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The Influence of Annealing on Optical and Humidity Sensing Properties of Poly(Vinyl Alcohol-Co-Vinyl Acetal) Thin Films †

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Abstract: Hydrophobically modified poly(vinyl alcohol)s of varied copolymer composition were tested as active media for optical sensing of humidity. Copolymer thin films were deposited on silicon substrate using water-methanol solution in a volume ratio of 20:80 and concentration of 1 wt%. Films were subjected to low (60 °C) and moderate (180 °C) temperature annealing in order to study the temperature influence on optical and humidity sensing properties. Refractive index, extinction coefficient along with thickness of the films were determined by non-linear minimization of the goal function comprising measured and calculated reflectance spectra at normal light incidence. The humidity sensing ability of the films was studied through reflectance measurements at different humidity levels in the range 5–95 %RH. The influence of temperature annealing on optical and sensing properties was demonstrated and discussed.

Keywords: thin films; poly(vinyl alcohol) copolymers; humidity; optical sensing

1. Introduction

A review of the health effects of relative humidity (RH) in indoor environments suggests that relative humidity can affect the incidence of respiratory infections and allergies [1,2]. Experimental studies have shown that by exposure to relative humidity between 40% and 70% the survival of airborne viruses and infectious bacteria is minimized. Epidemiological studies have examined the relationship between the number of respiratory infections and the relative humidity in people homes, offices and schools and have shown that the number of respiratory infections is lower among people working or living in medium-humidity environments than people in high or low relative environments humidity. One of the most important findings from the 1960s is that for the wound healing process to accelerate, the wound should be kept moist. Since then, the moisture of the wound is made a key parameter in the development of patches [3]. However, further advancement in wound monitoring and management requires improvements in personalized medicine and also more availability of diagnostic tests, parameters and data to facilitate wound management decisions. This should be established with easy-to-use sensors for humidity for the medical staff or otherwise these diagnostic parameters will not be available for clinical decisions.

Traditional humidity sensors are based on the electrical measurement and suffer from high working temperature, lack of selectivity and relatively low accuracy due to the cross-temperature feature. Optical sensing, where detection is based on change of color in response to particular analyte, offers simple and power saving method. Various measuring methods have been developed that operate on different basis. For example - holographic grating, fibre-optic technology, surface plasmon resonance, photonic crystals, Fabry-Perot resonances, etc. Great variety of materials that change their refractive index, extinction coefficient or thicknesses are implemented as sensitive media [4–6] but polymers are a material that stands out. Their qualities like easy deposition in form of thin films and relatively low cost, tailored functionality and fast response due to the short diffusion path length [7] makes them extremely suitable for implementation as active media in easy-to-use color sensor for humidity.

We have already shown in our previous work that chemical structure and composition, as well as macromolecular architecture of the copolymers plays a crucial role in their optical and humidity-sensing behavior [8]. Varying the copolymer characteristics was demonstrated to influences both the sensitivity and hysteresis level of thin polymer films when exposed to humidity. In attempt to continue the development in the field and to expand the range of polymer structures studied for optical sensing application poly(vinyl alcohol) (PVA) was selected as hydroxyl-functionalized building block based on its valuable physico-mechanical and film-forming properties. In the literature, a number of papers report on the application of PVA-based composite films as active media for humidity sensing [9–12], but to the best of our knowledge PVA copolymers were not tested in optical sensors. We have already shown that films of poly(vinyl alcohol-co-vinyl acetal)s of varied copolymer compositions annealed at 60^{o}C can be used as active media for optical sensing of humidity [13]. The comparison with pure PVA thin films confirms the positive influence of acetal fraction in the copolymer on sensing properties.

In this paper, humidity sensing properties of hydrophobically modified PVA copolymers, namely poly(vinyl alcohol-*co*-vinyl acetal)s used in a form of nanometer-sized thin films deposited on Si substrates by spin-coating method are further studied. Samples are thermally treated in air at two different temperatures—60 °C and 180 °C. The influence of annealing temperature on the optical and humidity sensing properties of the thin films obtained from copolymers with different degree of acetalization is investigated.

2. Materials and Methods

Hydrophobically modified PVA copolymers were synthesized by reacting a portion of hydroxyl groups of PVA (average polymerization degree 1600) with acetaldehyde in aqueous solution as already described elsewhere [13]. The copolymer composition was controlled by PVA-to-acetaldehyde molar ratio and determined by ^{1}H NMR spectroscopy. Four different samples of poly(vinylalcohol-*co*-vinylacetal) (PVA-Ac) with increasing acetal groups content were obtained. The copolymers were labeled PVA-Ac18; PVA-Ac19; PVA-Ac24; PVA-Ac28, where the number in the code denoted the mole percent of acetal groups in the copolymer composition.

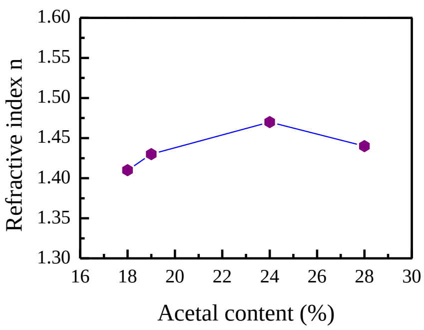
Polymers thin films of PVA and with different acetal content were deposited on silicon substrate using water-methanol solution in a volume ratio of 20:80 and concentration of 1 wt% (2 wt% for pure PVA). Thin polymer films were deposited by spin-coating method (speed 4000 rpm, time 60 s) using 0.250 mL of the solution and annealed at 180 °C for 30 min in air.

All films have thickness *d* around 70 nm, calculated using previously developed two-stages nonlinear curve fitting method using measured reflectance spectra with UV-VIS-NIR spectrophotometer (Cary 5E, Varian) [14]. Refractive index *n* and extinction coefficient *k* of the films were calculated also by using the same method and sensing properties of the films were studied by measuring reflectance spectra at low and high levels of relative humidity (from 5 % to 95 % RH). Humidity sensing experiments were conducted by using homemade bubbler system that generates vapors from liquids and cell with humidity sensor integrated in it [15].

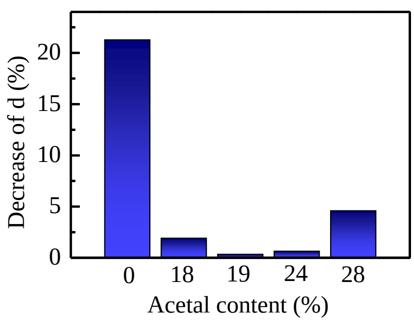
3. Results and Discussion

Figure 1a shows refractive index values of thin films of poly(vinyl alcohol-co-vinyl acetal)s as a function of the acetal content. It is seen that the values of *n* are in the range 1.41-1.47 with the highest value of 1.47 observed for the sample of acetal content of 24 %. So in this case, the highest *n* is observed for the copolymer of intermediate modification degree, unlike samples annealed at 60 °C, in which case the refractive index was found to decrease gradually with increasing acetal content [13].

Figure 1b shows the percentage decrease in thickness of films annealed at 180°C compared to films annealed at 60 °C [13]. From the calculated values it can be seen that the thicknesses of all films decrease when they are annealed at 180 °C. It is seen that the increase in temperature has the strongest effect on the pure PVA sample—21.3% decrease of *d*. For other acetal containing films, the change of *d* is within the range of 0 to 5%, with the smallest change—1.47% and 1.43%—in thickness for films with acetal content 24% and 19%, respectively. This could be explained with the high inter- and intra-molecular hydrogen bonding capability of PVA and its increased crystallinity upon heating above the glass transition temperature and subsequent cooling. The hydroxyls of the PVA chains are small enough to fit into the lattice whereas the presence of bulkier acetal rings hampers the copolymer chain ordering depending on the degree of acetalization.



(**a**)



(**b**)

Figure 1. Refractive index at wavelength of 600 nm of poly(vinyl alcohol-*co*-vinyl acetal)s thin films annealed at 180 °C as a function of the acetal content (**a**); Decrease of thickness *d*(%) for poly(vinyl alcohol-*co*-vinyl acetal) thin films with varied acetal content (0–28%) when the annealing temperature is increased from 60 °C to 180 °C (**b**).

The suitability of polymer films for optical humidity sensing was studied by monitoring the change of reflectance signal of the film with change of the relative humidity from 5 to 95 %RH and vice versa (the curves are not shown here). Usually curves measured for increasing and decreasing humidity exhibit difference, called hysteresis, that is unwanted properties because in that case the measured values of the same levels of humidity will be different depending on whether the humidity decreases or increases. For comparative purposes the percentage of hysteresis *H* was calculated as:

$$H(\%) = \frac{max|R_{up}-R_{down}|}{\Delta R_{max}} . \frac{\Delta RH_{hyst}}{\Delta RH} . 100, \quad (1)$$

where R_{up} and R_{down} are reflectance values measured for increasing and decreasing humidity, respectively, ΔR_{max} is the reflectance change in the whole range ΔRH of measured humidity and ΔRH_{hyst} is the humidity range where hysteresis is observed.

Recently, on the basis of the calculated values of *H* for samples annealed at 60°C it was concluded that thin films of pure PVA annealed at 60 °C are not suitable for optical sensing of humidity because of very high hysteresis levels [13]. The comparison of values of *H* for samples annealed at both temperatures is presented on Figure 2. It is seen that with increasing of annealing temperature there is an improvement in hysteresis for PVA, PVA-Ac18 and PVA-Ac28 (magenta arrow) and a deterioration for PVA-Ac19 and PVA-Ac24 (green arrow). The most significant improvement is obtained for pure PVA films. Interestingly, there is a correlation between the thickness change due to annealing at 180 °C and the degree of hysteresis improvement. A decrease of *H* is observed exactly for thin films with a greater thickness change: PVA, PVA-Ac18 and PVA-Ac28 (Figure 1). While in both films PVA-Ac19 and PVA-Ac24 exhibiting minimum decrease in thickness (), even deterioration of hysteresis is observed (green arrow). It is seen from Figure 2 that from all samples tested and annealed at 60 °C and 180 °C, the lowest percentage of hysteresis was observed for samples PVA-Ac18 annealed at 180 °C and PVA-Ac24 annealed at 60 °C. It is clear from here that the annealing at 180 °C has the strongest influence on the hysteresis percentage on the pure PVA (0% acetal content) film.

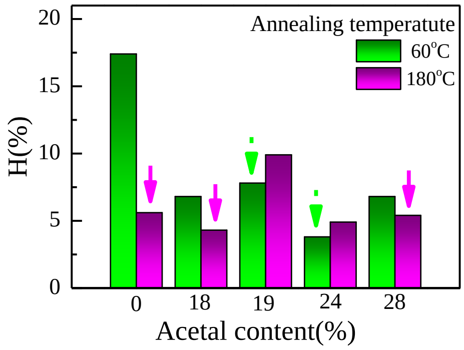


Figure 2. The percentage of hysteresis *H* (%) as a function of acetal content in the polymer films for samples annealed at 60 °C (green column) [13] and 180 °C (magenta column).

4. Conclusions

The optimization of humidity sensing abilities of thin films from hydrophobically modified PVA copolymers through annealing at temperature of 180 °C is demonstrated. The comparison with films annealed at low temperatures (60 °C) shows a decrease of the degree of hysteresis for films with acetal content of 0, 18% and 28% mostly pronounced for neat PVA films (0% acetal content). The observed enhancement correlates with the degree of volume reduction of the films due to annealing: the highest shrinkage of the film leads to the highest decrease in hysteresis percentage. Generally, the most suitable poly(vinyl alcohol-co-vinyl acetal) films for optical sensing of humidity are those modified with 18% and 24% of acetal annealed at 180 °C and 60 °C, respectively.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Arundel, A.V.; Sterling, E.M.; Biggin, J.H.; Sterling, T.D. Indirect health effects of relative humidity in indoor environments. *Environ Health Perspect* **1986**, *65*, 351–361.
2. Strelec, R.P.; Ivanišić, I.; Jurković, V.; Jurković, Z.; Ugarčić-Hardi, Ž.; Sabo, M. Influence Of Temperature And Relative Humidity On Grain Moisture, Germination And Vigour Of Three Wheat Cultivars During One Year Storage. *Poljoprivreda* **2010**, *16*, 20–24.
3. Gomez, D.; Morgan, S.P.; Hayes-Gill, B.R.; Correia, R.G.; Korposh, S. Polymeric optical fibre sensor coated by SiO2 nanoparticles for humidity sensing in the skin microenvironment. *Sensors and Actuators, B: Chemical* **2018**, *254*, 887–895.
4. Zhang, J.; Zhong, J.; Fang, Y.; Wang, J.; Huang, G.; Cui, X.; Mei, Y. Roll up polymer/oxide/polymer nanomembranes as a hybrid optical microcavity for humidity sensing. *Nanoscale* **2014**, *6*, 13646–13650.

5. Naydenova, I.; Jallapuram, R.; Toal, V.; Martin, S. A visual indication of environmental humidity using a color changing hologram recorded in a self-developing photopolymer. *Appl Phys Lett* **2008**, *92*, 031109.
6. Naydenova, I.; Grand, J.; Mikulchyk, T.; Martin, S.; Toal, V.; Georgieva, V.; Thomas, S.; Mintova, S. Hybrid Sensors Fabricated by Inkjet Printing and Holographic Patterning. *Chemistry of Materials* **2015**, *27*, 6097–6101.
7. Wei, M.; Gao, Y.; Li, X.; Serpe, M.J. Stimuliresponsive polymers and their applications. *Polym. Chem.* **2017**, *8*, 127–143.
8. Lazarova, K.; Vasileva, M.; Ivanova, S.; Novakov, C.; Christova, D.; Babeva, T. Influence of Macromolecular Architecture on the Optical and Humidity-Sensing Properties of Poly(N,N-Dimethylacrylamide)-Based Block Copolymers. *Polymers* **2018**, *10*, 769.
9. Khanikar, T.; Singh, V.K. PANI-PVA composite film coated optical fiber probe as a stable and highly sensitive pH sensor. *Optical Materials* **2019**, *88*, 244–251.
10. Mahapure, P.D.; Aiyer, R.C.; Gosavi, S.W.; Adhyapaka, P.V.; Amalnerkara, D.P. Studies on self supported film of PMMA, PMMA-PVA and PMMA-(PVAAg) nano composite for highly linear response over wide range of humidity. *1st International Symposium on Physics and Technology of Sensors (ISPTS-1)* **2012**, 244-248.
11. Zhao, Y.; Tong, R.J.; Chen, M.Q.; Xia, F. Relative humidity sensor based on hollow core fiber filled with GQDs-PVA. *Sensors and Actuators B: Chemical* **2019**, *284*, 96–102.
12. Cajlakovic, M.; Lobnik, A.; Werner, T. Stability of new optical pH sensing material based on cross-linked poly(vinyl alcohol) copolymer. *Analytica Chimica Acta* **2002**, *455*, 207–213.
13. Lazarova, K.; Bozhilova, S.; Christova, D.; Babeva, T. Poly(vinyl alcohol)– based thin films for optical sensing of humidity. *J. Phys.: Conf. Ser.* ***2019***, submitted.
14. Lazarova, K.; Vasileva,M.; Marinov, G.; Babeva, T. Optical characterization of sol-gel derived Nb2O5 thin films. *Opt. Laser Technol.* **2014**, *58*, 114–118.
15. Lazarova, K.; Awala, H.; Thomas, S.; Vasileva, M.; Mintova, S.; Babeva, T. Vapor responsive one-dimensional photonic crystals from zeolite nanoparticles and metal oxide films for optical sensing. *Sensors* **2014**, *14*, 12207–12218.