Chapter-IV

Humidity Sensing Properties of Drop Casted PMMA Films
Using Direct Optical Transmission Method

4.1 Introduction

The electrical response for humidity variations has been attributed to both chemi-sorption and capillary condensation of water molecules [1]. Over the years, different sensing methods have been developed by measuring a variety of humidity-related parameters [2]. Each of these has unique advantages and limitations and is suitable only in certain applications. The range of applications in which humidity measurements are needed is endless and is increasing with time because with the advancement of technology new information is required on the effects of humidity on quality and cost the product as well as safety, comfort, and health of the human beings. The conventional materials used for sensing humidity are electrolytic metal oxides, alumina thin films, and ceramics. [3] However, polymers are identified as good candidates for practical applications because High sensitivity, Low cost, Simple fabrication technique. There is a wide choice of molecular structures for improving their properties. However there are shortcomings of polymer’s e.g. low stability at high humidity, too high impedance at low humidity and drafting etc. To overcome these problems some techniques are developed such as grafting, cross linking and embedding of nanoparticles etc.

Polymers are having two main properties; they (i) act as surface capping agents & (ii) provides matrix to disperse nanoparticles. They are compatible with oxides and ceramics, because of their low cost, flexibility, light weight, and easy processibility. They can be used at room temperature. [4, 5] Various polymers have been used to fabricate humidity sensors. From their basic principles, they are classified into two categories based on (1) changes in the electrical properties of the materials due to the absorption of water vapor and (2) gravimetric changes in the materials after absorption of water vapor. The first category is divided into two types: -resistive type and capacitive type. Generally hydrophilic polymers are used for resistance type humidity sensors, whereas hydrophobic polymers are preferred for the capacitance type [6]. Nowadays, a variety of polymers doped with suitable molecules or dyes
are being used in optical humidity sensing applications [7]. Based on the changes in electrical or optical properties, different humidity sensors are popularly studied.

Different polymers like PANI, PVA, PVP and PPMMA in neat or doped with various acids or mNa and with nano-metal polymer composites are reported for humidity sensing [8-14]. Sensors based on evanescent waves are well reported [15-20]. In those planar optical wave guide based and plastic optical wave guide based are well studied. Another simple but the most sensitive optical method reported is direct transmission of laser beam through the humidity sensitive film [5,18] The method is applicable only for the materials which are optically transparent to the laser beam used unlike that of optical waveguides, which are applicable to any material, that can be in the form of a film and works as an optical clad.

PMMA is reported as a humidity sensitive material based on its electrical properties [21]. To the best of our knowledge it is for the first time is evaluated in the form of drop casted films for their Humidity sensitive behavior using Direct Optical Transmission Method. Characterization of the deposited films is done by SEM, FTIR.

4.2. Characterization of Material:
The drop casted films having 1, 2, 3 and 4 drops denoted as A, B, C, and D respectively, were characterized by SEM and FTIR in the presence of different percentage of Relative Humidity.

4.2.1 SEM:
The SEM pictures show uniformity of the film surface. For the layer one (A Type), there are bigger voids. The number of surface sites appears to be small in number. One can expect small contribution from surface and intra grain sites. The B type sensors show large number of grains with micro voids. The C type have more number of micro voids than those in type B while the D type has agglomerated grains with bigger voids. The same is reflected in the sensitivity curves. The results summarized in table 4.1 are supported by SEM pictures.
4.2.2 FTIR:

The FTIR spectra show the effect of humidity. With increase in humidity, the % transmission decreases and new peaks are introduced. At low humidity of about 12% RH and 33% RH, PMMA samples show peaks at 1530 cm⁻¹, 2350 cm⁻¹, 3740 and 3840 cm⁻¹ and broad band at about 1600-1800 cm⁻¹. The bond in the region 1600-1800 is due to C=O stretching. The peak at 2350 cm⁻¹ is attributed to gaseous CO₂ that represents asymmetrical stretching [22, 23]. This bond is instrumental error. The weak bonds at higher wave number i.e. 3840 and 3740 might be due to attachment of OH bond with surface [24].

With increase in humidity the broad band in the region 1600-1800 cm⁻¹ becomes sharp at 1640⁻¹. The broad band is introduced at 1240-1470⁻¹ which is centered at 1330⁻¹. A strong peak in the region 1240-1470⁻¹ is associated with the asymmetric stretching vibration of the carbonate anions [25] due to bonding between carbon and two -OH groups [26]. The strong and broad absorption band at a higher wave number (2800-3700⁻¹) in the FT-IR spectra is attributed to the O-H stretching.

4.3 Optical response of PMMA:

After depositing PMMA solution on 1.0 cm x 1.0 cm borosilicate glass, film thickness was measured by using following equation,

\[ P = \frac{M}{V} = \frac{M}{A \cdot t} \ldots (1) \]

Where \( P \) is the density of the PMMA (1.17 g/cc), It is assumed that the density of PMMA films is constant irrespective of the film thickness. \( M \) is the weight of the film in gm, \( V \) is the total
volume of the PMMA film in CC which is equal to the area A of the film covered (1.0cm x 1.0cm size glass samples were used) and 't' thickness of the PMMA film.

The characteristic response of PMMA as a function of relative humidity is shown in Fig. 4.3.

![Graph](image)

**Fig. 4.3.** Variation in transmitted output Vs Relative humidity for different thicknesses.

(a) Output (b) Normalized output

Fig. 4.3. (a) shows the typical response, i.e. the change in transmitted light intensity measured in mili volts (mv) with RH% variation for various thicknesses of PMMA films whereas (b) shows normalized response normalized with respect to the output at the lowest humidity for inter comparison. It is observed that, in general, the transmitted intensity of light decreases which effectively decreases the output voltage with increase in RH%. It is also seen that all the sensors roughly exhibit three to four regions of sensitivity. The sensitivity is lowest in region 2 for sensors A and B, in region 1 they exhibit higher sensitivity than in region 2. In the region 1 the sensitivity comes from the surface sites, whereas in region 2, it is contributed by the surface sites as well as intra grain boundaries. The higher sensitivity in region 1 means that surface sites are more dominating than surface sites plus intra grain occupation of water molecules. Sensors of A type exhibit 3 regions in their response against the Relative Humidity; third region is because of capillary condensation. The sensors of B, C, and D type exhibit 4 regions. The last region is because of capillary condensation, the second region is because of combination of surface sites plus intra grain sites. The third region is attributed to intra grain surface sites as well as capillary condensation. At the thickness of 26.3μm (C type) the maximum response is seen for regions 2, 3 and 4. The highest sensitivity is exhibited in the first region by sensors D. The region wise sensitivity is tabulated in table 4.1
Table 4.1 Sensitivity as a function of film thickness (region wise)

<table>
<thead>
<tr>
<th>Layer No</th>
<th>Region</th>
<th>%RH</th>
<th>sensitivityymV/RH</th>
<th>Region</th>
<th>%RH</th>
<th>sensitivityymV/RH</th>
<th>Region</th>
<th>%RH</th>
<th>sensitivityymV/RH</th>
<th>Region</th>
<th>%RH</th>
<th>sensitivityymV/RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (A)</td>
<td>2-9</td>
<td>0.43</td>
<td>9-67</td>
<td>0.22</td>
<td>67-85</td>
<td>2.77</td>
<td>--</td>
<td>6-85</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2(B)</td>
<td>2-7</td>
<td>0.4</td>
<td>7-50</td>
<td>0.24</td>
<td>50-68</td>
<td>1</td>
<td>69-85</td>
<td>3.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3(C)</td>
<td>2-28</td>
<td>0.5</td>
<td>28-45</td>
<td>0.81</td>
<td>45-69</td>
<td>1.95</td>
<td>69-85</td>
<td>3.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4(D)</td>
<td>2-15</td>
<td>1</td>
<td>15-41</td>
<td>0.5</td>
<td>41-69</td>
<td>0.54</td>
<td>69-65</td>
<td>3.21</td>
<td></td>
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</tr>
</tbody>
</table>

The results can be explained as follows. At a lower humidity, first region of the sensitivity spectra, water gets chemisorbed on the surface sites for few mono-layers. The thickness of these mono-layers is negligibly small in comparison with the wavelength of used light used for study. Therefore the change in transmitted light intensity is negligibly small. The amount of sorbed water increases with an increase in RH. At higher humidity (second region) the water molecules get adsorbed on the surface of the already chemisorbed water layers, the water molecules are loosely bound on the film surface. Therefore they occupy intra grain sites. With the increase in number of micro-pores, the amount of sorbed water also increases. This reduces the transmitted intensity of light more than that in the first region. In the third and fourth region, because of the contribution from capillary condensation, the refractive index of the film increases with adsorption of water, the transmitted intensity is absorbed by the condensed water and light also gets scattered at higher humidity as condensed water forms a meniscus [27].

The weight of the film at room humidity and at highest humidity was measured. The gravimetric change in these weights is given as an inset in SEM pictures. The change in the weight is a measure of the porosity of the film. The porosity of the film goes on increasing as a function of thickness.

Fig. 4.4. Adsorbed water as a function of thickness of the film
The model to describe the water absorption process is explained by a model given in Figure 4.5.

![Figure 4.5](image)

**Fig. 4.5.** The adsorption phenomena of water molecules on film (a) at lower humidity (surface adsorption); (b) at intermediate humidity (adsorption on capillary walls) surface sites plus intra – grain adsorption (c) at higher humidity (full capillary condensation).

The response time of the sensor is 10s and recovery time of the sensor is 20 s which are faster than the reported values of 30 seconds [28] for PMMA Fig.4.6.

![Figure 4.6](image)

**Fig.4.6 Response and Recovery Time of C film.**

The fast response of the sensors can be attributed to the fast penetration of water molecules into the film. The slow recovery in the response is a result of the slow desorption process and capillary forces [29]. The maximum response is evidenced for thickness of 26.3μm which gives the maximum output voltage change (133mv) for the whole humidity range (2 to 85%RH).

The thickness of 26.3 μm gives a maximum sensitivity (109.01mV/%RH).
To understand the role of thickness of the films the percentage moisture content was measured by weighing the samples at room humidity and at highest humidity and using following equation, [30], the moisture content was calculated.

\[ \text{Moisture (\%) } = \left[ \frac{(W_x-W_0)}{W_0} \right] \times 100 \ldots (2) \]

The sample was exposed to 85% RH for around 10 min. and then immediately weighed (Wx). The weight of the sample was .44944gm. Then the same sample was vacuum dried and weighed again at room humidity (42%RH). The weight of the sample was 0.44931gm. The percentage moisture content was calculated using equation (2). The weight change obtained for A, B, C and D type films is shown in Fig. 4.7. The plot is linear. However the humidity sensitivity is not increasing proportionately. This is because number of sites, number of voids, their sizes are different. The height of the capillaries is also different.

![Graphs showing change in weight with humidity for samples A, B, C, and D.](image)

Fig 4.7 Change in weight with humidity for sample : a) A b) B c) C d) D.

It is observed that water content increases with the film thickness, which also indicates that, the porosity of the films increase with thickness. The weight is saturated with increase in humidity. By using this change of weight values, it is possible to calculate percentage moisture content in each film. The association of water increases the refractive index and effectively dielectric permittivity of the film as free air is replaced by adsorbed water [13]. This also indicated that losses at higher humidity are due to absorption as well as scattering on input intensity.
**Conclusions:**

In conclusion, drop casted films of PMMA were evaluated for their thickness dependent relative humidity sensing properties using direct transmission of laser light. The films show response to wide range of humidity (2 to 85%RH). The C type films show the highest sensitivity.

**References**