Water Detection and Quantification in Polymers Using a Non-destructive Microwave Technique

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Abstract
A basic aspect of a component’s quality is the water content in the material. Water detection with non-destructive test methods is a current subject of research in many companies and research institutes. The presence of water in polymer materials like polyamide or epoxy can be an issue in many applications (e.g. adhesive bonding, extrusion processes). Only a fast and accurate water measurement technique suitable for on-line or laboratory application ensures a high product quality in combination with low expenditure. In this communication, it is reported how a non-destructive and portable device based on a microwave resonator technique accurately detects and quantifies water in the abovementioned polymers. Polyamide-6 and epoxy samples were saturated at 70 °C and 0% rh, 11% rh, 30% rh, 50% rh, 62% rh, 75% rh, 95% rh and, 100% rh, respectively. Epoxy samples were produced using Araldit GY250 as resin and isophorone diamine (IPDA) as hardener while commercially available thin polyamide-6 films (0.35 mm thickness) were used. Parameters related to the real (\(\varepsilon'\)) and imaginary (\(\varepsilon''\)) part of the permittivity were used to quantify the water content in these polymers. Both parameters depend on the specific gravity of the material, their ratio, however, is density independent. A linear correlation has been found between the moisture content in the epoxy samples (from 0.54 wt% to 2.48 wt%). For polyamide-6, a non-linear correlation was found allowing water quantification from 0.56 wt% to 8.14 wt%. Based on these results and due to the importance of the determination of water in composite materials, further research is in progress in order to determine the amount of water in carbon fiber reinforced polymer (CFRP) and other fibre-reinforced composites using the same technique.

Keywords: epoxy, polyamide, water detection, microwave resonator.

Introduction
A fundamental property of a component is the water content in the material. The presence of water in polymer materials like polyamide or epoxy can be a problem in different applications (e.g. adhesive bonding or extrusion processes) from a technical and economical point of view [1].

The early non-destructive techniques for water detection were based on the relation between the electrical conductivity in a material and its water content. These methods were soon supplemented by methods using electromagnetic radiation, for example, microwaves. The first water sensors based on microwaves were applied in agriculture and food industry [2,3,4]. Later on, microwave devices were also adapted to and applied in the tobacco and rice sector [5,6,7].

To analyze the moisture content in polymers, also several other techniques have already been used: from gravimetric methods to more complex techniques such as nuclear magnetic resonance (NMR) or infrared spectroscopy (IR) [8]. Gravimetric methods are very useful as reference techniques but they are considered as destructive tests. IR and NMR are not only accurate methods for quantifying water, but also provide information at molecular scale about interactions between polymer chains and water [9]. However, their information depths, depending on the investigated material, are usually much lower than for the used microwave device, which can also measure moisture content inside the material. Moreover, the water characteristic bands shown in the IR spectrum are very often overlapped by other bands of the polymer chain or surface contaminants.
Moisture measurements using dielectric methods in the microwave range are indirect measuring methods since they do not measure the amount of water in the material directly. The complex permittivity of a tested material can be measured by microwave techniques. It is not only influenced by the moisture content \( MC \), but also by density variations \( \Delta \rho \) and temperature \( T \), among others. In microwave transmission measurements, the attenuation \( A \) and phase shift \( \phi \) are used as parameters which are closely related to the relative permittivity. In resonator-based techniques, the frequency shift \( \Delta f \) and the change of bandwidth \( \Delta BW \) are widely used, both also depending on the relative permittivity. Methods based on one or two parameters using transmission or resonant properties have been developed [1].

Numerous efforts have already been devoted to the application of microwave techniques in agriculture and food, tobacco and rice industries [2-7]; however, in materials science technology applications for detecting water are sparse [1].

In this paper, we report on the results for water detection and quantification in polymers using a two-parameter method and resonator technique.

**Experimental part**

In the following chapter, the sample preparation, sample conditioning and the measuring method are described for an epoxy resin and polyamide-6.

**Sample preparation**

Epoxy samples were prepared using Araldit GY250 as resin and isophorone diamine (IPDA) as hardener with a molar ratio of 1:1. The components were mixed for 90 seconds at 3000 rpm using a SpeedMixer™ DAC 150 FVZ and then filled in circular aluminum containers (Ø 7 cm) and cured. The curing cycle consisted of three steps: (1) heating from RT to 140 °C for 57 min; (2) at 140 °C for 1 h; and (3) cooling down to RT.

Thin polyamide-6 samples (nylon-6, thickness 0.35 mm) were purchased from Goodfellow (AM301350).

**Conditioning**

For the preparation of the epoxy samples with specific moisture content, the cured samples were first dried in a sealed box at 70 °C using silica-gel until the sample mass was constant. The dry samples were then stored at 70 °C at a specific relative humidity (0% rh, 11% rh, 30% rh, 50% rh, 62% rh, 75% rh, 95% rh, and immersion in water). The different relative humidity were generated using oversaturated salt solutions (LiCl (11% rh), MgCl\(_2\)-6H\(_2\)O (30% rh), NaBr (50% rh), KI (62% rh), NaCl (75% rh), K\(_2\)SO\(_4\) (95% rh)) [10]. After four weeks, the samples reached constant mass and the gain of mass (water uptake) was gravimetrically determined at room temperature. The moisture content \( (MC) \) was then calculated as shown in Equation 1:

\[
MC = \frac{m_w}{m_d} \cdot 100
\]

Where \( m_w \) is the water uptake and \( m_d \) is the mass of the dried material.

Thin polyamide-6 film samples with specific \( MC \) were prepared accordingly. But in this case, it is important to avoid longer storage at high temperature and at high relative humidity because
this leads to a degradation reaction of the polyamide-6 [11]. Therefore all polyamide-6 samples were measured directly after 48h of saturation.

In Table 1, the final moisture content (MC) of the epoxy and polyamide samples is given:

<table>
<thead>
<tr>
<th>Relative humidity [%]</th>
<th>MC_{Epoxy} [wt%]</th>
<th>MC_{Polyamide-6} [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>11</td>
<td>0.13</td>
<td>0.56</td>
</tr>
<tr>
<td>30</td>
<td>0.54</td>
<td>2.04</td>
</tr>
<tr>
<td>50</td>
<td>0.92</td>
<td>2.74</td>
</tr>
<tr>
<td>62</td>
<td>1.11</td>
<td>3.73</td>
</tr>
<tr>
<td>75</td>
<td>1.43</td>
<td>3.91</td>
</tr>
<tr>
<td>95</td>
<td>2.11</td>
<td>6.03</td>
</tr>
<tr>
<td>In water</td>
<td>2.48</td>
<td>8.14</td>
</tr>
</tbody>
</table>

**Measuring method**

The interaction of electromagnetic waves with non-magnetic materials can be described by the complex permittivity \( \varepsilon = \varepsilon' + j\varepsilon'' \) which is a scalar for isotropic materials. In general, the permittivity of a given material is a function of the frequency \( f \), temperature \( T \), and density of the dry material \( \rho_d \). For a moisture-containing material, \( \varepsilon \) will additionally depend on the moisture content for a given frequency \( f \) and temperature \( T \), as shown by Meyer and Schilz [6]:

\[
\varepsilon(\rho_d, MC) = \varepsilon'(\rho_d, MC) + j\varepsilon''(\rho_d, MC) \tag{2}
\]

The real part \( \varepsilon' \) of the permittivity of free water at 20 GHz is about \( 80 \text{ A} \cdot \text{s} \cdot \text{V}^{-1} \cdot \text{m}^{-1} \) while most of the usual porous solids exhibit values around \( 2 \text{ A} \cdot \text{s} \cdot \text{V}^{-1} \cdot \text{m}^{-1} \) and \( 7 \text{ A} \cdot \text{s} \cdot \text{V}^{-1} \cdot \text{m}^{-1} \). This is why microwave techniques are quite sensitive to moisture.

Based on experimental results, the following empirical equations for \( \varepsilon' \) and \( \varepsilon'' \) have been derived [4]:

\[
\varepsilon' - 1 = f_1(MC) \cdot g_1(\rho_d); \quad \varepsilon'' = f_2(MC) \cdot g_2(\rho_d) \tag{3}
\]

Where \( g_1 \) and \( g_2 \) are functions of density and \( f_1 \) and \( f_2 \) are functions of \( MC \).

Assuming that the density functions \( g_1 \) and \( g_2 \) can be approximated by linear functions or linearly related power series, the following density-independent function can be derived [6]:

\[
\frac{\varepsilon' - 1}{\varepsilon''} \approx \text{constant} \cdot \frac{f_1(MC)}{f_2(MC)} = K \cdot f(MC) \tag{4}
\]

With \( K \) as proportionality constant and \( f(MC) \) as function depending on the moisture content.

Using microwave resonator techniques, the shift of the resonant frequency (parameter \( A \)) and the change of the full width at half maximum (parameter \( B \)) are measured according to the ‘Two-Parameter Method’ developed by Meyer and Schilz. Based on the linearity observed experimentally between \( A \) and \( B \) by changing the material mass, a density-independent function to measure moisture in solid materials was obtained and empirically used (Equation 5) [6]:

\[
K \cdot f(MC) = \frac{B}{A} \tag{5}
\]
The measurements were performed using a MW4310 instrument from TEWS Elektronik with a planar open-ended resonant cavity as sensor and a frequency of 2300 MHz, applying a specific density-independent equation patented by TEWS (Equation 6) [12,13]:

\[ K \cdot f(MC) = \arctan \left( \frac{B}{A} \right) \] ..........................(6)

Twenty-five measurements were done for each epoxy sample at different temperatures (RT, 40 °C, 50 °C, 60 °C and 70 °C) for eight different moisture contents (0.00 wt%, 0.13 wt%, 0.54 wt%, 0.92 wt%, 1.11 wt%, 1.43 wt%, 2.11 wt%, and 2.48 wt%). Ten measurements were performed for each polyamide-6 sample at RT for eight different moisture contents as well (0.00 wt%, 0.56 wt%, 2.04 wt%, 2.74 wt%, 3.73 wt%, 3.91 wt%, 6.03 wt%, and 8.14 wt%). Temperature-dependence studies for polyamide-6 were not possible since the thin samples cooled down very fast when removed from the oven. Polyamide-6 and epoxy samples immersed under water were dried with a paper tissue and tested five minutes after being removed from the storage box.

Results and Discussion

Epoxy: Dependency of \( \arctan(B/A) \) on the moisture content

To analyze the evolution of \( \arctan(B/A) \) with changing \( MC \), \( \arctan(B/A) \) was measured at RT for eight different moisture contents (0.00 wt%, 0.13 wt%, 0.54 wt%, 0.92 wt%, 1.11 wt%, 1.43 wt%, 2.11 wt%, and 2.48 wt%).

In Figure 1, the increase of bandwidth (\( B \)) versus change of resonance frequency (\( A \)) for samples with different moisture content is shown. For one \( MC \), the different data points result from different thicknesses of the material. The higher the sample thickness, the higher \( A \) and \( B \). If the epoxy samples for a specific \( MC \) would have had the same thickness, the measurements would have plotted a specific point instead of a linear distribution [14]. A linear regression analysis was performed (see Fig. 1 and Table 2). The results demonstrate a linear relation between the change of resonance frequency (\( A \)) and the increase of bandwidth (\( B \)) for each \( MC \), confirming the assumed density-independence (see Equation 4) and thus, the validity of Equations 5 and 6. The results showed that with increasing \( MC \) in the sample, the slope monotonically increases. Consequently, arctan\((B/A)\), which is the angle between the linear regression and the x-axis, can be used for a well-defined calibration independent of the thickness of the sample.

### Table 2. Results of the linear regression analysis for epoxy with different \( MCs \)

<table>
<thead>
<tr>
<th>Moisture content [wt%]</th>
<th>Linear regression equation</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>( B = 0.0558A - 0.0886 )</td>
<td>0.9399</td>
</tr>
<tr>
<td>0.13</td>
<td>( B = 0.0542A - 0.1892 )</td>
<td>0.9765</td>
</tr>
<tr>
<td>0.54</td>
<td>( B = 0.0679A - 0.1771 )</td>
<td>0.9036</td>
</tr>
<tr>
<td>0.92</td>
<td>( B = 0.0699A - 0.0804 )</td>
<td>0.9932</td>
</tr>
<tr>
<td>1.11</td>
<td>( B = 0.0713A - 0.1030 )</td>
<td>0.9865</td>
</tr>
<tr>
<td>1.43</td>
<td>( B = 0.0752A - 0.1186 )</td>
<td>0.8586</td>
</tr>
<tr>
<td>2.11</td>
<td>( B = 0.0949A - 0.2482 )</td>
<td>0.9607</td>
</tr>
<tr>
<td>2.48</td>
<td>( B = 0.1180A - 0.4906 )</td>
<td>0.8157</td>
</tr>
</tbody>
</table>

For clarity, the results at 11% rh, 50% rh, and 62% rh were omitted.
Based on these results, the density-independent parameter $\arctan(B/A)$ is used for the determination of the moisture content in the following. In Figure 2, $\arctan(B/A)$ according to the $MC$ is depicted for epoxy samples at room temperature. The $\arctan(B/A)$ value is the average of 25 single measurements on different spots of the same sample for each $MC$. The observed standard deviations and a linear regression analysis are also shown in Figure 2.

The results show a linear dependency of $\arctan(B/A)$ on $MC$. The observed standard deviations are satisfactorily small (with a maximum deviation of $\pm 0.0019$ for dry epoxy samples).
The linear behavior allows the calibration of the measuring device using the following equation ($R^2 = 0.9864$ for the regression analysis):

$$\arctan\left(\frac{B}{A}\right) = 0.0183 \cdot MC + 0.0504 \ldots$$  \hspace{1cm} (7)

Thus, for $MC$ Equation 8 is obtained:

$$MC = \frac{\arctan\left(\frac{B}{A}\right) - 0.0504}{0.0183} \ldots$$  \hspace{1cm} (8)

As shown in Figure 2, the value of $\arctan(B/A)$ cannot be discriminated for $MC$s of 0.00 wt% and 0.13 wt%. This basically means that $MC < 0.13$ wt% cannot be detected, so dry could also mean 0.13 wt%. Samples containing $MC$ between 0.13 wt% and 0.54 wt% would be needed to more precisely estimate the detection limit, which is thus considered to be 0.13 wt%.

**Epoxy: Dependency of $\arctan(B/A)$ on the temperature**

As outlined before, the permittivity also depends on the temperature. In order to investigate the effect of the temperature on the moisture measurement, $\arctan(B/A)$ was measured for a series of $MC$ at different temperatures (see Figure 3)$^2$. The dependence of $\arctan(B/A)$ on the $MC$ is linear for each tested temperature and the determined slopes are practically the same (Table 3).

These results indicate that the linearity between $\arctan(B/A)$ and $MC$ is always given, independent of the temperature in the epoxy case. Analyzing the y-intercept of the linear regression equations, an increase of 0.006 units for each 10 °C temperature increase is observed. This dependence of the $\arctan(B/A)$ on the temperature was reported before by Kraszewski et al. [4] and is material-dependent. In order to perform a set of reliable measurements, all of them must be carried out at the same temperature.

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$^2$ Samples were conditioned and measured at 40 °C, 50 °C, 60 °C, and 70 °C.
Table 3. Results of the linear regression analysis for epoxy at different temperatures

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Linear regression equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$\arctan(B/A) = 0.0184(MC) + 0.0503$</td>
<td>0.9768</td>
</tr>
<tr>
<td>40</td>
<td>$\arctan(B/A) = 0.0200(MC) + 0.0563$</td>
<td>0.9970</td>
</tr>
<tr>
<td>50</td>
<td>$\arctan(B/A) = 0.0210(MC) + 0.0608$</td>
<td>0.9924</td>
</tr>
<tr>
<td>60</td>
<td>$\arctan(B/A) = 0.0229(MC) + 0.0665$</td>
<td>0.9930</td>
</tr>
<tr>
<td>70</td>
<td>$\arctan(B/A) = 0.0219(MC) + 0.0737$</td>
<td>0.9694</td>
</tr>
</tbody>
</table>

**Polyamide-6: Dependency of arctan(B/A) on the moisture content**

As for the epoxy resin, the dependence of $\arctan(B/A)$ on the moisture content was investigated for polyamide-6 at RT. For that purpose, measurements were performed for different thicknesses of the samples (0.35 mm, 0.70 mm, and 1.05 mm) and different moisture contents (0.00 wt%, 0.56 wt%, 2.04 wt%, 2.74 wt%, 3.73 wt%, 3.91 wt%, 6.03 wt%, and 8.14 wt%).

In Figure 4, the frequency shift versus bandwidth increase is shown for some polyamide-6 measurements depending on the moisture content and the sample thickness (0.35 mm, 0.70 mm, and 1.05 mm).³

The results demonstrate a linear relation between the change of resonance frequency ($A$) and the increase of bandwidth ($B$) for samples with different thickness and same moisture content. Thus, Equations 5 and 6 are validated for the $MC$ calibration in polyamide-6. A linear regression analysis was performed (see Fig. 4 and Table 4).

³ For clarity, the results at 11% rh, 50% rh, and 62% rh were omitted.
Table 4. Linear regression equations and $R^2$ for polyamide for different moisture content

<table>
<thead>
<tr>
<th>Moisture content [wt%]</th>
<th>Linear regression equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>$B = 0.0230A - 0.0170$</td>
<td>0.9921</td>
</tr>
<tr>
<td>0.56</td>
<td>$B = 0.0221A - 0.0322$</td>
<td>0.9910</td>
</tr>
<tr>
<td>2.04</td>
<td>$B = 0.0302A - 0.0442$</td>
<td>0.9951</td>
</tr>
<tr>
<td>2.74</td>
<td>$B = 0.0306A - 0.0379$</td>
<td>0.9933</td>
</tr>
<tr>
<td>3.73</td>
<td>$B = 0.0373A - 0.0071$</td>
<td>0.9881</td>
</tr>
<tr>
<td>3.91</td>
<td>$B = 0.0599A - 0.0762$</td>
<td>0.9955</td>
</tr>
<tr>
<td>6.03</td>
<td>$B = 0.0934A - 0.0022$</td>
<td>0.9873</td>
</tr>
<tr>
<td>8.14</td>
<td>$B = 0.1936A - 0.0485$</td>
<td>0.9992</td>
</tr>
</tbody>
</table>

Similar to the measurements for epoxy samples, Figure 5 shows arctan($B/A$) versus $MC$ in polyamide-6 samples at room temperature. The arctan($B/A$) is the average of 10 single measurements on different spots of the same sample for each $MC$. The standard deviations are again satisfactorily small (with a maximum deviation of ±0.0081 for a $MC$ of 6.03 wt%).

However, unlike the epoxy resin, the experimental data can be best described by a second-degree polynomial equation ($R^2 = 0.9922$ for the regression analysis). The following equation allows the calibration of the measuring device for polyamide-6 films:

$$\arctan\left(\frac{B}{A}\right) = 0.0024 \cdot MC^2 + 0.0029 \cdot MC + 0.0031 \quad \text{................. (9)}$$

Thus, for $MC$ Equation 10 is obtained:

$$MC = \frac{-0.0029 + \sqrt{0.0029^2 - 0.0096 \cdot (0.0031 - \arctan\left(\frac{B}{A}\right))}}{0.0048} \quad \text{................. (10)}$$

This different behavior shows that the dependence of arctan($B/A$) on the $MC$ is material-dependent and an appropriate calibration has to be performed for each polymer material.

Furthermore, the results show that discrimination between different $MC$s is not possible for low moisture contents (see Fig. 5). 0.00 wt% and 0.56 wt% cannot be distinguished, so $MC < 0.56$ wt% cannot be detected and dry could be understood as polyamide-6 containing 0.56 wt%. Samples containing between 0.56 wt% and 2.04 wt% would be needed to better estimate the detection limit, which is thus considered to be 0.56 wt%.

The detection limits for epoxy and polyamide-6 are different because the abovementioned calibration is material-dependent. Moreover, the different hydrogen bond interactions depending on the polymer network could also be considered as an influencing parameter. In polyamide-6 the presence of amide groups will increase the interaction between the polymer network and the water molecules which in low amounts will be bonded. Free water is detected at GHz frequencies (microwaves), while more restricted bonded water is detected at MHz frequencies (short radiowaves). The used resonator sensor works in the range of microwaves (2.3GHz), so free water will be more easily detected [15].
Conclusions

Within the described work, we have investigated whether a microwave resonator-based technique is suitable to detect the moisture content of polymers for material science applications. To that purpose, two polymeric materials (epoxy and polyamide-6) have been analyzed. From the interaction of the microwaves with the polymers, the change of the resonance frequency ($A$) and the increase of the bandwidth ($B$) have been determined. The derived value $\arctan(B/A)$, as density-independent quantity, has been used to quantify water in epoxy and polyamide-6.

We could show that the method is suitable to detect and quantify the amount of water in polymeric materials, i.e. epoxy and polyamide-6, using the linear equation $\arctan(B/A) = 0.0183 \cdot MC + 0.0504$ and the second degree polynomial equation $\arctan(B/A) = 0.0024 \cdot MC^2 + 0.0029 \cdot MC + 0.0031$, respectively.

Furthermore, the detection limits were estimated to be between 0.13 wt% and 0.54 wt% for the epoxy and between 0.56 wt% and 2.04 wt% for the polyamide-6. Further work is in progress to obtain more experimental data and precisely estimate the detection limits.

It has also been shown that the linearity between $\arctan(B/A)$ and $MC$ is given independent of the temperature for the epoxy. Nevertheless, the reference measurements for calibration have to be performed at the same temperature, which is an important factor to keep in mind when measurements are carried out.

These results show that the applied non-destructive microwave resonator-based technique is suitable for the quantification of the moisture content in a wide range of polymeric materials and applications, providing that a proper calibration has been done for each material. Application of the introduced method for water detection in CFRP is also in progress.
Acknowledgements

The authors want to thank TEWS Elektronik for technical support and fruitful discussions.

References