Humidity regulating films made of blends from PLA and PP with $CaCl_2$

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Introduction

The relative humidity in closed packagings can vary due to temperature fluctuations and water vapour released by food products. Critical are a high relative humidity and water vapour condensation because they cause microbial growth and agglomeration of powdery and chunky food products. Therefore a humidity regulating packaging material is desirable that stabilizes the relative humidity in packagings.
In our research we are working with salts that are dispersed in polymer matrices [1]. Hygroscopic salts absorb reversible high amounts of water vapour. Thus they can buffer fluctuations of the relative humidity.

Experimental

Calcium chloride ($CaCl_2$) was dispersed in polylactid acid (PLA, 2002D, Nature Works) and polypropylene (PP, Moplen HP525J, LyondellBasell) by compounding with a concentration of 0.06 g $CaCl_2$ per one gram of polymer. From the compounds films with a thickness of 150 µm (PP) to 200 µm (PLA) were extruded. To immobilize salt solutions forming by water vapour absorption capillaries were created in the films by biaxial orientation at stretching ratios of 2.5 x 2.5 (Figure 1). The prior dried samples were stored at 60% relative humidity and 23 °C as triplicates.
The weight of absorbed water m_t at the time t normalized to the water vapour absorption in equilibrium m_∞ was depicted as a function of the square root of the time divided by the thickness l. When for values $m_t * m_\infty^{-1} < 0.5$ a straight line results the water vapour absorption is diffusion controlled [2]. The diffusion coefficient D can be calculated for semi-infinitive flat films by applying an simplified equation derived from Fick's laws by Crank (equation 1) by which the absorption velocity can be described for values $m_t * m_\infty^{-1} < 0.5$ [2]. Equation 1 is valid if Fick's laws and Henry's law apply when strictly following the preconditions for its derivation.

$$\frac{m_t}{m_\infty} = \frac{4}{\sqrt{\pi}} \cdot \sqrt{\frac{D \cdot t}{l^2}} \qquad (1)$$

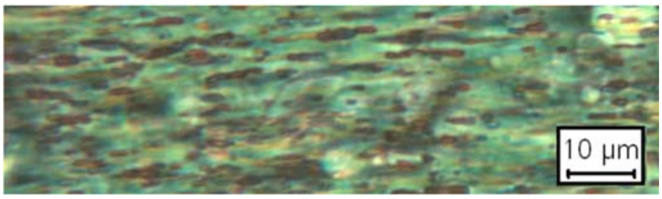

Figure 1: Microscopic picture of PLA film with 6 % w/w $CaCl_2$ in the polymer matrix, biaxially oriented at stretching ratio of 2.5 x 2.5

Results and Discussion

The films made of PLA and PP absorbed 0.085 g water vapour per one gram of film. ($CaCl_2$ powder absorbed 2.3 g water vapour per one gram of film under these conditions.) The depiction of the water content $m_t * m_\infty^{-1}$ as a function of the square root of the time divided by the thickness l resulted in a straight line for values $m_t * m_\infty^{-1} < 0.5$ (Figure 2). Thus the absorption was diffusion controlled.

The calculated diffusion coefficients for water vapour at PLA films with six weight percentage of $CaCl_2$ at 23 °C were:

- at PLA $(3.07 \pm 0.61) \cdot 10^{-9}$ $cm^2 \cdot s^{-1}$ and
- at PP $(4.54 \pm 1.77) \cdot 10^{-11}$ $cm^2 \cdot s^{-1}$.

Thus PLA causes a faster water vapour absorption of the structure. From the diffusion coefficients the water vapour absorption as a function of time was calculated by applying equation 1 (Figure 3). The results show that equation 1 describes the velocity for water vapour absorption well for an absorption of $m_t * m_\infty^{-1} < 0.5$.

The PLA films with six weight percentage of $CaCl_2$ were stored in recurring 60% and 0% relative humidity conditions at 23 °C. The films were reversibly absorbing water vapour proofing that by dispersing salts in polymer matrices humidity regulating films can be produced thereof (Figure 4).

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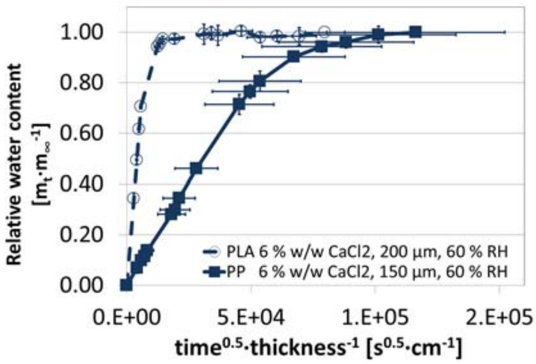

Figure 2: Water vapour absorption as a function a function of the square root of time divided by the film thickness of biaxially oriented films containing $CaCl_2$ in the polymer matrix at 23 C

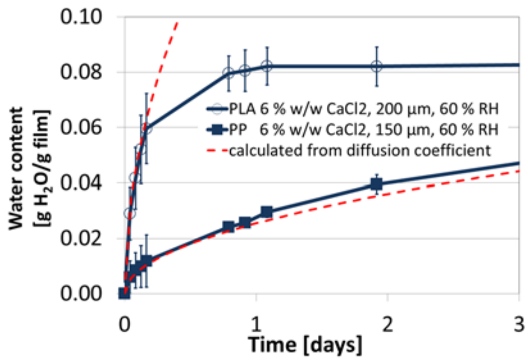

Figure 3: Measured and calculated water vapour absorption as a function of time at 23 C

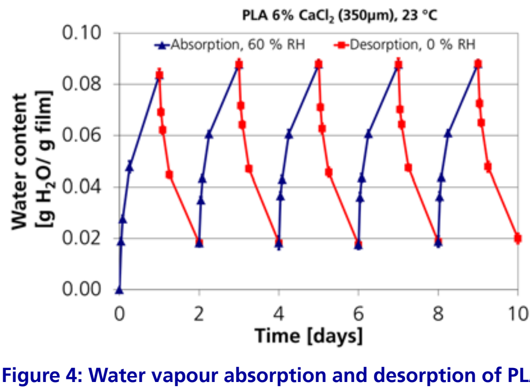

Figure 4: Water vapour absorption and desorption of PLA film with $CaCl_2$ at alternating relative humidity

References

[1] H.-C. Langowski, S. Sängerlaub, T. Wanner, Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., Patent WO/2007/121909, **2007**

[2] J. Crank, The Mathematics of Diffusion. 2nd ed., Oxford University Press, **1975** pp. 244-245