Automatically and Electronically Controllable Hydrogel Based Valves and Microvalves – Design and Operating Performance

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Summary: This paper describes automatically and electronically controlled valves and microvalves based on smart hydrogels. The operating performance of such devices will be discussed in dependence on various design parameters. Furthermore, it will be shown that hydrogel based valves are showing an outstanding possibility of miniaturization, a leakage free switching behavior up to a pressure drop of 8.4 bar, and a pronounced particle tolerance.

Keywords: automatic control; electronic control; hydrogel; microvalve; operating performance; valve

Introduction

In the last two decades a lot of hydrogels which are sensitive to temperature, ion and substance concentrations were developed. The distinction of the so-called stimuli-responsive or smart hydrogels is the property to change their volume reversible and reproducible by more than one order of magnitude even through very small alterations of certain environmental parameters. Therefore, an enormous importance for many technological and scientific applications was expected [1]. Particularly special mostly bio medical applications such as drug delivery systems suggest the rightness of this prediction. A first technological breakthrough at the development of hydrogel based valves and microvalves could be observed. An automatic valve for process engineering applications with sensitivities against the temperature, pH value, and contents of organic solvents was presented [2, 3]. In [4] an automatic microvalve was presented which possesses an automatic function to control a micro flow in dependence of pH value. Other hydrogel based microvalves can regulate micro flows as a function of pH value and

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concentrations of glucose [5], and temperature [6]. However, a detailed description of the operating performance of hydrogel based valves, the influence of design parameters, and phenomena at volume phase transition of hydrogel actuators are mostly outstanding. However, their knowledge is absolutely essential for developing well functioning systems. The paper summarizes our research on the development of automatically and electronically controllable hydrogel based valves.

Experimental

Synthesis of Gel

The actuator material poly(*N*-isopropylacrylamide) (PNIPAAm) was prepared at following procedure. The crosslinking agent was *N,N'*-methylenebisacrylamide (BIS). The initiator and accelerator for the polymerization reaction were potassium peroxidisulfate (KPS) and *N,N,N',N'*-tetramethyl-ethylenediamine (TEMED) (both from Aldrich Chemical Co.). NIPAAm and various amounts of BIS (1mol% to 10mol%, BIS4 – 4mol%) were dissolved in deionized water. The total monomer concentration was 0.53 mol/l. To initiate the polymerization reaction 0.3 mol-% of KPS and TEMED, respectively, were added to the oxygen free (bubbled with N_2) solution. After polymerization (ca. 12 h at room temperature) the PNIPAAm gel was immersed in deionized water for about one week to wash out non-reacted reagents. After drying the PNIPAAm BIS 4 gel the particles were obtained by milling and subsequent fractionating into different particle sizes using test sieves. The particles are irregular shaped.

The photo crosslinkable hydrogels were prepared from PNIPAAm copolymers bearing 4.5 mol-% light sensitive chromophores based on dimethyl maleimide. The copolymer solution (20 wt-% in butanone), containing 2 wt-% thioxanthone with respect to the polymer weight as photo sensibilisator was spin coated onto the SiO_2-support pretreated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as an adhesion promoter. The film was subsequently dried and irradiated with a UV lamp (Hg lamp 400 W, wavelength 360 to 450 nm). Irradiation of the polymer resulted in an irreversible crosslinking by a [2+2]-cycloaddition. The non-crosslinked polymer was removed with a water alcohol mixture (20 wt-% ethanol, 80 wt-% water).

Microvalve Fabrication

The microvalves (see Fig. 1) are consisting of a channel structure support (5), a Pyrex glass cover (invisible in Fig. 1), and a circuit card (7) for electrical contacting. The channel geometry (3) and the actuator chamber (4 in Fig. 1a) are generated by a two-side etching process. Applied materials were Si wafers, or Pyrex glass wafers. Heating elements (110 nm in thickness, resistance 50 Ω, not shown in the Fig. 1a) and temperature sensors (8) were prepared by a platinum-thin-film system with lift-off patterning. A heating element (6) is located below the actuators on the channel structure support, while the temperature sensor is placed on the rear of the Pyrex glass cover. The microvalve can be controlled electronically by these elements. All layers were coupled by a combinated flip-chip and gluing technology.

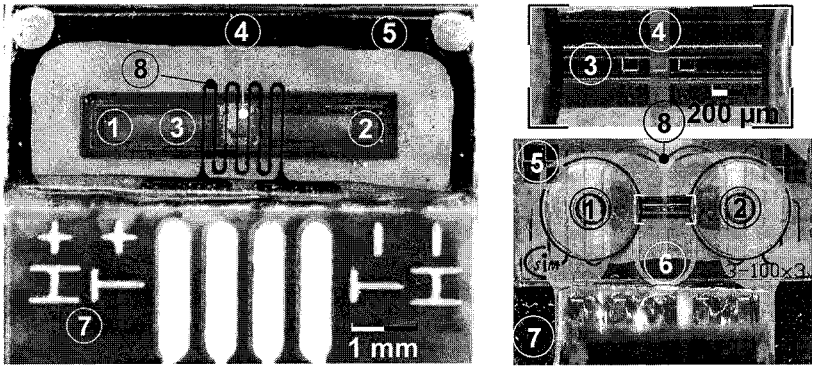

Figure 1. Photographs of hydrogel based microvalves; a) (left) – particle based microvalve, b) (right) - photopatterned microvalve; 1 – inlet; 2 – outlet; 3 – flow channel; 4 – actuators; Fig. 1a: actuator chamber filled with hydrogel particles, Fig. 1b: three actuator dots; 5 – structure layer; 6 – heating meander; 7 – circuit card; 8 – temperature sensor.

To assemble the microvalve body with the actuator hydrogel particles based on the homopolymer PNIPAAm (Fig. 1a) were manual incorporated into the actuator chamber. The microvalve shown in Fig. 1b contents three hydrogel dots. They were placed directly into the channel by photo-patterning using the photo crosslinkable PNIPAAm copolymer. This valve set-up does not require an actuator chamber. A satisfying adhesion of the hydrogel dot to the underground structure was achieved by an adhesion promoter [7].

Macrovalve Design

This valve is made from stainless steel (see Fig. 2). The design is consisting of a big tube, which is the flow channel with inlet (1) an outlet (2). The actuator chamber, which is filled with hydrogel particles (3), is placed inside the flow channel. Two steel meshes (4) on both sides of the actuator chamber prevent the outflow of particles. A small tube is used as a bypass (5). All parts are connected via welding or screwing.

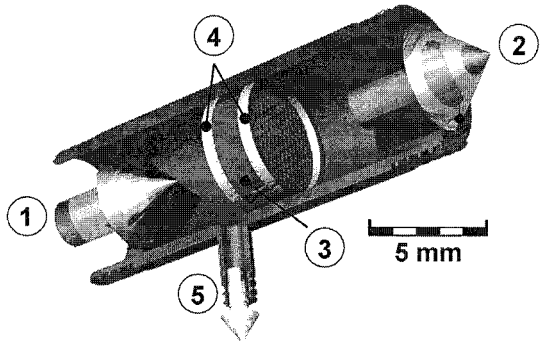

Figure 2. Schematic design of a automatic hydrogel based valve; 1– inlet, 2 – outlet, 3 – actuator chamber filled with hydrogel particles, 4 – steel mesh, 5 – bypass.

Results and Discussion

Operation Performance

A. Electronically Controllable Microvalves

By the direct placement of the hydrogel actuator in a flow channel the actuator has incessantly contact with the process medium, which acts as swelling agent as well. PNIPAAm and its photo crosslinkable copolymers exhibit lower critical solution temperature (LCST) behavior with a volume phase transition temperature (T_C) of approximately 33 °C (PNIPAAm, see Fig. 3a) or 21 °C to 29 °C (photo crosslinkable NIPAAm copolymers), respectively. Below T_C, e. g. at room temperature, the hydrogel is swollen, and above T_C the hydrogel is deswollen. In the normal case the medium temperature is below the T_C and the hydrogel seals the flow channel completely ("normally closed" function).

An electronic control of the valve shown in Fig. 1 was achieved by the heating element. To open the valves the gel actuators was warmed up above T_C with the heating element. The hydrogel actuator deswells and allows the fluid to flow through the channel. In order to obtain controllability of the valve, between completely opened and closed, a temperature sensor was integrated into the set-up to maintain a standard temperature.

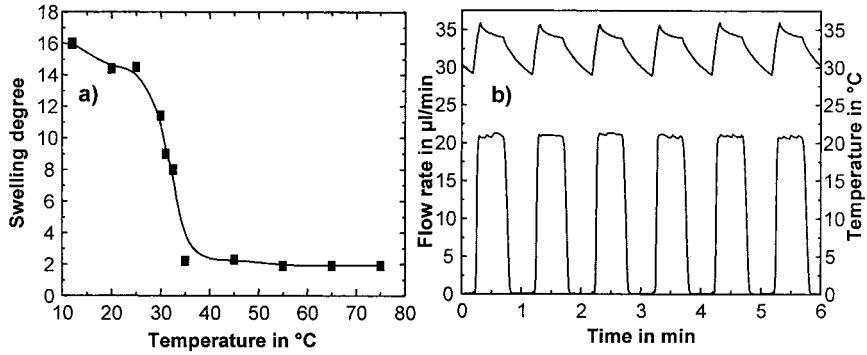

Figure 3. Principal behavior of PNIPAAm BIS 4; a) Swelling degree of PNIPAAm BIS 4 in dependence on temperature; b) Behavior of an electronically controllable microvalve with PNIPAAm BIS 4 particle actuator (size 500x500x50 µm³) at power modulated work (power peak at 380 mW for 500 ms, retaining power 150 mW). Upper curve: temperature vs. time, lower curve: flow rate vs. time.

Fig. 3b shows the opening and shut-off behavior of an electronically controllable microvalve with an actuator chamber size of 500 µm x 500 µm x 200 µm filled with PNIPAAm BIS 4 particles (diameter of (82 ± 8) µm). In order to control the water flow rate the valve was temporarily warmed up with 380 mW to 35 °C. Subsequently the temperature was kept constant within 1 K with 150 mW. The fastest switching times, obtained for the particle based microvalves, were 300 ms at 350 mW for opening. Presently, the spontaneous shut-off time was approximately 2 s. The valve closes within 1 s when an external fan for cooling was used. The response times of the photo patterned valves are slower. This circumstance is probable caused by a smaller amount of groups which induce the phase transition behavior. A microvalve with dots of the size (250 µm x 250 µm x 50 µm is opening in 4 s and closing in 10 s.

B. Automatically Controlled Valve

The macrovalve which is illustrated in Fig. 2 is designed for an automatic function of hydrogel actuator. Hence, a large valve chamber and a bypass to the source of process medium is supposed. In the open state the process medium is passing the actuator chamber. If the valve is closed the solvent can flow back to the inlet using the bypass. This intake shunt guarantees a persistent presence of the actual stimulus at the hydrogel actuator.

The homopolymer PNIPAAm is likewise showing sensitivities to contents of alcohols in water (see Fig. 4a).

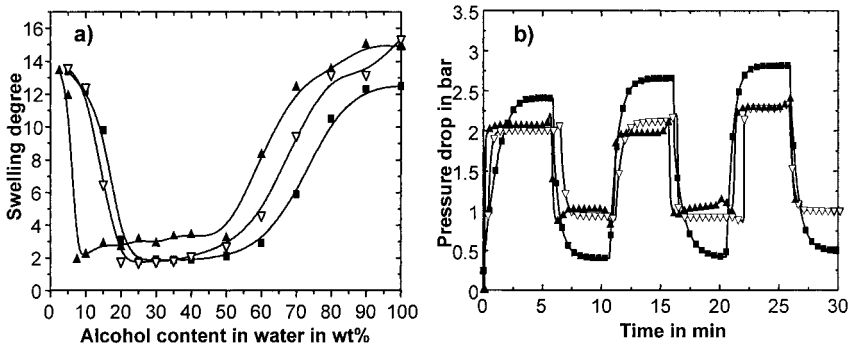

Figure 4. Behavior of PNIPAAm BIS 4 in dependence of alcohol concentration in water at room temperature (21 °C); a) Swelling degree of PNIPAAm depends on alcohol type and content; b) Behavior of a macrovalve loaded with PNIPAAm particles in dependence of alcohol content in water which was switched between 0 and 40 wt-% (■ - methanol, ▽ - ethanol, ▲ - 1-propanol).

It can be seen from Fig. 4a that two regions exist, which owe a volume phase behavior. The region at lower alcohol contents shows a decrease of the swelling degree with increasing alcohol concentration. The larger the carbon number of alcohol, the lower the concentration to obtain similar swelling degrees. The region at higher alcohol contents shows an inverse behavior.

This volume phase transition behavior of PNIPAAm can be used to obtain an automatic function of hydrogel based valves towards alcohol content in aqueous solutions. As shown in Fig. 4b in the range of the low concentrated phase transition the behavior of the valve is reproducible. The

opening time is about 40 s while the closing time is ca. 25 s. The response time increases with lowering the carbon number of alcohol. At the higher concentrated volume phase transition the valve is closing at higher alcohol contents in water, and opening at lower alcohol contents.

Material, Design, and Operational Parameters

The swelling and deswelling process of hydrogels is diffusion controlled. Hence, the effective dimensions of hydrogel actuators influence strongly their switching behavior. To obtain small effective dimensions we use thin films of hydrogels or hydrogel particles as actuator material. In the last case the switching time is stronger dependent on the dimensions of particles than on the total actuator volume. However, only for macrovalves the particle size has a strong influence on the switching time (see Fig. 5a). For microvalves with a ratio of particle size to chamber size between 0.075 and 0.15 is the influence on the particle size of switching time negligible.

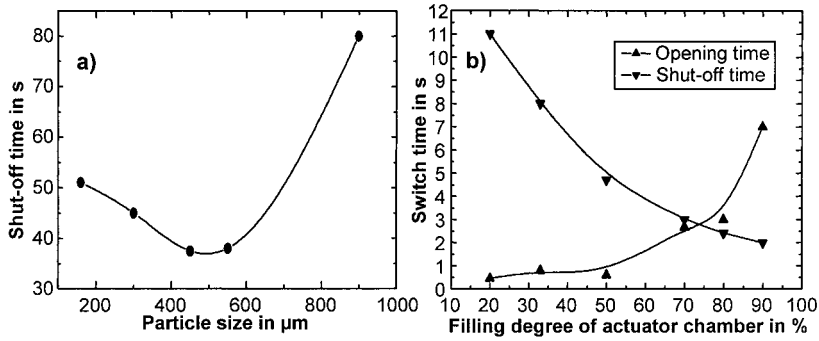

Figure 5. Switching time of hydrogel particle based valves in dependence of various design parameters. a) Shut-off time of an thermal stimulated valve with an actuator chamber of Ø 5mm x 4 mm, particle material PNIPAAm BIS 4; b): Switching time of a particle based microvalve in dependence on the filling degree of the actuator chamber, size of actuator chamber (800x800x200)µm³, actuator material PNIPAAm BIS 4, dry particle size (82.5 ± 7.5) µm.

The most important parameter which influences the switching time of hydrogel actuator is the filling degree of the actuator chamber with dry hydrogel particles (see Fig. 5b). A small filling degree allows to obtain short opening times but the closing time is high. Up to a filling degree of 50% the opening time remains constant. A further increase of this parameter is resulting in small

shut-off times while the opening time increases. In dependence on the priority of opening and shut-off time this parameter has to be optimized.

Another weighty design parameter is the size of the actuator chamber. The larger the actuator chamber the higher the switching time of a valve (see Fig. 6b). This figure shows also the effect of another design parameter, which is important for temperature stimulation. An increase of the heat capacity of valve body (valve with the actuator chamber size (800x800x200)µm³ induces a higher consumption of heating power to obtain fast opening times.

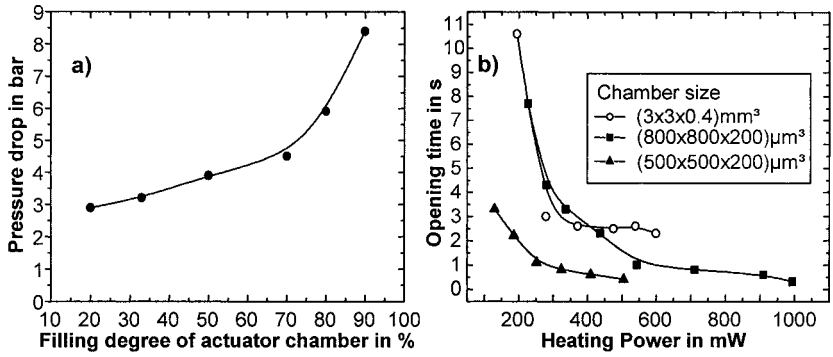

Figure 6. Leakage free pressure resistance in dependence on filling degree (a) and opening time in dependence on applied heating power for various hydrogel particle based microvalves (b).

The softness of hydrogels suggests that a leakage flow should be avoided because the actuator chamber can be fully filled with the swollen hydrogel. In fact, the maximal possible pressure drop, which is not showing a leakage flow, is a strong function of the filling degree of the actuator chamber with hydrogel particles (see Fig. 6a). At a filling degree of 90 % a leakage free pressure drop of 8.4 bar is obtainable. If the maximal pressure drop is exceeded the valve is mostly irreversible breaking through because the hydrogel particles were flushed out. Only at a very small filling degree the leakage flow is proportional to the increase of pressure drop.

For electronically controllable microvalves, which are using a thermal electronic interface, the temperature gradient is the most important operational parameter. Particularly the deswelling process and the opening time, respectively, are strongly dependent on the applied heating power (see Fig. 6b). Though, this dependence decreased after exceeding an angular point, which

depends on the heat capacity of valve body. A further increase of heating power induces only a slight opening time decrease.

The softness of hydrogel actuator indicates a pronounced particle tolerance of hydrogel valves. A process medium, which includes splinters from polystyrene (irregular shape particle diameter less than 60 µm), did not impair the shut-off function of a microvalve with a chamber size of (800x800x200) μm^3. A leakage flow could not be observed. However, single splinters can remain in the actuator chamber. To remove such particles a flushing step must be executed.

At constant environmental and process conditions the behavior of hydrogel based valves is reproducible and shows a maximum error in reproducibility of less than 1 %. However, such stable conditions are not given. For neutral gels which include the most temperature sensitive hydrogels such as PNIPAAm a lot of cross-sensitivities are known. By contact with the process medium particularly salts and pH may shift the phase transition temperature of hydrogel actuators. Also cross-sensitivities to a number of organic solvents are known. This might cause serious malfunction if the composition of the process medium is not properly chosen. It is necessary to choose an appropriate hydrogel for a specific fluid.

Conclusion and Outlook

Presented results are showing that smart hydrogel based valves can offer four advantages:

- automatic sensor – actuator functions to various environmental parameters,
- outstanding possibility of miniaturization,
- leakage free switching behavior up to a pressure drop of 8.4 bar, and
- pronounced particle tolerance.

The actual switching times of hydrogel based microvalves (300 ms for opening and 2 s for shut-off) are sufficient for a lot of applications. However, switching frequencies higher than 10 Hz are hardly realizable. Hence, hydrogel based valves and microvalves cannot be used in highly dynamic applications.

The valve design which includes an actuator chamber could be very easy loaded with particles based on any hydrogel. Hence, it is a basic design usable to realize automatically controlled valves. However, integrated sensor – actuator functions could be only successfully realized if possible cross-sensitivities caused by composition of process media or environmental parameters

will be respected. We believe that hydrogel based actuators can generate manifold developments in microfluidics, bio technology, chemical, and medical engineering.

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