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Microcalorimetry for characterization of film formation and cure of coatings and adhesives

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Abstract

A new microcalorimeter with eight parallel channels using robust, low cost sensors for characterization of coatings and adhesives is described and first experiments on coatings and adhesives are presented. The calorimetric sensors are based on thin glass plates (20 mm × 20 mm, thickness 150 μm) with heater and thermocouple sputtered on the surfaces (calorimetric active area of about 9 mm^2). The setup allows heating and cooling experiments as well as isothermal measurements in the temperature-modulated mode with up to eight sensors in parallel. The measured quantities are the real (C'_p) and imaginary part (C''_p) of the complex heat capacity ($C^*_p = C'_p - \mathrm{i}C''_p$), the related absolute value of the heat capacity ($|C^*_p|$) and the heat flow ϕ. An industrial computer (NI PXI system) with specific software for calibration and data recording controls the electronic components. Sensors can be embedded in a temperature controlled oven (heating and cooling by Peltier elements) or alternatively in a climatic cabinet with controlled temperature and humidity.

The method has been applied successfully to monitoring of film formation of aqueous polymer dispersions (styrene-acrylate copolymer) and curing of coatings.

Keywords: Microcalorimeter; Temperature-modulated calorimetry; Thermo-physical properties; Coatings; Adhesives; Film formation; Curing; Humidity

1. Introduction

During film formation and cure of coatings and adhesives changes in physical properties and chemistry of the material occur. For material development and characterization, one has to consider the complex interplay between drying, chemical reactions and vitrification. In order to get a deeper insight into the mechanisms of film formation, it is desired to monitor the changes of the physical properties in real time.

Calorimetry, particularly *D*ifferential *S*canning *C*alorimetry (DSC), belongs to the standard techniques for polymer characterization. DSC measurements allow detecting glass and phase transitions, melting and crystallization temperatures, specific heat and heat of reaction. With extensive laboratory automation and use of combinatorial methods for material development, there is an increasing interest in fast and/or parallelized methods for industrial laboratories. Therefore, calorimeters with automatic sample changers have been developed [1] to achieve higher throughput. Alternatively, sensor arrays [2] for parallel measurements have been developed. These arrays often show a thermal coupling of different channels and are not yet optimized from a calorimetric point of view.

Moreover, one of the limitations of calorimeters for characterization of coatings is the difficulty to study films with open surfaces (e.g. drying of coatings) at defined relative humidity and temperature.

In this paper, we describe a recently developed multi-channel microcalorimeter with flat calorimetric sensors enabling such analysis [3]. The sensors are based on standard cover slides for microscopy with heaters and thermocouples sputtered on upper and lower side, respectively. The principle is similar to so-called thin film calorimeters [4–6], but the sensors are more robust and therefore easier to handle in the environment of a test laboratory.

The hard and software arrangement allows isothermal measurements and experiments with well defined cooling or heating rates. For all types of experiments, temperature-modulated

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experiments are possible. The setup allows measuring the real and imaginary part of complex specific heat capacity (from the amplitude and phase of the heat flow) and latent heats due to drying, phase transformation or chemical reactions. The setup has been applied successfully to monitoring of film formation of aqueous dispersions and solvent-based coatings, curing of thermosets, hardening of solvent-based and crystallizing adhesives and IR curing of powder coatings.

2. Basics

The measurement of the heat capacity C of a sample is based on the detection of the temperature increase ΔT after addition of a defined amount of thermal energy (heat) δQ:

$$\delta Q = C \cdot \Delta T. \qquad (1)$$

For the realization of a calorimeter, a heater and a thermometer are needed at the very least. Both have to be coupled sufficiently good to the sample. It has to be noticed, that Eq. (1) is only defined for adiabatic conditions. Since for defined cooling experiments a heat sink is necessary, this assumption is not valid. In good approximation, the energy balance for such a case is given by:

$$\Phi(t) + (C(T) + C_0)\frac{\mathrm{d}T}{\mathrm{d}t} = P_0 - \xi(T(t) - T_{\mathrm{Env}}). \qquad (2)$$

$\Phi(t)$ is the latent heat flow, $C(T)$ the heat capacity of the sample, T the actual temperature of the sample, C_0 the heat capacity of the heated part of the sensor, P_0 the heater power and ξ represents the heat exchange with the environment (temperature: T_{Env}). For time intervals where the heating rate $\mathrm{d}T/\mathrm{d}t = 0$, ξ can be calculated from the actual heater power and the measured temperature difference between sample ($T(t)$) and environment (T_{Env}) [5], if the latent heat flow is zero.

Eq. (2) allows calculating the heat capacity of thin polymer films (where the heat transport in the sample can be neglected) for large heating or cooling rates. For such measurements, separation of the contribution of latent heat and heat capacity is not possible as a matter of principle. Therefore, contributions of latent heat of the sample are usually included in the apparent heat capacity. If the heating or cooling rate $\mathrm{d}T/\mathrm{d}t$ is constant for a given time segment, the heat capacity of the sample can be estimated by:

$$C(T) = \frac{P_0 - \xi(T(t) - T_{\mathrm{Env}})}{\mathrm{d}T/\mathrm{d}t} - C_0. \qquad (3)$$

In addition to non-isothermal temperature scans (heating or cooling ramps), the microcalorimeter can also be used for isothermal experiments. For this case ($\mathrm{d}T/\mathrm{d}t = 0$), the contribution of the heat capacity disappears and the latent heat flow can be calculated by:

$$\Phi(t) = P_0(t) - \xi(T - T_{\mathrm{Env}}). \qquad (4)$$

In order to keep the temperature constant, here the heater power P_0 has to be controlled and becomes a function of time (power compensation mode). In a modified operation mode the heater power is kept constant and small deviations from the set temperature are detected (heat flow mode). This temperature difference has to be small so that the experimental conditions remain almost isothermal. For exothermal processes this leads to an increase of the temperature above the set temperature, whereas the temperature for endothermal processes becomes somewhat smaller. For this case, the latent heat is given by:

$$\Phi(t) = P_0 - \xi(T(t) - T_{\mathrm{Env}}). \qquad (5)$$

The possibility of performing fast cooling and heating cycles allows monitoring of slow processes (e.g. drying, curing and crystallization) by combining time-dependent measurements of latent heat and heat capacity. In this type of experiments (realized, e.g. in the temperature-modulated or AC calorimetry) the latter can be estimated from the ratio of amplitudes of the periodic heating power (input) and the resulting temperature oscillations (output) [7–13]. If a periodic, e.g. sinusoidal heater power $P_{\mathrm{A}} \exp(\mathrm{i}\omega t)$ with the amplitude P_{A} and the angular frequency $\omega = 2\pi f$ (frequency: $f = 1/t_{\mathrm{period}}$, period: t_{period}) is superimposed with a constant heater power P_0, it follows:

$$\Phi(t) + (C(T) + C_0)\frac{\mathrm{d}T}{\mathrm{d}t} = P_0 - \xi(T(t) - T_0) + P_{\mathrm{A}} \exp(\mathrm{i}\omega t). \qquad (6)$$

For the assumptions, that (i) ξ can be approximated by a linear function of temperature in the range of temperature-modulation:

$$\xi(T_0 - T_{\mathrm{Env}} + \Delta T) \approx \xi(T_0 - T_{\mathrm{Env}}) + \left.\frac{\mathrm{d}\xi}{\mathrm{d}T}\right|_{T_0} \Delta T, \qquad (7)$$

(ii) the heat capacity can be assumed to be constant in this temperature range and (iii) the changes of the latent heat flow are considerably slower than the period of the sine, the output signal is a sinusoidal temperature change with the amplitude T_{A}, which has a phase shift φ relative to the input power:

$$T(t) = T_0 + T_{\mathrm{A}} \exp(\mathrm{i}\omega t + \varphi). \qquad (8)$$

Incorporation of Eq. (8) into the equations above and rearrangement yields the heat capacity:

$$C^*(T, \omega) = \frac{P_{\mathrm{A}} \exp(-\mathrm{i}\varphi) - T_{\mathrm{A}}(\mathrm{d}\xi/\mathrm{d}T)|_{T_0}}{\mathrm{i}\omega T_{\mathrm{A}}} - C_0. \qquad (9)$$

In general, the real (C') and imaginary (C'') part of the frequency dependent complex heat capacity $C^*(\omega) = C'(\omega) - \mathrm{i}C''(\omega)$ can be calculated from the ratio of the complex Fourier coefficients of input power P_{A}^* and temperature T_{A}^* according to:

$$P_{\mathrm{A}}^*(\omega_k, t) = \int_t^{t+t_{\mathrm{Period}}} P(t')(\cos \omega_k t' + \mathrm{i} \sin \omega_k t')\,\mathrm{d}t', \qquad (10)$$

$$T_{\mathrm{A}}^*(\omega_k, t) = \int_t^{t+t_{\mathrm{Period}}} T(t')(\cos \omega_k t' + \mathrm{i} \sin \omega_k t')\,\mathrm{d}t', \qquad (11)$$

with $\omega_k = 2\pi k/t_{\mathrm{Period}}$ ($k = 1, 2, \ldots$) by

$$C^*(\omega, t) = \frac{P_{\mathrm{A}}^*(\omega, t) - T_{\mathrm{A}}^*(\mathrm{d}\xi/\mathrm{d}T)|_{T_0}}{\mathrm{i}\omega T_{\mathrm{A}}^*(\omega, t)} - C_0, \qquad (12)$$

which is an extension of Eq. (10).

For isothermal monitoring of drying, film formation or curing the angular frequency $\omega = 2\pi f$ is usually set constant and the