Chapter V

Fiber optic sensor for determining relative humidity of the environment

5.1 Introduction

Water vapour is a natural component of air and the amount of water vapour in the air is described by the term “humidity.” The mass of water vapour in a given volume of air (i.e. density of water vapour in a given volume, usually expressed in grams per cubic meter) is defined as Absolute humidity while ratio of the percentage of water vapour present in air at a particular temperature to the maximum amount of water vapour the air can hold at that temperature is called relative humidity. It is often expressed as a percentage using the following equation [1]

\[ RH = \frac{P_W}{P_{WS}} \times 100\% \]

where \( P_W \) is the partial pressure of the water vapour and \( P_{WS} \) is the saturation water vapour pressure.

As humidity is a very common, continuously changing component of our environment, the measurement and control of humidity is necessary in a range of areas like air-conditioning, structural health monitoring, horticulture, meteorological services, chemical and food processing industry, paper and textile production, semiconductor manufacturing process etc [1]. The requirements for humidity monitoring may vary according to the application and hence various techniques from the simplest way of exploiting the expansion and contraction of materials such as human hair to the most sophisticated techniques, such as using a miniaturized electronic chip, have been explored over many years to obtain meaningful humidity measurements [1-4].

Generally, humidity sensors can be divided into two major groups namely electronic and optical, those that measure changes in electrical and optical properties of the sensing material upon interaction with moisture. Materials that have been studied for humidity sensing purposes include
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polymer, composite and ceramic, each of which has its own merits and specific conditions of application. Since this subject has been studied for some time, excellent reviews can be found in the literature on the principles and preparation techniques of different humidity sensors [1-4].

Electronic humidity sensors are either capacitive or resistive type which works on the electrical properties of the sensing material. Capacitive humidity sensors consist of a substrate on which a thin film of polymer or metal oxide is deposited between two conductive electrodes. The sensing surface is coated with a porous metal electrode to protect it from contamination and exposure to condensation. The incremental change in the dielectric constant of a capacitive humidity sensor is proportional to the relative humidity (RH) of the surrounding environment. Capacitive sensors are characterized by low temperature coefficient, ability to function at high temperatures (up to 200°C), full recovery from condensation, and reasonable resistance to chemical vapours [2-7]. In capacitive type sensors the distance of the sensing element from the signal conditioning circuitry is limited due to the capacitive effect of the connecting cable with respect to the relatively small capacitance changes of the sensor.

Resistive humidity sensors measure the change in electrical impedance of a hygroscopic medium such as a conductive polymer, salt, or treated substrate. Resistive sensors usually consist of noble metal electrodes either deposited on a substrate by photo resist techniques or wire-wound electrodes on a plastic or glass cylinder. The substrate is coated with a salt or conductive polymer. Alternatively, the substrate may be treated with activating chemicals such as acid. The sensor absorbs the water vapour and ionic functional groups are dissociated, resulting in an increase in electrical conductivity. A distinct advantage of resistive RH sensors is their repeatability, which allows the electronic signal conditioning circuitry to be calibrated by a resistor at a fixed RH point. This eliminates the need for humidity calibration standards and hence resistive humidity sensors are generally field replaceable. In residential and commercial environments, the life expectancy of these sensors is greater than 5 years, but exposure to chemical vapours and other contaminants such as oil mist may lead to premature failure. Another drawback of some resistive sensors is their tendency to shift values when exposed to condensation if a water-soluble coating is used. Resistive humidity sensors have significant temperature
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dependencies when installed in an environment with large (>10°F) temperature fluctuations [2-4,8-10].
The most important specifications to keep in mind when selecting a sensor are accuracy, repeatability, interchangeability, long-term stability, resistance to chemical and physical contaminants, size, packaging, cost effectiveness, field and in-house calibrations, and the complexity and reliability of the signal conditioning and data acquisition (DA) circuitry. Generally electronic sensors are inexpensive and have low power consumption, covering a wide humidity range with good repeatability but suffer from temperature dependency and cross-sensitivities to some chemical species. Their performance is limited owing to their inability to remote and distributed sensing, multiplexing, deployment in harsh environments, and their susceptibility to electromagnetic and radio frequency interference. Fiber optic type sensors can overcome these disadvantages and can be constructed by utilizing the humidity sensitive variation in optical properties of sensor materials. Optical fiber humidity sensors have been already used to facilitate the remote sensing and continuous monitoring of humidity in diverse applications such as the baking and drying of food, cigar storage, civil engineering to detect water ingress in soils or in the concrete in civil structures, medical applications and many other fields [1,11-22]. However, the limitations of the operating range and accuracy of the FO-based humidity sensors are some of the drawbacks which researchers are striving to continue to address.

Various fiber optic sensor techniques based on absorption [16,23,24], fluorescence [25,26], evanescent wave [14,18,21,27-29,30-35], fiber gratings [11-13,36-38] and interferometry [39,40] have been exploited over the years in the design and development of optical fiber RH sensors. Potential materials and chemical reagents like cobalt chloride (CoCl₂) [16,23,41,42], cobalt oxide (Co₃O₄) [43], Rhodamine B [44], titanium dioxide (TiO₂) [22,33,39,45], tin dioxide (SnO₂) [46], silicon dioxide (SiO₂) [20,47], calcium chloride (CaCl₂) [48] etc have been reported based on their humidity-dependent optical absorption properties. Zhou et al. [16] who have demonstrated an in-line absorption-based humidity sensor using a porous optical fiber segment doped with CoCl₂. The use of the absorption characteristics of the same compound contained in a variety of materials such as gelatine and cellulose has also been discussed by various authors
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[41,42]. Tao et al. [23] have demonstrated an active fiber core optical sensor (AFCOS) for humidity detection using an in-line absorption sensing concept. An air-gap design configuration with Rhodamine B (RB) and hydroxypropyl cellulose (HPC) coated fiber tip was reported by Otsuki et al. [44]. Titanium dioxide, also known as titania (TiO$_2$), is the naturally occurring oxide of titanium and has been extensively investigated as a hygrosensitive material for humidity sensing applications. Humidity sensor based on TiO$_2$ overlay on side-polished fiber is reported by Alvarez-Herrero et.al [33]. Depending on the refractive index value of the overlay, the wavelength of the resonance shifts accordingly to fulfill the phase matching condition. This forms the basis of the sensing scheme and the sensor has shown a linear wavelength shift for 0 to 15%RH, with a sensitivity of 0.5 nm/%RH. A fiber optic humidity sensor with a response time of 5 sec and a dynamic range of 20%RH to 80%RH based on the moisture dependence absorption of light by the phenol red doped polymethylmethacrylate (PMMA) film was reported by Gupta et al. [18].

The use of long period fiber grating (LPFG) for humidity sensing was first reported by Luo et al. [49] and in their work carboxymethylcellulose (CMC) hydrogel was covalently attached to cladding of a LPFG to form the humidity sensor. A similar LPFG-based humidity sensing scheme was demonstrated by Tan et al. [37] using a gelatine-coated LPFG and Konstantaki et al. [38] proposed a LPFG humidity sensor utilizing polyethylene oxide (PEO)/CoCl$_2$ hybrid overlay as the moisture sensitive coating. An optical fiber humidity sensor based on LPFG coated with a silicon dioxide (SiO$_2$) nanosphere film was reported by Viegas et al. [20]. Studies by Venugopalan et al. [13,50] have shown the use of polyvinyl alcohol (PVA) film as a sensing material for LPFG-based humidity detection. A long-period fiber grating coated with hydrogel for humidity measurement was developed by LiweiWang et al. [51].

Although various materials are used as humidity sensitive coatings in fiber optic humidity sensors, polymer film based sensors have attracted a great deal of interest due to their inherent advantages. They are compatible with oxides and ceramics, low-cost, flexible, light weight, easily processible and can be used at room temperatures. In general, polymers provide useful mechanical properties to the sensor design and hygroscopic polymers like Poly-aniline [52,53], PVA [13,17,32,50], Chitosan [54,55],
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Polyethyleneoxide [56], PMMA [18], Polyimide (PI) [57], etc., are being used in optical sensors.

Gaston et al. [32] have proposed an evanescent wave type humidity sensor based on a single mode, side-polished fiber with a PVA overlay and got a linear response in the RH range 70% to 90%. The humidity sensitivity of PVA was successfully utilized for the construction of LPFG based humidity sensors [13,50]. The commercial polyimide-recoated FBGs were found to respond linearly over a wide humidity range [57]. The sensor was reported to respond well to a humidity range of 10–90%RH and display good repeatability. Razat Nohria et al. [52] worked on humidity sensors based on ultrathin poly(aniline) film deposited using layer-by-layer nano-assembly. They used layer-by-layer (LbL) nano-assembly for deposition of ultrathin poly(anilinesulfonic acid) (SPANI) films and the change in electrical sheet resistance of the sensing film was monitored as the device was exposed to humidity. In their work on humidity sensors based on polymer thin films, Sakai et al. [59] had explained the humidity sensing behaviour of hydrophilic polymers like poly-(2-acrylamido-2-methylpropane sulfonate) and poly-(2-hydroxy-3-methacyloxypropyi trimethylammonium chloride) impregnated in microporous polyethylene film. A humidity sensor with nanostructure Co dispersed in poly(aniline) deposited as a clad, having quick response of 8 s (20–95%RH) and recovery time of 1 min (95–20%RH) was reported [53]. Effect of changes in relative humidity and temperature on ultrathin chitosan films were studied by Murray et al. [54] while Jinesh et al. [55] was successful in constructing a fiber optic evanescent wave based humidity sensor using chitosan as the clad and macro bend fiber coated with Poly (ethylene oxide) [56].

Chitosan is a natural polysaccharide formed by alkaline deacetylation of the second most abundant naturally occurring chitin of crab and shrimp shells [60]. Since it is inexpensive, non-toxic and possesses potentially reactive amino functional groups, chitosan has been evaluated for numerous applications, including medicine, food, cosmetics and wastewater treatment [61] and has also showed its potential as hygroscopic coating for fiber optic humidity sensor [54,55]. Though the response of the chitosan coated evanescent wave sensor is linear its humidity sensitivity is found to be poor. Poly (vinyl alcohol) is a non-toxic, water-soluble synthetic polymer that has good film forming ability. It has a large number of hydroxyl groups which
allows it to react with many types of functional groups. This advantage makes it suitable for biocompatible materials and has found use in the fabrication of fiber optic humidity sensors [13,17,32,50]. The PVA coated humidity sensor has shown better sensitivity but the operating range is 50% - 90% RH [32].

The humidity sensitivity of polymers depends on the availability of hydrophilic head groups and their degree of swelling. Development of membranes with both sensitivity and mechanical strength has been deemed extremely difficult. The mechanical strength of PVA can be enhanced by acetalization. However, the degree of water absorption is considerably lessened along with the increase in mechanical strength. Therefore, it is extremely difficult to obtain polymer membranes which are satisfactory in water sorbtion and mechanical strength. Addition of chitosan to PVA improves hydrophilic head groups along with the improvement in mechanical strength. If the proportion of chitosan is less than 10%, the beneficial effect achievable by addition of chitosan will be significantly reduced. On the other hand if the proportion becomes more than 60%, any additional effects will hardly be obtained. Moreover chitosan will be leached away in an acidic medium if the membrane is higher in its chitosan content. Chitosan/PVA blend has been found to be miscible in all composition and El-Hefian et.al [62] has shown that the blend with 50% PVA has maximum degree of swelling compared with pure polymers.

It is observed that the presence of metal oxide ions increases the humidity sensitivity of hydrophilic polymers. Khijwania et. al. [19] have reported a RH sensor based on U-shaped probe coated with anhydrous CoCl\textsubscript{2} and PVA. It has a response time of 1 sec with a sensing range of 1.6% RH to 92% RH. Recently an optical fiber humidity sensor based on TiO\textsubscript{2}-nanoparticle doped nanostructured thin film as the fiber sensing cladding was reported by R Aneesh et.al.[22]. Stannic oxide (SnO\textsubscript{2}) nanoparticles suspended polyvinyl alcohol (PVA) matrix was used for humidity sensing by Hatamie et.al. [63]. Enhancement of the humidity-sensing properties of poly(methyl methacrylate) (PMMA) with the addition of alkali salts (KOH and K\textsubscript{2}Co\textsubscript{3}) was reported by Su et.al [64].

In this work we have tried to find out the humidity sensing behavior of PVA-chitosan blend by coating the polymer over an exposed core region of a plastic clad silica fiber. The response of the evanescent wave fiber optic
humidity sensor thus constructed is presented. Also we have tried to improve the sensitivity and operational range by dispersing TiO\textsubscript{2} in the PVA-chitosan blend. The fabricated sensor exhibits good characteristics, such as sensitivity, range and time response.

5.2 Chitosan and PVA

Chitosan is a biopolymer derived primarily from deacetylation of chitin, found in the shells of crustaceans and insects [60,61,65-67]. Structurally, both chitosan and chitin are linear polymers composed of 2-amino-2-deoxy-(1,4)-β-D-glucopyranose with different degrees of N-acetylation, which differentiates them. The molecular structure of chitosan is shown in figure 5.1.

![Molecular structure of Chitosan](image)

Figure 5.1 Molecular structure of Chitosan

Alkali treatment of chitin replaces the acetyl side group on the chitin repeat units with an amine group, converting them to chitosan. The degree of N-acetylation in chitin, is the ratio of 2-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D-glucopyranose structural units. Chitosan is the universally accepted non-toxic N-de acetylated derivative of chitin. In chitin, the acetylated units prevail (degree of acetylation typically 0.90). Chitosan is the fully or partially N-deacetylated derivative of chitin with a typical degree of acetylation of less than 0.35. Thus the percentage of repeat units with acetyl side groups is specified as the degree of acetylation (DA), with pure chitin corresponding to DA-100% and pure chitosan corresponding to DA-0% [65-67]. The degree of deacetylation (DD) is defined as DD=100-DA. Chitosan is insoluble in water at neutral pH but it can be dissolved in weakly
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Acidic aqueous solutions and be made into hydrogels. The hydrogel form of chitosan can absorb up to 2000% of its own weight in water. For applications that require mechanical rigidity and improved stability with respect to changes in relative humidity, it is preferable to convert chitosan to chitin, and this is typically accomplished by exposing the chitosan to acetic anhydride. Unfortunately, the toxic nature of acetic anhydride makes the chemical conversion of chitosan to chitin environmentally unfriendly.

To improve mechanical properties and pursue the wider utilities of chitosan, poly(vinyl alcohol) (PVA) is mixed with chitosan which cause an increase in the Young’s modulus [68]. Poly (vinyl alcohol) (PVA) is a nontoxic, watersoluble, biocompatible, and biodegradable synthetic polymer, which is widely used in biochemical and biomedical applications [69]. PVA is a hydrophilic and good fiber-forming polymer which adsorbs moisture from the environment [32]. The molecular structure of PVA is shown in figure 5.2.

![Molecular structure of poly vinyl alcohol (PVA)](image)

Figure 5.2 Molecular structure of poly vinyl alcohol (PVA)

Blends of chitosan and poly vinyl alcohol (PVA) with good miscibility have been reported to provide good mechanical properties and have biomedical applications [68,70,71]. The schematic of intermolecular and intramolecular hydrogen bonds that occurred after blending PVA with chitosan is shown in figure 5.3.
The fiber used for the sensor element fabrication is a multimode, step index, plastic clad silica fiber of core diameter 400 μm with a numerical aperture of 0.37. In order to have efficient light coupling from the source to the fiber and the fiber to the detector, fiber ends were prepared properly to get optically flat end faces, perpendicular to the axis of the fiber. The ends of the fibers are wet polished with 600-grain sandpaper and alumina powder to maximize the optical power coupling to the fiber probe. Since evanescent wave is to be used, 5 cm length of the cladding was removed from the central portion of the fiber.

Since the optic fiber is immune to the relative humidity, a moisture sensitive polymer need to be coated onto the fiber as a transducer material to convert the chemical relative humidity into a physical phenomena which the fiber can sense. PVA and chitosan are two polymers whose refractive index is found to be dependant on the amount of water trapped in the polymer matrix.

The degree of swelling for pure chitosan and pure PVA films are 89% and 674% respectively while that of the chitosan/PVA blended films...
ranges from 1047% to 2117% [62]. This is because PVA is a water-soluble polymer and the blending of chitosan with PVA tends to increase the water intake due to the increasing of hydrophilic groups (-OH) in the blends. Also, the PVA chains are physically entangled with the chitosan chains leading to the formation of a hydrogel network [62,71]. Thus the chitosan/PVA blend is a better transducer for humidity than pure polymers and it is shown that the blend containing 50% each of chitosan and PVA has the highest degree of swelling. So in this work we have used a blend polymer film containing equal concentration of chitosan and PVA.

Chitosan with a degree of deacetylation (DD) of 96% was purchased from a commercial source. PVA with an average molecular weight of 195 x 103 g mol⁻¹ was also used in this work. Distilled water was used to prepare all solutions. All chemicals were used without further purification and freshly prepared solutions were used in all experiments.

A 10 gm L⁻¹ solution of chitosan was prepared by dissolving 5 gm of chitosan in 500 mL acetic acid (0.1 M) followed by stirring and heating at 40°C for 6 hours. A similar 10 gmL⁻¹ solution of PVA was prepared by dissolving 5 gm of PVA in 500 mL of preheated ultra pure water. The solution was then stirred and kept at about 60°C for 2 hours. The aqueous PVA solution was added drop by drop to the chitosan solution, under continuous stirring at around 60°C and stirring was allowed to continue for
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30 min after mixing. Proper amount of amorphous TiO$_2$ powder is then incorporated into this chitosan/PVA matrix and stirred continuously for 30 minutes to form the polymer composite. Air bubbles were eliminated by keeping the solutions at room temperature for two hours and figure 5.5 shows the entire process as a flow chart.

Before coating with the sensing material, the fiber needed to be calibrated and hence the fiber behavior towards exterior refractive index change was gathered. The fiber was fixed straight and a diode laser output was coupled to one end while the other end was connected to a power meter. The power meter was interfaced with a computer to record time varying output. Different oils and ethylene-glycol-water mixtures were used as mediums to
vary the refractive index around the decladded region of the fiber. An Abbe refractometer was used to measure the refractive index of the prepared solutions. The output power was recorded by embedding the decladded region with the prepared liquids. After taking the reading for first liquid the recording was stopped. The decladded region was cleaned using iso-propanol and then the reading was continued with second liquid. The outputs were recorded for all the prepared refractive index samples. The output was converted in to dB scale and is shown in figure 5.6. Figure 5.7 depicts the optical power loss in decibels versus the refractive index of the medium around the fiber.

Once the characterization of the prepared fiber was done, it was considered ready for the next step in sensor fabrication viz the deposition of a suitable polymeric layer. The dip coating method was used to deposit the TiO$_2$ immobilized polymer film onto the bare fiber core. The decladded fibers are dipped in the prepared polymer solutions and pulled out at a constant speed using computer controlled set-up. The probes were then dried at room temperature for two days and were thoroughly washed with NaOH solution.
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and water. After drying, good homogeneous films firmly adhered to the fiber were obtained.

Figure 5.7 Fiber output as a function of ambient refractive index

Figure 5.8 Experimental setup to determine humidity sensitivity
This polymer composite coated probe was then fixed in an in-house-made plexi-glass humidity chamber in such a way that the sensing region was in the middle of the chamber. The chamber had provisions for passing the dry and moist air into it. A commercial moisture sensor was used for calibration and its sensor head was fixed inside the chamber. The schematic diagram of the experimental setup for humidity measurement is shown in Figure 5.8. In order to change the humidity inside the chamber to different levels, an aerator was used to pump air into the chamber via ethylene glycol (dry air) or water (humid air). Air bubbled through water will create a humid environment in the chamber while dehumidification is achieved by passing air through ethylene glycol. One end of the fiber was coupled to a diode laser operating at 632.8 nm while the other end was coupled to a low power silicon photo detector (Newport 818-IR). Outputs of the power meter (Newport, Model 1815C) were monitored in a real time using a computer based data acquisition system developed using Lab View. A constant temperature of 25 °C was maintained throughout the experimental investigations for all sensing probes.

5.3 Theory

We have used polymers as humidity sensitive transducer for which refractive index varies upon adsorption of water molecules. The amount of water molecules adsorbed is proportional to its concentration and hence the refractive index change is proportional to ambient humidity of the surrounding volume.

Thus the moisture mass in unit volume of the polymer, \( C_m \) is proportional to ambient humidity \( H \),

\[
C_m = S \cdot H \quad (5.1)
\]

where \( S \) is the moisture solubility of the polymer.

The variation in the refractive index \( n \) of these swelling polymers with respect to humidity \( H \) is given by [72]

\[
\frac{\delta n}{\delta H} = \frac{(n^2 + 2)^2}{6n} k_m S \left( 1 - \frac{f}{f_c} \right) \quad (5.2)
\]

where \( k_m \) is the molar refraction divided by the molecular weight of water, \( S \) is the moisture solubility of the polymer, parameter \( f \ (0 < f < 1) \) is the fraction of the absorbed moisture that contributes to an increase in polymer volume.
In the case of $f=0$, the polymer exhibits no change in its volume as it sorbs moisture. On the other hand, in the case of $f=1$, the volume of the polymer increases by the same amount as that of the sorbed moisture. $f_c$ is a critical value which defines the variation in refractive index. When $f<f_c$, the refractive index, $n$ increases as $H$ increases, while $n$ decreases as $H$ increases when $f>f_c$. If $n_p$ is the refractive index of the polymer without any moisture and $\rho_m$ density of water $f_c$ is defined by the relation [72]

$$f_c = k_m \rho_m \frac{n_p^2 + 2}{n_p^2 - 1}$$  \hspace{1cm} (5.3)

When light propagates in an optical fiber, a fraction of the radiation extends a short distance from the guiding region into the medium of lower refractive index that surrounds it. This is the evanescent field and the evanescent energy may interact with analytes that attenuate it by means of refractive index changes, absorption or scattering.

The output power ($P_{out}$) of the optical fiber sensor head with respect to the refractive index ($n$) of sensing layer is given by [73,74]

$$P_{out} = P_{in} \frac{n_1^2 - n^2}{n_1^2 - n_2^2}$$  \hspace{1cm} (5.4)

where $n_1$ is the refractive index of the core, $n_2$ is the refractive index of the cladding, $P_{in}$ represents the total power injected into the guided modes of the fiber from the source. It is evident from this equation that power coupled to the fiber after the sensing region decreases linearly with the increase in $n_2$.

The amplitude $E(x)$ of the evanescent field decreases exponentially with the distance $x$ from the core–cladding interface according to the equation

$$E(x) = E_0 e^{-x/d_p}$$  \hspace{1cm} (5.5)

where $d_p$ is the penetration depth.

The penetration depth describes the distance from the interface where the intensity of the evanescent field has decreased to $1/e$ of the initial intensity $E_0$.

The magnitude of the penetration depth is given by [73,74]
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\[ d_p = \frac{\lambda}{2n_1 \left[ \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right]^{1/2}} \quad (5.6) \]

where \( \lambda \) is the vacuum wavelength, \( \theta \) is the angle of incidence and \( n_1, n_2 \) are the refractive index values of the core and the cladding, respectively. From equation 5.6 it is clear that the penetration depth \( d_p \) increases with the cladding refractive index, indicating an increase in the magnitude of the electric field present in the cladding medium and thus a reduction in the electric field within the core.

The normalized frequency (fiber \( V \)-parameter) is given by [73, 74]

\[ V = \frac{2\pi a}{\lambda} \sqrt{n_1^2 - n_2^2} \quad (5.7) \]

where \( a \) is the core radius. This equation shows that the \( V \)-parameter decreases when the cladding refractive index increases. Since the number of modes \( N \) propagating within the fiber is proportional to the square of the normalized frequency, it can be inferred that increasing the refractive index of the cladding reduces the number of modes propagating within the fiber.

5.4 Results and Discussion

Humidity response of PVA was studied by Gaston et al. [32] and he did his experiments using a side polished fiber coated with PVA. It was explained that PVA has a refractive index of 1.53 which is higher than that of the fiber cladding. Upon increase in humidity, the refractive index of PVA starts to decrease and hence the output decreases first and once the refractive index drops below that of cladding, the output starts to increase. A similar type of response (i.e. decrease in refractive index with respect to increase in humidity) is observed by Venugopal [13] by coating PVA over an LPFG. Chitosan as a humidity sensitive polymer for fiber optic sensors was studied by Jinesh et. al [55]. It was observed that upon increase in humidity the coupled power increases.

We have evaluated the response of Chitosan/PVA composite layer as a function of change in relative humidity. The polymer coated fiber probe was placed in the humidity chamber and the humidity level inside the
chamber was brought down to 45% RH by bubbling air through ethylene glycol. We were not able to bring the relative humidity below 45% due to the limitation of our setup. A constant temperature of 25 °C was maintained throughout the experimental investigations for all sensing probes. Afterwards the humidity was slowly increased to the maximum possible value by bubbling air through water and the output power was recorded using a PC at fixed time intervals of 1 sec. The result thus obtained is depicted in figure 5.9

![Figure 5.9](image)

Figure 5.9. Response of PVA-chitosan blend as a function of relative humidity

As can be observed from this result, initially fiber output decreases as the humidity increases within the chamber. On further increase in humidity, the output starts to raise and reach a saturation level. On the introduction of dry air, it is evident from the graph that the output power drops along with humidity. At 45% RH, the optical output reaches the same value as before
but it can be observed that the reverse response is different from the forward path. The dip observed during the forward path is absent in the reverse path.

To check whether the initial drop in output power is due to optical absorption, we measured the absorption characteristics of the film. The polymer blend was coated on a glass slide and using an absorption spectrometer we took the absorption spectrum of the film. The glass slide was then kept in a humid environment and repeated the absorption measurement. The result obtained is depicted in figure 5.10 and is obvious that the trapping of water molecules in the polymer matrix has very little effect on optical absorption.

It has been shown that the blend contains 50% each of chitosan and PVA has the highest degree of swelling on adsorption of water molecules [62]. This volume expansion of the polymer, when exposed to humidity, induces a strain effect on the fiber. Since the strain sensitivity of a bare fiber is very small, this cannot be a reason for the drop in intensity.

Figure 5.10. Absorption spectrum of PVA-chitosan blend film in dry state and upon adsorption of water
The evanescent type fiber optic sensors have been extensively studied and the transmitted optical power depends on the refractive index of the material in contact with the decladded region. The general shape of this variation is similar to the one shown in Figure. 5.7 for the fiber sample used in the experiments. It is evident that the maximum change in output occurs when the external refractive index varies between 1.4 and 1.5. Minimum transmittance occurs when the external refractive index matches the value of the fiber core, a situation in which the guiding conditions are lost.

Under dry conditions the polymer chains tend to curl up into a compact, coil form. On the other hand, at high humidity, polymer adsorbs water molecules and gets hydrated uncurling of the compact, coil form into straight chains that are aligned with respect to one another. This in turn contributes towards the change in refractive index. Watanabe et.al [72] did studies on humidity dependence of the refractive index of polymethylmethacrylate (PMMA) and found that the refractive index of PMMA increases as humidity increases at room temperature, while it decreases as humidity increases at temperatures higher than 60 °C. As mentioned in equation 5.2 and 5.3, if the f parameter of the polymer is less than $f_c$, the refractive index, n increases with increase in humidity (RH), while n decreases as RH increases when $f>f_c$. It has been shown by Gaston et.al[32] and Venugopalan et al [13] that the refractive index of PVA decreases with the increase in ambient humidity, which means it has the f parameter greater than fc. A higher value of f indicates a larger volume increase. Since the degree of swelling of PVA-chitosan blend is much higher than that of pure PVA [62], it can be deduced that the f parameter of PVA-chitosan blend is greater than fc and hence its refractive index decreases with increase in humidity.

Refractive index of chitosan/PVA blended film is around 1.5 [71] in its dry state and hence the fiber coated with the film acts as a lossy medium. As humidity increase water molecules diffuse into the polymer matrix and get adsorbed in the pores. This causes a reduction in refractive index and hence the output decreases till the refractive index reaches that of the core. It is evident from figure 5.4 that a further decrease in polymer refractive index increases the output. Since the response of chitosan/PVA blend is not linear for humidity variation, it cannot be effectively used for humidity sensor.
Titanium Dioxide itself is a hygrosensitive material and has been used by many authors in different ways as humidity sensors. We tried to evaluate the effect of TiO$_2$ on the humidity sensitivity of polymers like PVA and PVA-Chitosan blend.

The titanium dioxide (TiO$_2$) embedded PVA film was then estimated for its humidity response in a similar way mentioned earlier. The response thus obtained for a titanium dioxide concentration of 1g/L in PVA is shown in figure 5.11.

Unlike in the case of pure chitosan-PVA film, the output starts to increase with the introduction of humid air. The coupled power increases till the ambient humidity reach saturation and on the introduction of dry air the output drops and reaches the initial value.

As we did before, the absorption spectrum of the TiO$_2$ embedded PVA film was taken in its dry state and after keeping it in humid environment. The result obtained is shown in figure 5.12. It is evident that absorption is
meager for 632 nm (wavelength of the laser used) and hence it can be concluded that the variation in output is due to change in refractive index.

![Absorption spectrum of TiO$_2$-PVA composite film](image)

Figure 5.12 Absorption spectrum of TiO$_2$-PVA composite film in dry state and upon adsorption of water

The humidity response of TiO$_2$ embedded chitosan/PVA film was then evaluated. Titanium dioxide powder was added to chitosan/PVA mix containing 50% each of chitosan and PVA to produce film with 1 gm/L TiO$_2$ concentration. Humidity inside the chamber was recorded using a commercial hygrometer, and the fiber output corresponding to a particular value of RH% was noted manually. Humid air was pumped into the chamber for a short interval and humidity was allowed to stabilize to a specific value. The process is continued till the humidity reached 95% and then dry air was blown at various steps to reduce humidity. During this process the power output from the coated fiber probe was recorded continuously and is reproduced in figure 5.13 while the sensor output as a function of relative humidity is shown in figure 5.14. It is clear from the graph that the sensor response is linear and reversible in the range 50% to 95% RH with a
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sensitivity of 0.1 μW/%RH. We were not able to record the response below 48% RH due to technical hurdles.

Figure 5.13 Output power of TiO$_2$-PVA-chitosan composite film for different ambient humidity

Figure 5.14 Output power of TiO$_2$-PVA-chitosan composite film as a function of relative humidity
The effect of titanium dioxide on the humidity sensitivity of PVA and Chitosan/PVA blend is compared. The polymer coated fibers were fixed in the chamber. After bringing down the humidity of chamber to 45%, humid air was pumped. The variation in output was recorded and Figure 5.15 shows the comparison of humidity response of TiO$_2$-Chitosan/PVA composite with that of TiO$_2$-PVA composite for a TiO$_2$ concentration of 1 gm/L. It is evident that, with equal concentration of TiO$_2$, the PVA-Chitosan blend film shows better sensitivity than TiO$_2$ embedded pure PVA film. The fiber output as a function of relative humidity for the two probes is presented in figure 5.16.

Figure 5.15 Response of TiO$_2$-PVA composite film and TiO$_2$-chitosan/PVA composite film as a function of relative humidity
It is obvious that the initial drop in intensity observed in the case of pure PVA-chitosan blend is absent in the case of TiO$_2$-PVA-chitosan composite. The addition of TiO$_2$ might have reduced the refractive index of the polymer composite below that of the fiber cladding. From the characterization response shown in figure 5.7, it is obvious that if the coating refractive index is less than that of cladding the output increases linearly with decrease in coating refractive index.

Shadie Hatamie [63] et al. have carried out studies on Stannic oxide (SnO$_2$) nanoparticles suspended in polyvinyl alcohol (PVA) matrix and have shown that the bonds of PVA does not alter after the formation of the composite film. Thus in the case of titanium dioxide polymer composites too, it can be assumed that the film formed was merely by embedding the TiO$_2$ particles in the polymer matrix, homogeneously. The TiO$_2$ particles are attached to the polymer chain by weak Vander Waal’s force of attraction.
The presence of the titanium dioxide molecules in the polymer matrix thus increases hydrophilic head groups and hence stimulates the rate of adsorption. Figure 5.17 shows the output power for TiO$_2$ embedded chitosan/PVA film for titanium dioxide concentrations of 1 gm/L and 0.1 gm/L. It is obvious that the polymer with higher titanium dioxide concentration shows a better sensitivity.

![Figure 5.17 Fiber output as a function of relative humidity for TiO$_2$-PVA-chitosan composite film for different concentrations of TiO$_2$](image)

The higher sensitivity of TiO$_2$ embedded chitosan/PVA blend film can be attributed to the fact that the chitosan addition to PVA increases hydrophilic head groups available per unit volume of the polymer. It is clear that the Chitosan/PVA blend film absorbs more water than pure PVA film and thus increases the sorption capacity of the film. Titanium dioxide too is hydrophilic and its addition to the polymer also helps in the enhancement of available hydrophilic head groups per unit volume. This enhancement in
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hydrophilic heads helps in adsorption of more water molecules which in turn causes a larger shift in refractive index and hence more output.

Conclusions

The design and fabrication of fiber optic humidity sensors using polymers like poly vinyl alcohol and chitosan blended poly vinyl alcohol as hygrosensitive coatings are discussed. The hygroscopic properties of PVA, chitosan and TiO$_2$ are discussed elaborately and the preparation and characterization of polymer and fiber probes are explained. Both PVA and chitosan/PVA blend are sensitive to humidity and their refractive index is found to decreases with increase in ambient humidity. Blending of PVA in chitosan helps to improve its mechanical strength and the available hydrophilic head groups per unit volume. Though found sensitive to humidity, the humidity response of the chitosan/PVA blend is not linear. Addition of titanium dioxide to the polymer produces a linear output variation for change in humidity. The TiO$_2$ particles added to the polymer does not alter the bonds and are attached to the polymer chain by weak Vander Waal’s force of attraction. Blending of titanium dioxide increases hydrophilic heads and increases humidity sensitivity. TiO$_2$ embedded Chitosan/PVA blend gives better humidity sensitivity than TiO$_2$ embedded pure PVA. The humidity sensitivity is found to increase with increase in TiO$_2$ concentration.

References

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