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Humidity in MA Boxes

Effect of cardboard coating and absorbers on humidity build-up and condensation

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Contents

1. Introduction

Modified atmosphere packaging uses the natural respiration of agricultural products in order to create a microclimate within the packaging which increases the shelf life of this packed produce. The produce will consume oxygen and produce carbon dioxide which will lead to increased CO_2 levels in the packaging and decreased O_2 levels compared to the natural composition of the atmosphere. For each type of produce there exist an optimal percentage of CO_2 and O_2 within the packaging, where the metabolic rate (and, thus, the aging process) of the produce is slowed down, and the shelf life is prolonged. In order to achieve an ideal modified atmosphere, packaging materials with a gas permeance suitable for the respiration rate of the produce are chosen. In recent years, Kappa Packaging succeeded in co-operation with ATO to develop and introduce solid board MA boxes with the optimal gas permeance values for different types of vegetables and fruits. While the gas permeance of these boxes could be optimized, it remains difficult to achieve an optimal water vapor transmission rate for the MA boxes. Ventilation holes, which are otherwise commonly applied to reduce the humidity and condensation inside boxes, conflict with the aim to achieve a specific (low) gas permeance. High humidity values in MA boxes are problematic, because condensation on the produce supports mould growth, and condensation on the transparent film which covers the box limits the visibility of the packed produces. A packaging solution which leads to too low humidity values inside the packaging (e.g. the application of a desiccant which is too efficient) is also problematic: dehydration will lead to a low product quality. In order to achieve optimal storage conditions for the product, it is therefore desirable to be able to control the humidity values inside a package within the interval which is optimal for the product. This applies not only for fruits and vegetables, but for most perishable products such as meat, poultry, fish, and flowers.

The control of humidity in packaging is not only important for retaining optimal product quality during storage and transport. The absorption of humidity in the packaging material influences the performance of the packaging: material properties of board such as stiffness and strength depend on its water content. Coatings and films (in particular bio-based polymers) can change their permeability at high water contents.

A good understanding of the effect of humidity in packaging is therefore essential for the development of advanced paperboard packaging solutions and will contribute to the knowledge base which is created in ongoing projects (e.g. Theodora, MA-packaging of tomatoes on the vine, MA packaging of fish, Applications for bio-coatings on board).

In this study we focus on the humidity build-up and possible condensation in MA boxes, and study ways to control humidity build-up and possible condensation by the construction of the MA box and the application of desiccants and absorbers for two types of produce.

2. Scientific background for transpiration, humidity build-up, and condensation

If free water is in equilibrium with its vapor phase (i.e. water vapor), the saturation water vapor pressure *p* is given by the Clausius – Clapeyron equation:

$$p(T) = p_0 \cdot e^{-\Delta h / RT} \tag{2-1}$$

where *T* is the temperature, *Δh* is the latent heat of vaporization, and *R* is the gas constant. The saturation water vapor pressure p at a certain temperature T corresponds to 100% relative humidity (RH). In other terms, the Clausius – Clapeyron equation describes which water vapor pressure corresponds to 100% RH at different temperatures. If the water vapor pressure exceeds the saturation value (100% RH), condensation will occur. Since the saturation value depends strongly on the temperature, temperature drops can lead easily to condensation.

For the following study, we are not only interested in the interaction between free water (e.g. condensation) and the headspace of the packaging, but – first of all – in the interaction between the product and the humidity in the headspace. Two aspects are important to consider:

- Which humidity values can be reached in the headspace if produce is present, and
- What are the dynamics of the moisture release (transpiration rate) of the produce?

Two factors contribute to the transpiration of produce:

(1) The surface of the product can be viewed as a thin layer of water or a water reservoir with a water activity of approximately 0.98 (i.e. this water reservoir is in equilibrium with an atmosphere of 98% relative humidity. The saturation water vapor pressure of the water reservoir is lowered due to solutes (e.g. minerals)).

(2) Fruits and vegetables usually still metabolize sugar and oxygen, and produce water and carbon dioxide. Therefore, the produce still releases small amounts of water, even if the headspace already reached 100% RH. The metabolic rate can be influenced by MA conditions (see section 5: Characterization of the produce: transpiration rates of tomatoes on the vine and chicory).

The product is strictly speaking never in equilibrium with its environment: within a perfectly tight container, the headspace will always reach the saturation water vapor pressure, and condensation will occur.

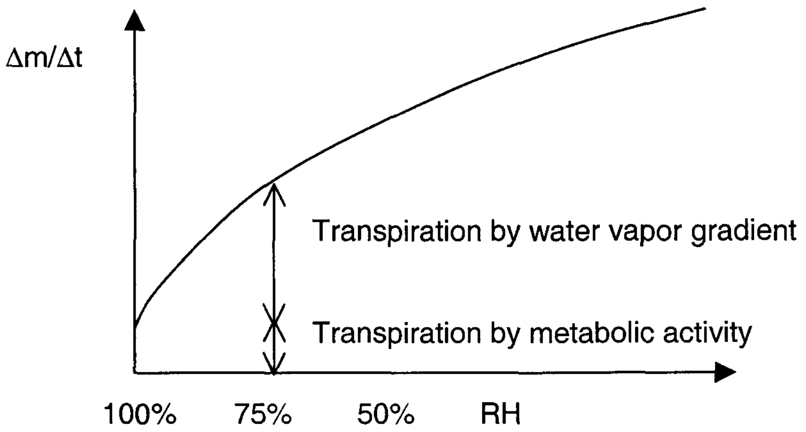


Figure 1: Schematic presentation of the loss of weight of the produce due to transpiration as a function of the relative humidity of the headspace.

The transpiration rate is a product specific property. It depends on the difference between the water vapor pressure of the headspace and the water vapor pressure corresponding to the activity of the water reservoir of the produce (approximately 0.98), the mass and the surface area of the product. Other factors which influence the transpiration rate are the age of the product, the air flow in the vicinity of the product and the intensity of light to which the product is exposed. Figure 1 shows schematically the transpiration rate $\Delta m/\Delta t$ as a function of the relative humidity. If the product is stored at low relative humidities, it will release more moisture than at a storage at high humidities. The transpiration rate is minimal at 100% RH. The transpiration rate will not increase linearly with the water vapor gradient.

If produce is packed in a cardboard container, the humidity will build-up and the rate of the build-up is depending on the transpiration rate of the produce. In addition, cardboard boxes are not impermeable for water vapor. Instead, they can absorb a certain amount of water, and can transmit water vapor to the surroundings. The absorption by the cardboard can slow down the build-up of the humidity inside the boxes until the material is saturated. If the water vapor which is released by the produce can be completely removed by permeation through the box, the relative humidity inside the box will not reach the saturation value but a lower 'steady state' value.

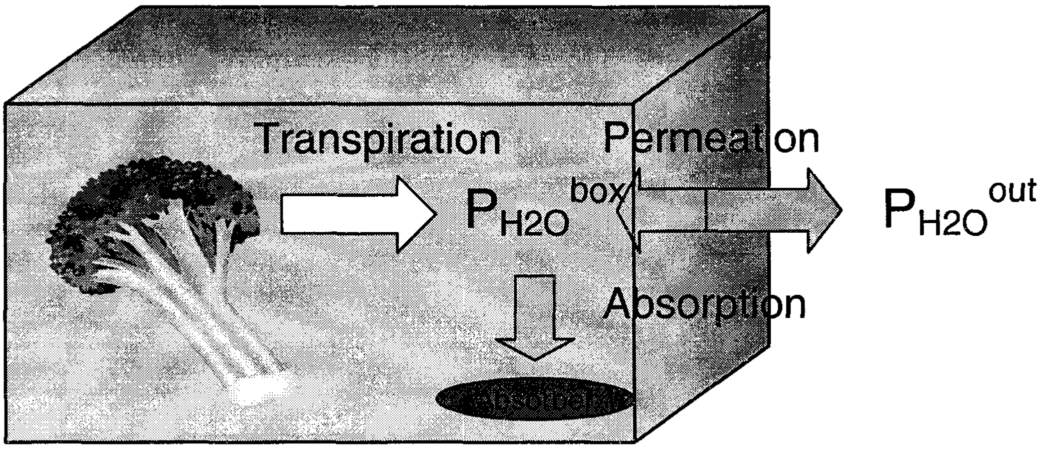


Figure 2: Moisture transport from the produce to an enclosed absorber and the surroundings.

The steady state value of the water vapor pressure p_{H2O}^{box} will depend on the transpiration rate of the produce at p_{H2O}^{box} and the water vapor absorption / transmission rate of the packaging (lower transpiration rates and the higher absorption / transmission rates will result in lower steady state values of the water vapor pressure). If the cardboard box does not transmit water vapor at a sufficiently high rate, the relative humidity in the headspace will reach 100% and condensation will occur. The water vapor pressure inside the box, the transpiration rate of the produce, the water vapor permeation rate of the packaging, and the water vapor pressure outside the box form a complex dynamical system: transpiration rate of the produce and the water vapor pressure inside the box depend on each other and are via the water vapor permeation rate linked to the water vapor pressure outside the box. The water vapor permeation rate can depend on the moisture content of the packaging material, which is again determined by the water vapor pressure inside and outside of this packaging (see Figure 3). In addition, permeation- and transpiration rates are usually temperature dependent.

If a sufficiently high water vapor permeation rate through the packaging can not be reached (e.g. the packaging material is not permeable enough, or the water vapor pressure gradient between box and surroundings is not high enough or can not be controlled reliably), a drying agent inside the box can be used to reduce the water vapor content in the headspace in order to reach a steady state below the saturation water vapor pressure. In this case, the water vapor pressure inside the box and the transpiration rate will influence each other and will depend on the absorption rate and capacity of the absorber (which, in turn, can depend on the water vapor pressure inside the box, see Figure 3).

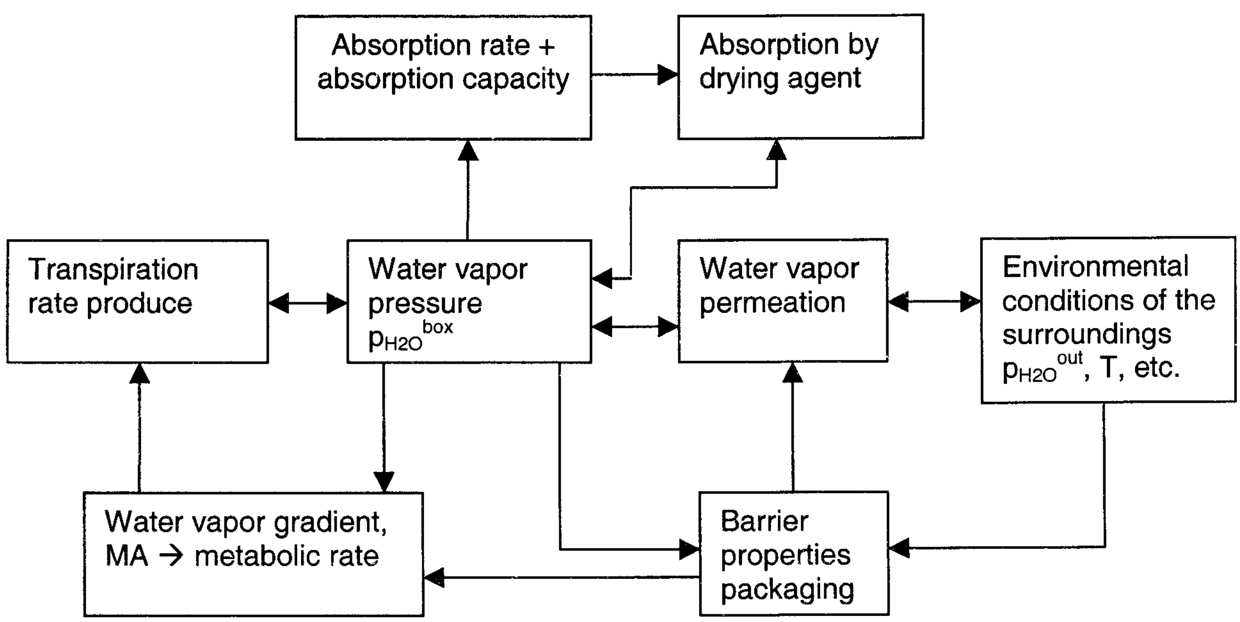


Figure 3: Flow chart describing the mutual relationships between the factors which influence the moisture transport in a packaging.

Practical experience with MA packed vegetables (e.g. broccoli, chicory) shows that the produce releases a significant amount of water during storage. Considering that the main driving force, the water vapor gradient, vanishes at the first occurrence of condensation (i.e. when the headspace reaches 100% RH), and considering furthermore that the metabolic activity of the produce (and therefore the 'metabolic' release of water) is slowed down by the MA conditions, the origin of the observed significant amount of moisture needs an explanation. A possible explanation for a continuing release of water by the product is the existence of a temperature gradient inside the packaging. The temperature gradient is created by the heat which originates from the metabolic activity of the produce. In the direct vicinity of the produce, the air will be warmer than close to the packaging material. As a result, the RH close to the produce decreases, and the product releases more humidity: the water vapor pressure close to the produce will increase. The resulting water vapor gradient between warmer regions (product) and colder regions (packaging) of the headspace will lead to a diffusion of water vapor from the product to the packaging material. There the water vapor will condense, if the water vapor pressure exceeds the saturation limit (see Figure 4). This mechanism leads to a constant transport of water from the product to the packaging and possibly leads to the significant degree of condensation which is observed in MA packaging.

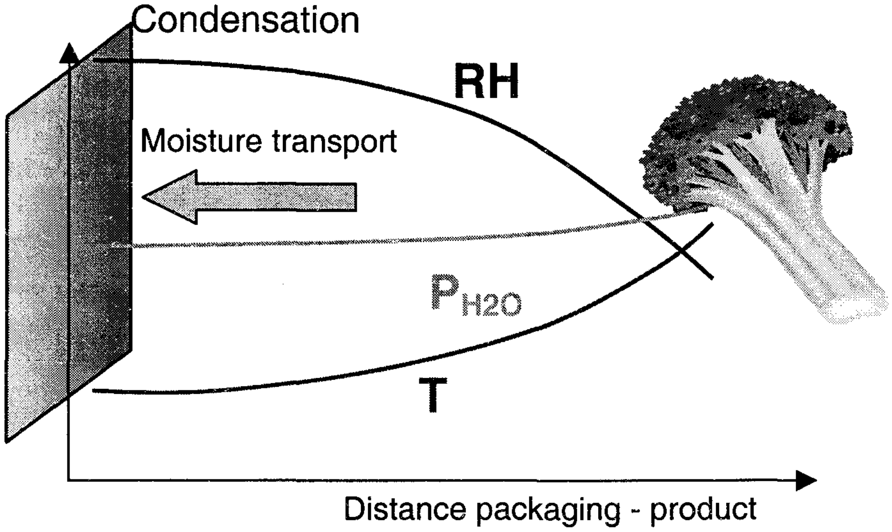


Figure 4: Moisture transport caused by a temperature gradient inside the packaging.

The above discussed model for the temperature-gradient driven moisture transport is a simplified model since convection phenomena which are caused by the metabolic heat of the produce are not included.

3. Aim of this study

Aim of this study is to investigate how the factors
- Transpiration of the produce;
- Water vapor permeability and water vapor absorption rate of the packaging; and
- Application of desiccants / absorbers

influence the build-up of humidity and the occurrence of condensation.

Specifically, we want to answer the following questions which are relevant for the design of novel 'modified atmosphere' packaging concepts with an active or passive humidity control:
- To which extend is it possible to control the build-up of humidity and condensation by the choice of different types coated board?
- Can desiccants and absorbers control the build-up of humidity and condensation over time periods typical for the distribution chain without leading to an (accelerated) dehydration of the product?
- Condensation can be caused by temperature jumps. What is the effect of temperature jumps on relative humidity values and condensation for packaging concepts using different types of coated board and / or absorbers and desiccants?

We chose for two types of products, tomatoes on the vine as a product with a low transpiration rate ('best case' product), and chicory as a product with a high transpiration rate ('worst case' product).
From Kappa GSF we obtained four different types of boxes (29×39×14 cm^3, made from solid board) with different water vapor transmission / absorption characteristics:
- *Type A:* not coated;
- *Type B:* PE coating on the outside;
- *Type C:* PE coating on the outside and the inside;
- *Type D:* 'Sandwich' coating (PE coating with paper liner on both sides) on the inside and the outside.

We tested two different types of desiccants / absorbers:
- Silica gel;
- Polyacrylate absorber embedded in a non-woven.

4. Experimental set-up

Relative humidity values were measured with the Vaisala sensors HMM 30D and HMP 31UT. The sensors employ a capacitive measurement of the relative humidity. All RH sensors were calibrated using 6 different types of saturated salt solutions resulting in equilibrium RH values ranging from 11 to 97% RH. The accuracy of the used humidity sensors is ± 2 % for RH levels below 90 % and approximately ± 3 % for RH levels above 90 %.
Temperatures were measured with constantan – copper thermocouples. The thermocouples were calibrated with a gauged mercury thermometer.
Temperature and RH values were recorded with Grant data-loggers in 5 or 10 minute intervals.
The occurrence of condensation was determined visually, or measured with a humidity sensor which is suitable for high humidity values. This sensor was positioned directly under the OPP film used for closing the MA boxes.
Weight of the produce and the cardboard boxes were measured by a Mettler balance prior and after the experiments.

5. Characterization of the produce: transpiration rates of tomatoes on the vine and chicory

We studied the build-up of humidity in MA boxes with two products: tomatoes on the vine as a 'best case' product with a low transpiration rate, and chicory as a 'worst case' product with a high transpiration rate. In order to gain some insight in the transpiration rates, we measured the mass losses (and, therefore, the moisture losses) of the two types of products under different conditions: tomatoes and chicory were placed on an automated Mettler balance which recorded the mass of the product at regular time intervals. In order to simulate a 'not packed product', we removed the top lid of the glass cover of the balance. The product is therefore in direct contact with the 'outside' environment. In order to simulate a packed product, the top lid of the glass cover was covered with an OPP film which was used in the subsequent experiments. In this case, the product is separated from the outside environment, and the transpiration of the product will lead to a build-up of the relative humidity inside this simulation packaging. In addition, we repeated the measurements under 'packed' condition and enclosed a desiccant or absorber. The relative humidity inside the glass cover of the balance was recorded during these experiments. The results of the measurements are listed in table 1.

Condition	Tomatoes on the vine		Chicory	
	$\Delta m_{product}$ [g day^{-1}kg^{-1}]	RH_{eq} [%]	$\Delta m_{product}$ [g day^{-1}kg^{-1}]	RH_{eq} [%]
'not packed'	2.7	65 - 70	31	~62
'packed'	1.6	70 - 75	21	75
'packed' + absorber	2.8	~65	28	65 - 70

Table 1: Transpiration rates of tomatoes on the vine and chicory 'packed' under different conditions and measured at 18.5°C. Transpiration rates are normalized for 1.0 kg product.

The measurements show that chicory has a significantly higher transpiration rate compared to tomatoes on the vine (the transpiration rate is a factor 10 - 13 higher). 'Packaging' the product increases the relative humidity in the vicinity of the product and results in a lower transpiration rate. Adding an absorber to the 'packed' product reverses this effect: the absorber decreases the relative humidity and leads in turn to an increased transpiration rate. The values listed above show a rough trend for the transpiration rates of chicory and tomatoes. It should be pointed out that the rates depend strongly on the RH in the vicinity of the product, which is influenced by the moisture transport (i.e. convection and diffusion of water vapor). However, a strict control of convection and diffusion of water vapor inside the balance remains difficult.

The production of water caused by the metabolic activity of the produce:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \Delta H$$

contributes for chicory and tomatoes only marginally to the transpiration at very low water vapor gradients. One kilogram tomatoes produce at 10°C and normal atmospheric conditions 0.147 mmol kg^{-1} h^{-1} water (= 63.6 mg day^{-1}kg^{-1}), one kilogram chicory produce 0.23 mmol kg^{-1} h^{-1} water (= 99 mg day^{-1}kg^{-1}).

6. Passive humidity control: effect of packaging material and product on the build-up of humidity

The aim of the research described in this section is to evaluate possibilities to control the build-up of humidity and condensation in MA boxes and the dehydration of the packed produce by using different types of coated solid board as packaging materials. The experiments were carried out for two types of produce with significantly different transpiration rates: tomatoes on the vine as a 'best case' product with a low transpiration rate, and chicory as a 'worst case' product with a high transpiration rate. The measurements were carried out for both products at two temperatures: at room temperature (18°C) and at the optimal storage temperature (12°C for tomatoes on the vine, and 4.5°C for chicory). Produce and boxes were conditioned at the experimental condition (T and RH) prior to the experiments.
We measured the temperature and relative humidity above the produce below the OPP-film which was used to close the boxes. For selected boxes, we measured temperature and RH values at the bottom of the boxes, below the produce. For all experiments the temperature and RH values of the environment of the boxes were recorded.
In order to investigate moisture transport and dehydration of the produce, the produce and the boxes were weighed before and after the experiments.

Tomatoes on the vine

The results of the measurements on tomatoes on the vine are listed in Table 2 and Table 3, and are shown in Figure 5 and Figure 6. RH_{eq} denotes the steady-state relative humidity, Δm_{box} is the increase in mass of the box (i.e. $\Delta m_{box} = m_{box,final} - m_{box,initial}$ corresponds to the moisture which was absorbed by the box), $\Delta m_{product}$ is the mass loss of the product (i.e. it is a measure of the dehydration of the product), and $\Delta m_{tot} = \Delta m_{box} + \Delta m_{product}$ is the total mass loss of box and product during the experiment and corresponds to the moisture content which was able to escape from the box. The mass balances determined in a single experiment do not contain information on the dynamics of the moisture transport since the weight of product and boxes was determined at two points in time only (before and after the experiment). Experiments with different duration provide insight into the dynamics of the moisture transport. There is a steady moisture transport from the headspace into the board and through board to the surroundings; the rate of this moisture transport depends on the permeability and the absorption capacity of the board. $\Delta m_{product}$ should be therefore given as $\Delta m_{product}$ per time interval.
In order to be able to compare the mass balances of different experiments, we normalized the time dependent mass losses for a time period of 24 hours.

Type	RH_{eq} [%]	Δm_{box} [g day^{-1}]	$\Delta m_{product}$ [g day^{-1}]	Δm_{tot} [g day^{-1}]	$\Delta m_{product}$ [g day^{-1} kg^{-1}]
Type A: not coated	75 - 85	0.53 ± 0.14	-4.9 ± 0.3	-4.4 ± 0.3	-1.81 ± 0.11
Type B: PE coating on the outside	87	3.2 ± 0.4	-3.9 ± 0.4	-0.7 ± 0.6	-1.44 ± 0.15
Type C: PE coating on both sides	96	0.99 ± 0.11	-1.62 ± 0.14	-0.64 ± 0.18	-0.60 ± 0.05
Type D: 'Sandwich coating' on both sides	91	1.9 ± 0.2	-2.52 ± 0.13	-0.6 ± 0.2	-0.93 ± 0.05

Table 2: Equilibrium values of relative humidity and moisture transport at 18°C for boxes filled with 2.7 kg tomatoes on the vine. Mass balances are converted for an experiment lasting 24 h. Values are means ± SEM (n = 4).

Type	RH_{eq} [%]	Δm_{box} [g day^{-1}]	$\Delta m_{product}$ [g day^{-1}]	Δm_{tot} [g day^{-1}]	$\Delta m_{product}$ [g day^{-1} kg^{-1}]
Type A: not coated	71	0.4 ± 0.2	-6 ± 2	-6 ± 2	-2.4 ± 0.9
Type B: PE coating on the outside	84	2.27 ± 0.10	-2.9 ± 0.3	-0.6 ± 0.3	-1.06 ± 0.10
Type C: PE coating on both sides	93	0.42 ± 0.06	-1.5 ± 0.2	-1.0 ± 0.3	-0.54 ± 0.09
Type D: 'Sandwich coating' on both sides	91	1.3 ± 0.4	-2.19 ± 0.17	-0.9 ± 0.4	-0.81 ± 0.06

Table 3: Equilibrium values of relative humidity and moisture transport at 12°C for boxes filled with 2.7 kg tomatoes on the vine. Mass balances are converted for an experiment lasting 24 h. Values are means ± SEM (n = 2).

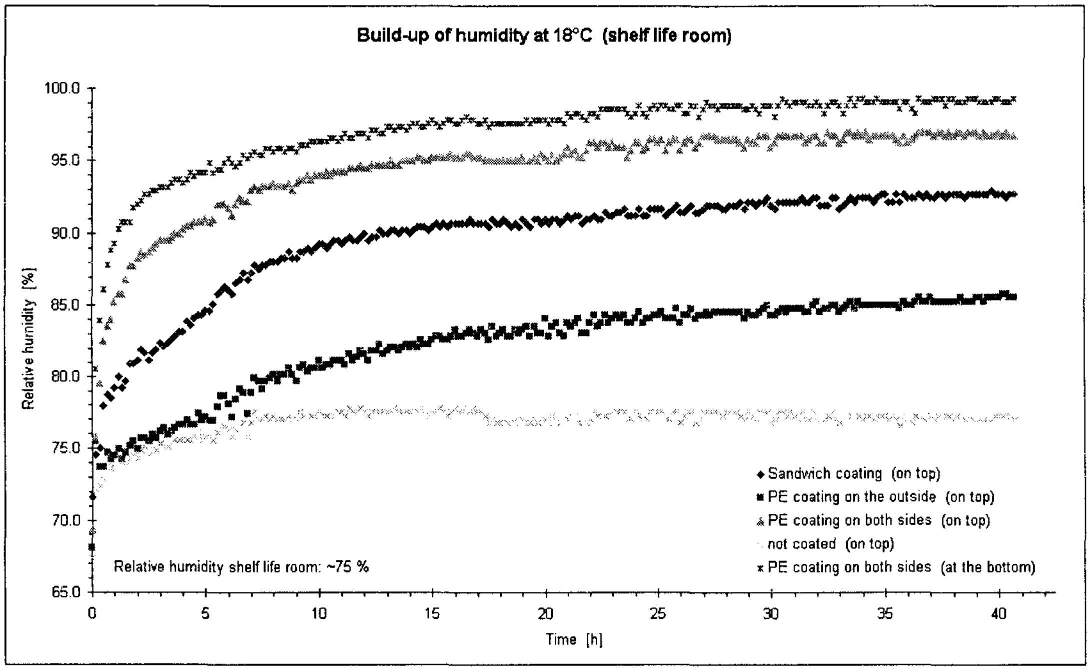


Figure 5: RH profiles for 2.7 kg tomatoes on the vine at 18°C packed in solid board boxes with different coatings.

RH – profiles

For tomatoes on the vine, the choice of packaging material (i.e. board with different coatings) has a significant influence on the build-up of humidity in the boxes. For experiments carried out at 18°C we observe the following RH profiles:

- If no coating is applied to the board (type A), the relative humidity inside the boxes increases only marginally. The water vapor permeability of the not coated board is high enough such that a significant amount of the moisture which is released by the tomatoes can be transmitted to the environment. The moisture transport from the product to the surroundings can be followed by the mass balances: the total weight of the product and the boxes decreases steadily in time. In addition, we observe that the water vapor pressure inside the boxes follows the variations in water vapor pressure of the surroundings (see Figure 6). In order to control the build-up of humidity by permeation of the moisture to the surroundings, a control of the water vapor pressure gradient (and, therefore, the water vapor pressure outside the box) is necessary. For example, the palletizing of boxes will have a significant influence on the water vapor gradient close to the box, and will alter the permeation rates.

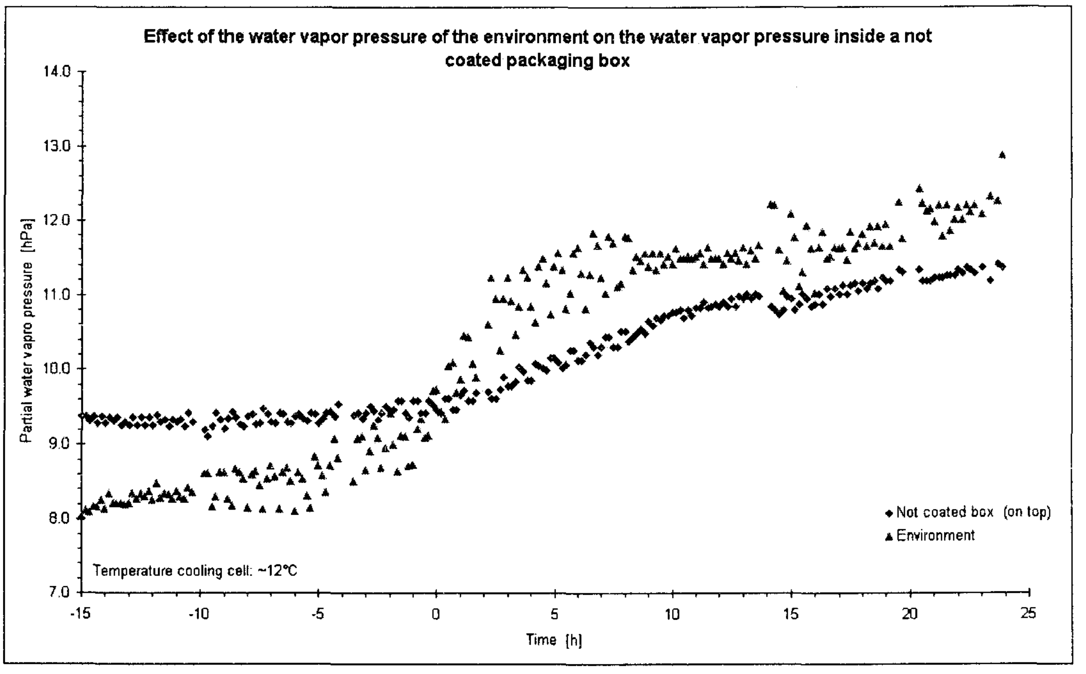


Figure 6: The effect of the water vapor pressure of the environment on the water vapor pressure inside a not coated packaging box filled with 2.7 kg tomatoes on the vine at 12°C.

- The results for tomatoes on the vine in not coated boxes contrast with the results for tomatoes packed in PE coated boxes: for box types C and D, the relative humidity reaches within 15 h values above 90 % RH. Within the accuracy of the RH sensors, there is no significant difference between box types C and D.
- The relative humidity builds up at a slower rate in boxes which have a PE coating on the outside only (type B) compared with the box types C and D. In addition, we observe that the board absorbs a significant part of the moisture which is released by the product: the packaging acts as an absorber. When we determined the weight increase of this box after different storage periods, we observed that the board has been saturated after approximately 3 days.

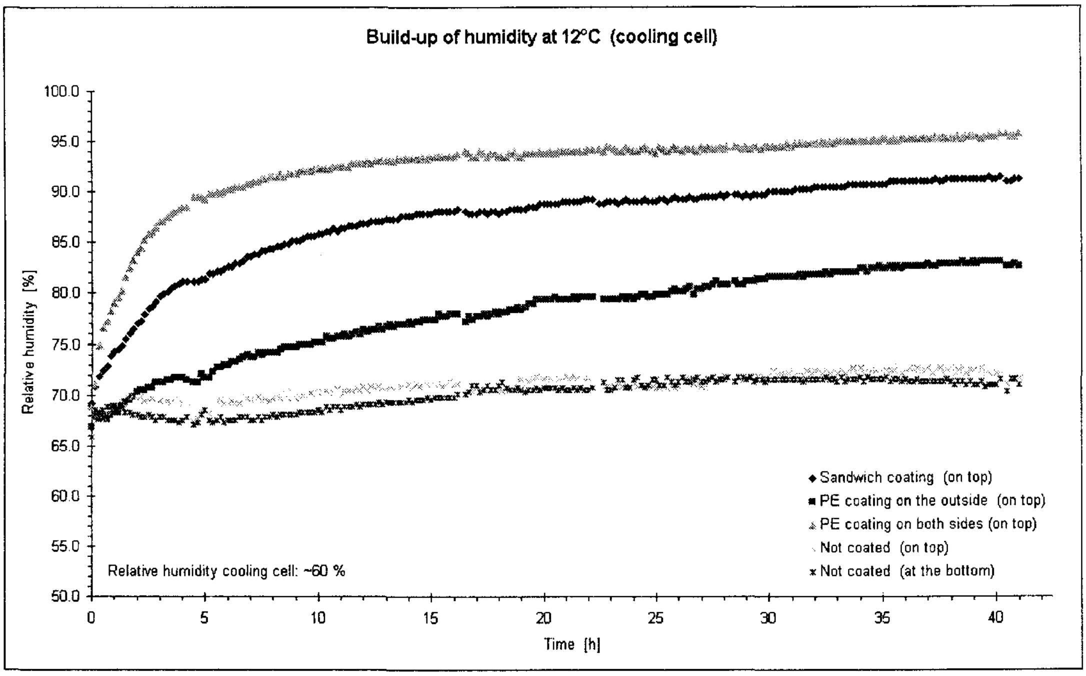


Figure 7: RH profiles for 2.7 kg tomatoes on the vine at 12°C packed in solid board boxes with different coatings.

- If we repeat the experiments at 12°C, we observe similar equilibrium RH values for the box types B, C and D (see table 3).
- The situation is different for box A which allows a continuous moisture transport from the product through the box to the surroundings. Here, the driving force for the transpiration (Δp_1, the difference between the saturation partial pressure and the steady state partial pressure) is a determining factor for the steady state RH. Δp_1 depends on the temperature: Δp_1 for e.g. a saturation RH of 98 % and a steady state RH of 75 % is 4.7 hPa at 18°C and 3.2 hPa at 12°C. The transpiration will be lower at lower temperatures for the same difference in RH values. In addition, the driving force for the water vapor permeation through the packaging material (Δp_2, the difference between the partial water vapor pressure in the box and the water vapor pressure of the surrounding) are not the same as for the experiments at 18°C. It remains therefore difficult to quantitatively compare the results for these boxes at different temperatures.
- In selected cases, we measured RH and temperature at different positions in the boxes. These measurements showed that the RH values at the bottom of the boxes usually differ from the values at the top of the boxes, right below the film. However, we observed that the water vapor pressure (which is the driving force for diffusion of water vapor) do not significantly differ throughout the boxes: the differences in relative humidity are caused by differences in temperature between the top and the bottom of the boxes which. The temperature gradient is caused by the heat which is generated by the metabolic activity of the produce.

Dehydration of the product

- The total mass balance Δm_{tot} for box A shows that the moisture which is released from the tomatoes on the vine is transported to the environment. The mass losses of the product inside the boxes is 1.81 ± 0.11 g day^{-1} kg^{-1} for tomatoes stored at 18 °C and 2.4 ± 0.9 g day^{-1} kg^{-1} for tomatoes stored at 12 °C. The mass losses for packed tomatoes on the vine at 18°C compares well with the mass losses determined in section 5 (1.6 g day^{-1} kg^{-1}).

- For box B we observe that the board has absorbed the moisture which is released by the tomatoes. Δm_{tot} is small compared to Δm_{box}. The mass losses of the product are lower than in box A (which is in agreement with the – compared to box A – higher RH values which are reached within this box: the driving force for the transpiration is lower). If we compare Δm_{box} for different time periods, we see that the cardboard saturates only slowly: after three days, Δm_{box} remains approximately constant. This explains the slow dynamics of the RH values which we observe for box B.
- For box types C and D we observe values for Δm_{tot} which are comparable with box B. The released moisture is partially absorbed by the board (for the double coated PE board to a much lesser extend than for the sandwich coated board, where the liner is in contact with the headspace), partially permeated through the packaging, and to a small extend used to build up the humidity in the headspace.
  - The mass balances for the box type C shows that at 12°C about 70 % of the released moisture has been transmitted to the outside, at 18°C this percentage is about 35 %. The dehydration of the product is small, about 0.6 g day^{-1} kg^{-1}, which indicates that the product is approximately in equilibrium with the high RH value inside the box.
  - The mass balances for the box type D shows that at 12°C about 40 % of the released moisture has been transmitted to the outside, at 18°C this ratio is about 20 % and the remaining released moisture was mostly absorbed by the board. The dehydration of the product is about 0.9 g day^{-1} kg^{-1}, which is higher then in box type C.
- Since tomatoes on the vine have a relatively low transpiration rate, dehydration is usually not a problem and does not limit the shelf life of the product.

Condensation
For all experiments with tomatoes on the vine, we do not observe any visual indication of condensation within the first three days of the measurements. In one case (box type C, 18°C), we observed after 5 days a slight haze on the packaging film which was caused by condensation.

Chicory
The results of the experiments conducted with 2.7 kg chicory at 4.5°C are listed in Table 4 and are shown in Figure 8.

RH profiles
- In contrast to the experiments with tomatoes, we observe for chicory no significant influence of the packaging material on the final equilibrium RH values. Within the accuracy of the sensors, the humidity reaches in all boxes a similar value above 90 % RH.
- If we repeat the experiments at 18°C, we observe similar equilibrium RH values.
- The results can be explained by the high transpiration rate of chicory. Compared with the transpiration rate of chicory, the water vapor permeability of box A or the absorption rate of the board of box B is too small in order to influence the RH profiles significantly.

Type	RH_{eq} [%]	Δm_{box} [g day^{-1}]	$\Delta m_{product}$ [g day^{-1}]	Δm_{tot} [g day^{-1}]	$\Delta m_{product}$ [g day^{-1} kg^{-1}]
Type A: not coated	94	17 ± 4	-17 ± 4	0 ± 6	-6.4 ± 1.5
Type B: PE coating on the outside	91	13 ± 2	-16 ± 4	-3 ± 5	-5.9 ± 1.6
Type C: PE coating on both sides	95	1.1 ± 0.4	-6 ± 3	-5 ± 3	-2.2 ± 1.1
Type D: 'Sandwich coating' on both sides	95	3.8 ± 0.3	-8 ± 2	-4 ± 2	-2.9 ± 0.8

Table 4: Equilibrium values of relative humidity and moisture transport at 4.5°C for boxes filled with 2.7 kg chicory. Mass balances are converted for an experiment lasting 24 h. Values are means ± SEM (n = 2).

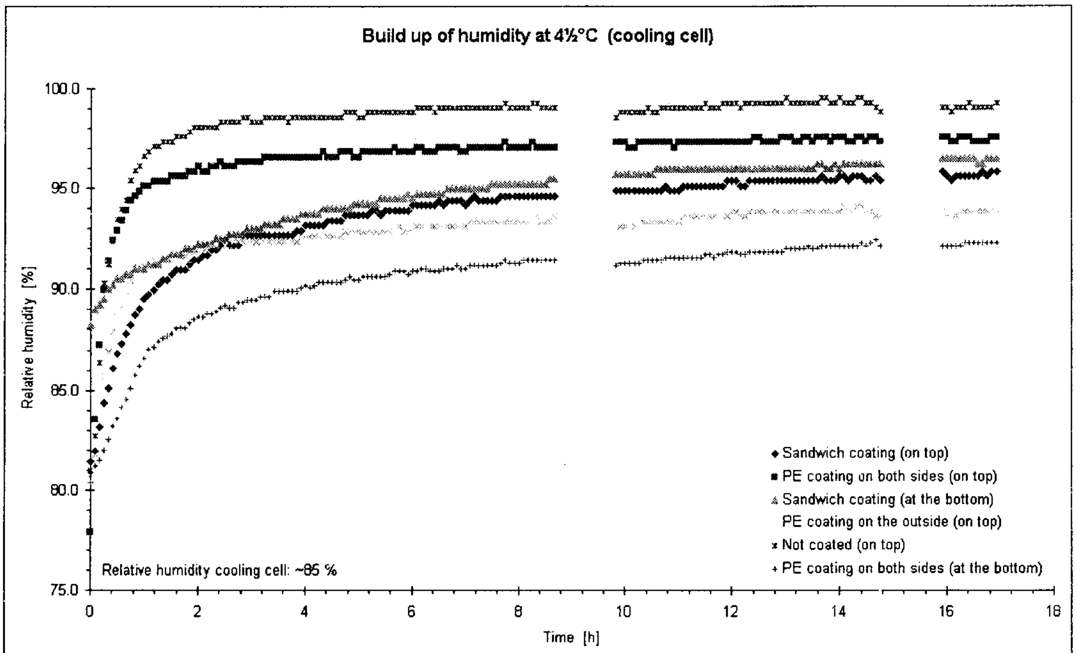


Figure 8: RH profiles for 2.7 kg chicory at 4.5°C packed in solid board boxes with different coatings.

Dehydration of the product

Some of our conclusions on the moisture transport in the experiments with tomatoes can also be applied for the experiments with chicory:

- The PE coating of boxes B – D limits the moisture transport to the surroundings.
- The board of the box with the PE coating on the outside (type B) acts as an absorber.
- For the experiments with chicory at 4.5°C, we do observe for the not coated box (type A) no significant moisture transports through the board. This is in contrast to the experiments with tomatoes at 18°C and at 12°C. During this experiment, the difference in water vapor pressure inside and outside the box (Δp_2 which is the driving force for the moisture transport) was too low in order to lead to a sufficient moisture transport to the surroundings ($\Delta p_2 \leq 1$ hPa at 4.5 °C (cooling cell), $\Delta p_2 \leq 6$ hPa at 18°C (shelf life room)). In addition, the water vapor permeability of the board might decrease when it is nearly saturated.
- If the experiment with chicory in box type A is repeated in the shelf life room at 18°C, we observe similar results as for tomatoes: within 24 h, 5.0 kg chicory

releases 34 g of moisture. The board absorbs 19 g water, and 15 g water are transmitted through the board.
- Chicory wrapped in PVC film (the currently used consumer packaging) exhibits a weight loss of 1% per week. The values we obtained for chicory packed in box A and B correspond to a weight loss of 4 % per week, and the values for box C and D correspond to 2 % weight loss per week.

Amount of produce
Experiments at 4.5°C with 5 kg chicory and 2.7 kg chicory do not show any differences in the equilibrium RH values. Considering the high transpiration rate of chicory, this is not a surprising result.

Condensation
In all experiments with chicory we observed within one hour water condensing on the film which was used to close the boxes. At the end of the experiment, the chicory felt wet: it was covered with a thin film of water.

Conclusions
The build-up of humidity, the occurrence of condensation, and the dehydration of the product are studied for four types of solid board and two types of produce. We obtained the following results:
- For produce with a **low transpiration rate**, we are able to control the build-up of humidity with the choice of an uncoated board which has a high water vapor permeability. No significant condensation occurred, if boxes and produce were packed and stored at constant temperature.
- For produce with a **high transpiration rate**, the choice of coating has no influence on the equilibrium RH values which are reached in the packaging. It is not possible to prevent condensation by the choice of a suitable packaging material, the produce is wet when it is unpacked.
- **Dehydration** of the produce can in general be controlled by the water vapor permeability and absorption capability of the board. A board with a high water vapor permeability which can be used to limit the build-up of humidity obviously will lead to higher moisture losses of the produce.
- Board which is only coated on the outside acts as an **absorber**. For produce with a low transpiration rate, the build-up of the humidity could be slightly delayed.
- If a board which is **permeable for water vapor** should be used in order to control the humidity inside the boxes, a detailed study of the **humidities of the surroundings** is necessary: the headspace in the box and surroundings influence each other. For example, the stacking of boxes on a pallet will have a significant influence on the exchange of moisture with the environment.

For practical applications, it should be possible to design a 'modified humidity' box for produce with a low transpiration rate using board with a high water vapor permeability (e.g. not coated board). However, it remains questionable whether the gas barrier of such a board is sufficient in order to obtain optimal MA conditions. A possible solution in order to optimize gas as well as humidity barrier would be to construct a box out of two different types of material: for example, a not coated lid with a coated box. For future research in this direction, the interaction between microclimate in the box and conditions outside the box has to be taken into account: the moisture exchange between box and surroundings is driven by the water vapor pressure difference between box and environment.

The results with the boxes coated on the outside, where the board acts as an absorber, indicate that absorbers can delay the build-up of humidity. However, the absorption capacity of the board is not sufficient in order to efficiently limit the build-up of humidity. In the following sections we will therefore investigate possibilities to actively control the humidity profile with absorbers or desiccants.

7. Moisture absorption characteristics of silica gel and polyacrylate absorber

In order to gain some insight into the behavior of drying agents which are suitable for modified atmosphere applications, we carried out several experiments to compare the behavior of silica gel and polyacrylate absorbers. Silica gel was obtained from Brocades ACF, Maarsen, and dried in an oven before use. The polyacrylate absorber which was obtained from Lantor, Veenendaal, consists of polyacrylate gel embedded in a non-woven sheet. The sheet had a weight of 240 g per m^2 and was used without any pre-treatment (i.e. directly cut 'from the role', which was protected with a film, a situation like in practical circumstances).
Characteristics which are important for the functionality of the drying agents inside the packaging are the rate at which the agent can take up moisture, the time which is needed to saturate the absorber (i.e. the time span during which the drying agent can effectively influence the humidity inside a packaging ($t_{saturation}$)), and the absorptive capacity (Δm / m) of the absorber. These characteristics are determined by measuring the weight of silica gel and polyacrylate samples as a function of time. During these measurements, which were carried out using an automated balance, the drying agents were exposed to air with different relative humidities. We carried out three types of experiments:

- In experiment A, the drying agent was in contact with the atmosphere of the surroundings (i.e., the protective cover of the balance was not closed, therefore, the absorber was not separated from the atmospheric conditions in the shelf life room (18°C, 70 % RH)).
- In experiment B, we attempted to simulate the situation in a modified atmosphere packaging. The drying agent was placed on the balance, and some product (e.g. one stem of chicory) was enclosed and suspended above the drying agent. The cover of the balance was sealed with an OPP packaging film such that the atmosphere inside this simulation packaging can only be influenced by the packed produce.
- Experiment C is a combination of experiment A and B. The polyacrylate absorber was first saturated under the atmospheric conditions in the shelf life room (18°C, 70 % RH). Subsequently, the characteristics of the absorber were measured under the conditions of experiment B (closed balance with product present). Aim of this experiment is to test the performance of the polyacrylate absorber if the absorber is not stored under dry conditions before it is used in a packaging. This will be the situation which is found in 'real life' applications. We want to answer the question whether the agent can lose its absorptive capacity during storage before being applied in a packaging. This experiment was only carried out for the polyacrylate absorber, since silica gel loses its absorption capability once it is saturated under the condition of the shelf life room.

In most experiments, we recorded the relative humidity inside the balance. Table 5 lists the final results of these measurements.

Agent	$m_{initial}$ [g]	Δm [g]	Δm/m [%]	$t_{saturation}$ [h]	Product	RH [%]
PA	17.3	2.3	13	~100	No product	~67 %
PA	11.3	~2.7	~24		No product	~65 %
PA	2.1	~0.6	~29	~30	Chicory	n.a.
PA	20.7	>7	>35	>240	Chicory	67 → 89 %
PA	1.35	0.52	39	18	Chicory	72 → 82 %
PA	21.3	>9	>40	>160	Chicory	n.a.
SG	20.2	3.5	17	85	No product	~65 %
SG	19.6	4.2	22	35	Chicory	62 → 89 %

Table 5: Characteristics of silica gel (SG) and polyacrylate (PA) drying agents.

In Figure 9, the weight increase of the polyacrylate absorber and the weight increase of silica gel are displayed, when the agents were placed in a closed balance with 0.3 kg chicory (experiment B). We can draw the following conclusions:

- Within the first 24 hours there is no significant differences between silica gel and polyacrylate in the rate at which both absorbers (about 20½ gram) takes up moisture,
- The absorptive capacity of polyacrylate is at least twice as big as the absorptive capacity of silica gel.
- The polyacrylate absorber is able to absorb over considerable longer time periods (at least a factor 4 longer) compared with silica gel. However, the absorption rate of the polyacrylate absorber decreases in time.

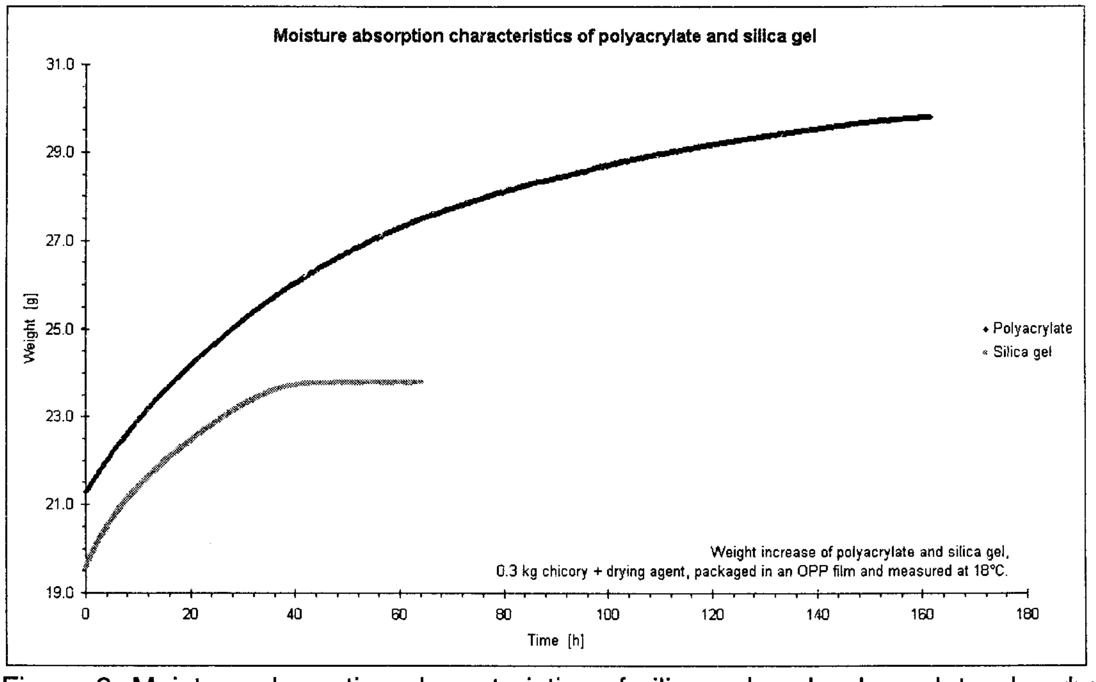


Figure 9: Moisture absorption characteristics of silica gel and polyacrylate absorber at the presence of product at 18°C.

Figure 10 displays the results of experiment C using polyacrylate absorber with an initial mass of approximately 17 gram. For this experiment we can draw the following conclusions:

- If the absorber is stored in contact with the atmosphere in the shelf life room, it saturates within 6 days.

- If the under the conditions of the shelf life room saturated absorber is exposed to higher relative humidities (e.g. in a closed packaging with a transpiring product), it still can absorb considerable amounts of moisture.
- The absorptive capacity (Δm / m) of the polyacylate absorber is a function of the RH values of the surrounding: at higher relative humidities, it can take up additional moisture. This explains the variations in Δm / m for the polyacrylate absorber listed in Table 5. The absorptive behavior of polyacrylate contrasts with the behavior of silica gel. In our experiments, silica gel absorbed all available moisture until it was saturated.

The development in time of the absorption can be modeled reasonably well by an exponential function:

$$m(t) = m(\infty) - \{m(\infty) - m(0)\} \cdot e^{-t \cdot \ln(2) / \tau} \qquad (7\text{-}1)$$

The dynamics of the moisture absorption can be therefore described by a few parameters: the degree of saturation ($m(\infty)$ - $m(0)$), and a 'half life time' (τ). A model which takes into account the characteristics of the absorber, the transpiration rate of the produce, and the permeation properties of the packaging should be ideally suited for screening different absorbers, and optimizing the humidity control by absorbers for different types of produce (see section 11).

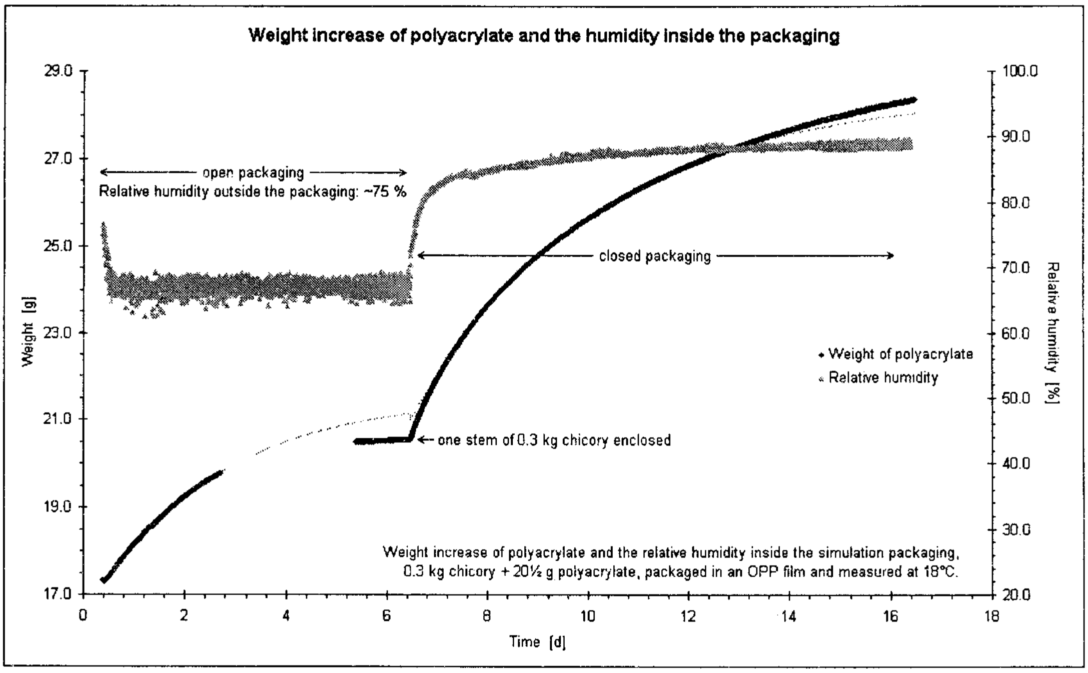


Figure 10: The weight increase of polyacrylate and the development of humidity during and after it has been exposed to the air (18 °C, ~75 % RH). After seven days, the balance was sealed with an OPP packaging film after one stem of about 0.3 kg chicory was enclosed.

Conclusions

These experiments show that polyacrylate absorber is - compared with silica gel - a superior absorber for applications in MA packaging.

- The same amount of polyacrylate absorber has at least twice the absorptive capacity than silica gel.
- Polyacrylate absorber can absorb moisture over a considerable longer period of time compared with silica gel.
- If polyacrylate absorber is stored under 'normal atmospheric conditions' (18°C, 70 % RH), it loses only part of its absorptive capacity.
- Future work on the optimization of absorbers should focus on exploring the packaging solution as an integrated system consisting of packaging, absorber, product, and surroundings.
  - A characterization of the absorber will include measurement of the absorption rate and capacity as a function of the water vapor pressure. The development of the humidity inside the box during a given period of time and the absorption of moisture by the drying agent will then be a result of the model, and will further depend on transpiration rate of the product, permeation properties of the packaging, and environmental conditions of the surroundings of the packaging.
  - In addition, future research can focus on controlling the flux of water vapor to the absorber (and, therefore, the absorption rate of the absorber) by a membrane.

8. Active humidity control: effect of desiccants and absorbers on the build-up of humidity and condensation

The experiments in section 6 showed that a 'passive' control of the humidity (i.e. the 'removal' of moisture by permeation through the packaging material) is possible for produce with a low transpiration rate in combination with a packaging material with a high water vapor permeability. In the previous section, we investigated the properties of two types of drying agents, silica gel and polyacrylate absorbers, which can possibly be used for an active control of the humidity. The central question which will be addressed in this section is whether it is possible to control the build-up of humidity actively in the cases where the passive control fails (e.g. for tomatoes on the vine in boxes with low water vapor permeability (box C), and for chicory in general). We will take the following steps to address the central question:

- Tomatoes on the vine packed in box C (PE coating on both sides) will be used to
  - Study the effect of drying agents on the build-up of humidity and the dehydration of the produce;
  - Investigate the difference in performance inside a packaging box between silica gel and polyacrylate absorber; to determine the superior drying agent;
  - Estimate the necessary amount of drying agent to control the build-up of humidity over a given period of time.

  We choose tomatoes on the vine for this part of the study since the very high transpiration rate of chicory will probably cover the differences in RH profiles for the drying agents enclosed in different amounts.
- Chicory packed in box C will be used to
  - Determine which drying agents can be used to control the build-up of humidity and prohibits the occurrence of condensation for produce with high transpiration rates;
  - Estimate the necessary amount of drying agent in order to control the humidity for a given period of time;

Silica gel was filled in petri-dishes and the polyacrylate non-woven was – if necessary – folded and placed inside the box. For selected experiments (see Table 6), we separated the polyacrylate sheet from the produce with an uncoated board (same material as box A). These experiments were carried out in the same way as the experiments described in section 6.

RH - profiles for experiments with tomatoes on the vine

Product	Absorber	Time [h]	RH profile	$\Delta m_{product}$ [g]	$\Delta m_{absorber}$ [g]	Δm_{box} [g]
2.7 kg tomatoes on the vine	No absorber	120	72 % → 97 % RH	-5.5	-	3.4
	82.5 g PA		72 % → 60 % → 66 % RH	-19.2	18.9	-0.9
	40 g SG		72 % → 56 % → 86 % RH	-12.1	9.8	1.2
	80 g SG		72 % → 45 % → 80 % RH	-17.4	16.6	-0.5
5 kg chicory	No absorber	70	75 % → 95 % RH	n.a.	n.a.	n.a.
	161 g PA		75 % → 92 % RH	-93.2	75.3	4.1

Table 6: Effect of drying agents on the relative humidity and dehydration of the product at 18°C.

Table 6 and Figure 11 show the effect of different types and amounts of drying agents in the build-up of humidity in box type C filled with 2.7 kg tomatoes.

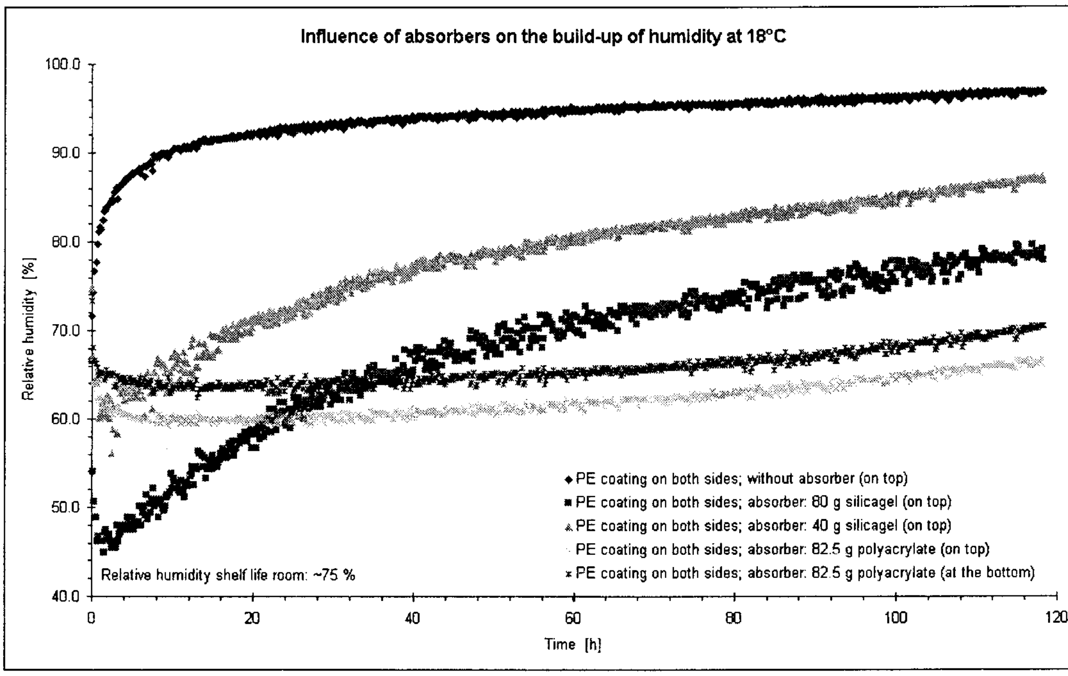


Figure 11: Effect of silica gel and polyacrylate absorber on the build-up of humidity in double coated boxes filled with 2.7 kg tomatoes at 18°C.

We can observe that the application of silica gel and polyacrylate absorber, respectively, lead to different dynamics of the build-up of the relative humidity, and result in different values for the relative humidity.

- Silica gel leads to a rapid decrease of the humidity in the boxes; the minimal values of the relative humidity are reached within 2 hours (40 g silica gel: 70 % RH → 56 % RH, 80 g silica gel 70 % RH → 45 % RH). After 2 hours, the relative humidity starts to 'recover' and reaches the initial 70 % RH for 40 g silica gel within one day, and 80 g silica gel within 3 days.
- Polyacrylate absorber lead to a rather moderate drop in relative humidity compared with silica gel: the relative humidity drops within 6 hours from 70 % RH to 60 % RH. In contrast to silica gel, the polyacrylate absorber stabilizes the relative humidity between 60 and 70 % RH: within 5 days, the relative humidity increases slightly from 60 % RH to 65 % RH. See Figure 11: effect of silica gel and polyacrylate absorber on the build-up of humidity in double coated boxes filled with 2.7 kg tomatoes at 18°C.
- 80 g of polyacrylate absorber are sufficient to keep the humidity in a box filled with 2.7 kg of tomatoes below 70 % RH for 5 days. Considering the slow increase of the measured RH values, and the results of the previous section, which showed that the polyacrylate absorber saturates only gradually without losing suddenly its absorption capability, we can estimate that the humidity in this set up can be stabilized below 75 % RH for several additional days.
- 40 g and 80 g silica gel also succeed to keep the relative humidity below 90 % RH over a period of 5 days. However, the silica gel saturated within the first days of the experiments (its color turned from blue to pink), and – based on our results in the previous section (see Figure 9) – we can assume that the silica gel ceased to absorb moisture before the end of the experiment. As a result, the RH values inside the boxes start to increase.

Dehydration of the produce

We gained insight into the humidity transport which occurred inside the boxes by weighing drying agents, produce, and boxes before and after the experiments. The following conclusions can be drawn:

- Moisture is transferred from the produce to the absorbers; moisture take-up of the double coated boxes is negligible.
- For tomatoes, 80 g of polyacrylate absorber and 80 g of silica gel lead within 120 hours to similar dehydration (≈ 18 gram). Since the dehydration is driven by the difference between the water vapor pressure inside the box and the water vapor pressure corresponding to the activity of the produce, we can conclude that most of the transpiration in the box filled with tomatoes and silica gel occurred during the first day, when the silica gel drastically lowered the RH. The polyacrylate absorber leads to stable RH values around 65% RH. For this reason we can assume that the tomatoes release moisture at an approximately constant rate of about 1.3 g day^{-1} kg^{-1}. This is slightly lower than transpiration rate for tomatoes on the vine (2.8 g day^{-1} kg^{-1} at 65 % RH) which is determined in section 5 and for transpiration rates of tomatoes packed in box A (1.8 g day^{-1} kg^{-1}) which is determined in section 6.

RH – profiles for experiments with chicory

The effect of silica gel and polyacrylate absorbers on the build-up of humidity in boxes filled with chicory is shown in Figure 12 and Figure 14. In the experiment shown in Figure 12, we placed the polyacrylate non-woven at the bottom of the box and separated it from the product with a non-coated board. The measurements show that the significantly higher transpiration rates of chicory lead to a qualitative different development of the relative humidity compared to the development observed for packaging boxes in which drying agent were enclosed and filled with 2.7 kg tomatoes on the vine. From these measurements the following conclusions can be drawn:

- The absorption rates of the drying agents are in general not able to match the transpiration rate of chicory. For this reason the drying agents do not cause a decrease in the initial relative humidity level. In general, we can state that we can not observe a longer lasting overall effect of 40 g or 80 g silica gel or 80 g polyacrylate absorber on the occurrence of condensation or build-up of humidity for the experiment displayed in Figure 12.
- An exception form the values which are obtained from the sensor which was positioned close to the polyacrylate absorber at to the bottom of the box: here we observe a decrease in relative humidity, which is caused by absorption of moisture by the enclosed polyacrylate sheet.

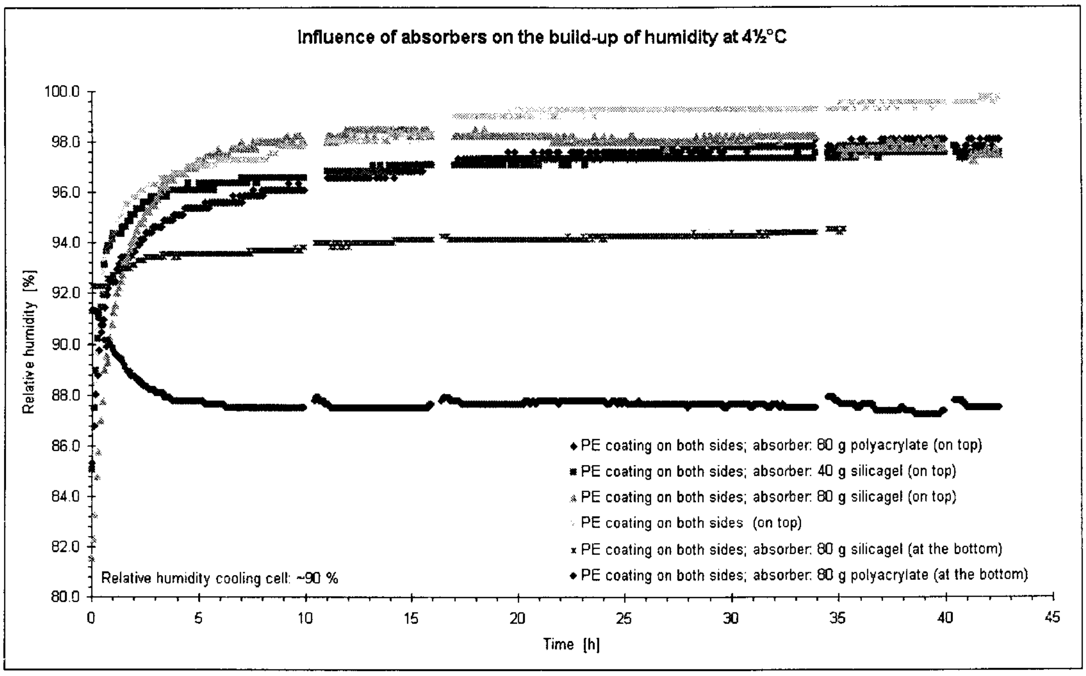


Figure 12: RH profiles for 5 kg chicory packed in a double coated box with silica gel and polyacrylate absorber at 4.5°C.

A packaging concept for chicory

The above mentioned observation led us to carry out the following experiment: we designed a box where the product was essentially 'enclosed' in two layers of polyacrylate non-woven. We placed one mat of non-woven (80.5 g) on the bottom of the box (type C) and covered this mat with a not coated board (same material as box type A). The product was placed on top of this board and covered with another not coated board. On top of this second not coated board, we placed another sheet of polyacrylate non-woven, and we sealed the box with an OPP film (see Figure 13).

The layout displayed in Figure 13 can be viewed as a model for a packaging with integrated polyacrylate absorbers. The development of the relative humidity was measured at four different positions in this box: (a) below the product, on top of the lower not coated board, (b) in between the product, (c) on top of the product, below the top not coated board, and (d) between polyacrylate non-woven and OPP packaging film. The results of these measurements are displayed in Figure 14.

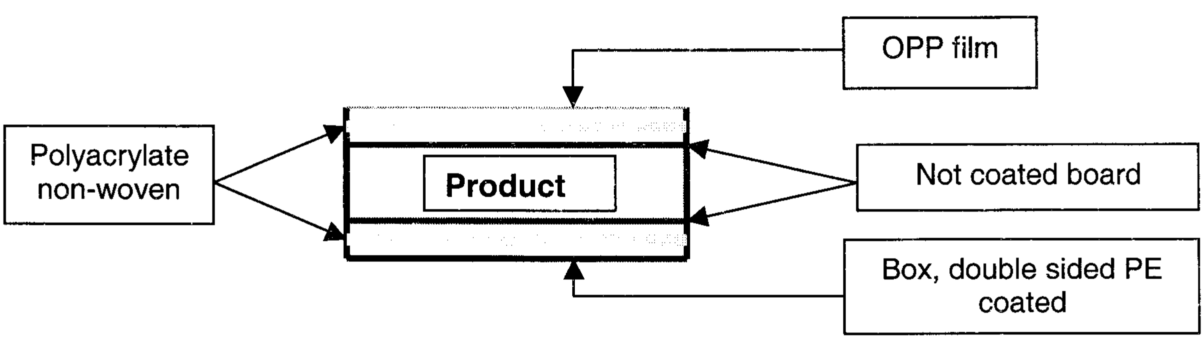


Figure 13: Layout of the experiment with two layers of polyacrylate non-woven.

RH-profiles

- The relative humidity close to the absorbers (position (a) and (c) of the sensors) remains during a period of three days below 95 % RH. Only in between the product (position (b) of the sensor) the relative humidity rises above 95 % RH, where condensation is likely to occur.
- The humidity between packaging film and absorber (position (d) of the sensor) is significantly reduced. The RH values increase gradually during the experiment; we assume that the values correspond to the degree of saturation of the polyacrylate absorber.
- When the product was unpacked after three days of storage, it felt dry. This is in clear contrast with the previous experiments: the product was wet when unpacked due to the occurrence of condensation on the OPP packaging film.
- The chicory loses about 6.5 g day^{-1} kg^{-1} (which corresponds to a weekly loss of 4.5 % of its weight). This corresponds to the weight losses observed for box A and B without absorber, and is about 2½ times as large as weight losses of chicory packed in boxes C and D or chicory wrapped in PVC film (the standard consumer packaging).

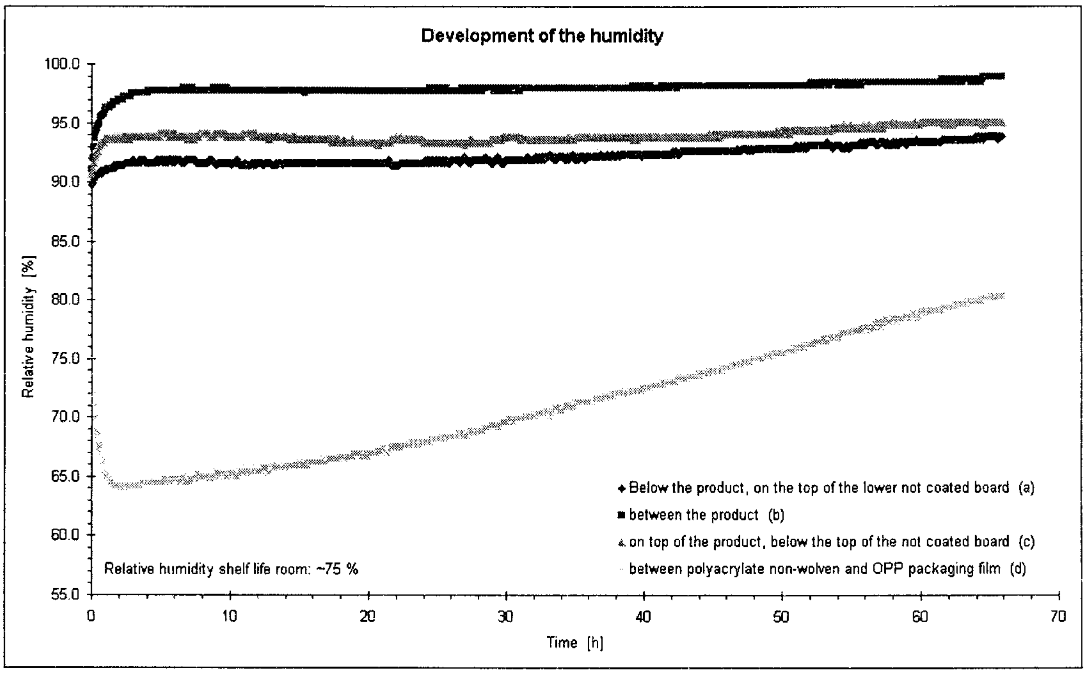


Figure 14: Influence of two layers of polyacrylate absorber (in total: 161 g polyacrylate non-woven) on the build-up of humidity (box type C, 5 kg chicory, 18°C)

We can therefore conclude that we are able to control the build-up of humidity and limit the occurrence of condensation by 'embedding' 5 kg chicory with 2 x 80.5 g of polyacrylate non-woven.

Considering the previous experiments with chicory without absorbers, and the experiences with MA packed produce which exhibits a high transpiration rate, one has to explain how this packaging concept prevents the condensation of substantial amounts of water.

- The transpiration rates of chicory which are determined in section 5 were measured at a relative humidity which was below 95 % RH. Inside the package we reached around 95 % RH which is close to the water activity of chicory. The driving force for transpiration is therefore significantly reduced.

- The experiments with polyacrylate absorbers in section 7 show that the absorptive capacity of these absorbers increases with increasing RH values of the environment.

We managed to steer the system which consists of product, micro-climate, and absorber into a region where the product transpires at a very low rate, and the absorber has its maximal performance, i.e. close at a relative humidity of 98 %.
The absorbers are placed at positions to which water vapor diffuses and where condensation is most likely to occur (according to our suggested model for transpiration and condensation which is driven by a temperature gradient caused by the metabolic activity of the product, section 2). The absorbers remove moisture from the headspace and absorb any free water originating from possible condensation. If condensation is absorbed immediately, it will not contribute to the build-up of humidity in the same way as free water.

If we investigate the partial water vapor pressures inside the box at different positions, we see that a stable water vapor pressure gradient forms: in the center of the box (in between the produce) the water vapor pressure values are the highest. Towards top and bottom of the box, the water vapor pressure values decrease slightly. The pressure gradient will lead to a diffusion of water vapor from the center of the box to the polyacrylate absorbers where the moisture or water vapor is absorbed. Between OPP film and polyacrylate sheet, the relative humidity builds up slowly: we assume that the build-up of humidity between film and nonwoven corresponds to the degree of saturation of the absorber.

Conclusions

- The control of the build-up of humidity in coated board boxes filled with tomatoes is in general possible.
- According to our experiments, the polyacrylate absorber is superior to silica gel: the same amount (weight) of absorber leads to lower and more stable RH values over a longer period of time.
- 80 g of polyacrylate absorber is able to limit the relative humidity values in box C filled with 2.7 kg tomatoes below 70% RH over a period for longer than 5 days. The actual RH values still have to be optimized for the type of produce.
- We designed a first prototype for a PE coated box for chicory in which 160 g of polyacrylate absorber is integrated. This prototype stabilizes the humidity at high values and prohibits the occurrence of condensation. In contrast to the experiments described in section 6, the chicory feels dry when it is unpacked.

9. Effect of temperature jumps on the development of relative humidity and condensation

In the distribution chain, packed produce is subjected to sudden temperature jumps and variations in the water vapor pressure of the environment. The relative humidity of the headspace and the water vapor transmission rate will be directly influenced by changes in the environmental condition. For example, sudden temperature drops can lead to condensation, high water vapor pressures of the surrounding will decrease the amount of water vapor which is transmitted through the packaging material. The experiments described in the previous sections are carried out under stable environmental conditions in order to study the factors which influence the humidity inside the packaging and the transpiration rate of the produce. In this study, we want to obtain a qualitative impression of the interactions between produce, packaging, and changing environmental conditions. We want to address the following questions:

- How the humidity and water vapor pressure is affected by sudden changes in the environmental conditions (temperature jumps and sudden changes in water vapor pressure of the surroundings);
- Under which circumstances do the changes in the environmental conditions result in condensation? Can absorbers create conditions inside a package such that condensation does not occur?

If the temperature of the surrounding of the box is decreased, the temperature of the headspace of the packaging will drop. As a result, the saturation water vapor pressure will be lowered, and condensation will occur when the dew point is reached. If the transport mechanisms for water vapor (e.g. permeation through the packaging material, absorption by absorbers) are not changed, we expect an increase of the RH values and a decrease of the water vapor pressure. If the temperature of the surrounding is increased, the headspace can take up more humidity: the RH of the headspace will drop temporarily, and the product will be stimulated to transpire at a higher rate (due to the increased water vapor gradient). As a result, RH and water vapor pressure will increase. The effects of temperature jumps on the development of humidity in boxes are displayed in Figure 15 for tomatoes on the vine for the temperature profile T = 18°C → 12°C → 18°C and in Figure 16 for chicory for the temperature profile T = 4.5°C → 18°C → 4.5°C. In both temperature experiments box type C (PE coated on both sides) was used. It takes roughly 8 – 10 hours until the temperature reaches its new equilibrium value; the relaxation times for RH values are in some cases even longer (approximately 20 h).

In the experiments as well as in realistic situations in the logistic chain, a change in the temperature of the surroundings is often accompanied by a change in the water pressure of the surroundings, which will have a significant impact on the permeation of water vapor through the packaging material and therefore on the RH and humidity profiles inside the packaging. In order to assess the impact of temperature jumps on the build-up of humidity and the occurrence of condensation, it is necessary to e.g. compare the amount of water which condenses from the headspace during a cooling step with the amount of water which is transported through the packaging material or absorbed by an absorber on the time scale which is typical for the cooling step. For a temperature drop T = 18°C → 12°C we observed for a box type C filled with 2.7 kg tomatoes a drop in water vapor pressure by approximately 5 hPa; this corresponds to the condensation of about 45 mg water. If we perform a temperature drop experiment T = 18°C → 4.5°C with a box type C filled with 5 kg chicory, approximately 90 mg of water is removed from the headspace by condensation.

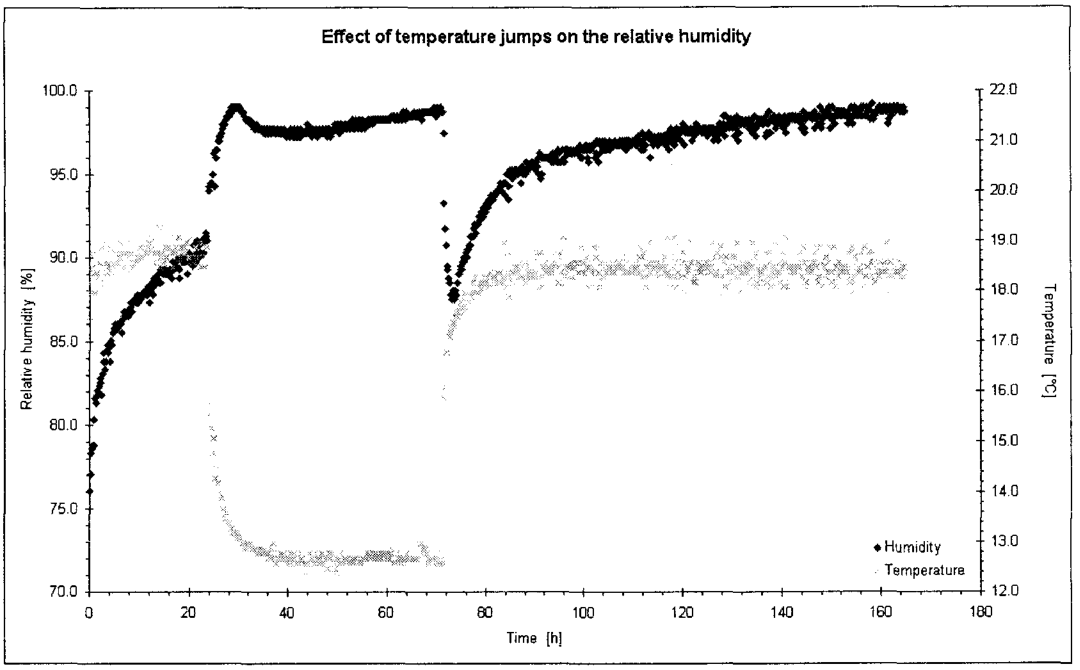


Figure 15: The effect of temperature jumps (18°C → 12°C → 18°C) on the development of humidity in a packaging box coated on both sides and filled with 2.7 kg tomatoes on the vine.

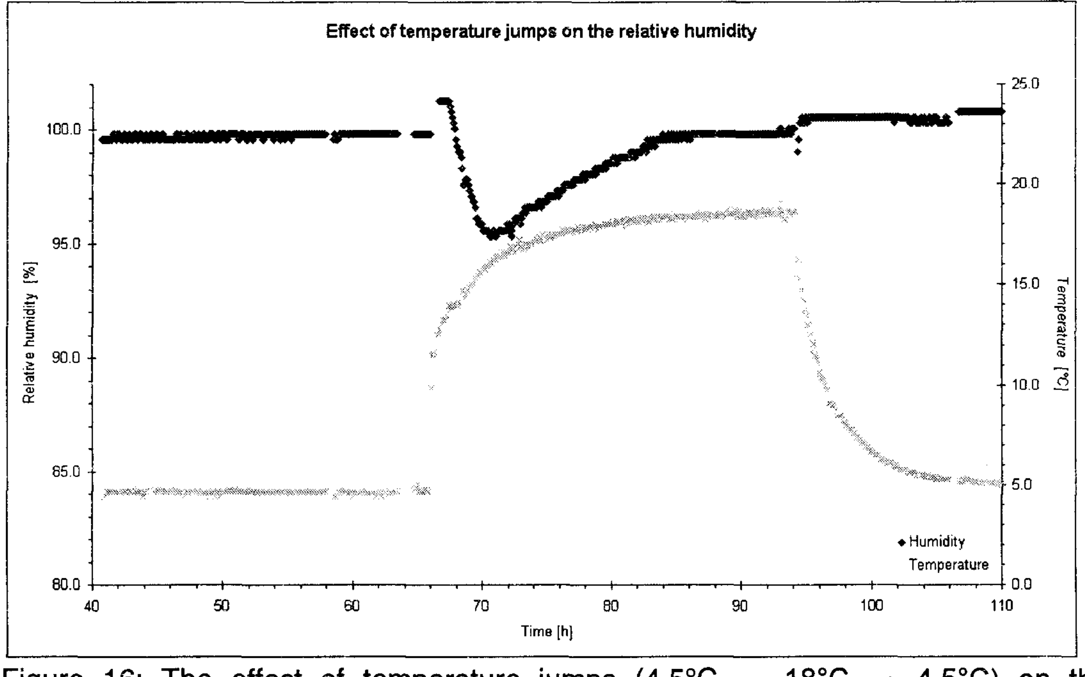


Figure 16: The effect of temperature jumps (4.5°C → 18°C → 4.5°C) on the development of humidity in a packaging box coated on both sides and filled with 5.0 kg chicory.

If we compare the amount of free water which condenses during a temperature drop with the amount of moisture which is permeated through the packaging material (see section 6) or which is absorbed by an absorber (see section 8), we can conclude that condensation due to temperature drops contributes only little to the overall transport of water from the headspace to absorbers or surrounding. An increased rate of permeation due to an increased water vapor gradient between headspace and

surroundings, or the presence of an absorber which removes moisture at a constant rate from the headspace will outweigh the effects on the RH caused by temperature jumps.
This effect is displayed in Figure 17. Two boxes (type C) filled with 2.7 kg tomatoes, are subjected to temperature jumps. One box contained a polyacrylate absorber. During the temperature drop, condensation occurred in the packaging box that did not contain an integrated absorber. In the packaging that contained an integrated absorber, the development of the relative humidity was apart from relaxation processes after the temperature jumps not affected by the change of temperature. In the box with absorber we observed no significant amount of condensation after the temperature drop.

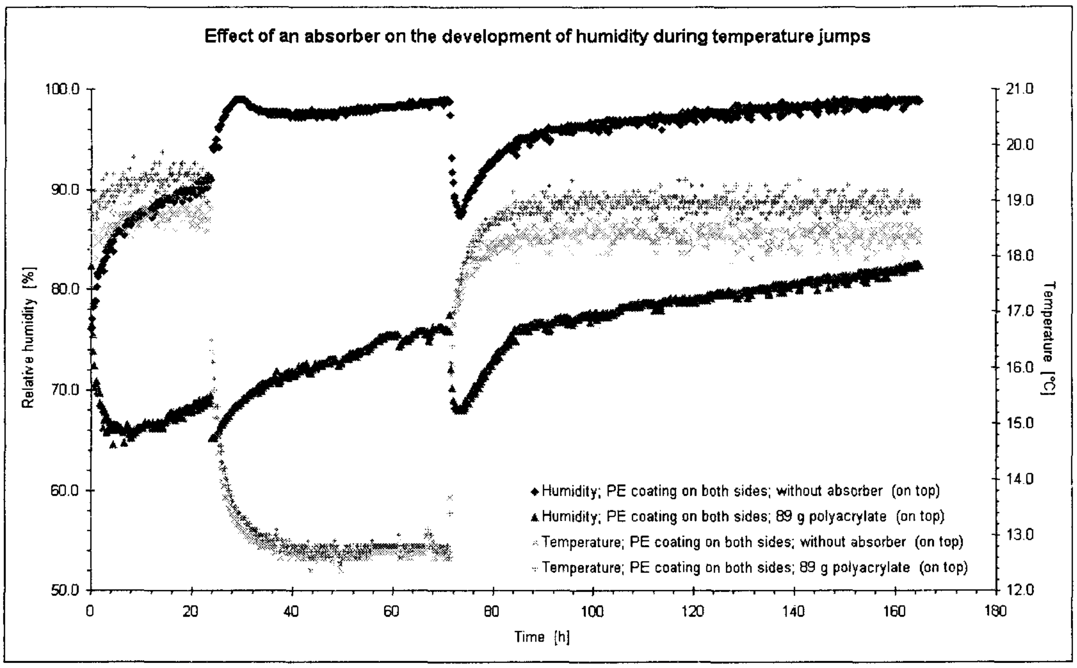


Figure 17: The effect of an absorber on the humidity build-up during temperature jumps (18°C → 12°C → 18°C) in a packaging box coated on both sides and filled with 2.7 kg tomatoes on the vine.

Conclusions

- We observed the following effects of temperature jumps on the humidity inside packaging boxes:
  - An increase in temperature results in a temporary decrease of the relative humidity,
  - In contrast, a temperature drop results in an increase of relative humidity. Condensation occurs if the water vapor pressure is equal to the saturation water vapor pressure. The amount of condensation due to the temperature drop is small compared with the amounts of water absorbed or permeated in a for the temperature drop typical time period,
  - An absorber which is integrated in the box stabilizes the RH values: the amount of moisture absorbed by the absorber is large compared with the amount water which condenses, and the absorption rate of the absorber is not significantly influenced by a change of the environmental condition of the surroundings of the packaging.

10. Conclusions & suggested future work

Aim of our study was to study factors which determine the build-up of humidity in MA packaging for fruits and vegetables, and to investigate possibilities to control humidity and condensation in packaging. A central result of the study is that

- The transpiring product,
- The relative humidity and the microclimate in the packaging,
- The packaging material and packaging design,
- The environmental conditions of the surroundings, and
- A drying agent which can be present in the packaging

form a complex dynamic system. The functionality and state of each component influences the behavior of the entire system. In order to control the humidity inside the headspace of a MA packaging an optimal choice of all important parameters is necessary.

Three aspects of the system were studied in detail:

- What is the influence of the packaging material and the product on the build-up of humidity?
- How can the relative humidity / condensation be influenced by drying agents?
- How stable is the system: What is the effect of temperature jumps on the relative humidity / water vapor pressure in the packaging?

The build up of humidity and the occurrence of condensation inside a packaging can be controlled by influencing the balance between transpiration rate and the rate at which humidity is removed from the packaging. From our study, we can draw the following main conclusions:

- Based on our experiments we suggest that a temperature gradient which is caused by the metabolic activity of the produce leads to an efficient transport mechanism for water vapor in the packaging, and can cause the condensation of significant amounts of free water in the packaging.
- The measures which have to be taken in order to control the build-up of humidity and occurrence of condensation are product-specific: The differences in transpiration rates for different types of produce are often large enough such that packaging solutions for the control of moisture have to be adjusted for each product. In order to obtain a working packaging solution for one type of product, it is necessary that the build-up of humidity can be controlled for produce with different initial quality.
- The control of the build-up of humidity by permeation of water vapor through the packaging material is only feasible for produce with a low transpiration rate (e.g. tomatoes on the vine). In order to succeed with controlling the build-up of humidity by permeation, a stable water vapor gradient between box and environment is necessary. This requires the control of climatic conditions of the environment.
- The build up of humidity and the occurrence of condensation can be controlled within a certain time period by the use of polyacrylate absorbers. For tomatoes on the vine (a product with a low transpiration rate) the presence of a polyacrylate absorber lead to a significant reduction of the relative humidity. For chicory (a product with a high transpiration rate), the build-up of humidity and the occurrence of condensation could be controlled by taking into account the transport mechanisms for humidity which are caused by the warming up of the produce due to its metabolic activity.
- Temperature jumps can cause condensation. However, the amount of free water which condenses during a temperature jump is in general small compared to the amount of water which is permeated through the packaging material or absorbed

by an absorber on a – for the temperature jump - typical time scale. The RH profiles during temperature jumps can be explained by changes in temperature gradients in the packaging or changes in external water vapor pressures. Absorbers can stabilize RH values during a temperature jump.

- The build-up of humidity in packaging can be simulated with a mathematical model. In appendix 1, a first model which integrates the transpiration of produce, the absorption of moisture by an absorber, and the permeation of water vapor through the packaging material is presented.
- The characteristics of various other absorbers are presented in appendix 2. The performance of polyacrylate absorbers can be optimized and tuned by mixing suitable salts with the absorber.

Future work

Focus of this study was to gain insight into the factors which determine the build-up of humidity in MA boxes and to obtain a 'proof of principle' whether it is possible to control the relative humidity inside a box for products with different transpiration rates by the use of an absorber. We obtained promising results for both high and low transpiring products; using a polyacrylate absorber, we obtained low RH values for tomatoes on the vine, and we could prevent condensation in a box packed with chicory. At the same time, we observed that product packed in a MA box forms together with an absorber and the surroundings a complex system. Many of the factors which determine the build-up of humidity are inter-related, and temperature, relative humidities and water vapor pressures are not completely homogeneous inside the packaging. Therefore, it is not possible to rely only on the specifications of a type of absorber in order to obtain an optimal packaging concept. Furthermore, the system is too complex such that a 'trial and error' approach for finding optimal product / packaging / absorber combinations would lead easily to success.

The humidity transport inside the packaging influences not only the product quality. Absorption of the humidity will for instance also influence the mechanical stability of the packaging and the gas permeance of the packaging material. The understanding and control of humidity in the packaging is therefore also closely related to the overall performance of the packaging in the logistic chain.

We therefore suggest to focus in the future on two areas of research:

For developing an optimized packaging solution which controls the humidity inside a packaging solution an integrated approach is necessary which takes into account relations between the transpiration and metabolic activity of the product, the microclimate inside the box, the performance of the absorber, the influence of the surroundings on product and packaging, and the effect of humidity on mechanical performance and barrier properties of the packaging. A suitable tool to address such a system would be a mathematical model for the moisture transport in MA boxes (comparable to the existing MA model for the gas composition in MA packaging). The set-up of such a model requires knowledge of the metabolic activity and transpiration of the product as well as the specifications of absorbers for different climatic conditions. The model can be used in order to test the performance and stability of a combined MA and MH (modified humidity) packaging solution for different types of produce and different types of packaging designs and absorber systems. It would yield information of the product quality, the efficiency of the absorbers, and the absorption of moisture in the board which can in turn be linked to models and experiments on the mechanical stability of the packaging.

Moisture plays in general an important role in designing advanced paper board packaging solutions. This report focused on moisture released by the packed product. We observed that the box design (i.e. the integration of the absorber into the box) plays an important role in optimizing the control humidity and condensation. Based on the results we obtained from the lab model of the chicory box, we gained the impression that certain parts of the packaging will be exposed to more humidity than others. Placing the absorber at the position where condensation is likely to occur maximizes the efficiency of the packaging solution. A topic of future research would be to study the effect of the environment of the box (pallet stacking, forced cooling, vibrations, etc.) on the transport of water vapor inside the box.

In addition, the packaging is not only exposed to moisture which originated from the transpiring product. Boxes and palletized boxes can for example be exposed to water originating from the environment, or from melting ice which is used to cool the product (e.g. fish). Again, only parts of a box or palletized boxes will be directly exposed to moisture, and techniques which are used to locally absorb 'internal' humidity for obtaining MH conditions can possibly be applied to protect packaging from 'external' humidity.

Aim of future research would be to design a packaging solution which provides both optimal MA and MH conditions for the packed product. The research would require experimental and computational work in order to optimize the box design with respect to keeping an optimal product quality and obtaining an optimal mechanical performance of the packaging under the conditions of the logistic chain.

Appendix I, A mathematical model to describe the moisture balance inside a packaging

A mathematical model is developed which can describe the moisture balance inside a packaging filled with produce and possibly provided with a moisture absorber. In this mathematical model the following assumptions have been made:

- The transpiration of biologically active products is modeled by describing both the metabolic transpiration and the partial pressure driven transpiration. The metabolic transpiration depends only on temperature while the pressure driven transpiration depends also on the vapor pressure inside the packaging;
- The absorption rate of the absorbers is supposed to be linearly dependent on the moisture content of the absorber and the partial pressure difference between the absorber and the atmosphere inside the package. The parameters for this absorption model are based on experimental data;
- If the absolute pressure inside the package exceeds the environmental or atmospheric pressure, an incidental leakage will cancel out this difference in pressure;
- If the relative humidity exceeds 100% condensation occurs. Subsequently, if the relative humidity decreases again, the condensed water will evaporate inside the packaging;
- The rate of permeation of gasses (and water vapor) through the packaging material is proportional to the concentration gradient (Fick's Law).

These submodels lead to a system of differential equations which can be solved using the fourth order Runge-Kutta method. Furthermore, the model can describe the change in concentrations of the permanent gasses (carbon dioxide, oxygen and nitrogen) inside a packaging due to permeation through the packaging material, due to absorption in the packed product and due to leakage. In addition, temperature and pressure fluctuations can be included in this mathematical model.

For this study, the build-up of humidity inside a 29 x 39 x 14 cm^3 MA cardbox filled with 2.7 kg tomatoes on the vine is simulated. The temperature of the product and the environment are 18°C; the environment has 87 % RH. The build-up in relative humidity inside the box and the moisture uptake by the absorber are simulated for 0, 20, 40 and 80 gram of in the packaging enclosed absorber (Figures 18 and 19). In this simulation the permeation of water vapor through the packaging material is neglected.

Comparing the obtained results with the experimental data as displayed in Figure 10 and 11, we can conclude that we succeeded to develop a first model which qualitatively simulates absorption and control of humidity in MA boxes. In order to refine the model, future research has to focus on the absorption characteristics of different absorbers.

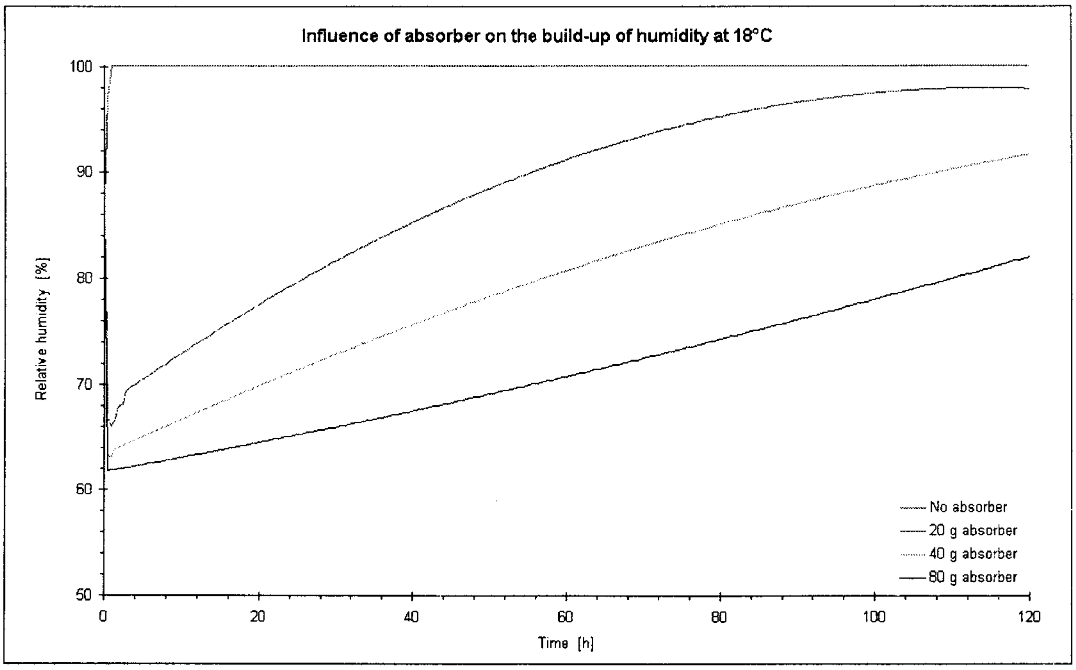


Figure 18. The simulated RH profiles for 2.7 kg tomatoes on the vine packed in a MA box with different amounts of absorber at 18°C.

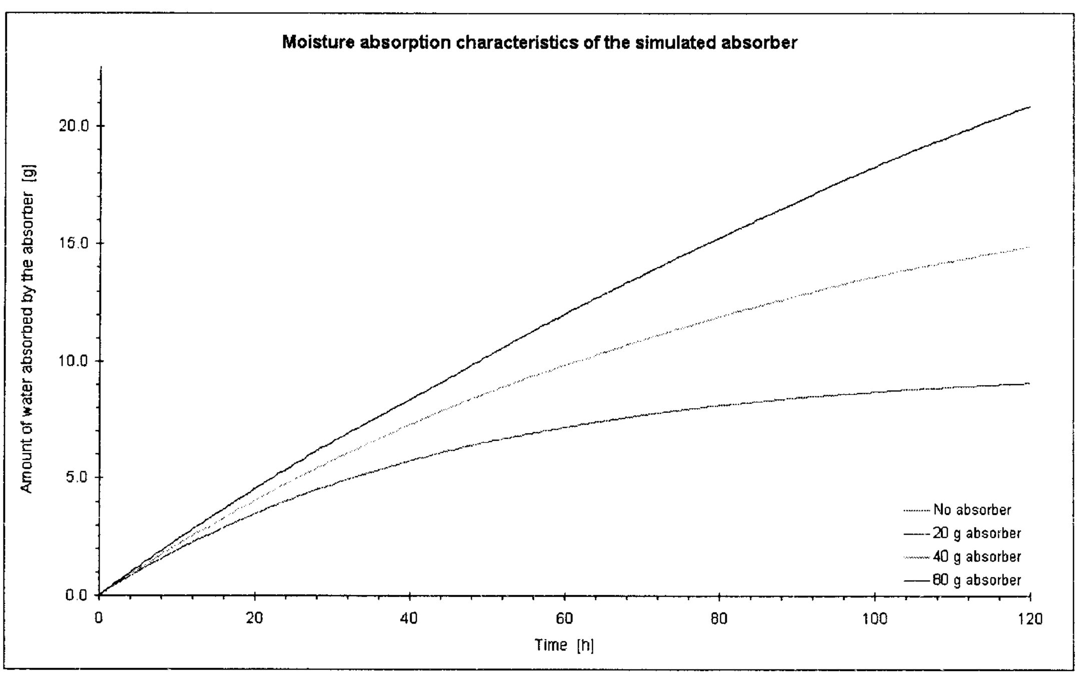
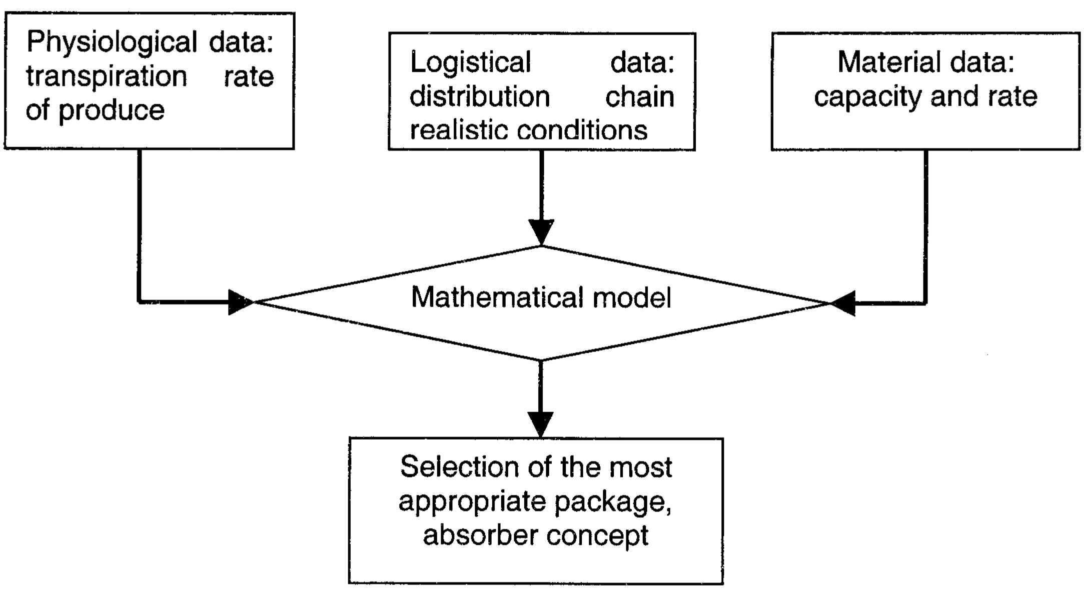


Figure 19. The simulated moisture absorption characteristics of the absorber enclosed in a MA box filled with 2.7 kg tomatoes on the vine at 18°C.

Appendix 2: Absorber composition as adjustment parameter to regulate humidity in packages.

Introduction

Moisture build-up and condensation in closed MA-boxes filled with perishables are complex, dynamic phenomena, as discussed in the report (Figure 3 of report). In order to gain control over these phenomena it is necessary to fine-tune the properties of absorbers and packaging materials to the needs of the packed produce. It would be desirable to have a limited amount of adjustment parameters that are used in a well-directed manner to fine tune the packaging concept.
For a generic solution of moisture problems in packages of perishables it is necessary to combine the knowledge of three disciplines: physiology, logistics and material science. Upon using a mathematical model of moisture build-up (appendix 1) the best adjustment parameters for absorber and packaging could be selected. Subsequently, experimental validation will be required to implement the packaging concept.



In this annex an overview is given of moisture absorbers, their properties and all their potential adjustment parameters. These experimental results can be used as input for the model.

Moisture absorbers

Two main methods are used to remove moisture from air:
- chemical by the use of drying agents and desiccants,
- electronical by the use of cooling elements.

The electronic method is not economical viable for consumer and transport packages of perishables. The chemical method is much cheaper, and hence more attractive.
Various chemicals are known or have been claimed to remove moisture from air. These are named: desiccants, drying agents and dehumidifiers. Well known examples are concentrated solutions of acids (sulphuric acid, phosphoric acid), polar

organic compounds (sorbitol, choline chloride), porous inorganic materials (zeolites, silica gel), inorganic salts (calcium chloride) and charged amorphous polymers. For applications in food packages, the absorption materials need to be safe and to comply with food regulations. Hence, the choice is limited to safe chemicals, that are named on the positive list and that do hardly migrate to the food (less than the migration limits). To minimise the risk of migration the choice is limited to: inorganic salts, porous inorganic materials and charged amorphous polymers.

Material properties of moisture absorbers

The performance of absorbers is determined by the following parameters: temperature, relative humidity and moisture content. This performance is determined by measuring absorption curves at fixed temperatures and relative humidity's. From these curves several relevant parameters are derived:

- maximum capacity [g/g],
- initial rate of absorption [g/g.h],
- half time [h] or other kinetic descriptors,
- threshold value of the relative humidity [%] at which the maximum capacity is 10 % of the capacity at 100 % relative humidity.

The desired properties for moisture absorbers in packages for perishables are:

- high maximum capacities (> 1.5 g/g), to lower the cost,
- high initial rates of absorption, to have a fast response on increasing humidity's,
- high half times, to remain active over many days,
- high threshold values (> 70 %) to reduce inactivation by moisture prior to use in the package.

Screening of absorbers

In order to make a fast comparison between absorbers, their absorption curves were determined at 22°C and three relative humidity's: 65, 85 and 100 %. Prior to this measurement the absorbers were dried in an oven of 120°C for 3 hours. The initial moisture content was calculated from the weight loss. The used absorbers are listed in table 7 and the measured absorption curves are depicted in figure 20-22.

Table 7: Applied moisture absorbers.

Name	Type	Origin	Initial moisture content, [%]
PAC / Favor 300	Polyacrylate gel	Stockhausen (D)	1.7
RSF	Starch derivative	ATO	8.5
CMC	Carboxymethyl cellulose sodium salt	AkzoNobel	7.8
$CaCl_2$ 2 H_2O	Inorganic salt	Merck	2
Zeolite A	Zeolite	PQ	6
ZSM-5	Zeolite	PQ	5
Mordenite	Porous clay		3.7
Molecular sieves 0,4 nm	Zeolite specially for water	Merck	0
Si-gel	Silica gel	Brocades ACF	n.d.

n.d. : not determined

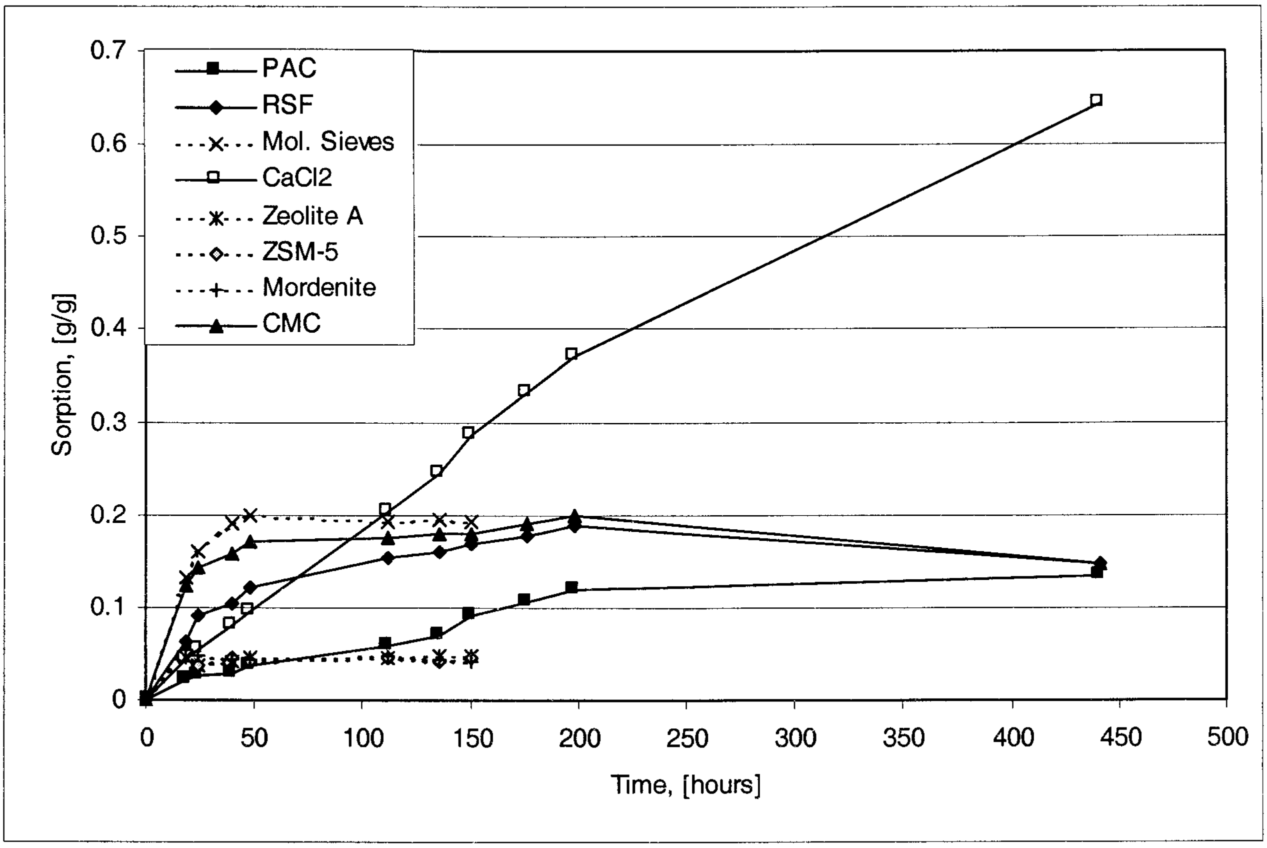


Figure 20: Absorption curves at 65 % RH and 22°C

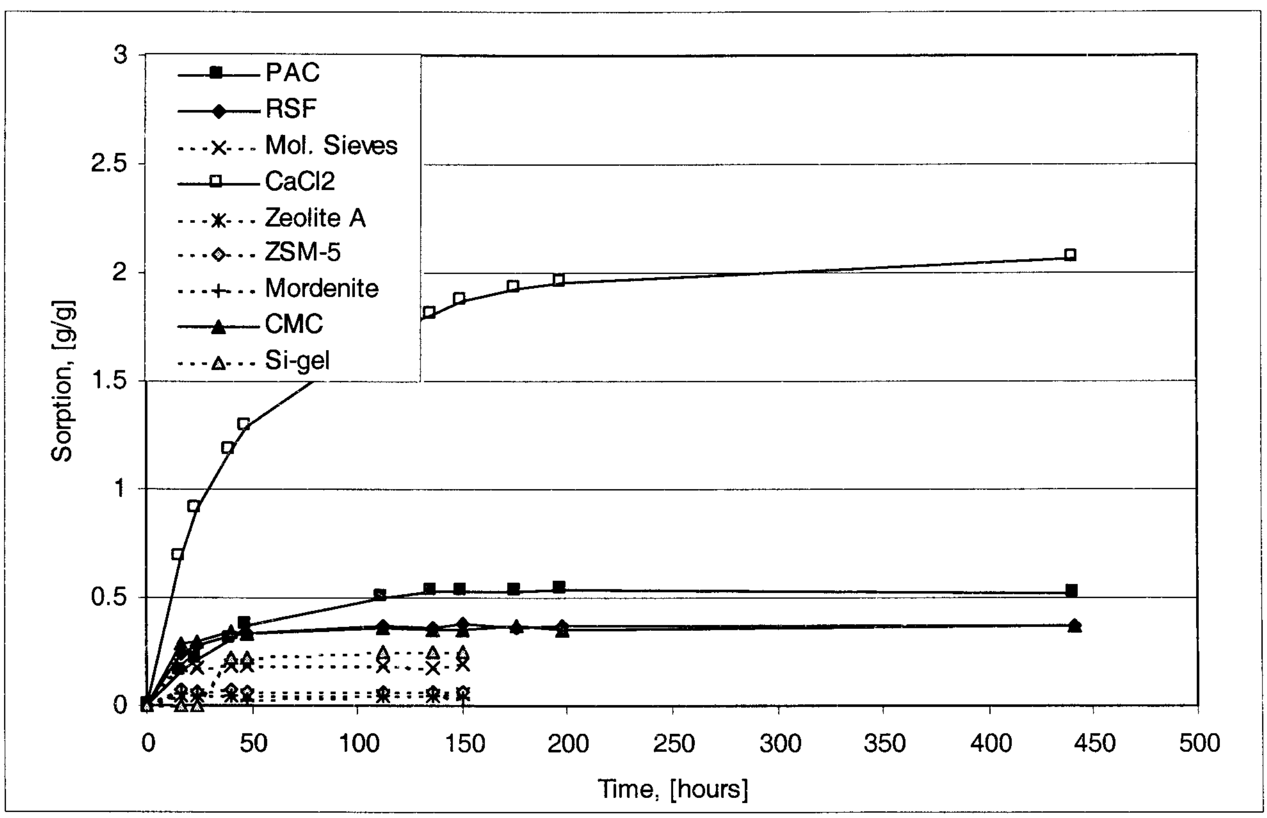


Figure 21: Absorption curves at 85 % RH and 22°C. The absorption of moisture in Si-gel started at 24 hours.

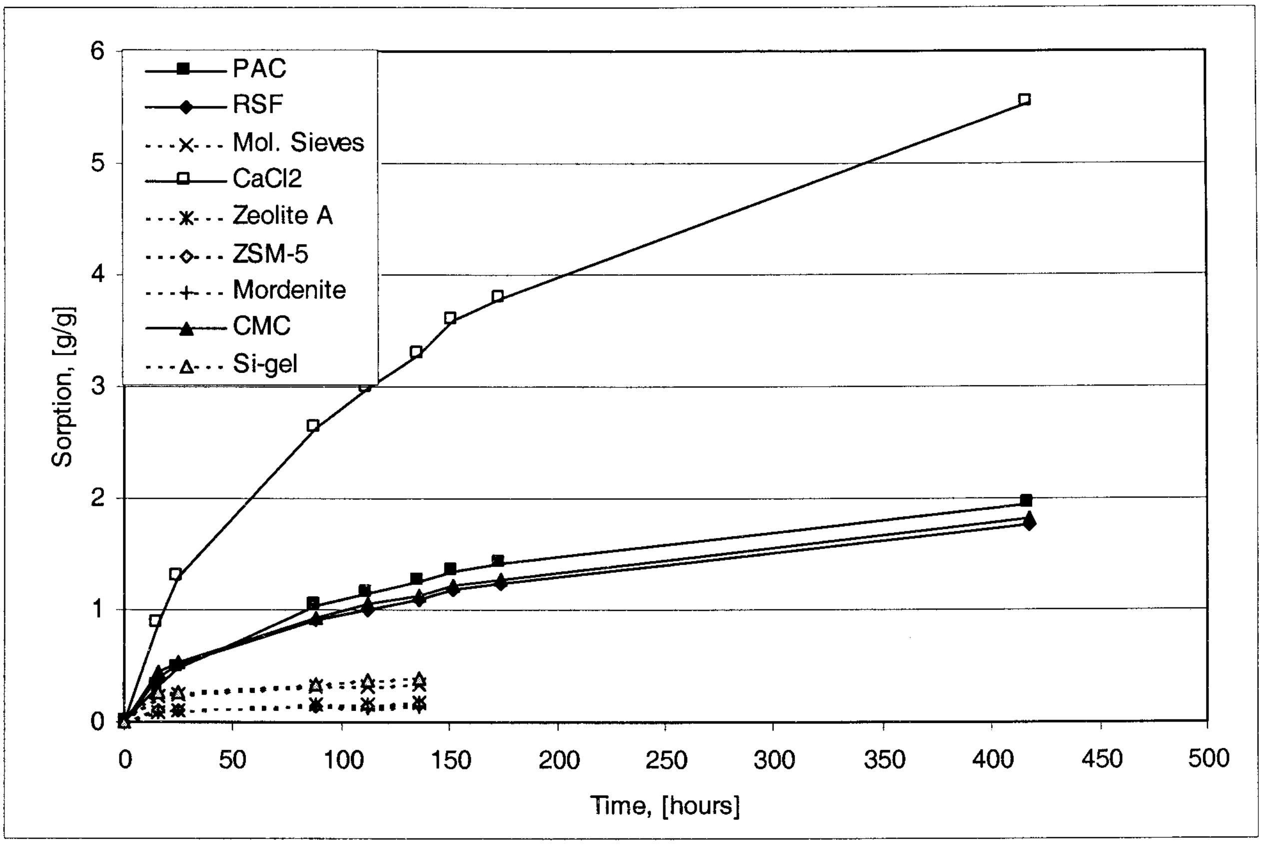


Figure 22: Absorption curves at 100 % RH and 22°C.

From these absorption curves the most important properties were estimated. These tabulated in table 8.

Table 8: Estimated absorber properties at 65, 85 and 100 % RH and 22 °C

Absorber	Max. capacity, [g/g]			Initial rate, [mg/g.h]			Half time, [h]			Threshold, [% RH]
	65	85	100	65	85	100	65	85	100	
PAC	0.13	0.53	1.9	1	9	18	80	30	60	>65
RSF	0.15	0.38	1.8	4	14	22	25	15	50	>65
CMC	0.15	0.37	1.8	7	16	25	15	5	40	>65
$CaCl_2$	>0.7	2.1	>6	2	38	49	-	25	-	<65
Zeolite A	0.05	0.05	0.18	2	2	5	<10	<10	<10	<65
ZSM-5	0.04	0.07	0.16	3	4	6	<10	<10	<10	<65
Mordenite	0.04	0.05	0.13	3	3	5	<10	<10	<10	<65
Mol. Sieves	0.2	0.2	0.3	7	10	13	15	<10	15	<65
Si-gel	n.d.	0.3	0.4	n.d.	13	15	n.d.	<10	15	<65

n.d. : not determined

From these results it is clear that three types of desiccants can be distinguished: calcium chloride, polymeric absorbers and inorganic absorbers.
Calcium chloride is the most powerful desiccant, having the highest capacity's and longest working time. A disadvantage of calcium chloride is that it binds so much water that it forms a solution, limiting it practical applicability.
The polymeric absorbers (PAC, RSF, CMC) usually have high maximum capacity's of 1.8 – 1.9 g/g at 100 % RH or more, their initial rate of absorption strongly increases with the RH and is about 20 mg/g.h at 100 % RH. This implies that they can react

quickly to increasing humidity's Their half times to saturation is high at 100 % RH, implying that they remain active over a long period of time. Their threshold values are near 65 % RH, meaning that they hardly loose absorption capacity in atmospheres of 65 % RH and lower. From the three polymeric absorbers that have been screened, polyacrylate gel, was found to have the best performance.
The behaviour of inorganic absorbers is markedly different. Their capacity's, half times and threshold values are much smaller than for the polymeric absorbers. Hence, inorganic absorbers are less well suited for the purpose of moisture absorbers in perishable packages.
These results are in agreement with the characterisation of polyacrylate gel and silica gel, described in the report, chapter 7.

It was decided to study polyacrylate gels in more detail, for three reasons:

- good performance
- acceptable price (5 Dfl /kg)
- food contact approved and is currently in use as drip pads for meat packaging

The aim of this more detailed study was to prove that the performance of the polyacrylate gel could be adjusted by minor chemical modifications. This will widen the working range for the acrylate gels as moisture regulators in food packages.
The most simple and straightforward strategy is mixing the polyacrylate gel with inorganic salts. This will increase the polarity of the gel and might increase the capacity and initial rate. Moreover, these salts could also influence the threshold value. Since various concentrated aqueous salt solutions are known to give well defined equilibrium RH values in the overlaying atmosphere and these gels can be regarded as bound aqueous solutions.

Seven different salts (lithium chloride, potassium carbonate, magnesium chloride, sodium chloride, potassium chloride, ammonium chloride and calcium chloride) were selected, based on their equilibrium RH values of saturated aqueous solutions, price and availability. In all cases the arbitrairly chosen mixing ratio of 4 : 1 polyacrylate : salt was used. The absorption curves were determined at 22°C and at three different RH values. These results are depicted in figure 23-25.

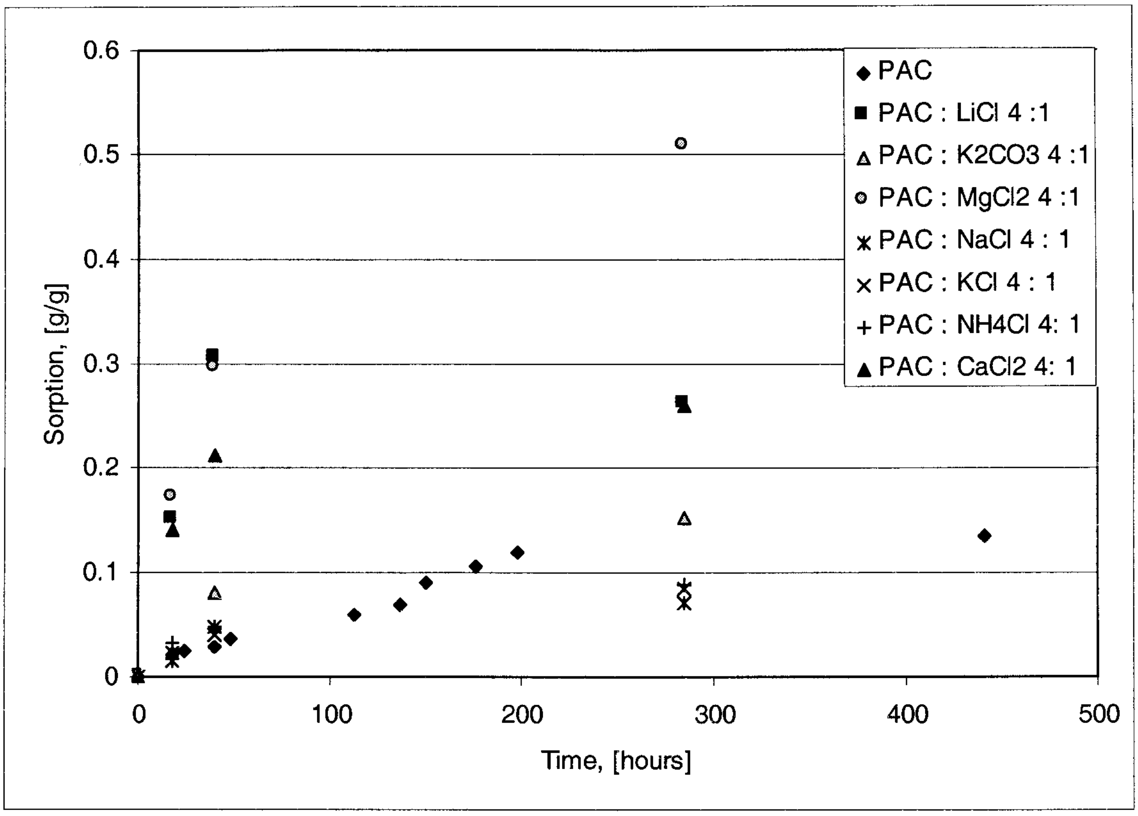


Figure 23: Absorption curves of mixtures of polyacrylate gel and salts at 65% RH and 22°C

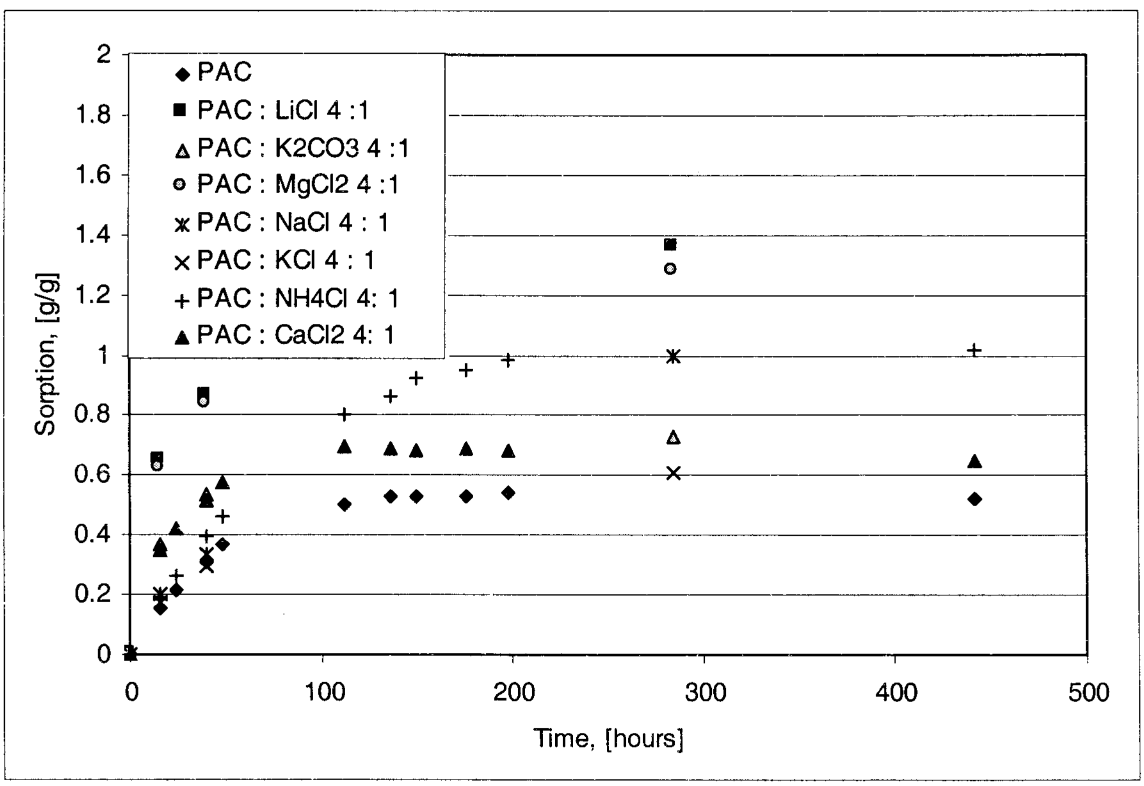


Figure 24: Absorption curves of mixtures of polyacrylate gel and salts at 85% RH and 22 °C.

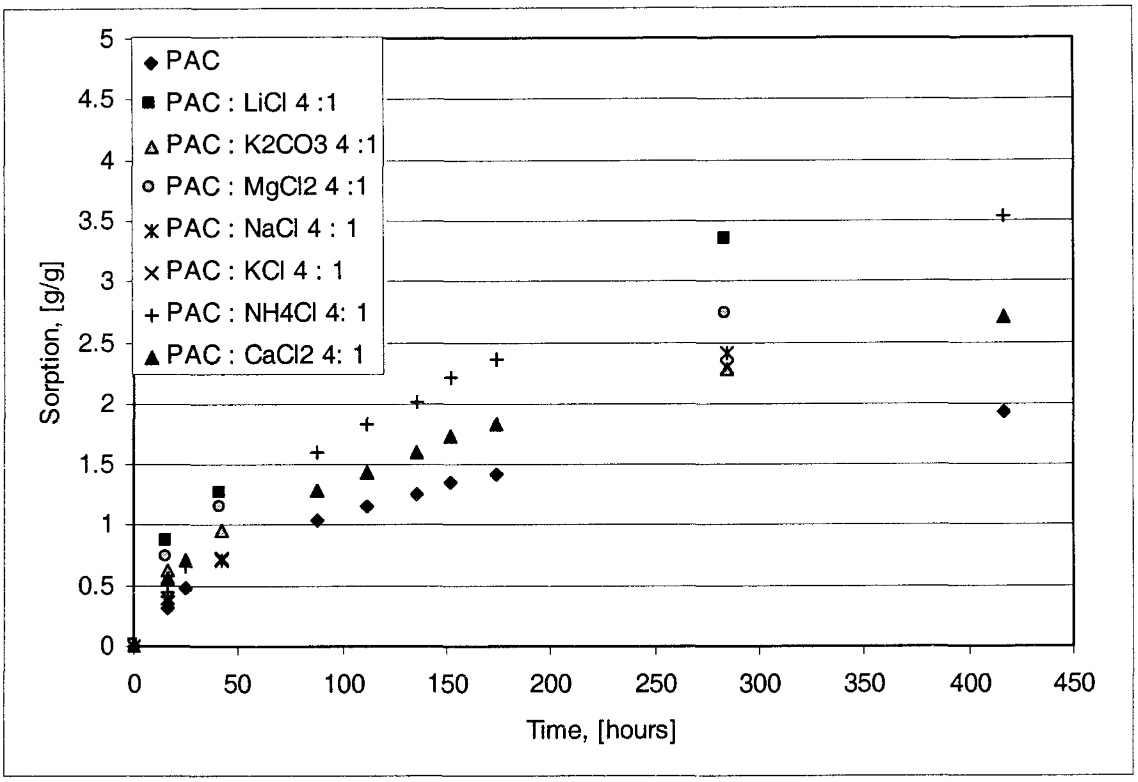


Figure 25: Absorption curves of mixtures of polyacrylate gel and salts at 100 % RH and 22 °C.

From these absorption curves the most important properties were estimated. Only most the half times were to difficult to estimate based on the current results. The results are tabulated in table 9.

Table 9: Estimated absorber properties at 65, 85 and 100 % RH and 22 °C

Absorber : salt 4 : 1	Max. capacity, [g/g]			Initial rate, [mg/g.h]			Half time, [h]			Threshold, [% RH]
	65	85	100	65	85	100	65	85	100	
PAC	0.13	0.53	1.9	1	9	18	140	30	80	>65
PAC : LiCl	0.26	1.4	3.3	8	41	53	<20	30	80	>65
PAC : K_2CO_3	0.15	0.7	2.3	1	23	40	40	15	70	>65
PAC : $MgCl_2$	0.5	1.3	2.7	10	39	46	35	20	80	<65
PAC : NaCl	0.07	1.0	2.4	1	13	25	30	60	100	>65
PAC : KCl	0.08	0.6	2.3	1	12	22	40	40	40	>65
PAC : NH_4Cl	0.09	1.0	3.5	2	12	28	35	50	120	>65
PAC : $CaCl_2$	0.26	0.7	2.7	8	22	35	15	15	90	±65

These results prove that salts are modifiers for polyacrylate gel moisture absorbers. All salts enhance the capacity of the absorbers at high relative humidity. Ammonium chloride and lithium chloride nearly double the capacity at 100 % relative humidity. Ammonium chloride performs better, since it increases the capacity only at high relative humidity.

Moreover, all salts increase the initial rate of absorption at high relative humidity. The effect on the half time is less clear. There seems to be no major influence of salts on the half time of absorption at 100 % RH. Hence, their effective working time remains to be about a week. The best salts (low price and good performance) as moisture absorption modifiers are: ammonium chloride, sodium chloride, magnesium chloride and calcium chloride.

The relative humidity over saturated salt solutions at 22 °C of the salts studied was found to correlate crudely with the measured maximal sorption capacities, see figure 26. In general it was found that the capacity was higher for salts which render lower relative humidity's over saturated aqueous salt solutions.

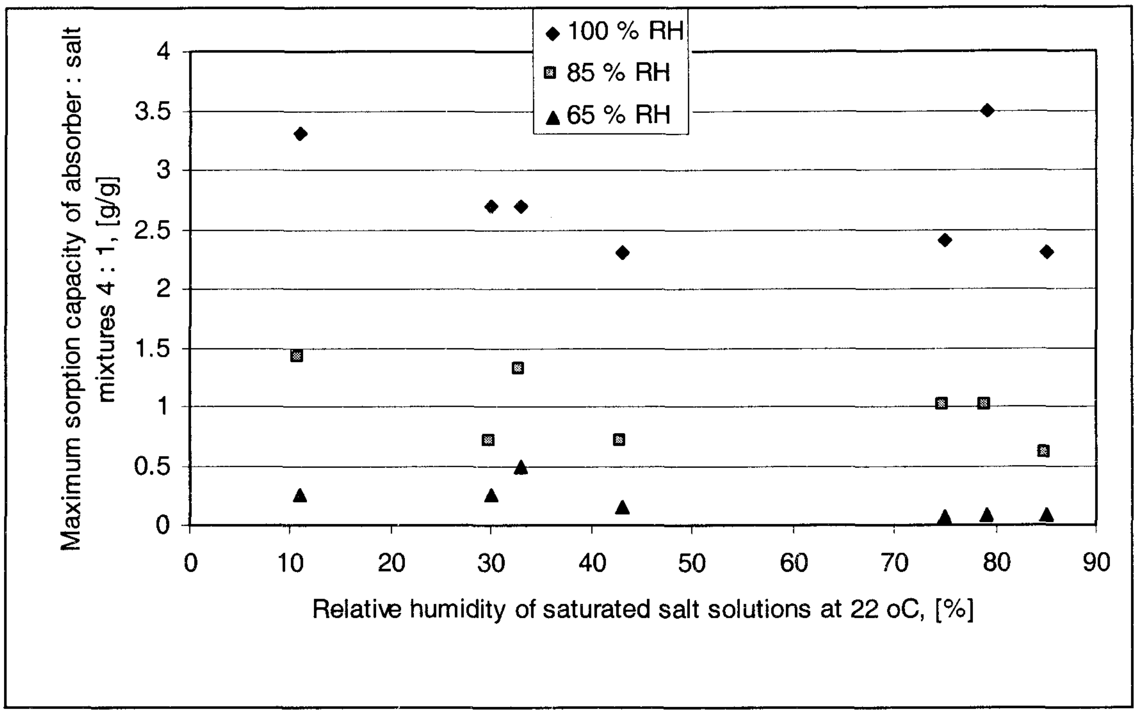


Figure 26: Relationship between maximum sorption capacities of absorber : salt 4 : 1 mixtures at three relative humidity's and the equilibrium relative humidity of saturated aqueous solutions of the same salts.

Another crude correlation was found between the size and charge of the ions and the performance as absorber modifier. Small ions bind water more strongly than larger ions: Li^+ > Na^+ > K^+. Also, double charged ions bind water stronger than single charged ions: Mg^{2+} > Na^+ and Ca^{2+} > K^+. Ammonium was found to give the absorber more performance (sorption capacity) at 100 % RH than can be accounted for by size and charge of the ion. Presumably, hydrogen bonding between ammonium and water renders the extra effect.

Potential adjustment parameters for moisture absorbers in boxes

The results of this exploratory research have shown that the composition of polyacrylate gel absorbers can effectively be used to tailor the moisture absorption properties. Hence, there are four adjustment parameters to tailor the performance of the absorber:

- total amount,
- position(s) in the box (design and integration),
- composition,
- permeability of the pouch to retard the moisture absorption

These adjustment parameters will have different influences on the absorber performance and hence the humidity in the box:

- The amount of absorber will predominantly affect the effective time of operation.
- The position in the box will affect the rate of absorption.
- The composition will affect the time of operation and the rate of absorption.
- The permeability of the sachet will control the rate of absorption.

Experimental packaging tests are required to establish which combinations of adjustment parameters are best for products. These results should be interpreted and fed into the mathematical model, as discussed in the introduction of this annex. By this approach, the complex interrelationships can be elucidated and more general rules for package design will be established. These results will be valuable input for the mathematical model. With the use of this upgraded mathematical model future packaging concepts can be tested under all relevant conditions. This will render an improved version, which is more robust and which has a better chance to succeed during the experimental validation.