Poly(vinyl alcohol)-based thin films for optical humidity sensing

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Abstract. The optical and humidity-sensing properties are studied of hydrophobically modified PVA, namely poly(vinyl alcohol-co-vinyl acetal)s of varied copolymer composition. Copolymers are synthesized by reacting PVA with acetaldehyde in aqueous solution, thus introducing cyclic acetal functionalities in the polymer chain. Thin polymer films are deposited by spin-coating and their optical properties are studied as a function of the copolymer composition, i.e., degree of acetalization. Reflectance measurements at different relative humidities in the range 5 – 95 % RH are conducted in order to probe the sensing behavior. The comparison with neat PVA thin films confirms the influence of the copolymer’s acetal fraction on the optical and sensing properties and degree of hysteresis. The feasibility of applying poly(vinyl alcohol-co-vinyl acetal) thin films for optical sensing of humidity is demonstrated and discussed.

1. Introduction
The accurate monitoring of humidity is essential in many areas, for example, in industry, where the quality of products is influenced significantly by the humidity, in museums or archives to preserve valuable artworks, and in office and residential buildings to secure comfortable and healthy environment. Thus, the need has arisen of developing sensitive humidity sensors working in a wide humidity range [1, 2]. Different materials and sensing schemes have already been implemented having various sensitivities and dynamic ranges [3, 4]. The ideal humidity sensor should work in a wide range of relative humidity, have a high sensitivity, and lack hysteresis. Being inexpensive, environmentally friendly and easily processable would be serious additional advantages of the sensitive material. The use of polymers instead of inorganic materials brings about the advantage of easy processability and mechanical flexibility [5].

Poly(vinyl alcohol) (PVA) is a water-soluble synthetic polymer widely used in various industrial fields, and in biotechnology and medicine. It is well known for its excellent film-forming ability and good adhesion to a variety of surfaces. PVA films possess remarkable mechanical and physical properties and could be used in a thin-film form on different substrates. PVA has been already used for sensing relative humidity through optical fibers [6,7]. To the best of our knowledge, hydrophobically-modified PVA copolymers have not been investigated as thin films for optical sensing of humidity.

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In this paper, we present a study of thin films of poly(vinyl alcohol-co-vinyl acetal)s of varied copolymer compositions regarding their applicability as active media for optical sensing of humidity. The comparison with neat thin PVA films confirms the positive influence of the acetal fraction in the copolymer on the sensing properties and degree of hysteresis. The feasibility of using poly(vinyl alcohol-co-vinyl acetal) thin films in optical sensing of humidity is demonstrated and discussed.

2. Experimental part
The poly(vinyl alcohol-co-vinyl acetal)s used in this work were synthesized according to a procedure described elsewhere [8]. In brief, a chosen amount of acetaldehyde was added dropwise to an aqueous PVA solution thermostated at 15 °C. The reaction was let to proceed under vigorous stirring at 30 °C for four hours. The copolymer obtained was isolated from the solution by precipitation at 60 °C, purified by several dissolution-precipitation cycles in deionized water, and finally dried in vacuum at 60 °C. A series of poly(vinylalcohol-co-vinylacetal)s of controlled copolymer composition were synthesized by varying the PVA-to-acetaldehyde molar ratio. The copolymer composition, i.e. the content of acetal groups, was determined by 1H NMR spectroscopy and is shown in table 1 along with the cloud points \( T_{\text{CP}} \) of 5 wt % polymer solutions in water. The latter parameter was determined from the transmittance curves of the solutions registered at the wavelength of 500 nm as a function of temperature. The higher the acetal content, the higher the hydrophobicity of the copolymer and lower the \( T_{\text{CP}} \).

| Code  | Acetal content (%) | \( T_{\text{CP}} \) (°C) | Increasing hydrophobicity |
|-------|--------------------|--------------------------|--------------------------|
| PVA1  | 28                 | 27                       |                          |
| PVA2  | 24                 | 30                       |                          |
| PVA3  | 19                 | 40                       |                          |
| PVA4  | 18                 | 48                       |                          |

Thin polymer films with an approximate thickness of 80 nm were deposited on silicon substrates by spin coating using 0.250 ml of 1-wt % of polymer solution in an 80:20 volume ratio of methanol-to-water solvent. In the case of the PVA film, a 2-wt % aqueous solution was used to prepare films with a similar thickness. The reflectance spectra of the films were measured at normal light incidence in the 320 – 900 nm spectral range using a UV-VIS-NIR spectrophotometer (Cary 5, Varian) and were further used to determine the refractive index, \( n \), extinction coefficient, \( k \), and thickness, \( d \), of the films through a nonlinear curve-fitting calculating procedure [9]. To probe the sensing ability of the films studied, they were placed in a measuring cell, and the reflectance signal at a fixed wavelength was monitored with the relative humidity (RH) being gradually changed from 5 to 95 % RH. The humidity in the cell was varied by using a homemade bubbler system that generates vapors from liquids [10]. The exact RH values were obtained from a reference humidity sensor placed in the measuring cell.

3. Results and discussion
As seen in table 1, increasing the acetal content reduces the cloud point. This means that as the hydrophobicity is increased, the phase separation occurs at lower temperatures. Although this property is intrinsic to a polymer solution in water, it may be expected that the optical properties of the deposited films and their sensing capabilities would also depend on the acetal content and the degree of hydrophobicity, respectively.

Figure 1 presents the refractive indices of the films studied. As seen, both the values of \( n \) and the shape of the dispersion curves change with the acetal content. The refractive index increases with the increase in the cloud point, which means that the hydrophobic films have a lower refractive index. Further, the dispersion becomes stronger for films with increased acetal content, which can be
associated with the hydrophobic films’ narrower band gap. Considering that the refractive index is related to the density, structure and polarizability of the films, it may be expected that the different films would exhibit different humidity response.

In order to study the suitability of the polymer films for humidity sensing, we measured the reflectance spectra of the films exposed to low (5 % RH) and high (95 % RH) relative humidity and determined the films’ optical constants and thickness. The exposure from low to high humidity leads to an increase of the films thickness because the polymer chains swell when humidity penetrates the polymer film. Simultaneously, the refractive index drops due to the reduced density of the films.

Figure 2(a) presents the thickness variation of the films studied when exposed to humidity from 5 % to 95 % RH. As the acetal content increases and the films become more hydrophobic, the humidity-induced changes in their thicknesses decrease. The highest thickness change of 44 % is obtained for the PVA film that is the most hydrophilic sample. To explore further the suitability of PVA for optical humidity sensing, we monitored the reflectance signal of the film when the relative humidity was changed gradually from 5 % to 95 % RH. The two curves registered for increasing and decreasing humidity are shown in figure 2(b). It is seen that the difference between the two curves, the so-called hysteresis, is very strong. This means that the sensor will measure different humidity values depending on whether the humidity increases or decreases. Therefore, the neat PVA is not suitable for optical sensing of humidity.

Figure 3 shows the similar curves of reflectance versus relative humidity measured for acetal-modified samples. As expected, the modification of PVA affected the sensing properties, especially the degree of hysteresis. The most suitable samples in what concerns their applicability to humidity sensing are PVA1 and PVA2, which exhibited two well-defined linear ranges.

To compare further the samples we defined the percentage of hysteresis parameter \(H\) as:

\[
H(\%) = \frac{\text{max} |R_{\text{up}} - R_{\text{down}}|}{\Delta R_{\text{max}} / \Delta RH_{\text{hy}} \times 100},
\]

where \(R_{\text{up}}\) and \(R_{\text{down}}\) are the reflectance values measured for increasing and decreasing humidity, respectively; \(\Delta R_{\text{max}}\) is the reflectance change in the whole range \(\Delta RH\) of measured humidity; and \(\Delta RH_{\text{hy}}\) is the humidity range where hysteresis is observed.
Figure 3. Reflectance versus relative humidity curves for thin poly(vinyl alcohol-co-vinyl acetal)s films of varied acetal content: (a) 18 %, (b) 19 %, (c) 24 % and (d) 28 % registered for increasing (solid black symbols) and decreasing (open blue symbols) humidity.

The calculated percentage of hysteresis as a function of the acetal content in the films is presented in figure 4(a). It is seen that $H$ decreases with the acetal content reaching the smallest value for the sample PVA2 (24 % acetal content). With the further acetal content increase, the percentage of hysteresis increases. This means that the optimal acetal content is around 24 % and the most suitable sample is PVA2.

To check the applicability of this sample for uses in color humidity sensing, we calculated the CIE color coordinates using the measured reflectance spectra of the sample at low (5 % RH) and high (95 %RH) [11] relative humidity and plotted them on the color scheme (figure 4(b)). It is seen that the two points that represent the colors of PVA2 at low and high humidity are well separated in the color space, thus enabling color sensing of humidity as well.

Figure 4. The percentage of hysteresis calculated by eq. 1 of poly(vinyl alcohol-co-vinyl acetal)s thin films with different composition (a); Color coordinates calculated for PVA2 at 5 % and 95 %RH (b). The polymers are described in Table 1.

4. Conclusions
The suitability is demonstrated of thin films of hydrophobically-modified PVA copolymers for optical sensing of humidity. The comparison with neat PVA film shows improved humidity sensing properties: a decrease of the degree of hysteresis and an increase of dynamic range for acetal modified
films are observed. On the basis of comparing the degree of hysteresis, the optimal value of acetal content in PVA is determined to be around 24%. All films have thicknesses of less than 100 nm, which guarantees fast and reversible sensing of humidity.

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