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Schmitt, Philip; Wedrich, Karin; Müller, Lutz; Mehner, Hannes; Hoffmann, Martin

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P Schmitt[1]**, K Wedrich**[1]**, L Müller**[1]**, H Mehner**[1,2] **and M Hoffmann**[1]

¹ Technische Universität Ilmenau, Ilmenau, Germany

² now with X-Fab MEMS Foundry GmbH, Erfurt, Germany

philip.schmitt@tu-ilmenau.de

Abstract. This paper describes a concept for a passive microfluidic time-temperature indicator (TTI) intended for intelligent food packaging. A microfluidic system is presented that makes use of the temperature-dependent flow of suitable food ingredients in a microcapillary. Based on the creeping distance inside the capillary, the time-temperature integral can be determined. A demonstrator of the microsystem has been designed, fabricated and characterised using liquid sugar alcohols as indicator fluids. To enable a first wireless read-out of the passive TTI, the sensor was read out using a commercial RFID equipment, and capacitive measurements have been carried out.

1. Introduction

One of the current global challenges is the waste of perishable goods. Recent European studies show that 20 % of the total EU food supply is being disposed although it is still esculent. This averages out at an annual food waste of about 173 kg per person [1]. The most important reason for discarding food in the private and reselling sectors are exceeding expiration dates that are usually printed on food packages. However, since the shelf-time of perishable goods depends on environmental conditions such as temperature and humidity, the labelled expiration date on packages can be seen as a cautiously estimated reference which does not strictly reflect the actual condition of the enclosed item.

In order to extend shelf-time of food, research on intelligent packaging has strongly increased, recently [e.g. 2]. Intelligent packaging systems focus on the replacement of the printed expiration date by the integration of passive sensors that measure and indicate the current spoilage condition of the enclosed perishable item.

Since quality deterioration of food is strongly impaired by elevated temperatures and the time the food is exposed to them, the integral of a time-dependent temperature profile can be used as an indicator for the condition of a perishable item. Passive time-temperature indicators (TTI) are therefore often used as monitoring devices on food packages. Existing and commercially available TTIs are typically based on chemical reactions, polymerisation or diffusion processes [3, 4]. By changing their colour, these non-electrical tags optically indicate the current state of the product.

However, a pure optical evaluation of the measurement makes it difficult to calculate and predict a new and adapted expiration date. Moreover, such sensors are usually placed at the outside of the package. Furthermore, an automated and electronic read-out of the sensor during handling or transportation within the supply-chain may be difficult by visual inspection, only.

In this paper we propose a new, optimised passive microfluidic TTI-system based on the works presented in [5]. The TTI-system can be connected to an RFID transponder enabling a wireless read-out. The proposed system is based on the progressive filling of a capillary by a dielectric fluid. Since the viscosity of the fluid is temperature-dependent, the filling speed of the capillary strongly depends on the imposed temperature. The covered distance of the fluid in the capillary consequently corresponds to the time-temperature integral. ~~Because choosing an indicator fluid featuring a high~~ dielectric constant, the creeping distance can be ~~...~~ es an electrical evaluation of the sensor. In the fra ~~...~~ of appropriate indicator fluids and their fluidic p ~~...~~ ly chosen from food ingredients: non-toxic and res ~~...~~

2. Method

The working principle of the microfluidic TTI i ~~...~~ is a capillary with rectangular cross-section. Alon ~~...~~ side walls so that a plate-capacitor is formed. A ~~...~~ te positioned at the beginning of the capillary. I ~~...~~ is initially either in a highly viscous or in a solid ~~...~~ al starts to melt, becomes less viscous and starts ~~...~~ re lowers, the viscosity increases again, forcing the ~~...~~ e depends on both the imposed temperature and the exposure time, the final creeping distance of the fluid can be seen as a measure of the time-temperature integral.

To read out the final creeping distance electronically, the capacity between the side-wall electrodes is measured. Since the indicator fluid features a higher dielectric constant than air, the capacity of the plate capacitor increases almost linearly with the creeping distance.
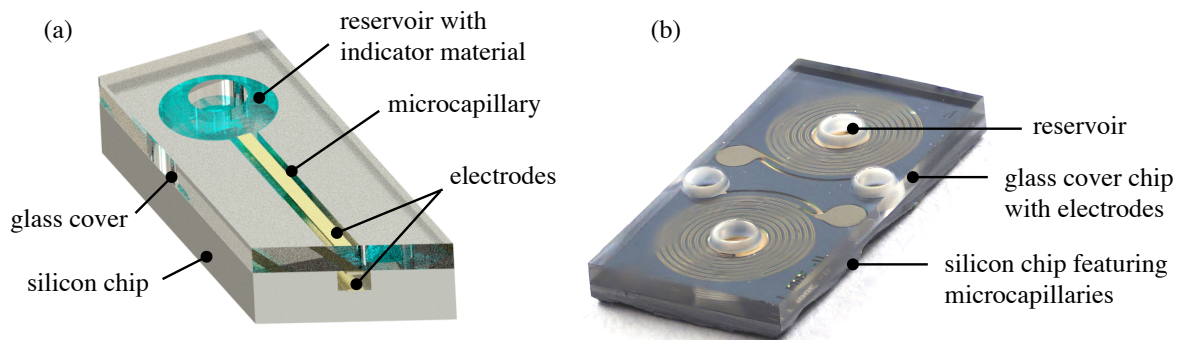

Figure 1. (a) Schematic illustration of the TTI; (b) fabricated microfluidic TTI demonstrator

2.1. Microfluidic model

To predict the dynamic behaviour of the fluid and the creeping distance x within the capillary, a microfluidic model based on the Navier-Stokes-Equation is derived. All significant forces that apply are visualized in figure 2. Taking the forces into account, a one-dimensional formulation of the Navier-Stokes equation can be given as:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(m\frac{\mathrm{d}x}{\mathrm{d}t}\right) = -F_{\text{weight}} - F_{\text{vis}} + F_{\text{capillary}} \tag{1}$$

Adapting the individual force-terms for a rectangular cross-section, the above equation can be reformulated to:

$$\varrho bhx\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + \varrho bh\left(\frac{dx}{dt}\right)^2 = -\varrho bh\mathrm{g}x - \zeta(n)\eta\, x\frac{\mathrm{d}x}{\mathrm{d}t} + 2\sigma_{\text{lg}}\cos\theta(b+h) \tag{2}$$

where ϱ is the density and η the dynamic viscosity of the fluid. σ_{lg} represents the fluid surface tension and θ is the contact angle as shown in figure 2. $\zeta(n)$ substitutes the following geometric function respecting the width b and the height h of the capillary:

$$\zeta(n) = \frac{12\,(bh)^2}{\min(b,h)^3\,\max(b,h)\left(1 - \sum_{n=1}^{\infty}\frac{1}{(2n\text{-}1)^5}\frac{192}{\pi^5}\frac{\min(b,h)}{\max(b,h)}\,\tanh\left((2n\text{-}1)\frac{\pi\max(b,h)}{2\min(b,h)}\right)\right)} \tag{3}$$

Since the diameter of the microcapillaries does not exceed the order of several microns, scaling effects have to be taken into account. After analysing the characteristic Bond and Weber numbers, the inertial force and the fluid's weight can be neglected in comparison to the capillary force, allowing a simplification of equation (2):

$$\zeta(n)\,U\,\frac{x}{\mathrm{d}t} = 2\sigma_{\mathrm{lg}}\cos(\theta)(b+h) \tag{4}$$

An analytical solution of the above differential equation can be found as:

$$x(t,T) = 2\left(\frac{\dots\cos(\theta(T))}{\dots}\right)^{\frac{1}{2}} \tag{5}$$

It is important to note that almost all material parameters are temperature-dependent, thus enabling the evaluation of the creeping distance x not only as a function of time, but also as a function of temperature.
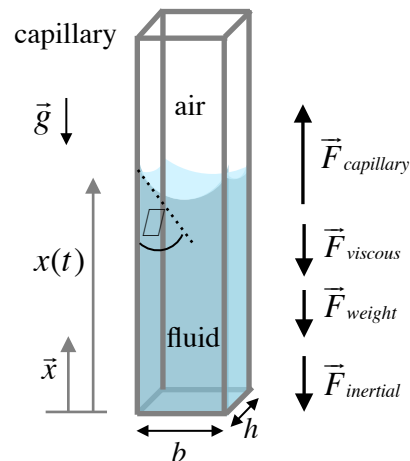

Figure 2. Illustration of relevant forces and geometric parameters in a vertically oriented capillary.

2.2. Capacitive measurement of the creeping distance

For the electrical read-out of the time-temperature integral, the associated creeping distance of the fluid has to be translated into an electrical signal. By using an indicator fluid with a high dielectric constant $\varepsilon_{r,fluid}$, the evaluation of the creeping distance can be achieved by measuring the capacity change of the plate capacitor. The total capacity as a function of the creeping distance can be approximated by:

$$C_{\mathrm{p}}(x) = \varepsilon_0\frac{b}{h}(L + x(\varepsilon_{\mathrm{r,fluid}}\text{-}1)) \tag{6}$$

where L is the length of the capillary and ε_0 is the vacuum permittivity.

3. Indicator material

The choice of a suitable indicator fluid is essential for a proper operation mode of the TTI. Many restrictions regarding fluidic and dielectric properties as well as safety and health issues have to be considered.

Since different perishable items are sensitive to different storage temperatures, the melting temperature or rather the glass transition temperature of the material should be adjustable, facilitating an easy adaption of the TTI for a wide range of products. Moreover, fluidic requirements such as a low contact angle or a high fluidic surface tensions must be fulfilled to enable a strong capillary force. In order to allow an increased sensitivity to capacitive changes, the indicator material should also feature a high dielectric constant and a low electrical conductivity. Furthermore, for being integrated in food packages, the fluid must not be toxic. Food ingredients are surely non-toxic and first choice.

Therefore, sugar alcohols like sorbitol or xylitol are ideal fluids to serve as indicator materials in the TTI-sensor. These food additives are usually used as artificial sweeteners in many food products and can be considered as harmless chemical products. Because of their polar molecular structure, sugar alcohols normally offer high dielectric constants what makes them suitable for capacitive measurements.

Another advantage is that they can appear either in a crystalline or in an amorphous state. Whereas the melting temperature of crystalline sorbitol was found to be 95 °C, the glass temperature of amorphous sorbitol is known to be –2.3 °C [6]. Therefore, and using the respective form of sugar alcohol, a wide range of temperatures can be covered. Furthermore, by dissolving sugar alcohols in water, the glass transition of the dissolution can be varied what allows an adaption of the indicator material for different temperature ranges as well. Moreover, the mobility of sugars and fats are responsible for the aging of ice cream and other products in an insufficiently cold storage.

Since sugar alcohols have not been considered as indicator material in a microfluidic sensor before, various dielectric and microfluidic experiments have been performed in order to characterise the material properties of molten sorbitol and xylitol. Pure D-sorbitol and xylitol purchased from Sigma-Aldrich were used for experimental investigations.

3.1. Permittivity measurement

Firstly, the frequency-dependent dielectric constant of amorphous sorbitol has been measured. Therefore, a cylindrical test-capacitor made of anodised aluminium has been used. The capacity of the *empty* capacitor has been measured utilizing an *Agilent E4980A* LCR-meter first. Subsequently, the test-capacitor was filled with molten amorphous sorbitol, and the capacitance measurement was repeated at a temperature of 40 °C. Another measurement at room temperature was repeated 24 hours later after the sorbitol had recrystallized.
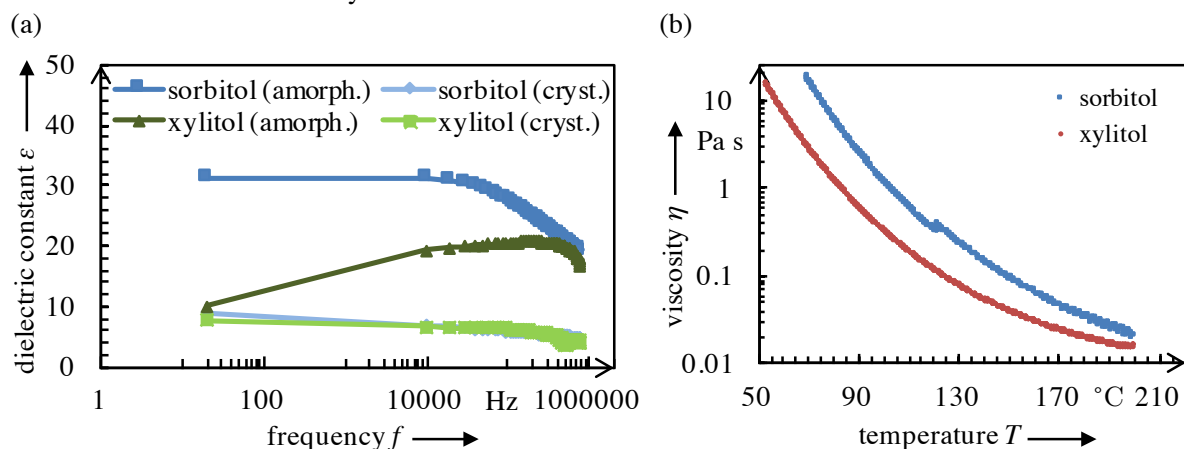

Figure 3. (a) Measured dielectric constant of sorbitol and xylitol in crystalline and amorphous state; (b) Temperature-dependent viscosity measurement of sugar alcohols.

3.2. Viscosity measurement

The most significant property which determines the temperature-dependent creeping speed of the fluid inside a capillary is the viscosity. Dynamic viscosity measurements were performed utilizing an *Anton Paar MCR 302*. Since the sugar alcohols were initially in a crystalline state, they have been molten first at high temperatures. The viscosity has then been measured for declining temperatures. The

For a microfluidic characterisation of the temperature- and time-dependent creeping distance, the experimental setup as shown in figure 4a has been used. Demonstrator chips were annealed to stationary specific temperatures, using a regulated hotplate. When the respective chip has reached the final temperature, crystalline sugar alcohol was filled into the reservoir of the demonstrator. The immediately starting creeping process has been measured with a known framerate so that the filling speed could be evaluated. Figure 4b shows the measurement results for the time-dependent creeping distance of sorbitol for two different temperatures in a $100\,\mu$m x $100\,\mu$m silicon capillary. The associated theoretical graphs in figure 4b are based on equation (5).
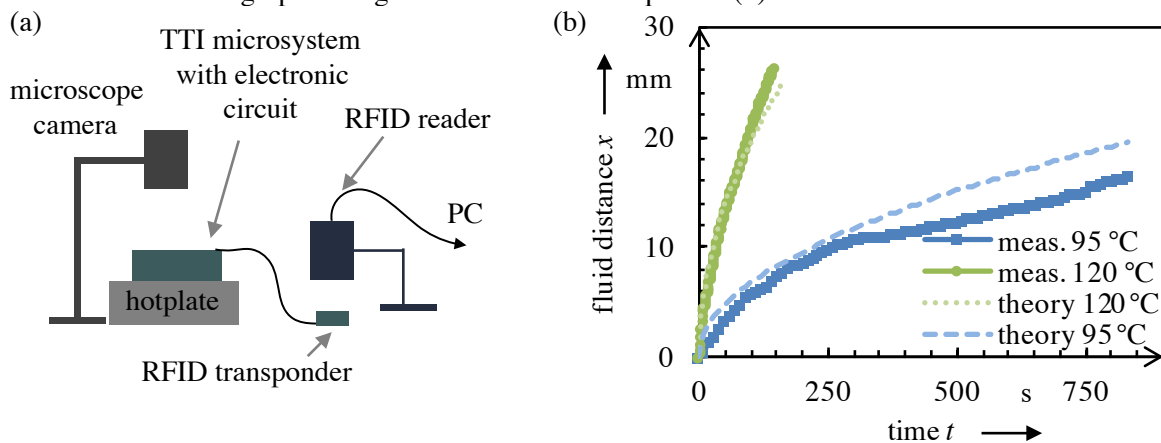

Figure 4. (a) Experimental setup used for system characterisation; (b) Measurement results of time- and temperature-dependent creeping distance of liquid sorbitol in a $100\,\mu$m x $100\,\mu$m capillary.

For reliable sensor applications, the creeping speed inside a capillary has to ensure a high reproducibility. By fabricating and testing microfluidic systems with multiple capillaries that start from the same reservoir, a high reproducibility could be verified as indicated in figure 5a. The presented *x-t*-profiles refer to the average creeping distance in six capillaries of the respective chip.

In order to test a first electronical wireless read-out of the passive TTI-sensor, the microfluidic system was connected to a capacity evaluation circuit based on commercial RFID equipment. As output, the RFID evaluation circuit provides a voltage which is proportional to the creeping distance. Measurement results, given in figure 5b, provide the proof of principle for capacitive read-out.
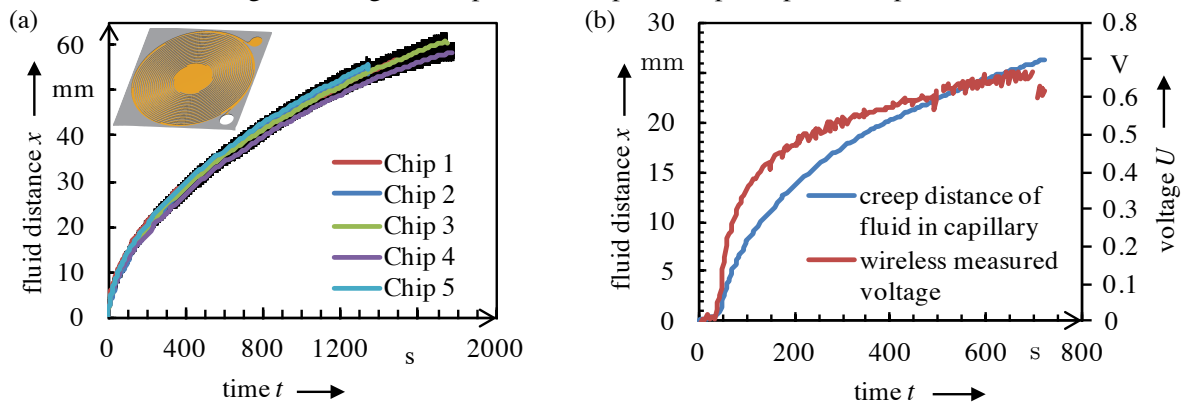

Figure 5. (a) Reproducibility testing using microsystems with multiple capillaries. (b) Electrical wireless read-out by RFID providing a corresponding voltage as reference for the creeping distance.

6. Conclusion

Non-electrical TTI-systems have been considered for a long time as reliable indicator for passive temperature surveillance of cool-chains or sterilisation processes. However, existing TTIs often allow only an optical evaluation of the measurement results. Furthermore, their adaption to different temperature ranges is limited. In this paper, a new microfluidic TTI concept has been presented that complements these missing features of today's commercially available TTI-solutions. The microfluidic system can be read out wirelessly using RFID technology.

The utilisation of pure sugar alcohols as indicator material in the TTI system has been assessed. Special attention was paid to their fluidic and dielectric properties. Measurement results show that sorbitol and xylitol offer great potential as indicator materials for high temperature applications like sterilisation processes. For low temperature applications such as cool-chain surveillance, water-based dissolutions of sugar alcohols could be applied. Further investigations and a fluidic characterisation concerning sugar alcohol dissolutions are pending.

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