melting behavior (melting temperature or melting range) of semi-crystalline polymers by capillary tube method

According to the official regulation EN ISO 3146, [1] polymers do usually not have a sharp melting point as known for low-molecular substances. Here, we demonstrate the feasibility to employ the M-565 for the melting range determination of semi-crystalline polymers by capillary tube method according to EN ISO 3146 (method A).

Semi-crystalline poly(tetrafluoroethylene) (PTFE) was chosen as test compound for the melting range measurements. For the analyzed PTFE samples we report a narrow melting range between 322.9 ± 0.4 °C and 326.0 ± 0.1 °C.

With the M-565 the melting process can be measured and recorded without modification of the instrument.

1. Introduction

The melting process of crystalline and semi-crystalline polymers is structure-sensitive. In addition, several parameters such as molecular weight, molecular weight distribution, mass respectively volume fraction of the crystalline materials/phase and thermodynamic properties may greatly affect the melting behavior of polymeric materials. [1] Also, the thermal history of the sample could influence the melting of the polymer. [1]

Due to the named parameters, we cannot expect an exact melting point of the polymer material but a melting range.

The melting range of a semi-crystalline polymer starts when the solid powder slightly changes shape and continues through a viscous transition before the crystalline phase disappears due to complete melting of the material (illustrated in Figure 1). [1]

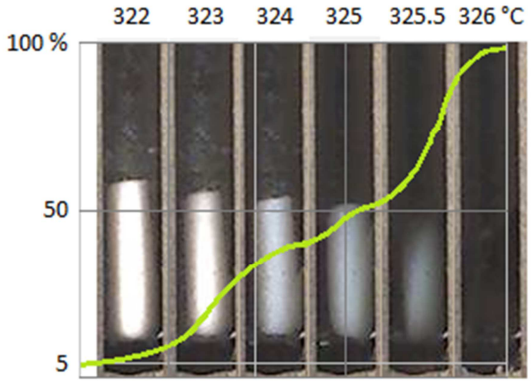

Figure 1. Temperature dependent melting process for PTFE. The green curve illustrates the corresponding melting grade recorded by the Melting Point Monitor 1.2 software. The melting range was observed between 322.9 ± 0.4 °C and 326.0 ± 0.1 °C.

2. Experimental

To approximate the melting temperature of the test compound, the capillary tubes were filled with the PTFE powder (Sigma Aldrich, powder, freely flowing, ≤ 12 µm particle size) using the Sample Loader M-569. PTFE was used as delivered and conditioned for 3 h at 25 °C room temperature with a relative humidity of 55 %.

Filled capillaries were placed in the Melting Point M-565 and a steep temperature gradient of 10 °C/min was applied. The average melting temperature of three samples was 328.1 °C.

To determine the exact melting range, a temperature gradient of only 2.0 °C/min was used for newly prepared samples. The melting process was recorded employing the Melting Point Monitor 1.2 software. By programming a heating ramp, starting 20 °C below to about 10 °C above the expected melting point of 328.1 °C, the process ran without supervision. Recorded data were analyzed after each run.

3. Results

Measuring six PTFE samples, prepared as described, revealed that the melting process started at a temperature of 322.9 ± 0.4 °C. Melting was completed at 326.0 ± 0.1 °C. As expected, with a heating gradient of 2.0 °C/min the melting is completed at a lower temperature compared to a heating gradient of 10 °C/min.

In Table 1 the results of all six samples are summarized; T_{start} is the temperature when the sample starts melting, T_{end} is the temperature when the melting process is completed. The melting process is illustrated in Figure 1. The green curve corresponds to the respective melting grade for each temperature.

Table 1. Melting range data of the six PTFE samples. Temperatures are given in °C.

sample	1	2	3	4	5	6
T_{start}	322.8	322.3	323.1	323.4	323.2	322.7
T_{end}	326.1	325.8	325.9	326.1	325.9	326.2
mean(T_{start})		322.9		**mean(T_{end})**		326.0
std(T_{start})		0.4		**std(T_{end})**		0.1

4. Conclusion

It was successfully demonstrated that the melting range of semi-crystalline polymers can be determined using the M-565 according to EN ISO 3146. Reproduction of the measurements was performed yielding a standard deviation of less than 0.5 °C – well complying with the EN ISO 3146 norm.

Clearly, the found results confirm that the M-565 can be applied to perform melting range measurements, in addition to its conventional use for the determination of melting and boiling points. This makes the M-565 an economic and versatile instrument for the quality control of crystalline and semi-crystalline polymers.

5. References

[1] EN ISO 3146 : 2002-06