# The influence of annealing on optical and humidity sensing properties of poly(vinyl alcohol-co-vinyl acetal) thin films

# Authors

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# Introduction

## Why humidity?

- ✓ Relative humidity can affect the incidence of respiratory infections and allergies.
- ✓ By exposure to relative humidity between 40% and 70% the survival of airborne viruses and infectious bacteria is minimized.
- ✓ For the wound healing process to accelerate, the wound should be kept moist - the moisture of the wound is made a key parameter in the development of patches.
- ✓ Atmospheric humidity affects the sense of comfort and is also an important parameter for ensuring optimum exploitation of warehouses for food and non-food goods, building materials, museum artifacts, etc.

## Why optical sensing?

- ✓ 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 of the thin film for example in response to particular analyte, offers simple and power saving method.

# Introduction

## Why polymers?

Great variety of materials that change their refractive index, extinction coefficient or thicknesses are implemented as sensitive media but polymers are a material that stands out.

Easy deposition in form of thin films

Relatively low cost

Tailored functionality

Fast response due to the short diffusion path length

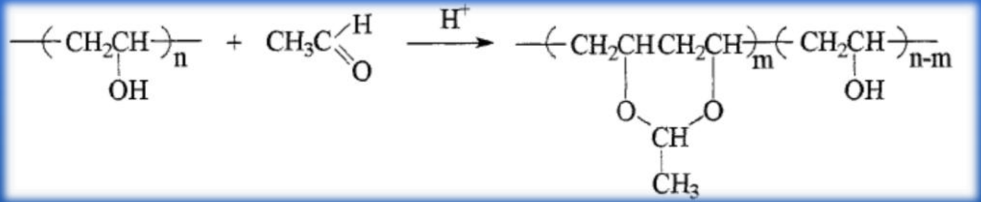
## What we do?

✓ Hydrophobically modified PVA copolymers, namely poly(vinyl alcohol-*co*-vinyl acetal)s, are synthesized and used in a form of nanometer-sized thin films deposited on Si substrates by spin-coating method.

✓ 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.

# Copolymer synthesis



- Poly(vinylalcohol-co-vinylacetal)s of varied copolymer composition were synthesized at mild reaction conditions in aqueous media at 30°C [1].
- The copolymer composition was controlled by PVA-to-acetaldehyde molar ratio.

- Obtained poly(vinylalcohol-co-vinylacetal)s are smart materials exhibiting reversible phase transition in aqueous solution with increasing temperature.
- The higher the acetal content, the higher the hydrophobicity and the lower the phase transition temperature, respectively.

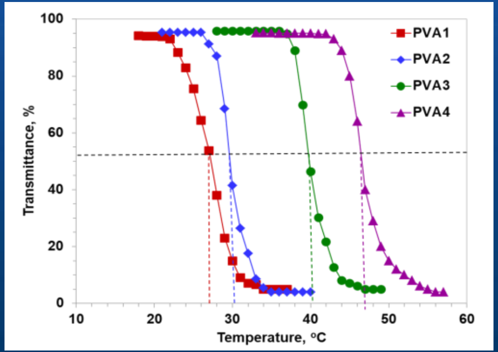
**References: [1] D. Christova, S. Ivanova, G. Ivanova, Polymer Bulletin, 50, 367-372 (2003).**

# Copolymer characterization

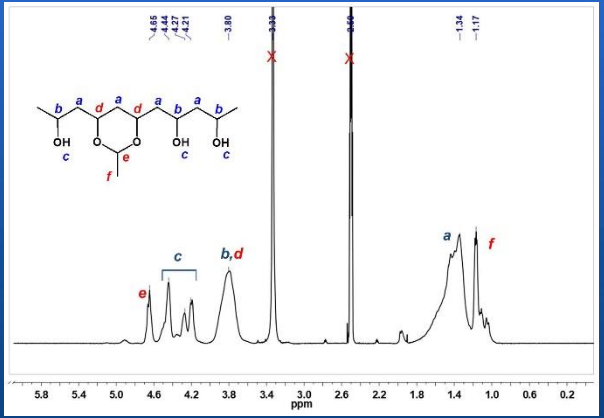
Poly(vinylalcohol-co-vinylacetal)s based on poly(vinyl alcohol) of M.W. 72000 (Fluka)

| Code | Acetal content, % (NMR) | $T_{cp}$ in water, °C (UV-VIS) | Increasing hydrophobicity |
|---|---|---|---|
| **PVA-Ac28** | 28 | 27 | |
| **PVA-Ac24** | 24 | 30 | |
| **PVA-Ac19** | 19 | 40 | |
| **PVA-Ac18** | 18 | 48 | |
| **PVA** | - | - | |

Clouding curves of the obtained co-polymers registered in transmittance mode at 500 nm.




$^1$H NMR spectrum of PVA4 (solvent DMSO-$d_6$)



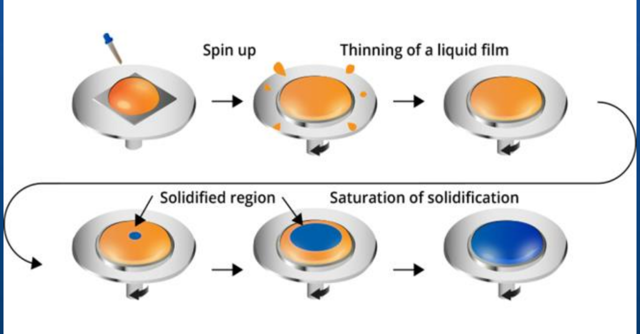

Copolymer composition, i.e. acetal content was calculated by comparing the area of the peak assigned to the methine protons (e) from the acetal group to those assigned to the methine protons in the PVA main chain (b+d).

# Thin film deposition

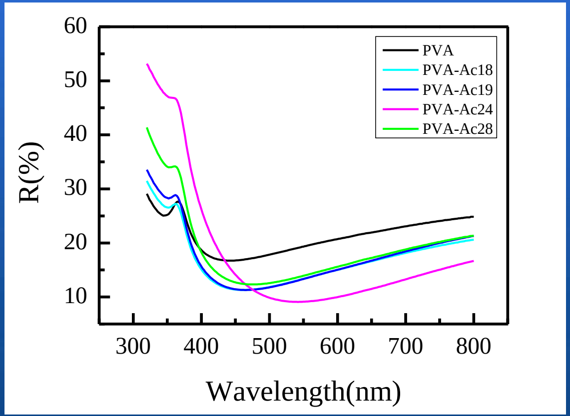
Thin polymer films with approximate thickness of 80 nm were deposited on silicon substrates by the method of spin coating using 0.250 ml of 1 wt% solution of polymers in 80:20 volume ratio of methanol-to-water solvent.

In the case of PVA film a 2 wt% aqueous solution is used in order to obtain films with similar thickness.

- **Spin coating: 0.250 ml drop, speed - 4000 rpm, time - 60s**
- **Postdeposition annealing: 30 min in air, *T* = 60°C and 180°C**
- **Substrates: Si-wafer**
- **Thickness: all films have thickness around 80 nm**



# Optical characterization of thin films




Reflectance spectra of poly(vinyl alcohol-*co*-vinyl acetal)s thin films with different acetal content annealed at 180°C.

- Reflectance spectra of the films were measured at normal light incidence in the spectral range 320-900 nm using UV-VIS-NIR spectrophotometer (Cary 5, Varian).

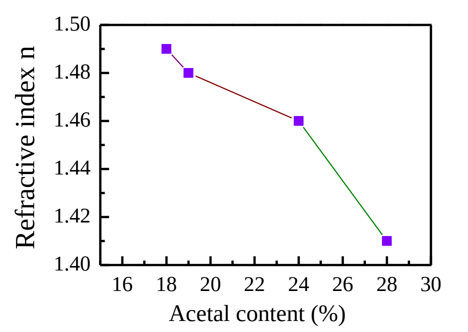
- Spectra were further used for determination of refractive index, *n*, extinction coefficients, *k* and thickness, *d* of the films through nonlinear curve fitting calculating procedure [2].


**References: [2] Lazarova K, Vasileva M, Marinov G and Babeva T 2014 Optics & Laser Technology 58 114.**

# Optical characterization of thin films

60°C

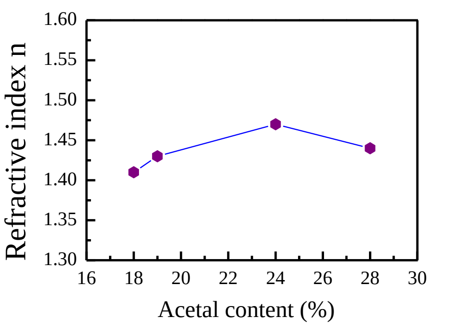
The refractive index of samples annealed at 60°C decreases with increasing acetal content.




Refractive index at wavelength of 600 nm of poly(vinyl alcohol-*co*-vinyl acetal)s thin films annealed at 60°C as a function of the acetal content.

180°C

The highest value of the *n* (1.47) is observed when acetal content is 24 and for the other samples values of *n* are lower, in range 1.41-1.43.

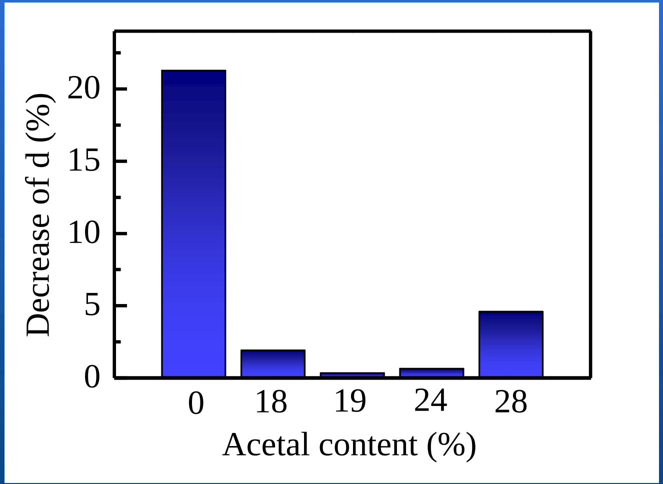



Refractive index at wavelength of 600 nm of poly(vinyl alcohol-*co*-vinyl acetal)s thin films annealed at 180°C as a function of the acetal content.

# Characterization of thin films

From the calculated values of the thickness it can be seen that the thicknesses of all films decrease when they are annealed at 180oC. 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 smallest change – 1.47% and 1.43% - in thickness for films with acetal content 24% and 19%, respectively.




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$^{o}$C to 180$^{o}$C

# Humidity sensing experiments

- The suitability of polymer films annealed at both temperatures 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.
- 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

Sensitivity (%/%RH)

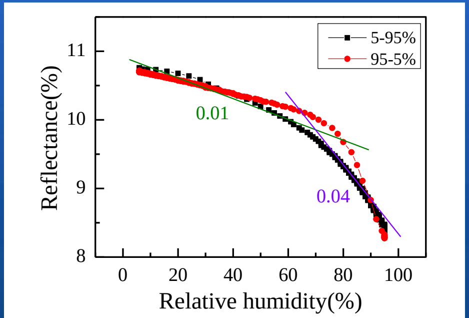
$$S = \frac{\Delta R}{RH_2 - RH_1}$$

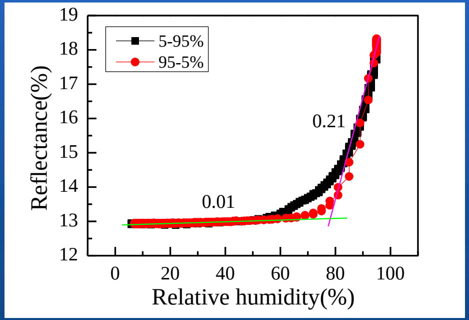
$\Delta R$ - change in Reflectance for variation of relative humidity from $RH_1$ to $RH_2$

60°C

PVA-Ac18

180°C



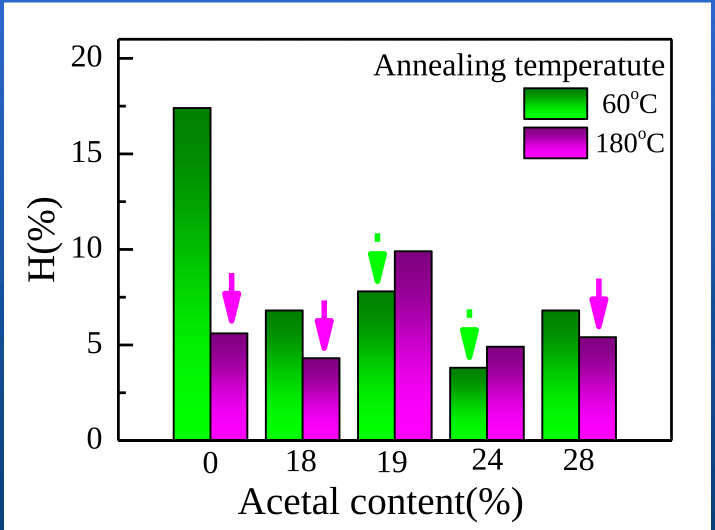




S=0.04

S=0.21

Sensitivity improvement at relative humidity above 60% is observed.

# Humidity sensing experiments




Percentage of Hysteresis H (%)

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

**60°C**

- ✓ The most suitable film for humidity sensing is the copolymer film with acetal content of 24 % because it has the smallest hysteresis and the highest sensitivity in the widest humidity range.

**180°C**

- ✓ Annealing at 180°C has the strongest influence on the hysteresis percentage on the pure PVA (0% acetal content) film.
- ✓ The copolymer film with acetal content of 18 % has the smallest hysteresis.

# Summary

1. Poly(vinyl alcohol-co-vinyl acetal)s of varied hydrophilic-hydrophobic balance are synthesized by reacting poly(vinyl alcohol) (PVA) with acetaldehyde in aqueous solution thus introducing cyclic acetal functionalities in the polymer chain.

2. Obtained poly(vinylalcohol-co-vinylacetal)s exhibit reversible phase transition in aqueous solution with increasing temperature. The higher the acetal content, the higher the hydrophobicity and the lower the phase transition temperature, respectively.

3. Thin polymer films are spin-coated successfully on silicon substrates using methanol-water solution in a volume ratio of 80:20 and concentration of 1 wt%.

4. Decrease of thickness *d*(%) is observed for all poly(vinyl alcohol-*co*-vinyl acetal) thin films when the annealing temperature is increased from 60$^{o}$C to 180$^{o}$C, most pronounced for pure PVA.

5. Refractive index decreases with increasing of hydrophobicity for films annealed at 60$^{o}$C. For thin films annealed at 180$^{o}$C the highest $n$ is observed for the acetal content 24%.

6. From all samples tested and annealed at 60$^{o}$C and 180$^{o}$C, the lowest percentage of hysteresis was observed for samples with acetal content 18 % annealed at 180 $^{o}$C and acetal content 24 % annealed at 60°C.

7. The annealing at 180$^{o}$C has the strongest influence on the hysteresis percentage on the pure PVA (0% acetal content) film.

# Thank you
# for
# the attention!

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