Equilibrium Moisture Content of Some Bioplastic Materials for Agricultural Use (Drip Tubes)

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ABSTRACT
This work focused on the determination of equilibrium moisture content (EMC) of some bioplastic materials that could be used for agricultural foil mulch as a source to produce biodegradable drip tubes. Equilibrium moisture content (EMC) is very important to determine the desirable conditions of microorganism’s growth, which causes material deterioration and degradation. Thus, this work aimed to determine the EMC of some commercial bioplastic mulch such as (Bioflex, Ecoflex, Chitosan, Mater-bi, and Bi-OPL). The bioplastic materials were put under different temperature (10-50°C) and relative humidity (43-95%) conditions. The data revealed that changing the relative humidity from 43 to 95% has a great effect on both of Mater-Bi and Chitosan, which the EMC increased by 9.87 and 12.22%, respectively. On the other hand, there is a small effect on the EMC with relative humidity changes on each of Ecoflex (1.41%), Bioflex (2.4%) and Bi-OPL (0.5%).

Keywords: EMC, bioplastic, Bioflex, Ecoflex, Chitosan, Mater-Bi, Bi-OPL, relative humidity.

1. INTRODUCTION
In the recent times, there has been tremendous interest in the use of bioplastic and biodegradable polymers. There were many attempts to use a bio-filler in thermoplastic polymers because it is a natural polymer, abundant, and a renewable resource.

The world consumption of low density polyethylene (LDPE) mulching films in horticulture is at present around 700 000 tonnes per year (Espí et al., 2006). After use, the films can be dirty with soil, organic matter and agro-chemicals. As a result, after use they need collection, and either disposal or recycling. Because of the high costs related to the regular process of gathering and discarding films, and the recycling process, plastic films are often discarded in a dump or burned with the subsequent emission of toxic substances both to the atmosphere and to the soil (De Prisco et al., 2002). Suitable alternative methods are presented by the use of biodegradable materials in agriculture (Malinconico et al., 2002; Imam et al., 2005; Kyrikou and Briassoulis, 2007; Tzankova Dintcheva and La Mantia, 2007; Kichavengkul et al., 2008a, 2008b; Malinconico et al., 2008). At the end of their life, biodegradable materials can be integrated directly into the soil where bacterial flora transforms them into carbon dioxide or methane, water, and biomass. Because biodegradable materials do not produce wastes that require disposal, they could represent a sustainable ecological alternative to LDPE films (Immirzi et al., 2003 and Kapanen et al., 2008).

With the development of degradable plastics, a group of materials was created with consideration for their disposal. However, for economic reasons, the use of degradable plastics is still
negligible. These plastics are suitable for waste management to close circular flow, save oil reserves, stabilize CO2 emission and offer consumers an environmentally friendly option (Tien et al., 2000).

Plastic films actually used for soil mulching have two serious drawbacks: they are manufactured with non-renewable oil based raw materials and produce large amounts of plastic wastes that require disposal. Biodegradable coatings that can be sprayed represent an ecological friendly alternative to synthetic petro-chemical polymers for soil mulching (Immirzi et al., 2009).

Molecules of water are constantly leaving and returning to the biomaterial surface. If the same number of molecules of water returns to as leave from the surface, an equilibrium condition exists. The moisture content of the material at equilibrium with the given environment, the relative humidity and the temperature, is called the equilibrium moisture content (EMC). The partial pressure of the water vapor in the ambient air equilibrates the partial pressure of the water vapor in the material.

The EMC of some agricultural produce for bio-plastic applications are reported in the literature. Starch was used as a bio-filler in thermoplastic polymers (Kaewta et al., 2008). Starch is used as filler because it is a natural polymer, abundant, inexpensive and a renewable resource. Starch is degraded by microorganisms and is suitable for blending with bioplastics and biodegradable polymers. Unfortunately, the mechanical properties of thermoplastic polymer/starch blends are very poor due to the incompatibility and hydrophilic nature of starch (Kaewta et al., 2008). Ashour (2003) reported that, the EMC of wheat straw increased with increasing the relative humidity but it decreased with increasing temperature. The equilibrium moisture content of barley straw was higher than that of the wheat straw. The relative humidity has greater effect on the change of moisture content of bales compared to the effect of the temperature. He reported that the EMC equilibrium moisture content ranged between (8.4-22.9%) for all conditions (5-30 °C temperature and 43-96% relative humidity).

Paetau et al. (1994) studied the effect of moisture level in molding soy isolate into plastic specimens at 125oC. The percent elongation of samples increased as water content increased in the molding material. The moisture content of the molding material was crucial for the rigidity and extensibility of the specimens. Moisture contents above 10% resulted in more extensible specimens with decreased tensile strength.

Swearingen (2001) reported that the composition of wood and straw are quite similar. Both consist largely of cellulose plus inorganic materials. At about 18% moisture content, fungi which are present in wood and straw as spores become active and begin breaking down cellulose, creating what we know as dry rot. Below 18% MC (dry weight basis), the active fungi go dormant.

Watts et al. (1995) found that the deterioration of straw can be a result of microbial activity, which is a function of such environmental variables as temperature, pH, oxygen, radiation and availability of moisture. The exact relationship between the equilibrium relative humidity and the moisture content of the straw was given by the moisture sorption isotherm as a function of the type of straw and the ambient temperature.
Fully amorphous bio-plastic applications are limited by the fact that a polymer's Tg (the glass transition temperature) is highly affected by the relative humidity (especially for hydrophilic polymers). Below the Tg the material is rigid, and above the Tg it becomes visco-elastic or even liquid. Below this critical threshold, only weak, non-cooperative local vibration and rotation movements are possible. Film relaxation in relation to temperature follows an Arrhenius time course. Above the Tg, threshold, strong, cooperative movements of whole molecules and polymer segments can be observed (Cuilbert et al., 2005).

Ritschkoff et al. (2000) studied mould contamination (at constant humidity and temperature conditions) for several wood-based materials, stone-based materials and insulation materials. All building materials tested were susceptible to mould growth in humidity higher than 90% RH at temperature above 15°C. However, building materials of different origin showed variable tolerance against fungal growth under the test conditions. In the stone-based materials the critical humidity level and exposure time needed for the initial fungal growth was higher than in the wood-based materials. In the material combinations the initial mould growth principally retarded in the contact surface. Equilibrium moisture content is very important factor in drying, storing the agricultural products and saving building materials such as wood.

Due to the lack of information about the thermal, physical and mechanical properties of some bioplastic materials using in agriculture, the main aim of this work was to obtain the EMC of some bioplastic materials as one of a series of research will be done to identify the properties of these materials and the possibility for using it as biodegradable drip tubes for developing and management of micro irrigation systems.

2. EXPERIMENTAL PROCEDURES

According to DIN EN ISO 12571 (1996), equilibrium moisture content was determined for five commercial bioplastic samples collected from market which were used as agricultural mulch film (Bioflex, Econflex, Mater Bi, Chitosan and Bi-OPL foil) to study the material stability and found which is better to use for produce the biodegradable drip tubes.

Ecoflex® F BX 7011 is a biodegradable aliphatic-aromatic copolyester based on the monomers 1,4-butandiol, adipic acid and terephthalic acid for film extrusion. It has been developed for the conversion to flexible films using a blown film or cast film process. Typical applications are packaging films, agricultural films and compost bags (BASF, 2007).

Bio-Flex® film compounds are innovative PLA / copolyester blends. The excellent processing qualities stem from the outstanding compatibility of the polymeric components polylactic acid (PLA) and the biodegradable copolyester. Bio-Flex ® film compounds do not contain starch or derivatives of starch (FKUR, 2008).

Chitin, a polysaccharide of animal origin, is obtained from seafood industrial waste material. It occurs in the skeletal material of crustaceans such as crabs, lobsters, shrimps, prawns and crayfish. Chitosan is the deacetylated product formed by treatment of chitin with concentrated (50%) caustic alkali. Thus Chitosan is safe (nontoxic), biocompatible and biodegradable (Yadav et al., 2004 and Radhakumary et al., 2005).
Mater-Bi® is a biodegradable thermoplastic material made of natural components (corn starch and vegetable oil derivatives) and of biodegradable synthetic polyesters. The material is certified as biodegradable and compostable in accordance with European Norm EN 13432 and with the national regulations UNI 10785 and DIN 54900 (Novamont, 2008).

Bi-OPL is biodegradable film mulching and produced from poly lactic acid (PLA) which made of degradable materials (corn) and compostable in accordance with DIN EN13432 (Oerlemansplastics, 2008).

Samples with 10 x 10 cm were taken and put on a wire mesh, then above a plastic dish containing a saturated salt solution. The samples, wire mesh and dishes were placed inside a basket. The basket was put in a plastic bag with an air-tight seal. These bags were put inside a climate chamber at different temperatures (10, 20, 30, 40, and 50°C) and in order to obtain different relative humidity values (43, 53, 65, 75, 85, and 95%) in the surrounding materials in the bags, the chemical substances listed in Table 1 were used. The development was controlled with combined T/RH sensors. After 2 or 3 weeks, until a constant relative humidity inside the bags were reached, samples were weighed and the moisture contents were calculated.

A climate chamber measuring 3.5 x 2.75 x 3.0 m was used to control the temperature conditions. Capacitive humidity sensors (Aluminum 12 mm φ ± 2 % for RH, and 1 K for temperature accuracy, made in Germany) contained a glass substrate with a humidity-sensitive polymer layer between two metal electrodes. With absorption of water, corresponding to the relative humidity, the dielectric constant, and as a result, the capacity of the thin-film capacitor, changed. The measuring signal is directly proportional to the relative humidity and is not dependent on the atmospheric pressure.

Moisture content for the materials was measured according to (ASHRAE, 1997). The materials were put in the drier until a constant weight was obtained. The following equation was used to calculate the MC:

\[ MC = \left( \frac{W_m - W_d}{W_d} \right) \times 100 \]

Where:
MC: Moisture content (% db)
Wm: Moist weight (kg)
Wd: Dry weight (kg)

Table (1): Chemicals substances used for adjusting different relative humidity values.

<table>
<thead>
<tr>
<th>Name</th>
<th>Materials</th>
<th>Relative humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium sulfate</td>
<td>Na2SO4.10 H2O</td>
<td>95</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>85</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>75</td>
</tr>
<tr>
<td>Sodium nitrite</td>
<td>NaNO2</td>
<td>65</td>
</tr>
<tr>
<td>Magnesium nitrate</td>
<td>(Mg NO3).6 H2O</td>
<td>53</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>K2CO3.2 H2O</td>
<td>43</td>
</tr>
</tbody>
</table>

3. RESULTS

3.1 Mater-Bi

Fig.1 shows the equilibrium moisture content (EMC, % db) of Mater-Bi at different predetermined relative humidity values and temperatures. The samples were placed under conditions of relative humidity ranging from 43–95 %, and temperatures of 10–50 °C.

The results revealed that the equilibrium moisture content of Mater-Bi increased with increasing the relative humidity but it decreased with increasing the temperature. It seems that the relative humidity has a greater effect on the equilibrium moisture content than the temperature, where, changing the relative humidity from 43 to 95% leads to an increase of 12.17 % in the moisture content of the material at 10 °C temperatures. On the other hand, increasing the temperature from 10-50°C caused a decrease of 4.3% in the equilibrium moisture content of the material at 43 % relative humidity, while at the higher temperatures and relative humidity (50 °C and 95 %), increasing the relative humidity from 43 to 95% at 50 °C caused an increase of 9.41 %, whereas it was 7.06 % when the temperature increased from 10-50 °C at 95 % relative humidity.

The average of EMC from 43 to 95% relative humidity ranged from 2.37 to 12.24 %, on the other hand it ranged from 8.10 to 4.78 % for 10 to 50°C. At low relative humidity (43 %) the maximum equilibrium moisture content was 4.30 % at 10 °C while it was a low of 0 % at 50 °C. As relative humidity rises, the equilibrium moisture content (EMC) reached a high of 16.47 % at 10 °C and a low of 9.41 % at 50 °C.

![Figure 1. Equilibrium moisture content of Mater-Bi](image_url)

3.2 Ecoflex

Fig.2 shows the equilibrium moisture content (EMC, % db) of material at different relative humidity values and temperatures. At low relative humidity (43 %) the maximum equilibrium moisture content was 5.88 % at 10 °C while it was a low of 3.53 % at 50 °C. As relative humidity rose, the equilibrium moisture content (EMC) reached a high of 8.24 % at 10 °C and a low of 7.06 % at 50 °C. It is also noticed that, changing the relative humidity from 43 to 95% lead to an increase of 2.36 % in the moisture content of the material at 10 °C temperature. On the
other hand, increasing the temperature from 10-50 °C caused a decrease of 2.35 % in the equilibrium moisture content of Ecoflex material, while at the higher temperatures and relative humidity (50 °C and 95 %), increasing the relative humidity from 43 to 95% at 50 °C caused an increase of 3.53 %, whereas it was 1.18 % when the temperature increased from 10-50 °C at 95 % relative humidity.

![Figure 2. Equilibrium moisture content of Ecoflex](image)

### 3.3 Chitosan

Fig.3 shows that the maximum equilibrium moisture content for Chitosan materials at low relative humidity (43 %) was 7.64 % at 10 °C while it was a low of 3.47 % at 50 °C. As relative humidity rises, the EMC reached a high of 19.44 % at 10 °C and a low of 13.19 % at 50 °C. It is also noticed that changing the relative humidity from 43 to 95% leads to an increase of 11.80 % in the moisture content of the material at 10 °C temperatures. On the other hand, increasing the temperature from 10-50 °C caused a decrease of 4.17 % in the equilibrium moisture content of Chitosan material, while at the higher temperatures and relative humidity (50 °C and 95 %), increasing the relative humidity from 43 to 95% at 50 °C caused an increase of 9.72 %, whereas it was 6.25 % when the temperature increased from 10-50 °C at 95 % relative humidity.

### 3.4 Bioflex

Bioflex has the same trend like Ecoflex and Mater-Bi, where the EMC is increased with increasing relative humidity, but it decreased with small rate in the case of increasing the temperature (Fig 4). The results revealed that at 10, 20, 30 and 40 °C had the same effect on the moisture content of Bioflex when changing the relative humidity from 43 to 95%, it lead to an increase of 2.37% in the moisture content. On the other hand, increasing the temperature to 50 °C caused a small decrease in the EMC, it lead to a decrease of about 0.2, 0.21, 0.14, 0.31, 0.3 and 0.08% when changing the relative humidity from 43 to 95%, respectively.
3.5 Bi-OPL

From the data plotted in Fig.5, it can be observed that Bi-OPL looks like Bioflex. In the case of changing relative humidity from 43 to 75%, and the temperature from 10 to 50 °C, we can find that the EMC was stable (1.03%). On the other hand, the mean of EMC increased to 0.12 and 0.5% when the relative humidity increasing to 85 and 95%. So we can find that neither temperature (10 to 50 °C) nor relative humidity (43 to 95%) had an effect on the EMC of Bi-OPL.
4. DISCUSSION

The results revealed that both Mater-Bi and Chitosan has a great affect by changing the relative humidity from 43 to 95%, which the EMC increased by 9.87 and 12.22% respectively. On the other hand, there is a small effect on the EMC by changing the relative humidity on each of materials: Ecoflex (1.41%), Bioflex (2.4%) and Bi-OPL (0.5%). This may be due to the fact that the moisture content is identical to the sorption isotherms, where water is adsorbed from the vapor of the ambient air, and the moisture content is in equilibrium with the ambient relative humidity. Two mechanisms are responsible for this sorption phenomenon, at low relative humidity values, water molecules are attached to the pore film wall forming a thin water film, as relative humidity rises, this film becomes thicker and capillary condensation starts taking place in the narrow pores, the two mechanisms overlap each other, but at high relative humidity, the capillary condensation becomes dominant (Kuenzel, 1991).

Equilibrium moisture content of bioplastic materials increases with the rise of relative humidity at the same temperature. That was due to the vapor pressure deficit (VPD) decreases with increasing relative humidity which creates an atmosphere close to saturation and that increases the ability of sheep thickness to absorb more moisture from the surrounding atmosphere. On the other hand, with increasing temperature from 10 to 50 °C, equilibrium moisture content decreases according to Künzel (1994) and Krus (1995).

5. CONCLUSION

The results revealed that the equilibrium moisture content of all materials under study increased with increasing the relative humidity but it decreased with increasing the temperature. The equilibrium moisture content of Chitosan and Mater-Bi was higher than Ecoflex and Bioflex and it was the lowest for Bi-OPL. The temperature and relative humidity play an important role in the microorganism activity which can attach and degrade the bio materials, so each of following: Ecoflex, Bioflex and Bi-OPL, may hold for a longer period of time than Chitosan and Mater-Bi as a mulch film. It may be better to use the same materials which use to produce each of Ecoflex, Bioflex and Bi-OPL to produce the degradable drip tubes for drip irrigation system.
6. FUTURE WORK
Further work should be done to measure the effect of soil type and the length of time for the degradation of these materials.

7. REFERENCES
Tzankova Dintcheva N., and F.P. La Mantia. 2007. Durability of a starch-based biodegradable polymer. Polymer Degradation and Stability, 92, 630–634.