Monitoring swelling and deswelling of thin polymer films by microcantilever sensors

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Abstract

Microcantilever based sensors are promising devices because they are fast, low cost, portable and allow measuring extremely small quantities of substances in gas or liquid phase that are not detectable by other methods. In this work we investigate the swelling and deswelling behavior of poly(hydroxyl ethyl methacrylate), PHEMA, films with three different average molecular masses deposited onto bare silicon microcantilevers, a hydrophilic substrate, and onto polystyrene (PS) coated microcantilevers, which is a hydrophobic substrate, under humidity cycles by monitoring the deflections resulting from differential surface stress. The results found in the present study demonstrate that the micromechanical response observed are related not only to the polymer molecular weight, but also to the polymer-interface phenomena and environment –polymer interface that can play a crucial role on the signal transduction. Ellipsometric measurements evidenced that the swelling of PHEMA films with intermediate molecular weight at 80% RH follows Fickian diffusion mechanism. Nevertheless, due to the weak optical contrast or film homogeneity shorter or longer chains than PHEMA-300 could not be investigated by ellipsometry. PHEMA films deposited onto PS surfaces presented dewetting, which limited the ellipsometric measurements. In comparison to ellipsometry, monitoring swelling behavior of PHEMA by nanomechanical responses is more advantageous because it is faster and less restricted.

Keywords: microcantilevers; poly(hydroxyl ethyl methacrylate); polystyrene; molecular weight; surface stress; humidity; ellipsometry

1. Introduction

Microcantilever (MC) based sensors are promising devices because they are fast, label-free, low cost, portable and allow measuring extremely small quantities of substances in gas or liquid phase that are not detectable by other methods [1, 2]. The main mechanical effects observed in MCs are surface stress, which causes static mechanical bending, and changes in the resonance frequency [3, 4]. The surface stress mechanical effect takes place, if only one of the both MC sides is coated with a film, this operation mode can be designed to follow the mechanical response in real time. If the top side of the MC is coated and the film expands, which might occur due to hydration, favorable/specific interactions or thermal transitions, the cantilever bends away from the coated side, resulting in compressive stress. On the contrary, as the film contracts, the cantilever bends towards the coated side, generating tensile stress. The dynamic response mode is characterized by resonance frequency changes caused by added mass of a given analyte on any of the sensor surfaces. Scheme 1 represents both operation modes of nanomechanical sensors.

In the field of biosensors, MCs have been used for the detection of specific bindings to proteins [5], DNA hybridization [6, 7, 8] or antibody–antigen interactions [9, 10, 11]. MC sensors can also be used for monitoring viscoelastic changes in thin polymer layers deposited on the upside of MCs. Jung and co-workers [12] used PS-coated silicon cantilevers to determine the thermomechanical and physical properties of the PS sample in the vicinity of the glass transition temperature. They found that the nanomechanical thermal analysis technique using polymer-coated silicon cantilevers can serve as a promising method to experimentally probe the volume expansion and contraction of amorphous polymers in the glassy state upon heating. Recently, the glass transition temperature (T_g) was determined for ultrathin films of poly(3-thiophene methyl acetate), P3TMA, deposited onto MC as 5.2 °C higher than the T_g value determined for the bulk polymer. Such effect was attributed to ordered molecular arrangement at polymer-air interface induced by the nanometer scale thickness [13]. The swelling and deswelling behavior of poly(methyl methacrylate), PMMA, brushes attached to MC was investigated in a fluid cell, where cantilever bending was monitored as solvent/non-solvent mixtures were injected [14]. Polymers can also be swollen by solvent vapor. The usual techniques to investigate swelling behavior of thin polymer layers by a given solvent vapor are reflectometry [15], gravimetry [16], quartz crystal microbalance with dissipation monitoring (QCM-D) [17], attenuated total reflection infrared (ATR-IR)

spectroscopy [18], optical interferometry [19] and AFM force versus distance interaction curves [20,21]. The use of bending responses of polymer coated MC under variable moisture levels has been used to understand the swelling behavior of polymeric networks with different crosslinking degrees [22] or to determine the diffusion coefficient of water in the thin polymer film [23].

Poly(hydroxyl ethyl methacrylate), PHEMA, a polymer widely used for contact lenses, is water-insoluble, but it swells in water or water vapor. The PHEMA based contact lenses should be always hydrated in order to avoid uncomfortable corneal dessication. Opdahl and co-workers investigated the surface stiffness and surface elastic modulus values of commercial crosslinked PHEMA hydrogel by means of AFM force versus distance interaction curves in the RH range of 36% to 87% [20,21]. They found that at low humidity (< 60% RH), the air exposed surface is dehydrated in comparison to the bulk, it is stiffer and behaves as a glassy polymer, whereas at high humidity (> 60% RH) water acts as a plasticizer, the surface softens and the viscous deformation increases [20,21].

In this work we investigate the swelling and deswelling behavior of PHEMA films deposited onto bare MC, which is a hydrophilic substrate composed of a native layer of SiO₂, or onto polystyrene (PS) coated MC, which is a hydrophobic substrate, under humidity cycles of 8 min, 15 min or 60 min, by monitoring the deflections resulting from differential surface stress. PHEMA with three different molecular weights (20 kg/mol, 300 kg/mol and 1000 kg/mol) were deposited on the upside of MCs. Thus the micromechanical effects explored in the present study are related not only to the environment-polymer interface but also to the polymer-substrate interface phenomena and to the polymer molecular weight. Ellipsometric measurements were used to monitor thickness and index of refraction of PHEMA films spin-coated onto Si wafers and PS coated Si wafers in the RH range of 25% to 80% for periods of time ranging from 5 min to 4 h.

2. Experimental

2.1 Materials

Poly(hydroxyethyl methacrylate) (PHEMA) samples with nominal viscosity average molar masses (M_v) 20,000 g.mol⁻¹ (PHEMA-20), 300,000 g.mol⁻¹ (PHEMA-300) and 1,000,000 g.mol⁻¹ (PHEMA-1000), polystyrene (PS) with M_v 300,000 g.mol⁻¹, toluene and methanol analytical grade were purchased from Sigma-Aldrich (USA). PHEMA and PS solutions were

prepared at 30 g L⁻¹ in methanol and toluene, respectively, in a sonication bath during 5 minutes.

2.2 Methods

Silicon microcantilevers (MC) (Mikromasch, Estonia) arrays rinsed with piranha solution were used as mechanical transducers. The cantilevers are 400 µm long, 100 µm wide and 1 µm thick. The variations of resonance frequencies within one array were less than 1%, indicating similar mechanical properties. Polymer solution at 30 g/L was deposited on the MC by spin coating (SÜSS Microtec Delta +10), $\omega = 10,0000$ rpm, 30 s). In the case of PHEMA-300, films were deposited not only on bare MCs, but also on MCs previously coated with a thin PS film (~ 4 nm thick); these films were coded as PS/PHEMA-300. The polymer films were homogeneously deposited on the cantilevers (Figure 1). One should note that less concentrated polymer solutions were not adequate because they led to discontinuous polymer films and would not generate a uniform stress. PHEMA or PS was removed from the MC backside by plasma treatment (80 W, $7.5 \cdot 10^{-9}$ torr, O₂ at 20 sccm, RIE Oxford Instruments Plasmalab 80 PLUS), because otherwise there is no cantilever deflection. One should note that plasma treatment caused no crosslinking, film thinning, or changes in surface roughness (Supplementary Information-Figure S1).

The resonance frequency and deflection of polymer coated MC were recorded as a function of air relative humidity (RH) in the experimental setup depicted in Figure 2. The nanomechanical response of the MC was measured by using a home-built apparatus equipped with an optical readout-technique and the automated two-dimensional scanning of a single laser beam by voice-coil actuators [24]. The beam of a 3 mW red laser diode (Edmund Optics) was focused on the MC end and the reflected beam was collected by a two-dimensional position sensing linear detector (PSD). The apparatus has an environmental chamber that allows the control of temperature (T) and RH. The RH control system is implemented with a humidity probe from Hygrosens (sensor) and two mass-flow controllers (MFC) from Aalborg. The measurement chamber has an inlet for dry/wet N₂. One of the MFCs provides a flow of dry N₂, and the other one provides a flow of wet N₂. Wet N₂ is obtained by passing the gas through a wash flask filled with distilled water. Both gas lines are mixed in a pre-chamber before reaching the measurement chamber. The temperature control system was implemented with a standard PT 100 resistance temperature detector located close to the microcantilever array in the measurement chamber and a cooling circulator (Huber Kaeltemaschinenbau GmbH) as shown in Figure 2.

For the humidity cycles, the relative humidity was varied from 0% to 80%, while the temperature was kept at 25 ± 1 °C. The humidity cycles were completed in 8 min, 15 min or 60 min. The resonance frequency of the microcantilevers was measured at 0% and 80% RH after the stabilization of the environment in the measurement chamber at the desired RH for 10 minutes.

Silicon wafers (University Wafers, USA) were cut into 1.0 cm X 1.0 cm pieces and rinsed with piranha solution and deionized water and afterwards dried under N₂ stream. Half of the Si wafer area was covered with a tape resistant to toluene and methanol. Polymer solutions were deposited onto Si wafers by spin coating (SÜSS Microtec Delta +10), $\omega = 10,000$ rpm, 30 s. The tape was removed and the mean thickness values of polymer films were determined by means of profilometry (Veeco Dektak 150). The measurement was performed at least at three different points of two different samples.

Ellipsometric measurements were performed with a vertical computer-controlled DRE-EL02 ellipsometer (Ratzeburg, Germany) with an angle of incidence ϕ of 70.0° and wavelength λ of 632.8 nm He–Ne laser. The mean thickness and index of refraction of the PHEMA layer were determined independently using the fundamental ellipsometric equation [25]:

$$e^{i\Delta} \tan \psi = (R_p/R_s) = f(n_k, d_k, \lambda, \phi) \quad (1)$$

where R_p and R_s are the overall reflection coefficients for parallel and perpendicular waves, respectively. The mean thickness d_k and refractive index n_k can be calculated from the changes of the ellipsometric angles Δ and Ψ , using iterative calculations and a multilayer model composed by the substrate, the unknown layer, and surrounding medium. The thickness of the SiO₂ layer was determined in air, considering the indices of refraction for Si as $n_{Si} = (3.88 - i0.018)$ [26], $n_{air} = 1.00$ and $n_{SiO_2} = 1.462$ [26] and “infinite” thickness for the Si and air layers. The mean thickness obtained for SiO₂ was (2.0 ± 0.1) nm. The mean thickness and index of refraction determined in air for PS films deposited onto Si wafers amounted to (136 ± 5) nm and (1.587 ± 0.004) , respectively. The PHEMA spin-coated onto Si wafers of PS coated Si wafers were inserted in a special cell made of poly(methyl methacrylate) and quartz windows with inclination of 70° [27]. The RH inside the ellipsometric cell was controlled by mixing dry N₂ and humid N₂ and measured by a humidity/ temperature meter Lutron HT 3006A. In the first set of experiments a desired RH value was adjusted inside the cell and the ellipsometric angles were measured after 4 h. In the second set of experiments the RH value was constant and the ellipsometric angles were measured as a function of time. All measurements were performed in a conditioned room with temperature at (24.0 ± 0.5) °C.

3. Results and Discussion

The procedure for polymer coating of MCs must consider the fragile suspended mechanical structures to avoid changes in the mechanical properties of the cantilever. Several methods can be used for coating MCs with homogeneous polymer layers, but the choice depends on the system. For instance, the ink-jet deposition method was used for poly(vinyl alcohol) depositions, while for poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), and poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) microarray spotting pins were applied [28]. Polymers can be polymerized onto MCs by plasma polymerization [22,23] or MCs can be functionalized to enable grafting of polymer brushes [14,29] or polymer colloidal particles [30]. In this work PHEMA was spin-coated on bare MCs and PS coated MCs and polymer residues were removed from the MC backside by plasma treatment. The reasons to choose this technique to coat the MC surfaces are (i) the necessity to coat only one side of the MC for the surface stress measurements and (ii) the quality and reproducibility of the polymer film acquired after the spin coating. As shown in typical optical micrographs in Figure 1, continuous and homogeneous polymer films were deposited onto MCs using a very fast and simple method.

The MC deflection setup used in the present work is schematically represented in Figure 2. Basically it consists of one side coated MCs, that act as mechanical transducers, and a deflection readout system confined in a chamber with controlled temperature and air relative humidity (RH). Figure 3a shows typical deflections of PHEMA-20, PHEMA-300 and PHEMA-1000 coated MCs as a function of RH cycles at $(25 \pm 1)^\circ\text{C}$. As reference, the deflection of PS coated MCs with RH cycles were also recorded (Figure 3a). PS was chosen as reference due to its hydrophobicity.

The deflections result from differential surface stress generated between opposite sides of MC. Upon increasing RH, PHEMA chains swell, increasing the viscoelasticity [19,21] and the osmotic pressure [29,30]. This effect causes compressive stress on the coated MC side and, consequently, MCs bend away from the coated side. Figure 3 shows clearly that increasing RH values from 0 % to 80 % the bending of PHEMA coated MCs increased with polymer molecular weight decrease (PHEMA-20 > PHEMA-300 > PHEMA-1000). These results can be explained with basis on the fact that the entropy change by swelling short polymer chains is larger than for long polymer chains [14]. This effect is alleviated in the MC as a larger curvature bending for the shorter polymer chains.

The deswelling ramps showed that at $\sim 20\%$ RH the original position of PHEMA coated MCs was achieved. For RH values lower than 20% the MCs coated with PHEMA-20, PHEMA-300 and PHEMA-1000 kept bending towards the coated side up to maximal values of $9 \pm 1 \mu\text{m}$ at $\sim 2\%$ RH, $6.6 \pm 0.5 \mu\text{m}$ at $\sim 2.5\%$ RH and $1.5 \pm 0.5 \mu\text{m}$ at $\sim 3.5\%$ RH, respectively. The tensile stress indicates that attractive forces dominate the intermolecular interaction on the MC surface. The polymer layer is expected to shrink at RH range of 2.5 % to 3.5 %, while it adopts a more extended conformation at 0% RH. A similar behavior has been observed and theoretically modeled for self-assembled monolayers of ssDNA, a polymer with strong affinity for water molecules [6, 31, 32]. Rabin et al. [32] proposed a model to explain polyelectrolyte monolayers shrinking upon adsorbing water; they considered that at low concentrations of water vapor, the adsorption of water is accompanied by enhanced expulsion of vacancies, and thus, compression of the monolayer. Swelling and deswelling cycles were also performed for PS coated MCs as control experiments (Figure 3a). The deflections were negligible, indicating that the behavior observed for PHEMA-20, PHEMA-300 and PHEMA-1000 in Figure 3a arises due to the favorable interactions between SiO_2 /PHEMA, SiO_2 /water and PHEMA/water.

Figure 3b shows the swelling and deswelling cycles determined for PHEMA-300, PS and PS/PHEMA-300 coated MCs. The deflections observed for PS/PHEMA-300 were much less pronounced than those observed for PHEMA-300. These results indicate the existence of a thick interfacial water layer between SiO_2 (bare MC) and PHEMA and a thin interfacial water layer between PS (deposited onto MC) and PHEMA that plays a substantial role on the signal transduction.

Figures 3a and 3b show MC responses to humidity cycles of 15 min. In order to evaluate the effect of period of time set for swelling and deswelling cycles on the MC deflections, the responses of PHEMA-300 coated MC were recorded for humidity cycles of 8 min, 15 min and 60 min (Figure 3c). The systems behaved similarly, indicating that the time needed to exchange the atmosphere in the environmental cell seems to be short in comparison to the periods of time between 8 and 60 min used for the humidity cycles.

Mechanical resonators are based on the change of the nanometer-scale vibration of a suspended MC when molecules adsorb on its surface. Mass changes can be determined accurately by following the MC resonance frequency if (i) the elastic properties of the MC remain unchanged during the molecules adsorption and (ii) damping effects are negligible [33]. The resonant frequency sensitively shifts in proportion to the mass of the molecules adsorbed on the MC. Moreover, the MC used in this study are homogeneously covered by the PS or PHEMA films (Figure 2) and considering that water absorption is also homogeneous in the

entire film, the simple harmonic oscillator model can be applied to estimate the amount of water absorbed by the polymeric films when exposed to high humidity. Table 1 shows the difference in surface stress between the upper and lower sides of the MCs, $\Delta\sigma$, calculated by the modified Stoney's formula [29]. $\Delta\sigma$ is related to the microcantilever deflection, Δz , the length of the cantilever, L , Poisson's ratio, ν , Young's modulus, E , and the thickness of the cantilever, h :

$$\Delta z = \frac{3(1-\nu)L^2}{Eh^2} \Delta\sigma \quad (2)$$

The resonance frequency was determined for each PHEMA coated MC at increasing RH ramp (see Supplementary Information Figure S2 for details). Table 1 shows the relative resonance frequency shift (Δf), which is the difference between the MC resonance frequency determined at 80 % RH and at 0 % RH. The largest Δf value was observed for PHEMA-20 and the smallest one was for PHEMA-1000, corroborating the deflection behavior observed in Figure 3a. The negative Δf values observed are related to mass increase (Δm) due to swelling:

$$\Delta f = \frac{1}{2\pi} \sqrt{\frac{k}{\Delta m}} \quad (3)$$

where k is the cantilever spring constant. The relative mass increases are presented in Table 1; the largest value was determined for PHEMA-20 coated MCs as $(5.1 \pm 0.8) \%$. The dependence of Δf and relative mass increase values on PHEMA molecular weight is presented in Figures 4a and 4b, respectively. Although there are only three data points, Δf and relative mass increase values suggest that PHEMA swelling tends to increase exponentially with the decrease of molecular weight. The Δf and relative mass increase values determined for PHEMA-300 and PS/PHEMA-300 are comparable, although $\Delta\sigma$ values are quite different, indicating that the amount of water is approximately the same, but the water molecules at the interface $\text{SiO}_2/\text{PHEMA}$ are arranged in a different way than at the interface PS/PHEMA. Moreover, the organization of water molecules in the system polymer/MC does not depend on the polymer layer thickness because PHEMA-300 and PHEMA-1000 have similar thicknesses, but presented quite different values of $\Delta\sigma$, Δf and relative mass increase. PHEMA-300 was deposited onto PS coated MCs, but dewetting of PHEMA-20 films impeached their use in the deflection curves under humidity cycles (see Supplementary Information Figure S3).

Hysteresis observed for swelling and deswelling isotherms determined for PHEMA-20, PHEMA-300 and PHEMA-1000 occurs when the water content in deswelling at the same water activity is higher than in swelling, indicating water retention in the system polymer/MC [34]. At low RH the persistence length increases and then the entropy penalty is lower and thus the

bending, at high RH chains explore a wider conformational space and thus the entropy penalty needs to be balanced by a larger bending.

The arrangement of interfacial water layer and polymer chain length seem to control the MCs deflections, since they result from differential surface stress generated between opposite sides of MCs. In the case of hydrophilic substrate, as SiO₂, water interacts with both, substrate and PHEMA, by hydrogen bonding. The hydroxyl groups of PHEMA will tend to orient to the water wetted SiO₂ surface, as schematically represented in Figure 5a. Such effect is favored for lower molecular weight PHEMA, which have smaller entropic constraints. On the other hand, hydrophobic substrates, as PS, are not wet by water and the PHEMA methyl groups are expected to be oriented to the substrate, driven by weak dispersion forces, as depicted in Figure 5b. Thus, the interfacial water layer between SiO₂ (bare MC) and PHEMA is more strongly bound than in the case of the interfacial water layer between PS (deposited onto MC), resulting in different signal transduction.

Ellipsometry, an optical technique very sensitive to changes in thickness (d) and index of refraction (n) of thin films, was used in order to obtain additional experimental evidences for the proposed model. For environmental conditions with RH < 80%, the changes in the ellipsometric angles (Δ and ψ) measured for polymeric films were too small, even after 4 h in contact with humidity (Supplementary Information Figure S4). Ellipsometric measurements were successfully performed for PHEMA-300 at 80% RH as a function of time. Figures 6a and 6b show the linear dependence of mean d and n values determined for PHEMA-300 onto Si-wafers as a function of square root of time. Such behavior is typical for Fickian diffusion mechanism, which describes the transport of molecules through matrix without any specific interactions between liquid molecule and polymer matrix. The fitting equations (4) and (5) allow estimating d and n values for 15 min as being 358.5 nm and 1.4536, respectively. The increase in d value corresponds to 1.3% of the initial value, which is due to the swelling. However, it is not possible to correlate directly with the amount of water in the PHEMA layer.

$$d \text{ (nm)} = 353.7 + 1.2389 t^{0.5} \quad (4)$$

$$n = 1.4652 - 0.003 t^{0.5} \quad (5)$$

The swelling degree can be estimated by the changes in the index of refraction of PHEMA layer:

$$n_x = n_{\text{PHEMA}} \varphi_{\text{PHEMA}} + n_{\text{water}} \varphi_{\text{water}} \quad (6)$$

$$\varphi_{\text{PHEMA}} + \varphi_{\text{water}} = 1 \quad (7)$$

where n_x is the index of refraction of a swollen PHEMA layer, n_{PHEMA} and n_{water} stand for the indices of refraction of PHEMA ($n = 1.465 \pm 0.005$) determined just after spin-coating and of distilled water ($n = 1.3334 \pm 0.0005$) determined with an Abbé refractometer at $(24 \pm 1)^\circ\text{C}$, respectively. ϕ_{PHEMA} and ϕ_{water} represent the volume fraction of PHEMA and water in the layer, respectively. Substituting n_x by 1.4536 in equation (6) and combining with equation (7), the ϕ_{water} value of 8.8% was calculated. It corresponds to approximately three fold the amount of water estimated by Δf in Table 1. On the other hand, exposing PHEMA-1000 during 4 h at 80% RH led to changes in order of the accuracy of the ellipsometric measurements ($\Delta \pm 0.1^\circ$ and $\psi \pm 0.05^\circ$), corroborating with the small deflections observed for MC coated with PHEMA-1000. Ellipsometric measurements for PHEMA-20 were not successful because the films became inhomogeneous (Supplementary Information Figure S3) and the laser beam was scattered from the surface to all directions. The spin-coater environment was conditioned with dried N_2 , so that just after spin-coating the short PHEMA-20 chains, particularly those in the uppermost layer, have larger mobility to expose the hydrophobic methyl groups to the low humidity environment (Figure 7a) than the long PHEMA-300 or PHEMA-1000 chains. Upon contact with high RH in the ellipsometric cell, the hydroxyl groups tend to orientate to the humid air (Figure 7b), causing molecular segregation on the surface and creating the morphological inhomogeneity observed (Supplementary Information Figure S3).

It was not possible to monitor the thickness or the index of refraction evolution for any PHEMA films deposited onto PS coated Si wafers by ellipsometry. Either the PHEMA films dewetted or became too inhomogeneous (Supplementary Information Figure S3).

The limitations of ellipsometry in comparison to the detection of nanomechanical response are the (i) low optical contrast between SiO_2 and PHEMA, which restricted the experiments to substantial swelling common to high RH levels and (ii) films inhomogeneity. Thus, MC sensors are advantageous because physical changes in the polymeric films can be detected in a much shorter period of time and in a broad RH range, regardless the film morphology.

4. Conclusions

Microcantilevers sensors are excellent sensors of physical surface phenomena and have great potential as a sensitive tool for the rapid characterization of thin films of diverse materials. We have studied systematically the swelling and deswelling behavior of PHEMA films with three different average molecular masses deposited onto bare MCs or onto

polystyrene (PS) coated MCs by monitoring the deflections resulting from differential surface stress under humidity cycles. We observe that PHEMA swelling tended to increase exponentially with the decrease of molecular weight, since short polymer chains have higher degree of freedom than long polymer chains. Ellipsometric measurements evidenced the swelling behavior of PHEMA-300 films under 80% RH as Fickian diffusion. However, due to the weak optical contrast or film homogeneity shorter or longer chains than PHEMA-300 could not be investigated by ellipsometry. Dewetting of PHEMA films deposited onto PS surfaces also impeached the ellipsometric studies. Therefore, in comparison to ellipsometry, monitoring swelling behavior of PHEMA by nanomechanical responses proved to be faster and less restricted.

5. References

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Figure Captions

Scheme 1 - Main operation modes of nanomechanical sensors: (a) static mode, this mode can be designed to follow the mechanical response in real time and (b) dynamic mode.

Figure 1 – Bright field images of polymer films prepared by spin-coating onto microcantilevers (a) PS, (b) PHEMA-20, (c) PHEMA-300, (d) PS/PHEMA-300 and (e) PHEMA-1000.

Figure 2 – Scheme of the experimental setup used for the experiments. The MC chip is mounted in a 2D voice-coil actuator for the displacement of the chip in the X and Y axis direction. The out-of-plane displacement of the mechanical system is along the Z axis. The incident laser beam is oriented orthogonally to the reflected laser beam and with one axis in the X-Z plane. The system is also an environmental chamber and automated RH and temperature control.

Figure 3 – Microcantilever response to humidity cycle of 15 min: (a) PS, PHEMA-20, PHEMA-200, PHEMA-1000 and (b) PHEMA-300, PS/PHEMA-300, PS. (c) PHEMA-300 coated MC response to humidity cycles of 8 min, 15 min and 60 min. PS covered MCs were used as reference sample due to its hydrophobicity.

Figure 4 - Dependence of (a) microcantilever frequency shift (Δf) and (b) relative mass increase values on PHEMA molecular weight due to an increase on the relative humidity (R.H.). The MC resonance frequency was determined at 80 % R.H. and at 0 % R.H.

Figure 5 – Scheme of the arrangement of interfacial water layer and polymer chain length at high and low R.H. when (a) PHEMA thin film was deposited onto a hydrophilic substrate (SiO_2) and (b) PHEMA thin film was deposited onto a hydrophobic substrate (PS). The gray rectangle represents the silicon microcantilever, the blue cycles are the water molecules, the green lines are represents the polymer PHEMA film and the orange line is the PS.

Figure 6 – Dependence of mean (a) thickness, d , and (b) index of refraction, n , as a function of square root of time determined for PHEMA-300 at 80 % R.H. and $(24 \pm 1)^\circ\text{C}$.

Figure 7 – Schematic representation of orientation of methyl and hydroxyl groups of PHEMA at (a) low R.H. and (b) high R.H.

Table 1 - Difference in surface stress between the upper and lower sides of the MCs calculated using eq. (1) for maximal Δz , $\Delta\sigma_{\max}$; the relative frequency shift (Δf) which is the difference between the resonance frequency determined at 80 % RH and at 0 % RH; relative mass increase determined with Δf and eq. (2).

Coating	$\Delta\sigma_{\max}$ (N/m)*	Δf (kHz)	Relative mass increase (%)	Thickness (nm)
PHEMA-20	10 ± 1	$-(0.20 \pm 0.03)$	5.1 ± 0.8	106 ± 4
PHEMA-300	7 ± 1	$-(0.13 \pm 0.02)$	3.2 ± 0.4	220 ± 14
PS/PHEMA-300	0.9 ± 0.3	$-(0.12 \pm 0.04)$	2.9 ± 0.6	207 ± 10
PHEMA-1000	1.4 ± 0.3	$-(0.06 \pm 0.01)$	1.5 ± 0.4	233 ± 17
PS	0.004 ± 0.003	$-(0.003 \pm 0.002)$	0.09 ± 0.06	223 ± 15

*calculated for the maximal Δz , $E = 160$ GPa, $\nu = 0.22$, $L = 400$ μm and $h = 1.0$ μm .

Temperature was kept constant at (25 ± 1) °C.

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Accepted Manuscript

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Scheme 1

(a) Static mode

Cantilever deflection – Real time

(b) Dynamic mode

Added mass

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 7

(a)

Low RH

(b)

High RH