A Novel Fiber-optic Sensor for the Determination of Melting Point of Solids

Abstract: A novel, rapid and automatic computer-controlled equipment based on the two-channel fiber optic refractive index sensor for determining the melting point of minute quantities of solid substances is described. The technique uses two optical fiber heads as serve sample holder and temperature sensor, respectively. Principle of the method is that there is a linear relationship between the temperature and the refractive index of the simethicone. The refractive index-time curve was recorded by the sensor, and the abrupt change point of the curve indicated liquidus and solidus transition. Combined of the two curves of the refractive index and the refractive index-time of simethicone, the melting point can be calculated easily. The results obtained with this new method showed good agreement with the results acquired from other methods, with relative standard deviations (RSDs) less than 2%. The automatic method based on fiber optic sensing has the following advantages: clever design, easy operation, good repeatability, accurate result, implying its potential for industrial application.

Keywords: Simethicone; Melting point; Refractive index sensor; Fiber optic

1 Introduction

The melting point is the most fundamental parameter influencing the properties and behaviors of materials, and it also plays a vital role in technical applications. Therefore, it is important to have a simple, accurate and rapid method for the determination of the melting point. In the past decades, many methods have been developed to determine the melting point [1,2], visual observation is used to determine the melting point, but its large errors are inevitable, the use of the optical instrument can make its results more accurate [3,4]. The capillary-tube methods by means of a thermometer immersed in the melt sample is usually used, but it is a tedious work, and the results of different observers, using the same apparatus and the same specimen, may suffer a large errors. Differential thermal analysis (DTA), differential scanning calorimetry...
A Novel Fiber-optic Sensor for the Determination of Melting Point of Solids

(DSC) [5-9], derivative thermogravimetry (DTG) [10], noise thermometry [11,12] were also applied to determine the melting point. Thermal analysis methods are rapid but less accurate [13], because they are subject to systematic errors coming from the small sample volumes [14]. Noise thermometry, which the mean square of the noise voltage developed in a resistor is proportional to T, can be variously applied at both high and low temperatures, and the temperature of this melting point depends on the surrounding atmosphere and its uncertainties are relatively high. A few new optical methods such as laser ultrasonic [15], step-shift method [16], and absolute spectral radiometric [17,18], infrared thermal camera technology [19], high-field electron paramagnetic resonance spectroscopy [20] are proposed for the determination of the melting point. Laser ultrasonic has a advantage of non-contact samples, the step-shift method can be determined by direct observation, the measurements of the absolute spectral radiometric are absolute. However, expensive equipments, complicated procedures and high-qualified staff limit their applicability for serial measurements. As a result, the determination of the exact melting point of a substance is a matter of some little difficulty and trouble.

An urgent need to find a method for determining melting-points of minute quantities of solid substances which is rapid and accurate, capable of giving strictly comparable and reproducible results, and potential for application by a relatively unskilled operator. Unfortunately, at present, no existing method can satisfy all above-mentioned criteria.

The objective of our work is to research a novel method for determining the melting points with lower price, easy to operation, precise and suitable to unskilled operator. What is more, the technique can be applied in industry.

In this paper, we present a novel and automatic method to determine the melting point of substances based on fiber optic refractive index sensing to detect the solid/liquid transition. One of two fiber optic heads holds minute quantities of solid sample, little simethicone is coated to another optic fiber head as a temperature sensor. Theory analyses and the experimental setup of the method are introduced in detail. With our method, melting point values of three kinds of substances were determined and compared with the results from other methods.

2 Principle of operation

In this paper, the temperature was measured using a fiber sensor based on a two-channel Fresnel reflection technique. The measurement principle of the sensor can be found in the literature [21]. Figure 1 is the set-up diagram.

The fiber head A is the reference arm, which is exposed to the air environment, used to eliminate the influence of light source fluctuation. In addition, the undesirable effects or the errors coming from the different losses of fibers and couplers and
environment temperature can be also decreased. There is a calibration process to get the constant K before formal test.

In this paper, the refractive index of air is 1.0003. The effective index $n_f$ of the fiber mode $n_f$ is 1.44961 at $\lambda = 1550$ nm.

3 Materials and Methods

3.1 Apparatus

Figure 1 shows the general arrangement of the apparatus. A schematic diagram of the electric heating chamber is also shown in Figure 1. The home-built heating chamber is made of copper, 10cm in high, 2cm in diameter, round the cylindrical surface is the heating coil inside asbestos. The heating current which pass through the heating coil is under micro-transformer control. The heating chamber is supported on a iron stand, the optic fiber heads pointing upwards are inserted into the chamber and heated in air.

Two Lightcomm OPM2012AA optical power meters connected to the computer via the RS-232C port is used for monitoring and collecting the reflective intensity-time (R-t) data. The apparatus is controlled by a MS Windows computer and home-built software written in C++, the signals are collected data in fixed intervals (can be adjusted), corresponding refractive indices are calculated and saved it as the excel format for further processing.
3.2 Materials

Simethicone and other samples were used for experiments and supplied by tianjin kemiou chemical reagent Ltd (China). All other analytical reagent grade chemicals and distilled water were used.

3.3 Methods

To carry out a determination, a minute quantity of the finely powdered solid, which was spread in the head A as thin as possible, the head B was coated a thin layer of simethicone. Then, the two heads located in the center of the chamber was heated in air atmosphere to the appropriate temperature by means of the heating coil at the rate of approximately 5~10°C per minute, the rise of temperature of the system may be easily regulated by applied voltage. The system was ensured a gradual and regular rise of temperature all the time. When the system approached certain temperature (approximately 5°C below the melting point, acquired by preliminary experiments), the heating rate was reduced to about 1°C per minute.

In order to obtain the relationship between the refractive index and temperature, the refractive indices of simethicone corresponding to a series of known temperatures were determined firstly, and a calibration curve can be obtained. A linear equation relating temperature and refractive index can be established. The temperature corresponding to a given refractive index was then calculated by aid of the equation.

At the melting-point, the molten substance spreaded the head A, the head A-molten substance interface was replaced by the head A –air interface, the light intensity reflected at the head A-molten substance interface occurred a sudden change, causing a abrupt change in the refractive index-time curve, the temperature corresponding to the refractive index of the abrupt point indicated the melting point.

4 Results and Discussion

Before the determination of the melting point, the refractive indices of simethicone versus temperature were measured, the results are shown in Figure 2. The straight line is the linear fit to measured data. It can be seen that the linear fit is in very good agreement with the experimental data.

It will be noticed that the relationship between the refractive index of simethicone and the temperature is a straight line, and for the fitting equation: \( n = 1.34448 - T \times 1.87881 \times 10^{-4} \), where \( n \) is the refractive index and \( T \) is the temperature. By the help of the equation, the apparatus is once set up, the melting-points of the sample may be readily obtained by simply measuring the refractive index of simethicone, the
inflection point of the refractive index-time indicates the temperature at which the sample begins to dissolve.

The measurement of the melting points were carried out for three kinds of samples (with different melting point) and the curve of refractive index vs time of diphenylamine is shown in Figure 3. The curve having two inflexion points and three line segments can be observed. The melting point is found by the first intersection of the two lines. The first segment corresponds to the curve of refractive index vs temperature of simethicone, the second rapid descending branch refers to the melting of solids. Combined with Figure 2, the temperatures can be determined from the refractive index of the first intersection. It can be seen from Figure 3, the observed transition is quite clear.

Figure 2. Plot of change in reflective index \( n \) of simethicone as a function of change in temperature \( T \), fitted with a linear function. The fitted equation and \( R^2 \) of fit are indicated.

Figure 3. Under the experimental conditions, plot of change in reflective index \( n \) of diphenylamine as a function of change in time.
The results obtained for diphenylamine, paraffin, benzil are given in the following Table 1.

Table 1. Melting points $T$ for the investigated substances compared with their literature values

<table>
<thead>
<tr>
<th>Materials</th>
<th>This work</th>
<th>Literature</th>
</tr>
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<tbody>
<tr>
<td>Diphenylamine</td>
<td>53.42°C±1.3%</td>
<td>53.00°C [21]</td>
</tr>
<tr>
<td>Paraffin</td>
<td>52.28°C±1.5%</td>
<td>52.52°C [capillary-tube method]</td>
</tr>
<tr>
<td>Benzil</td>
<td>93.75°C±1.9%</td>
<td>94.40°C [22]</td>
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</table>

*All values are the means of seven determinations ± relative standard deviation

The mean of three determinations, by standard capillary tube method, the heating rate of the bath was 1°C/min at the beginning, when approaching the melting point, the rate reduced to 0.5°C/min until the sample began to melt.

Seven determinations of the melting-point of each substance were made, and the values recorded above represent the mean of these results.

A comparison with literature data suggests a satisfactory overall performance of this fiber-optic sensing technique. The agreement between the values determined by this technique and these measurements, such as DSC, DTG, and capillary-tube method is rather good and demonstrates that the melting point can be easily determined in a wide range of samples for solids.

Conventional melting point analyses should be avoided those methods, which subject to large error, complex, tedious, expensive. Classical methods, such as thermal analysis, are accurate, but prone to system error coming from a little sample volume, spectral methods involves expensive equipment and professional operators, their applications have been limited. In this report, we describe a method that is fast and easy to use, testing requires only a small amount of sample and the melting can be obtained easily. The method is useful for labor and time savings to yield reliable results of the melting points.

In this paper, it was found from Table 1 that the relative standard deviations of the melting point of the three samples were never more than 2%, which shows that good reproducibility can be obtained and the performance of this technique is very stable, the reason is that the reference signal received by reference head A can be used to eliminate the influence of light source fluctuation, the undesirable effects can be also decreased. Thus, in this paper, long term stability can be effectively guaranteed.
5 Conclusion

A new automatic computer-controlled device for convenient and accurate determination of melting points is described. Its reliability evaluated by comparison with other methods.

Some advantages of the fiber optic sensing technique can be identified.

- The great advantage of the method is the automatic determination and the melting point can be obtained easily.
- A thermometer is not required.
- Unskilled observers can obtain results with a small error.
- Air bath instead of liquid bath and stir is cancelled.
- The two optic fiber heads being touched by the sample and the simethicone respectively, and the temperature of the sample is certain to be of exactly the same as the simethicone’s. So the Results are close to the actual melting point.

One apparent limitation of the technique is that the melting range cannot be obtained.

The experimental results illustrate that this approach is capable of providing melting point measurements that are in good agreement with the data from other methods.

This paper shows the high potential of the technique to study liquidus and solidus transition, and it opens a new way to determining the melting points in industrial application.

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References

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