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Test Method

Development of a faster hot-stage for microscopy studies of polymer crystallization

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ABSTRACT

A new design of hot-stage (temperature controlling cell) and methodology were developed for investigating the kinetics of fast phase transitions of polymers at higher supercooling. The contact cooling rate of the hot-stage can be increased up to 1000 °C/s (between 200 °C and 80 °C) by means of flowing liquid cooling, the response rate of the whole device due to immediate temperature measurement and an original automation unit. This design enables one to study isothermal crystallization of polyethylene down to 80 °C, and its relative simplicity makes it suitable for routine measurements. Description of the parameters of the automation unit and the heating/cooling cell are reported.

1. Introduction

In polymeric products, the material is mostly used in a metastable state and the performance properties greatly depend on how the state was reached, i.e. on the mode/rate of crystallization during processing. In order to systematically study the strongly temperature-dependent crystallization process, it is important to cool the sample fast enough to reach the given temperature before crystallization has taken place, and to record the microscopic (morphological) changes and measure the temperature of the sample at intervals considerably shorter than the duration of the crystallization process. Primary obstacles to this are thermal *inertia* due to the mass of the sample and the substrate and insufficient thermal contact between the sample and the temperature sensor.

Many crystallization studies, e.g. as referred to in [1,2], have used commercially available heating and freezing stages. One of the most efficient of them is the Linkam THMS600 [3] with its water cooled silver heating element and platinum temperature resistor sensor, the cooling rate reaching 130 °C/min and response time 0.1 s at 30 °C/min. In [4] an apparatus was developed and tested for obtaining real time experimental data of polymer crystallization under high cooling rates – the sample was quickly shifted from the electric oven zone to the liquid (water) spraying zone, fast thermocouples were inserted in the 50–100 m thick sample itself, yielding a cooling rate of 35 °C/s, and the temperature control mechanism was one-way (no heating after the shift). While with a great number of polymers the cooling rate of commercially available hot-stages is sufficient, some polymers, including the much used polyethylene, require considerably faster instrumentation due to the inherent fast crystallization mechanism. Calculation models from [5,6] make it possible to estimate the necessary minimum cooling rate for crystallization studies at a certain temperature. For example, with polyethylene, to be able to follow most (99%) of the crystallization process at 122 °C, one has to cool the sample at 100 °C/min, but to reach 80 °C (which would still be higher than in real injection moulding or film blowing), the sample has to be cooled at 1000 °C/s.

There are reports of faster techniques to change the temperature of the sample. For calorimetric studies of small

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samples [7–9], in order to increase time resolution and signal to noise ratio, the mass of the measuring system was reduced by using calorimetric chips capable of heating the sample and cooling it down to the surrounding temperature at an impressive rate of 10^6 K/s. Some chip models are applicable for optical studies as well [9]. Authors of the current paper have used the last mentioned type of gauge for combined calorimetric and light scattering studies, but it is hardly applicable with a microscope. Also, with its microscopic semiconducting heater and a semiconducting thermopile on a thin (500 nm) SiN_x membrane composed by integrated-circuit (IC) technology, neither it nor its calibration can be considered as routine. Use of short (picosecond scale) laser pulses to excite a ligand or a near-infrared dye additive in the sample raises the heating rate up to 10^{12} K/s [10,11]. However, when studying crystallization, additives are generally not acceptable. Also, the method would require a laser system of two parallel optical amplifiers pumped by a femtosecond Ti/Sapphire amplifier, and control of vibrational cooling is even more complicated.

This working group has made several attempts to increase the cooling rate, at the same time keeping the design simple and convenient to use for serial measurements. The type of hot-stage described in [12] is based on gas as both the heating and cooling agent, and its cooling rate up to 1000 °C/min allows for isothermal crystallization studies of polyethylene no lower than 110 °C, avoiding crystallization in the cooling phase. The current design of hot-stage aims at going considerably lower. In addition to the cooling rate itself, it is even more important to be able to detect the actual temperature of the sample and thus control the cooling. To improve the cooling rate and measurement of the real temperature, the new design of hot-stage uses the known linear dependence between temperature and electrical resistance of many metals and also transparent metal oxides, thus enabling one to measure changes in temperature by measuring changes in resistance. The advantage is that no extra instruments (such as thermocouples) are needed and the response is faster than with thermocouples (always having a certain time lag). Temperature measurement and electrical heating can be carried out by means of the same transparent resistor.

2. Method and device

In order to follow the growth of crystalline structures in a polymer sample, hot-stage microscopy is used. Bearing in mind the need for fast controlled temperature movements, heat capacity (and thus dimensions) of both the sample and the heater are made relatively small (as was suggested in [9]), compared to the cooler.

The polymer sample (1 in Fig. 1) is heated by a transparent resistor heater (2) – e.g. a 65 nm ITO (indium titanium oxide) layer on a thin glass substrate (by Präzisions Glas & Optik GmbH, Germany). Alternative heaters include 10 nm vacuum deposited Au/Pd or Pt films, but their transparency and surface hardness are less than with ITO. However, a thin Al_2O_3 layer makes the metal layer mechanically more endurable. Electrical resistance of the ITO-layer, which depends on its thickness and configuration, is chosen to suit the temperature range necessary for

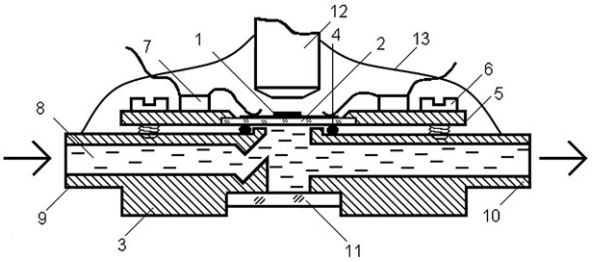

Fig. 1. Temperature controlling cell for optical studies of material morphology (not to scale).

the crystallization studies (e.g. for polyethylene 20 °C–200 °C). Both ends of the resistor film are gilded to ensure a good electrical contact with the soft graphite electrodes (7) connecting it to the external circuit. The electrodes are fastened to the flange (5) but electrically isolated. The heater is tightened against the body (3) by a thermoresistant packing o-ring (4), flange (5) and screws (6). The cooling liquid (water solution of ethylene glycole etc, 8) is externally thermostated at −15 to +10 °C; it enters the tubular cell through inlet nozzle (9) and its flow is directed against the substrate glass as perpendicular as possible to ensure best cooling efficiency. The cooling agent leaves the cell through outlet (10). Coaxial to the ITO-glass, there is a glass window (11) in the bottom of the cooler liquid channel for the light beam to pass through the sample. The objective (12) of the microscope approaches the sample from above. Tight against the objective, there is a rubber hood (13) to be flushed with dry nitrogen gas in order to avoid oxidation of the object, condensation of moisture and disturbing air movements. The cooling liquid is kept flowing at a constant rate throughout the experiment and, for temperature control, only the heating voltage is changed. Voltage on the heating regulator is controlled by an analogue output of a PC-connected data aquisition board DT 9086 by Data Translation™ and a virtual instrument designed in LabVIEW™ (National Instruments™). A special multifunctional temperature measuring and control unit (Fig. 2) was designed for the sake of speed and accuracy.

In order to measure relative changes in resistance, the controller device uses the analogue-multiplication circuit

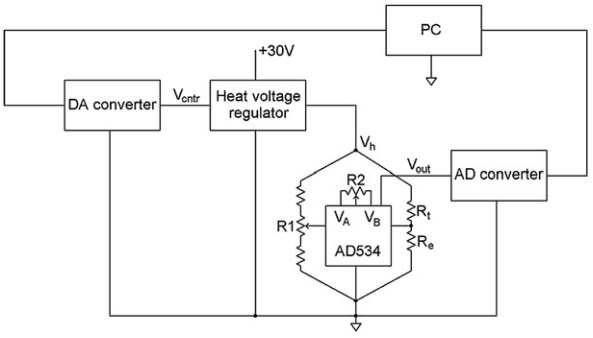

Fig. 2. Simplified schematics of the temperature measurement and control unit.