Thesis 2018

Water sorption in polyethylene films produced with different protocoles

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1.Abstract

This thesis will make a characterization of four LDPE membranes. Each one representative of a different point of the final membrane production process.

The objective, to find out at which point of the process the capacity of water absorption in the membrane increases considerably.

The thesis part of the values obtained in "McCall 1983 Solubility and diffusivity of water in LDPE"[12] where the water absorption values are 50 ppm and "2017 Influence of water uptake on the electrical DC-conductivity of insulating LDPE / MgO nanocomposites "[4] where the values of water absorption in a LDPE membrane are much higher.

It will proceed to perform membrane saturations with water in gas phase to different controlled water activities and to perform desorption with vacuum pump to calculate the volume of water absorbed and thus characterize the membranes.

2.Introduction

With the development of new technologies is needed to carry current over longer distances. To avoid losses the voltage increases, but thermal and electrical losses also increase. To compensate these losses have to resort to a better insulator to involve the cable. Years ago the strategy to improve an insulating was purifying the polymer [3] to avoid the electron conduction. Nowadays, it is dispersed small fractions (1-3 wt.%) of inorganic nanoparticles in the LDPE in order to reduce conductivity to 1 -2 order of magnitude. The physical explanation is still under discussion. [4]

The thesis starts from an article published in 1983 "McCall 1983 Solubility and diffusivity of water in LDPE"[12] where the absorption of liquid water in Low-Density Polyethylene (LDPE) vas studied.

Afterwards, a similar study was performed "2017 Influence of water uptake on the electrical DC-conductivity of insulating LDPE / MgO nanocomposites "[4] where absorption gas water on a LDPE treated nanoparticles MgO was made. MgO was modified superficially with octyl (triethoxy) silane (C8) reacting the MgO with Silane for 24 h [5]. After nanoparticles MgO powder were mixed with LDPE, antioxidant (Irganox 1076) dissolved in n-heptane. The suspension was stirred for 60 min and dried at 80 ° C. Dried mixture was blended at 150 ° C and 100 rpm for 6 minutes in a compressor. It was degassed at 100 ° C, and it was compression molded films.

The second study was intended to obtain a similar absorption amount to the first due to the membranes were mostly the same material. However, considerably higher absorption values it was obtained.

Therefore, in the present thesis it will be proceed to try to find why there is such a difference between LDPE and LDPE / MgO treated. In order to do that, four membrane samples are analysed. Every sample will be a step in the production process of the final membrane, pure LDPE, pure LDPE treated hydraulic press, pure LDPE press prepared with 3 mL of heptane and pure LDPE treated in press 0.02 W + Y and Amino Acid

It is intended to find which processes, from all of those done to LDPE, it does increase absorption of water. Previously to the experiment the main hypothesis it is that when LDPE is treated with hexane there are some nanobubbles that stay trapped in the form of in the structure of LDPE, and this nanobubbles are the ones absorbing the amount of water that makes the experiment different.

3.material

Nanocellulose

The nanocellulose is a material made by fiber, these fibers are composed of smaller fibers that are as well composed of smaller fibers up to a fiber that is only made by one celluloses chain. Thus there is a significant relation between length-diameter because its diameter is between 10 to 20 nanometers and its length is ten times bigger. [1] [2]

The image (figure 1) bellow shows the celluloses in the nanocellulose chain forming a polymer. It can be seen that its structure is mostly nonpolar molecule, and therefore hydrophobic. The goal is to create a polymer that can absorb water, modifying nanocellulose with the amino acid arginine. Alcohol radicals replace arginine in a variable percentage. Studying how it affects this percentage difference.

To this, cellulose pulp will be created and it will be mixed with different percentages of Arginine, then it will be heated until the Arginine will react with the cellulose chain replacing the OH in the polymer, the OH will form water and will evaporate.

This process is not carried out and described in this thesis, although this cellulose pulp made previously in a Swedish laboratory that appears in the literature [12] it will be used. However, the present paper is going to study the water uptake analysing the different pressures and concentrations.

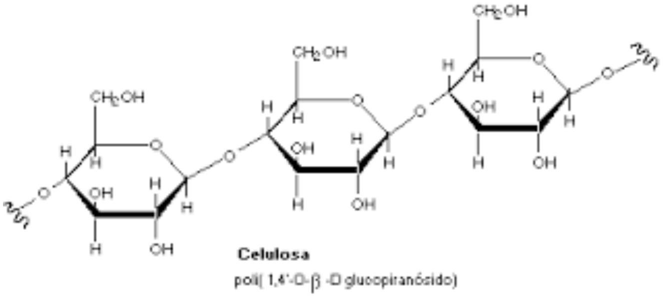


Figure 1.Cadenade nanocellulose

The new polymer will be polar because some of the OH will replace by Arginine and the polymer characteristics will depend on the concentration of Arginine.

The nanofibrillated cellulose (NFC) membrane with 30% concentration of Arginine will be the first to be analysed.

Low-Density Polyethylene (LDPE)

The Low Density Polyethylene (LDPE) is the material to be used mainly in this study, it is a thermoplastic formed of ethylene monomers. The polymer is not a single chain but it has big radicals that form a net, this is the difference with High Density Polyethylene (HDPE) [6]

Figure 2. Structure of LDPE

Comparing LDPE with HDPE formed by a single chain of ethylenes, LDPE's degree of compaction will decrease due to the large radicals. Every polymerization process consists of three parts: initiation, propagation and termination. The case of LDPE process, it should be worked at high pressures. The most important characteristics of polyethylene are low reactivity and easily recyclability. [7]

Low price, high processability and easy recycled process makes these polymers very present in many industries, i.e., in bags, bottles, laboratory equipment... So much so that in 2013 LDPE industry generated 33 billion US $. [8]

Mounting

Assembling consists of a cylindrical column with a concentric jacket for maintaining the temperature. Sample is placed in the column together with an aluminium strip hung from a spring and the system is brought to the operating conditions. The column is the principal object where the conditions and measurements will be manipulated.

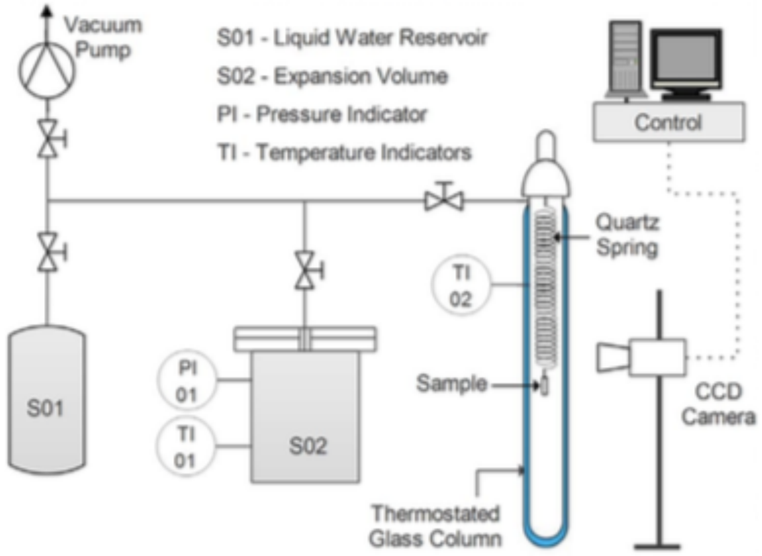


Figure 3. Diagram of the complete assembly

The cylindrical column has a water inlet and outlet for the jacket, a stream of water heated to 35.5 ° C (process temperature), the jacket maintains the temperature during the process. In order to avoid temperature changes and therefore losses in pressure (activity) and taking into account that the process is carried out with gases and it takes a lot of time, the entire assembly is going to be wrapped in insulating material. Otherwise the experiment will be biased.

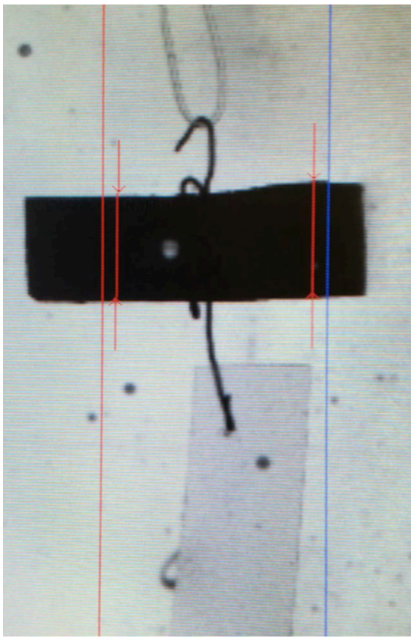
The system has another inlet of water, water is taken from a tank heated to 35 °C, this will evaporate and enter directly to the column, it will not be outlet because it shall be stored in the column until the end the experiment.

Pressure will be reduced to 0 Atmospheres with a vacuum pump. Due to the low pressure when the valve of the tank (S01) will be opened water will simultaneously aspirate and change to gas phase to fill the tank (S02). When the desired humidity is reached in the expansion tank (S02) the inlet valve to the column will be opened letting the water gas enter in the cylindrical column where the sample is located.

Figure 3. Vacuum pump

Telecamera measures the variation in height of the sample by analysing the difference in brightness, because the samples used are transparent the difference in brightness is captured on the aluminium strip previously placed with the sample. The sample displacement due to increased weight absorbed water will cause an elongation in the spring that holds it. To correctly measures the height variation it is placed a white panel behind the sample.

Telecamera works by measuring the variation of brightness along an axe therefore detect brightness variations at the edges of aluminium foil. Telecamera makes a measurement every x seconds. Telecamera uses five variables to assess the variation in height: time, height1 and height2 (both are the point of variation in brightness of two predefined axes), reference1 and reference2 (which are the size of the aluminium strip).



The image shows the sample (white film) aluminium foil (dark film) and four variables; height1, height 2 (blue and red line) Ref1, Ref2. (red segments)

The telecamera measures over blue and red lines.

References 1 and 2 are necessary, because the telecamera takes measurements in pixels. Acordingly the measure of the aluminium strip in mm and the measure of the strip in pixels (reference1&2) it is a reference to convert all values of height variation to millimetres. With the logical ratio pixels/mm.

Figure 4 shows and aluminium strip viewed by the telecamera.

As it is been said, the telecamera works by variation of brightness in the red and blue axis (figure4), i.e. the camera evaluates brightness changes only in the axis and the made a graphic, the water bubbles are seen in the image belong to the shirt and contribute to the error of the camera.

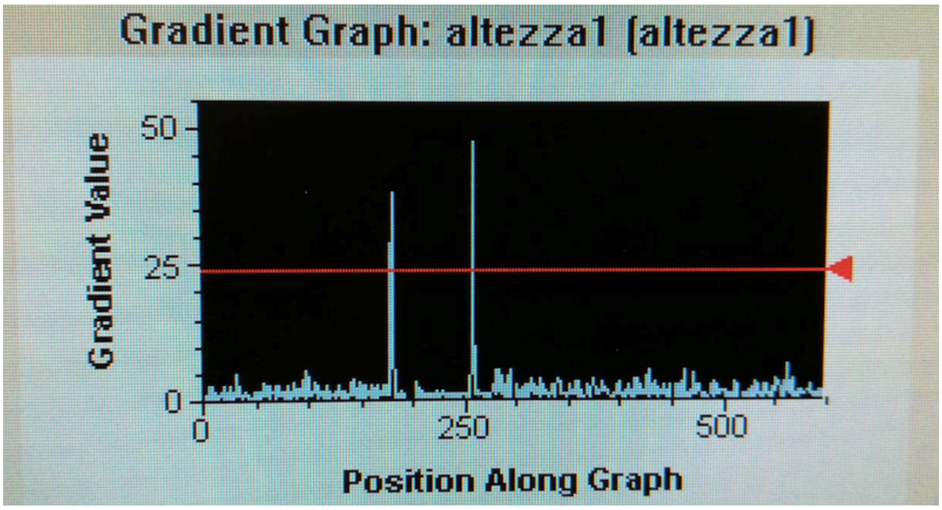


Figure 5. Brightness difference sample view the program

Telecamera detects the relevant data at the edges of the aluminium strip.

It should be noted the crucial importance of the heating system to try to keep the temperature as stable as possible. Because when working with gases a variation of half degree causes a change in water humidity and it will affect the data obtained by the telecamera, especially when the system is left working overnight. That's why there are different systems to maintain constant temperature.

Therefore, all the system and pipes will be covered with insulating material and the heating water system will be connected to the column jacket and the expansion tank. Likewise, a resistance will heat the top of the column because a small condensation would put the results on risk and even break the sample. The resistance also heat tripod telecamera because it has been detected undesired height variations due to temperature changes in tripod.

Gas expansion

When water vapor is loaded in the expansion tank, the value pressure must be charged to a higher value than the working pressure value because logically when opening the inlet valve to the column it will increase the volume and lower the pressure.

Calculations relevant to this part are as follows, assuming that it behaves as an ideal gas.

Situation 1

$$P_{C0} = 0 \qquad P_{T0} = \frac{n_T RT}{V1} \qquad \mathrm{P_{Total0}} = \frac{\mathrm{n_T RT}}{\mathrm{V1 + V2}}$$

Situation 2

$$P_{C1} = \frac{n_c RT}{V2} \qquad P_{T1} = \frac{n_T RT}{V1} \qquad \mathrm{P_{Total1}} = \frac{\mathrm{n_c RT}}{\mathrm{V1 + V2}} + \frac{\mathrm{n_T RT}}{\mathrm{V1 + V2}}$$

$$P = \frac{n_c RT + n_T RT}{V1 + V2}$$

And so on we can obtain the desired pressure with this calculation.

Flotation coefficient

It is called Archimedes' principle, it states that the buoyant force of an object is equal to the fluid displaced by the object. Knowing that the sample is dissolved in air as working fluid there is a component of the weight of the sample that cannot be attributed to its actual weight (pressure 0), so as it will work to different pressures must calculate the buoyancy force on function of pressure to make a correct analysis of the different activities.

Because of that a simple experiment will be performed, the sample will be 0 atmospheres and will return to atmospheric pressure so the difference in height will be floating force because it will not absorbed anything at all.

$$F_{bouyancy} = V_{desplazado}\,\rho_{fluido}\,g(\frac{g\,m}{s^2})$$

The buoyancy force is equal to the product of the volume of fluid displaced fluid density and gravity.

$$PV = nRT = \frac{m}{M_{air}}RT \qquad \frac{m}{V} = \rho_{fluido} = \frac{PM_{air}}{RT}$$

It is needed to find the ratio of the density with pressure by the ideal gas law. Replacing:

$$\frac{F_{bouyancy}}{g}(P) = V\frac{PM_{air}}{RT}(g)$$

Expressing equation in grams, knowing that everything weight variation due to the variation of buoyant force and adapting it to our experiment where the fluid is water gas.

$$\frac{F_{bouyancy}}{g}(P) = V\frac{PM_{water}}{RT}(g)$$

Experimentally must satisfy the equation:

$$\left(h_f - h_0\right)k + \frac{F_{bouyancy}}{g} = \left(h_f - h_0\right)k + \frac{VPM}{RT} = 0$$

All the weight difference is due to the buoyant force. Where k is the spring constant. The only unknown value that we cannot find experimentally is the volume:

$$V = \frac{\left(h_0 - h_f\right)k}{PM_w/RT}$$

In this way we obtain the value of the buoyant force for all experiments.

Hooke's law

In order to obtain an increase in mass due to the variation in the elongation of the spring, Hooke's law will be used.

$$M = k(x - x_0) + F$$

Where M is the mass increase, (x-x0) is the variation in height of the sample, F is a flotation coefficient determined in another experiment, k is the constant to be obtained and its units are g/mm. In this experiment it will be taken into account the bouyancy but obviously it will be a very small value compared with the variations of the absorbed water.

Water activity

Water activity is the ratio of the water pressure and the saturation pressure at the same temperature:

$$\mu(p_w, T) = \frac{p_w(T)X}{p_{vap}(T)}$$

Being p_w the partial pressure of gas and X the mole fraction of water, X = 1 in all cases to be treated. Relative humidity is the percentage of water in the system regarding the maximum capacity.

$$H_R(p_w) = \frac{p_w}{p_{vap}} * 100$$

During this study, humidity or activity will be used for referring to the same thing.

Antoine law

Although the experiment will be performed at the same temperature, small changes will change the saturation pressure of water and thus the activity, so that will be considered all time.

Antoine's law relates the saturation pressure of the water temperature, the values A, B and C calculated empirically bibliographic data are made.

$$\log_{10} p = A - \frac{B}{C + T}$$

Diffusivity

Diffusivity is the process by which particles of a substance introduced into a medium. There is a transfer between two adjacent systems always from the higher concentration to lower concentration. The diffusivity measures the speed of this transfer. To calculate the diffusivity Fick's law it will be used, this law states that solute will move to the less concentrated medium proportionally to the concentration gradient, a single spatial dimension values. [9]

$$J = -D\frac{dC}{dx}$$

Being "J" the diffusion rate as amount of substance per unit of area, "C" concentration, “x” thickness penetrated and “D” the diffusivity. [10]

Applied to the case study, a rectangular plate of known thickness, it will be researched literature data for the same situation so that the equation developed is the following. [11]

$$\frac{M}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{D(2n+1)^2\pi^2 t}{L^2}\right)$$

Being “L” characteristic of the sample “M” and “M_{inf}” data obtained in experiments. It is going to be possible to iterate to get the diffusivity of each of the experiments.

4.Process

Process

First of all, the laboratory membrane will be held with gloves to avoid contaminating it, a rectangular piece will be held from the edges without deforming. It will be weighed and will be determined their thickness. For both tests, a series of measurements will be made and the average value of them will be considered. Then, the sample will be placed within the assembly hanging from the spring with the aluminium strip.

After placing the sample within the assembly will be generated vacuum, the goal to do this it is dry completely the sample. Generating 0 atmospheres inside the column sealed and then modify the pressure. Generating 0 atmospheres initially, it can be assumed that all the gas within the column is steam.

During the process of generating vacuum in the column and thus in the expansion tank, the sample is observed by telecamera, the sample will go up as it loses water because when it loses mass and weight the spring that holds it will be compressed. Actually, at first due to the buoyancy of every material in a fluid, it will show a descent but overall the sample will rise. At the moment it will be no water inside, according to Hooke's law, the mass of the sample will be dried and it will be possible to evaluate the first point of the first pressure equilibrium.

Then, the system will have 0 atmospheres, pump will stop and all valves will close. After, expansion tank water will be filled with the desired water activity (pressure). valves S01 and S012 will be opened very slowly to prevent unwanted condensation or cooling. Water is absorbed to the tank and it is evaporated immediately because the system is at 0 atm. With a manometer connected to the expansion tank S02 it will evaluated the pressure and it will be able to reach the pressure and water activity desired.

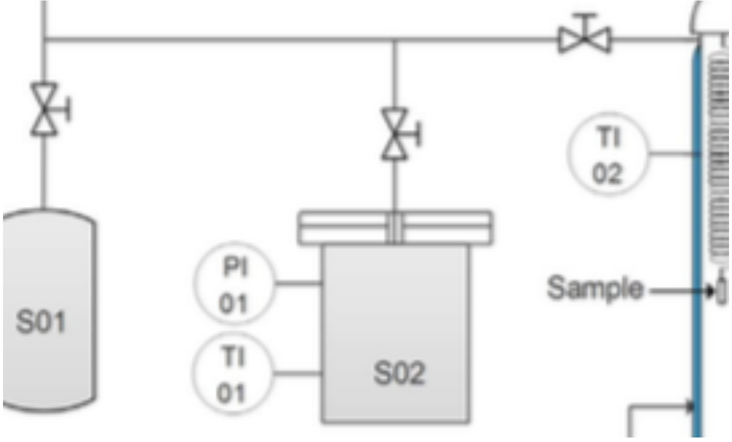


Figure 6. Diagram Valve

When the desired activity is reached, the valve S01 will be closed, and the access valve to the column will be opened. The gas will expand through the two volumes and it will be obtained the pressure and work activity.

Moreover, the sample will be exposed to a specific water activity and the process of water absorption of the sample will begin. Depending on diffusivity and water activity it will absorb faster or slower. With telecamera will be evaluated again the difference in the height of the sample. The sample will descent until the maximum amount absorption of water (equilibrium state).

Analysing the dry mass of the sample and the mass of water that it is able to absorb in every step of the experiment, it will be known the amount of water absorbed by the sample under specific conditions.

When one step finish, access valve to the column will then be closed, it will be re-opened the valves S01 and S02 to load another water pressure in the expansion tank once loaded the desired pressure it will be closed S01 and the inlet to the column valve will be opened subjecting the sample to a different and higher activity. When it will reach equilibrium state it will get another pressure-absorbed mass point.

It will be loaded the expansion tanks with different activities the number of times necessary to evaluate the diffusivity.

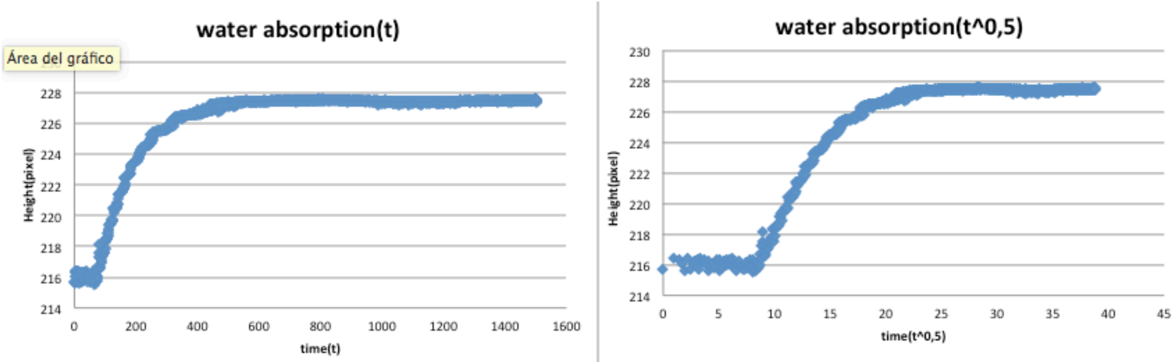
When the experiment ends the system should be brought to an atmospheric pressure before handling anything and before changing the sample.

Data processing

The assembly provides a series of data, from these data the behavior of the membrane will be interpreted. After obtaining data it only will be used Excel tool for manipulation and interpretation of it.

Telecamera synchronized with the computer provides the values it has been already seen, height1, height 2, reference2, reference2 and time. To evaluate the data, it can be used just one height and one reference but always corresponding with each other.

First, the data will be manipulated to generate columns of data and the height will be represented as a function of time. Knowing that the experiment ends when the sample stops falling and therefore it has absorbed the maximum amount of water. As height versus time will be inaccurate, it will be plotted height against the root of time.

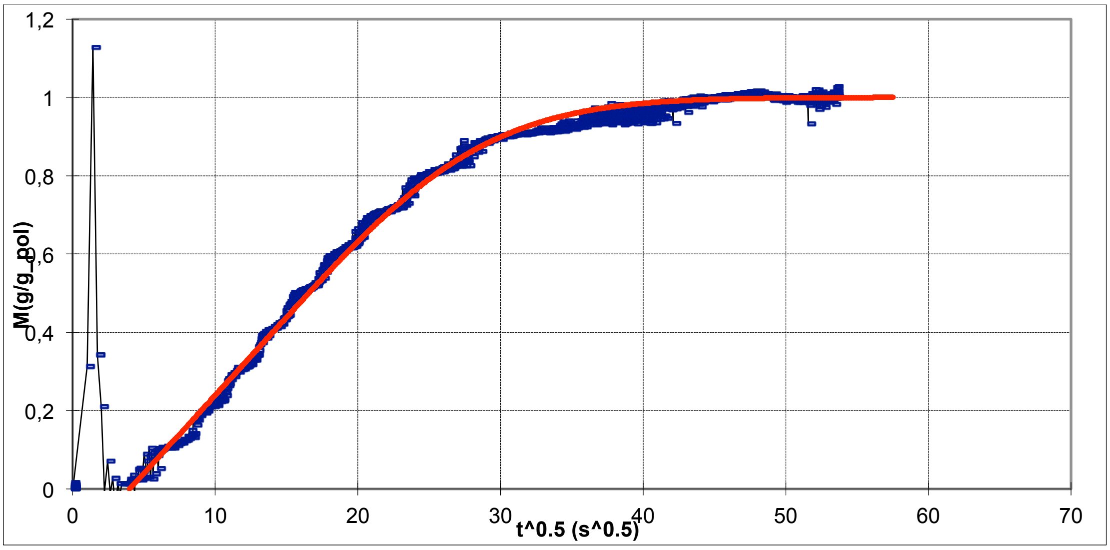


Graph1. Graphics comparison Height-t, height-$t^{0.5}$

As it can be seen in the graph 1 the slope is less with the root of time, which helps us to distinguish whether the system reached equilibrium.

Each experiment of the study will be made with a different membrane, each experiment will be divided into different steps. From each step you can obtain all the values provided by the telecamera and the initial and final pressures of the step. Therefore, the manipulated variable will be the initial activity of the water, the first step will always be to empty the column, then 25%, 45%, 55% ... or any other value, the objective is to obtain several values of activity.

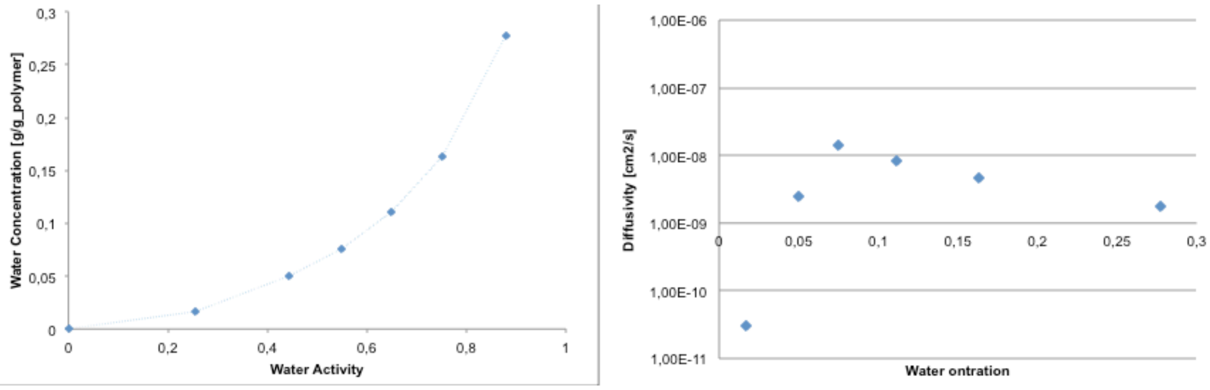
Then the amount of water absorbed as a function of sample mass (blue line) is expressed. Will iterate following the laws of diffusivity to model the behavior of the membrane (red line).



Graphic2. Example g_agua/g_polímero function of $t^{0,5}$

When all diffusivities and concentrations are calculated the final two tables will be made, which will serve to compare with other experiments are performed.

The disturbance that is seen in the initial times is due to the opening of the access valve to the column. The strong pressure change causes the spring to oscillate violently until it stabilizes. Mark the starting point of the experiment



Graph 3. Example of concentration of water based activity and diffusivity depending on water concentration.

5. Discussion of Results

This section contains all the results obtained in the different experiments will be evaluated; graphs and observed anomalies are discussed.

Nano-cellulose fibers with 30% arginine

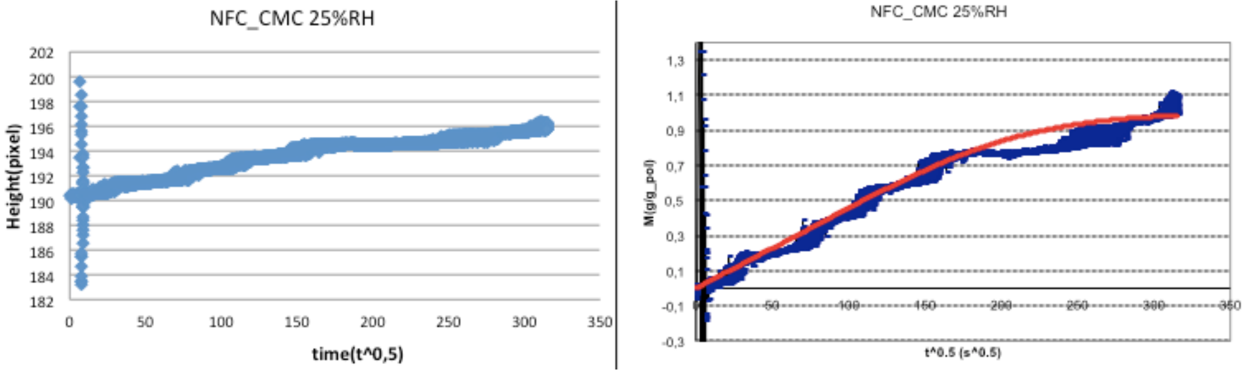
This is the experiment from which the greatest water absorption is expected. It has polarized nano-membrane cellulose fibers by treating with arginine. The first step starts from 0 atm, therefore from 0% of initial activity, but leave the rest starts of the previous step and therefore there is an amount of water already absorbed.

At all times the mass absorbed respond to the equation.

$$g_{abs} = (h - h_0) * S.f * k$$

Where k is the spring constant expressed in (g / mm) and the Sf Scale factor different in each experiment and expressed in (mm / pixel).

Water activity 25%

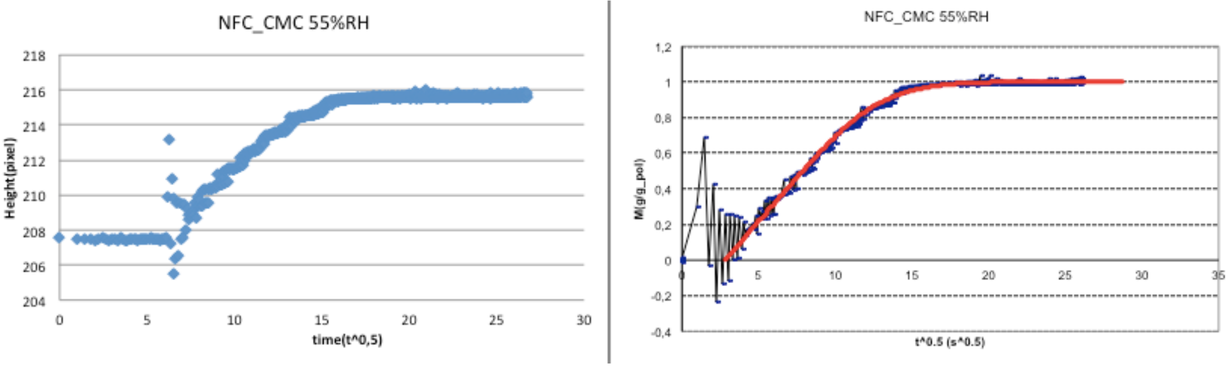


Graph 4. Water absorption 25% activity

At 25% activity, the minimum activity to be worked on, the speed of absorption is the slowest. Furthermore this is the membrane more water can be absorbed, so it is the slowest experiment. The column was vacuum valve opened and, after a few seconds an initial pressure of 13.98 mbar scored. It was left for 29 hours reaching a final pressure of 14.08 mbar. The height difference is 196-190 = 6.

You can see in Figure 4 as the system does not reach equilibrium completely. In the graph of mass absorbed they can clearly see the oscillations of the spring. And an abnormal area differs diffusivity model (red line), just at night when the temperature drops system inevitably. The diffusivity is 3 * 10^{-11} cm / s2.

Water activity 55%



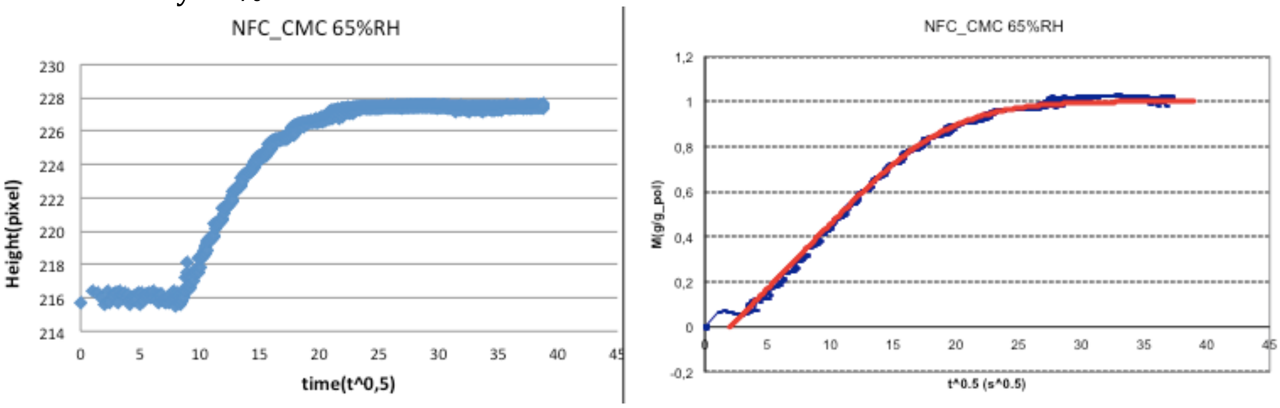
Graph 5. Water absorption 55% activity

The speed of the second experiment is much faster, since the diffusivity increases exponentially with the pressure. The previous pressure of the column was 24.72 mbar. The expansion tank was filled to generate an activity of 55% in the system.

The initial pressure of the system was 30.57 mbar. It was left 24 minutes reaching a pressure of 30.46 mbar.

From the graph we can see that reaches equilibrium by drawing a perfect line from $s^{0,5}$ = 20. Continue to be felt the oscillations of spring, the diffusivity is 1.4 * 10^{-8} cm/s2. The height difference is 215.6 to 207.4 = 8.2.

Water activity 65%

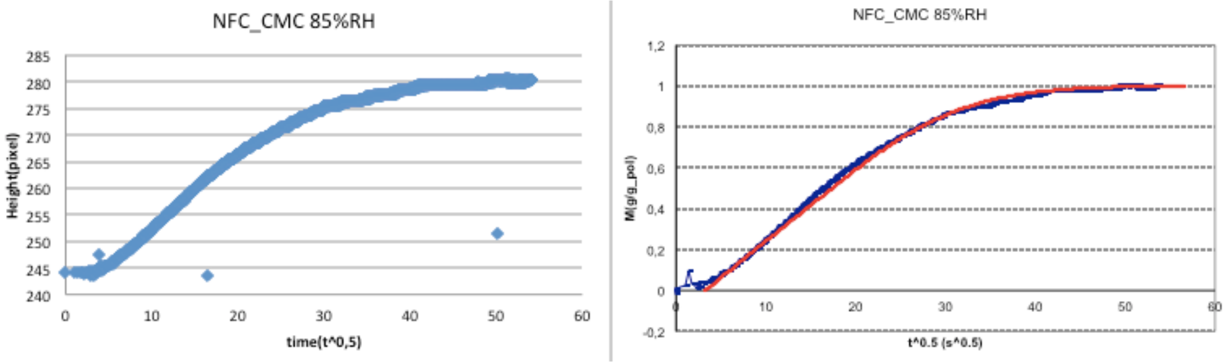


Graph 6. Water absorption 65% activity

It increases the activity under absorption becomes much faster. The initial pressure in the column was 30.46. After filling the expansion tank and open the valve of access to the column initial pressure was 36.3 mbar, after 25 minutes the pressure was 36.3 mbar.

Diffusivity coefficient is 8.5 *10^{-9}cm/s2. The height difference 227.47-216.03 = 11.44.

Water activity 85%

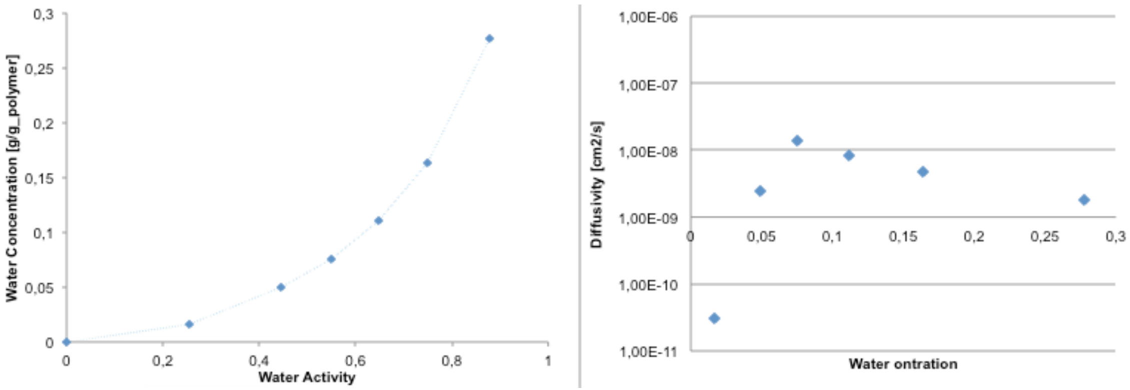


Graph 7. Water absorption 85% activity

The previous pressure in the column was 42.04. After filling the expansion tank and open the valve of access to the column initial pressure was 55.5 mbar, after 49 minutes the pressure was 56.1 mbar.

Diffusivity coefficient is 8.5 * 10^{-9} cm/s2. The height difference from 280.24 to 244.10 = 36.13.

Activity and diffusivity



Graph 8. Concentration-activity and concentration-diffusivity

Finally, the summary table will serve to compare this experiment with others. It should be noted the high concentration of water absorbed against subsequent experiments.

LDPE

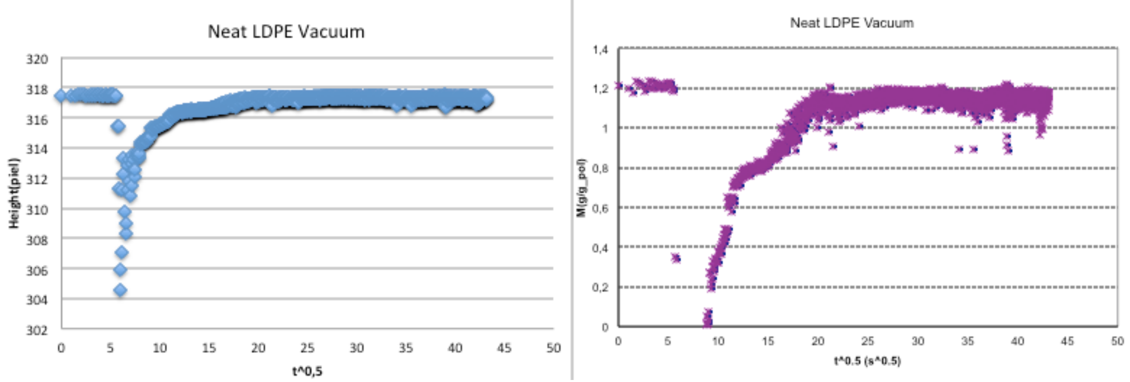
As has already been said, this thesis will try to analyze when the LDPE production process increases the absorbent capacity of the material. Four samples analyzed membrane. Neat LDPE, LDPE Neat pressing LDPE + 3 mL of heptane and LDPE + Antioxidant.

There was an experimental problem in the first experiments, the data were difficult to interpret. To solve it, a lens was used for the telecamera with much more magnification, the membrane was approached to the membrane and the size (mass) of the membrane doubled. It went from 35.5 grams samples of 80 grams.

35.5 mg Neat LDPE

Neat LDPE is the most basic membrane. It is expected according to the article "Solubility and Diffusion of Water in Low-Density PolyethyleneDavid W. McCall "a variation of 50 ppm is a variation of 0.134 pixel to 5 * 10^{-5} gH20/gLDPE.

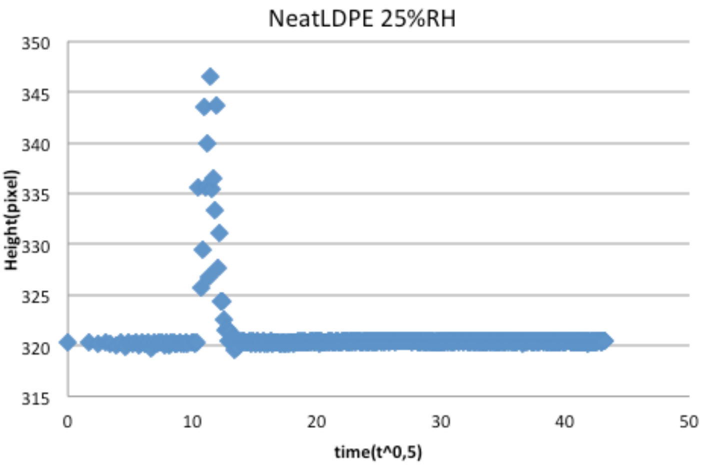
Vacuum



Graph 9.Vacuum of the sample

A vacuum pump is used to bring the sample to 0 atmospheres, at which point we can say that there is no water in the system. The initial pressure was atmospheric pressure, the final 0 atmospheres. There is a loss of height due to the buoyancy force and the loss of the little water that can be in the sample. The height difference was 317 to 314.6 = 2.33 pixels.

Water activity 25%

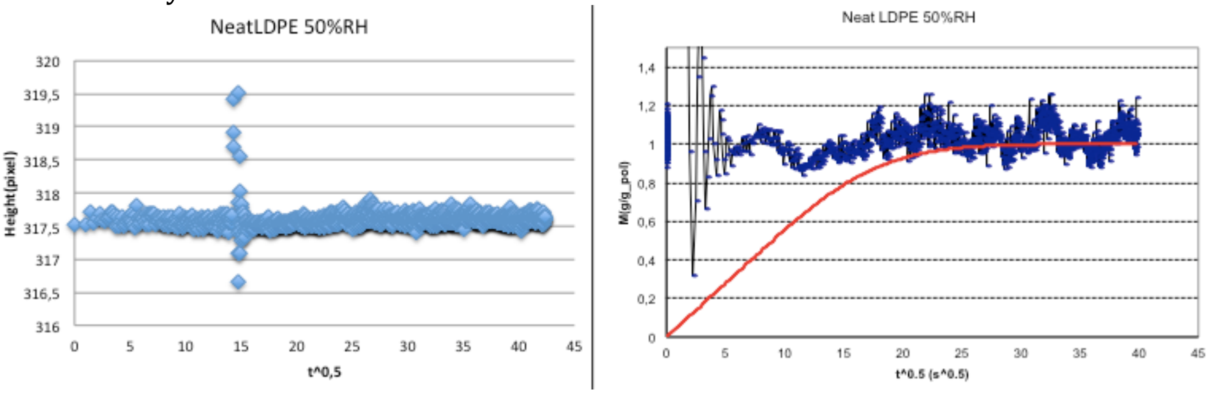


Graph 9. Water absorption 25% activity

From this point the water absorption is very small. The interpretation of the graphs becomes increasingly difficult. Image Neat LDPE absorption 25% RH hardly any variation of 320.39 to 320.20 = 0.19 pixel. Which implies a very small amount of water.

The initial pressure was 25.5 mbar system, after 40 minutes the final pressure was 25.3 mbar.

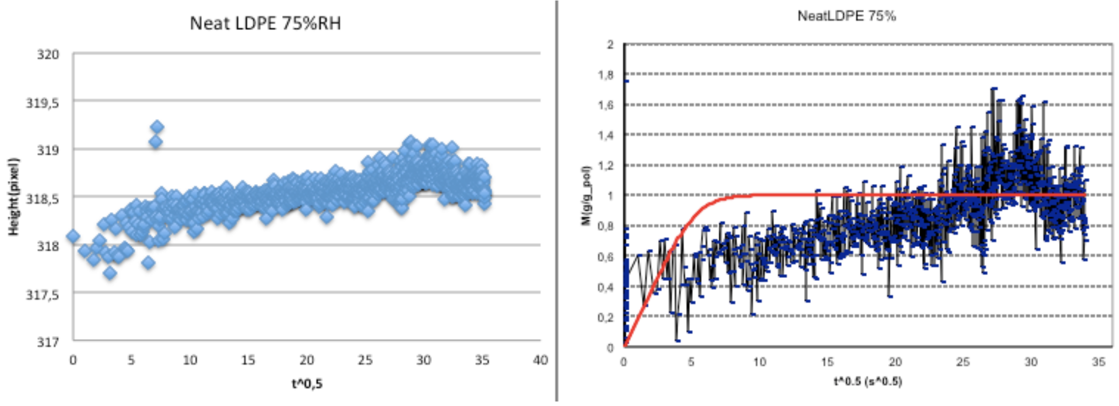
Water activity 50%



Graph 10. Water absorption 50% activity

The height variation continues to be almost imperceptible. From the average of the points before the opening of the valve and when it reaches equilibrium (the end points), the variation of the height is obtained 317.6-316.35 = 1.25 pixel. The initial pressure was 28.17 mbar after 25 minutes it was 27.96 mbar. While the diffusivity 3,2 * 10^{-8} cm/s2.

Water activity 75%

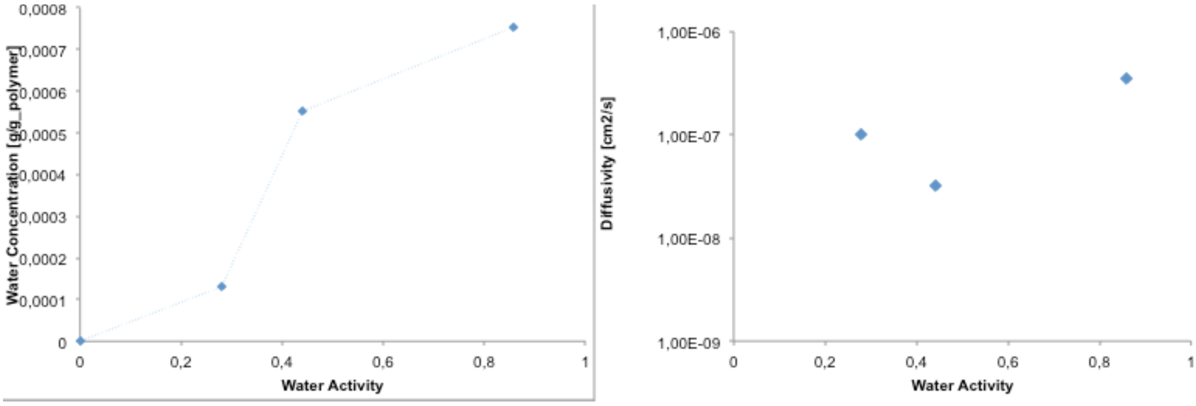


Graph 11. Water absorption 75% activity

The initial pressure was 50.66 mbar after 41 minutes the pressure was 51.43 mbar. The variation in height of 318.64 to 318.26 = 0.3823 was pixel. And diffusivity 3.5 * 10^{-7} cm/s2.

As seen in Figure 11 the variation in height is minimal the problem is that the oscillation of the spring is larger than the height difference to be measured. These data are difficult to interpret are the ones we need to bring an improvement in the process.

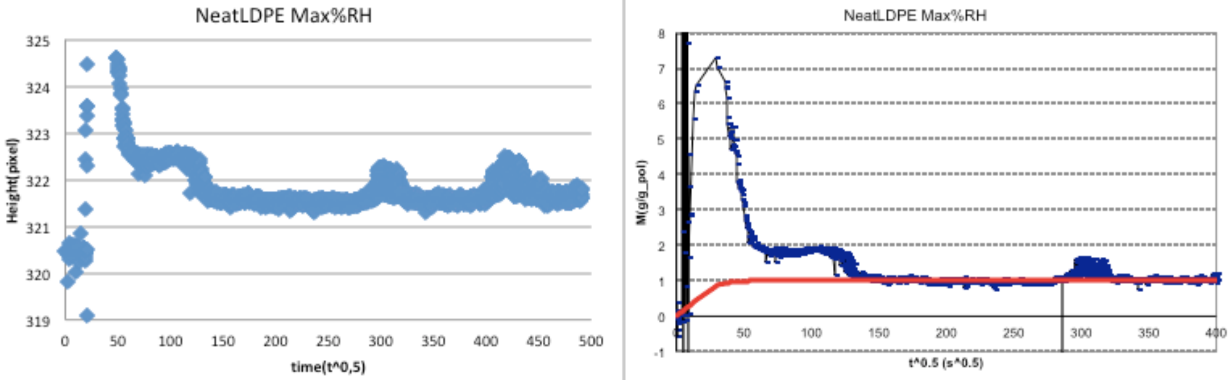
Activities



Graph 12. Concentration-graph activity and diffusivity-concentration

Comparative mode graphic summary of the experiment.

Maximum Activity



Graph 13. Water absorption maximum% activity

To finish the experiment the maximum possible activity was reached and absorption was caused from 0 atm. The goal was to make the biggest jump possible. To do this, after carrying out the vacuum, the water was evaporated with the valve of the column open, maximizing the volume.

The experiment had an initial pressure of 57,58mbar after leaving it to rest all weekend 2 days and 18:50 hours the pressure was 50,49 mbar. The difference in height of 321.52 to 320.45 = 1.07 pixel. Diffusivity 1 * 10^{-8} cm/s2.

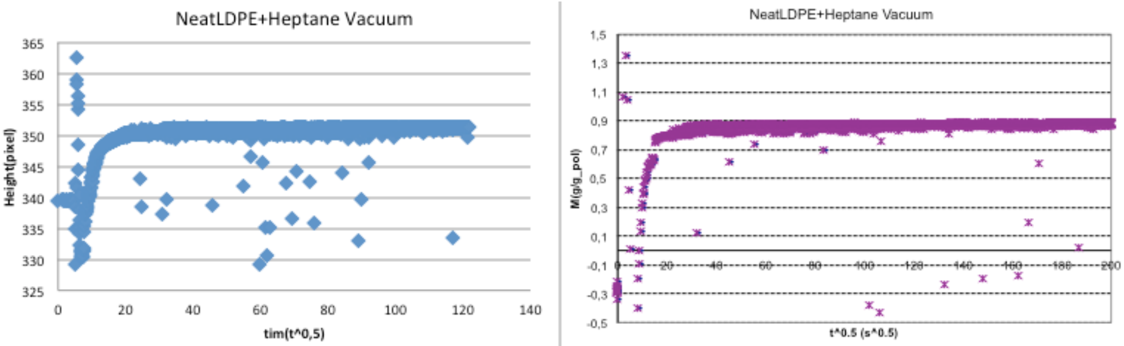
In the graph you can see how during the night the height varied considerably, it is logical due to the inevitable temperature drop. Obviously, the oscillations in the initial times are much larger because the difference in pressures is the greatest experienced.

LDPE + 35.5 mg Neat 3 mL heptane

The next step in the production process, treat LDPE with heptane. This experiment absorption 50 ppm is also expected (0.134 pixel to 5 * 10^{-5} gH20/gLDPE) as that obtained with LDPE Neat.

The tests were also carried out various activities and completed with maximum activity as in the previous experiment.

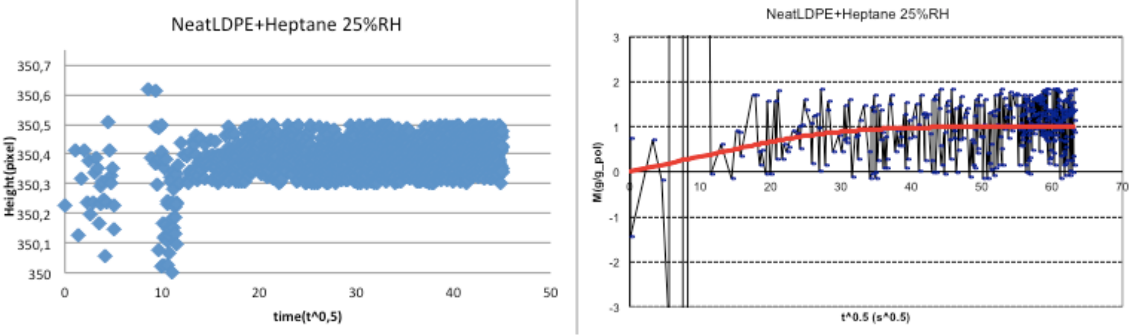
Vacuum



Graph 14. Vacuum of the sample

A vacuum pump is used to bring the sample to 0 atmospheres, at which point we can say that there is no water in the system. The initial pressure was atmospheric pressure, the final 0 atmospheres. There is a loss of height due to the buoyancy force and the loss of the little amount of water. The difference in height was 349.64 to 339.44 = 10.20 pixels.

25% activity

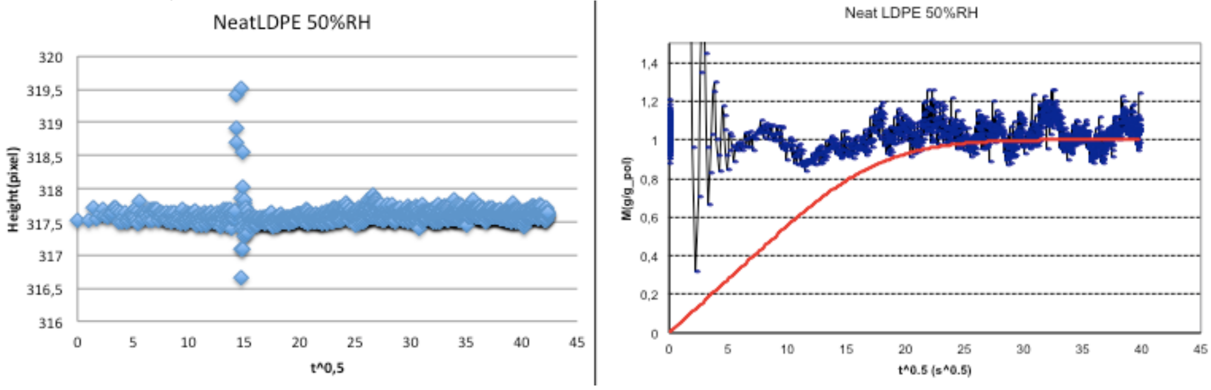


Graph 15. Water absorption 25% activity

The variation in height was 351.38-351.35 = 0.038 pixel. The initial pressure was 13.87 mbar after 1 hour 19 minutes was 13.98 mbar. While the diffusivity 1* 10^{-8} cm/s2.

As you can see there remains a slight variation in height.

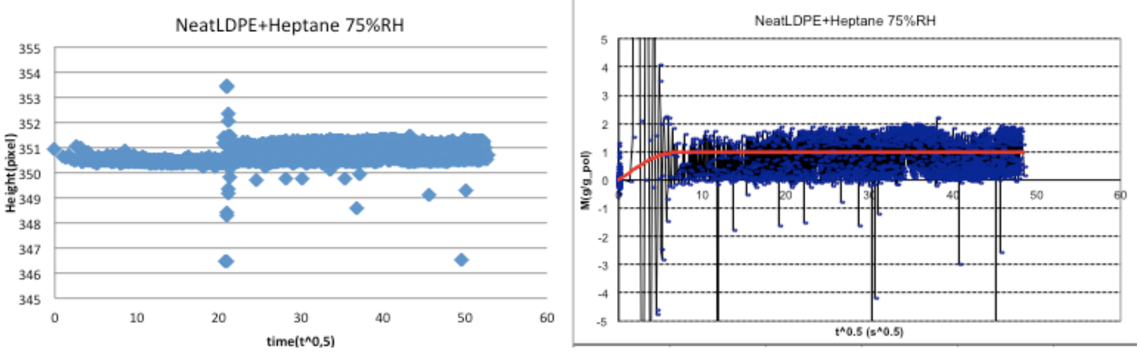
Water activity 50%



Graph 16. Water absorption 50% activity

The variation in height of 350.56 to 350.06 = 0.5 was pixel. The initial pressure was 32.44 mbar after 44 minutes was 32.44 mbar. The diffusivity 3.2 * 10^{-8} cm/s2.

Water activity 75%

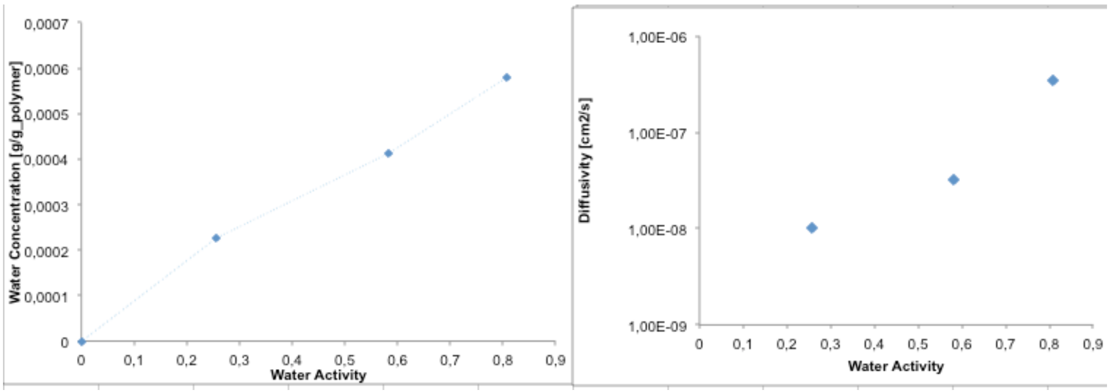


Graph 17. Water absorption 75% activity

The initial pressure was 43.71 mbar after 39 minutes the pressure was 44.75 mbar. The variation in height of 350.92 to 350.56 = 0.4538 was pixel. And diffusivity 3.5 * 10^{-7} cm/s2.

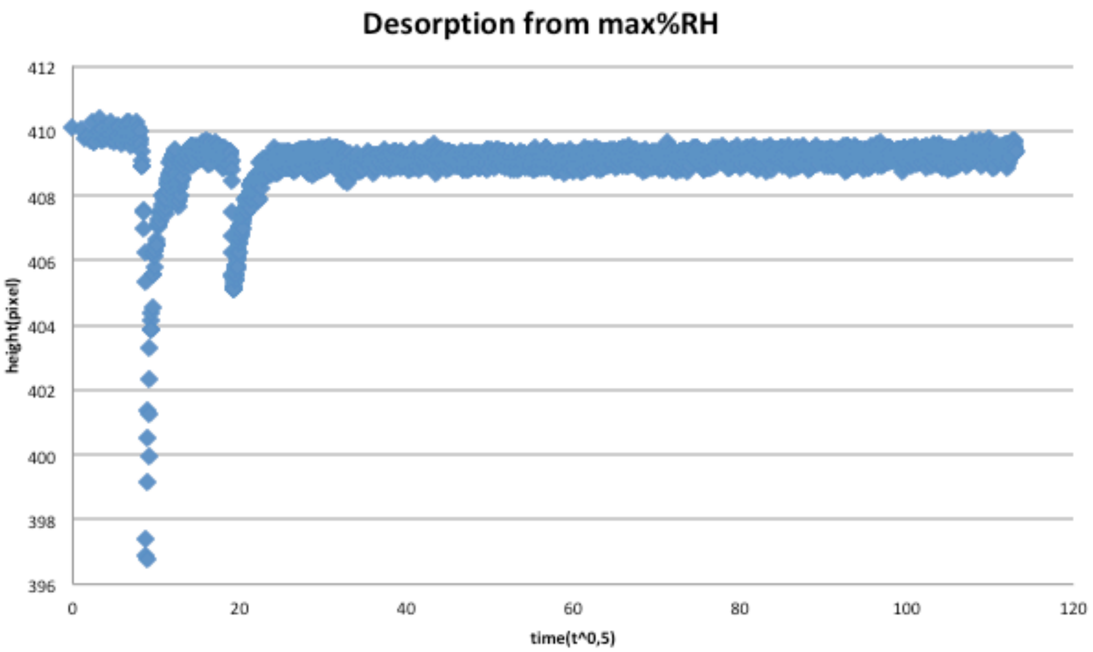
As shown in the graph 17 to a high activity there is no high absorption. The graph makes clear that there is great difficulty in interpreting the data, which will lead us to stop the experiments and remodeling process.

Activities



Graph 18. Concentration-graph activity and diffusivity-concentration
Comparative mode, the summary graph of the experiment. It is visualized as increasing humidity increases diffusivity and water absorption.

Maximum Activity



Graph 19. Water absorption maximum % activity

Again the maximum capacity was performed. With the valve of the column open, maximizing the volume.

The difference in height was 409.91 to 409.28 = 0.6366 pixel.

Change in procedure

This was the last experiment in these conditions. A variation of 50ppm (0,134pixel) was expected, between the oscillations and changes in temperature the difference that wanted to measure was smaller than the experimental error. The graphical explanation is as follows.

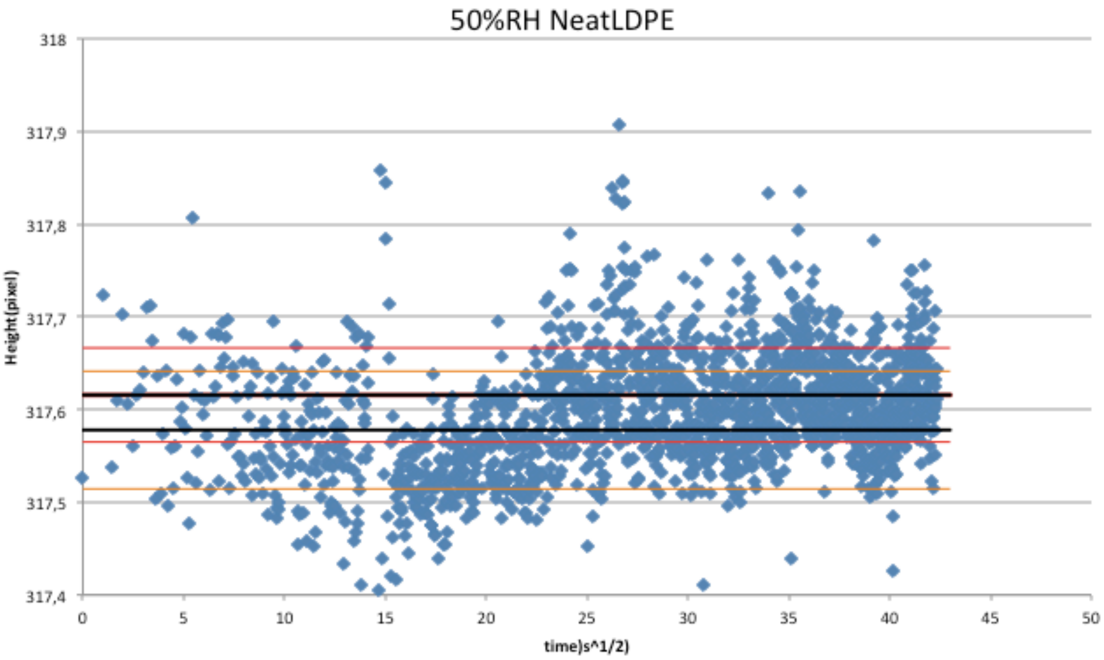
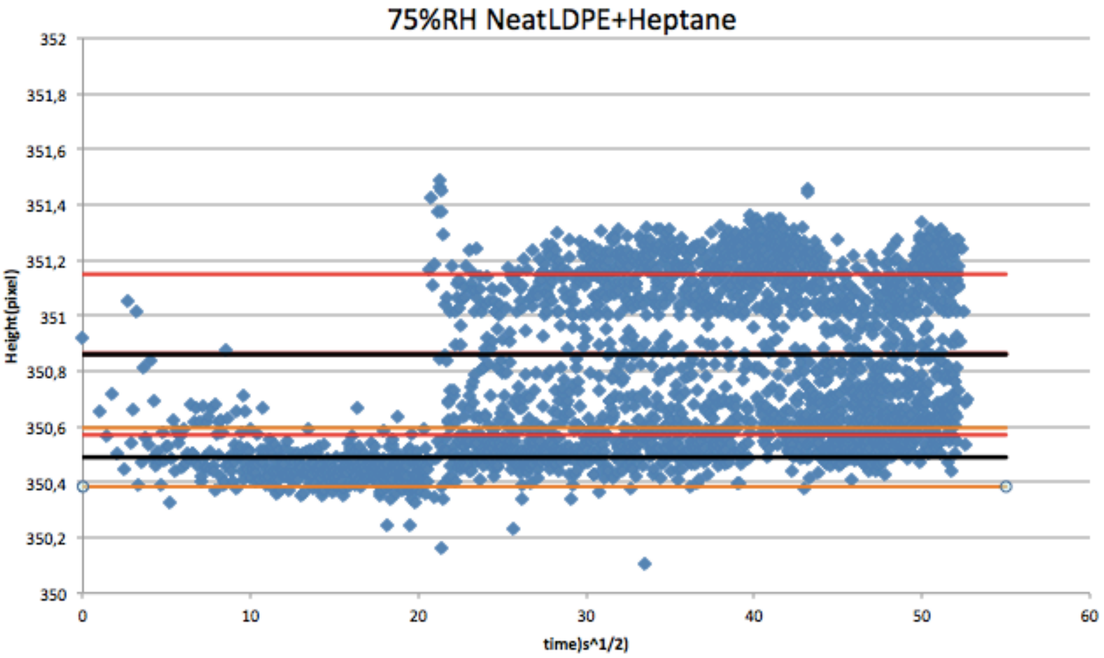


Figure 20. Experimental error 50% NeatLDPE

The graph shows the water absorption of the membrane NeatLDPE 50% of activity is represented. As we have already said they are very difficult to interpret. The bottom black line represents the average height of the sample before subjecting the sample to the absorption. Yellow lines, the standard deviation of the data (error). The upper black line represents the average height of the sample at the end of the absorption and the red lines its standard deviation (the error). The error overlaps almost completely, which makes a change in the procedure necessary.



Graph 21. Experimental error 75% NeatLDPE + heptane

Increasing the activity reduces the overlapping error part. But it is not avoided, making all data unacceptable from the statistical point of view. Although the biggest problem as we have already said the error is larger than the value you want to measure.

To solve the experimental problem, a lens was attached to the camera with much more magnification, the membrane was approached to the membrane and the size (mass) of the membrane doubled. It went from samples of 35.5 grams to 80 grams.

When applying a new objective and bringing the camera closer we will have more increases, a pixel will correspond to more centimeters. As the sample size increases, a greater amount of water will be absorbed, increasing the mm that the sample must descend when absorbing the maximum amount of water. With 35mg they were 00875mm and with 80mg 0.02mm.

Finally we will make only the maximum possible jump. We will produce the minimum possible humidity and we will make a total desorption.

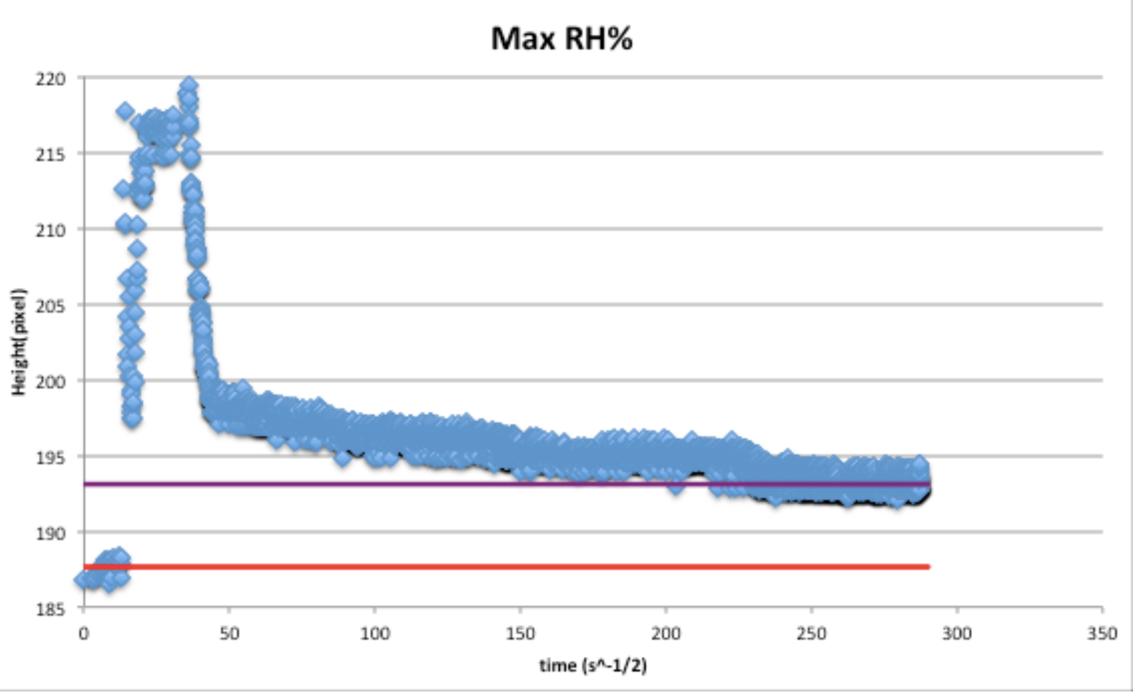
Final experiment

After the commented modifications, the experiment was carried out paying special attention to the standard deviation. Expected results change as well. Since according to the article "Solubility and Diffusion of Water in Low-Density PolyethyleneDavid W. McCall "a variation of 50 ppm is expected. We will expect an absorption of 4E-6gH2O, which will mean a variation in the spring of 0.02 mm and 0.833 pixels.

The procedure to be followed was the following, first the buoyancy of the sample was evaluated. Then the sample was saturated with the maximum possible humidity that in no case reached 100%.And finally desorption was performed with the vacuum pump causing the maximum possible jump.

80 mg of NeatLDPE

Saturation

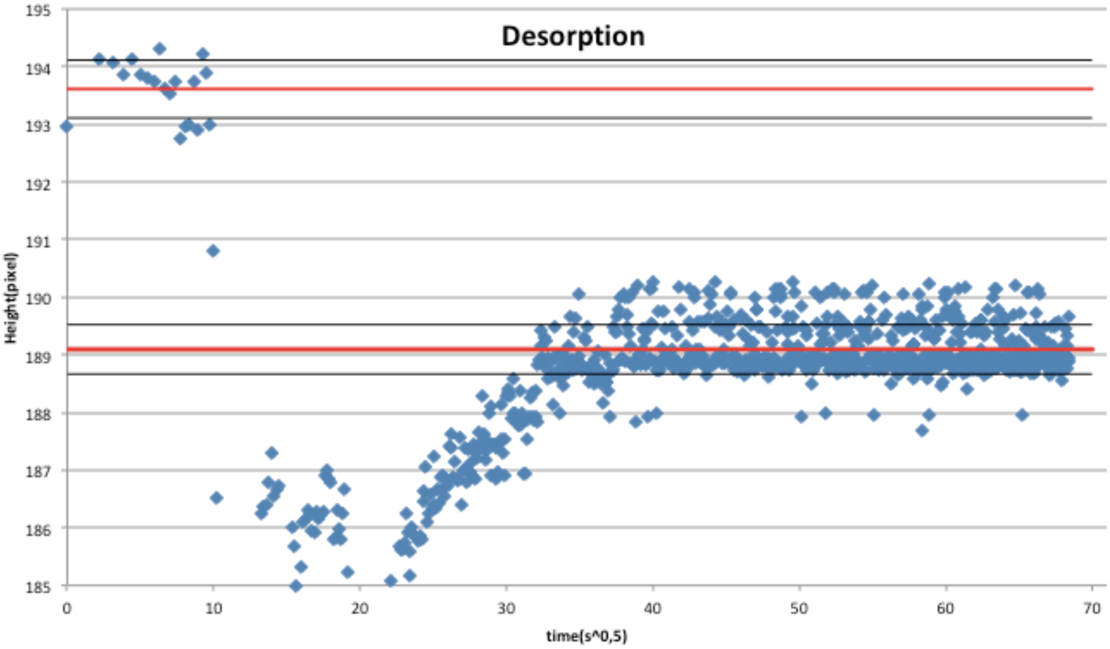


Graph 22. Exposure to high humidity NeatLDPE

The red line represents the average height at the beginning of the experiment, purple the final height. A variation of 5.454pixel, 2,65E-05gH2O, 331,349ppm.

An acceptable variation since we are working with water in gas phase

Desorption



Graphic 23. Desorption of NeatLDPE

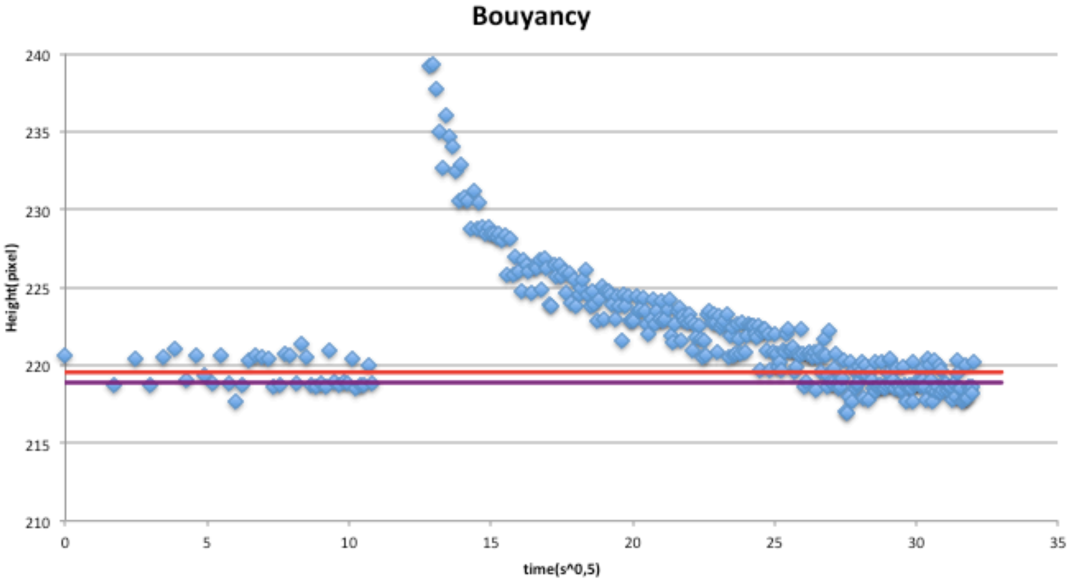
The jump in the desorption experiment must be equal in amount of water saturation experiment. We see that the error lines are clearly separated.

According to the experimental data, the difference between the average of the height at the beginning and end of the experiment was 4,515pixel, 2,19E-05gH2O, 273,978ppm.

Practically the same as previous experiment.

LDPE pressed

Buoyancy



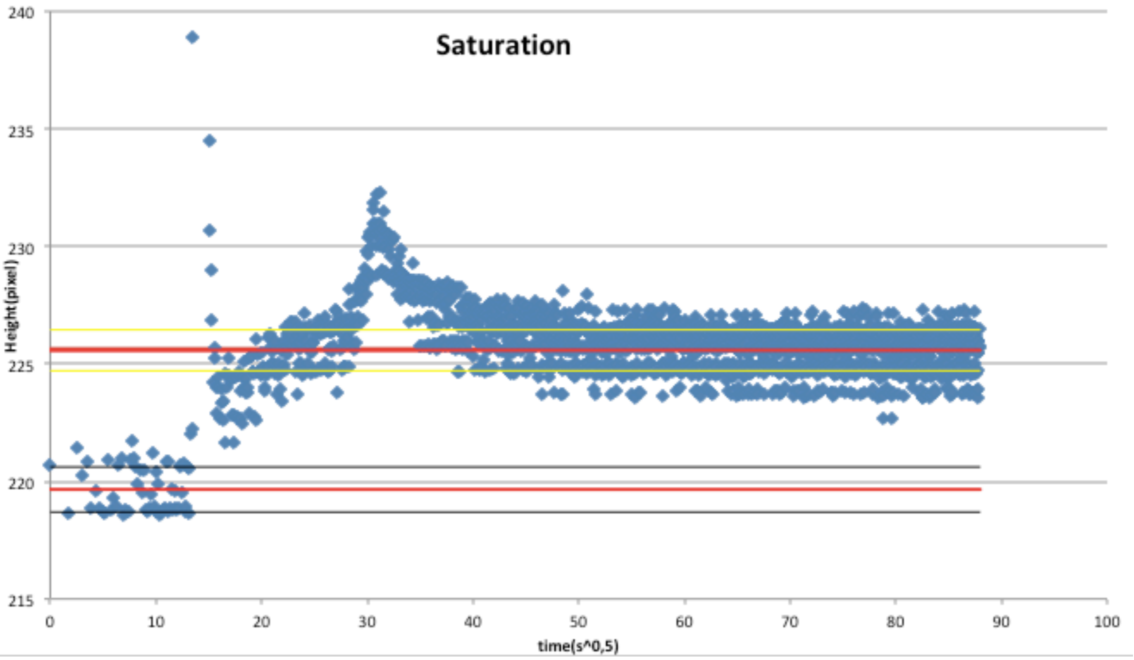
Graph 24. Buoyancy pressed LDPE

The variation between the start and end in experiment buoyancy is almost negligible because the influence of the buoyancy force of the membrane in the air is low.

It experienced a variation of 0,662pixel, 2,92E-6gH2O, 36,6ppm.

Very small compared with other experiments.

Saturation



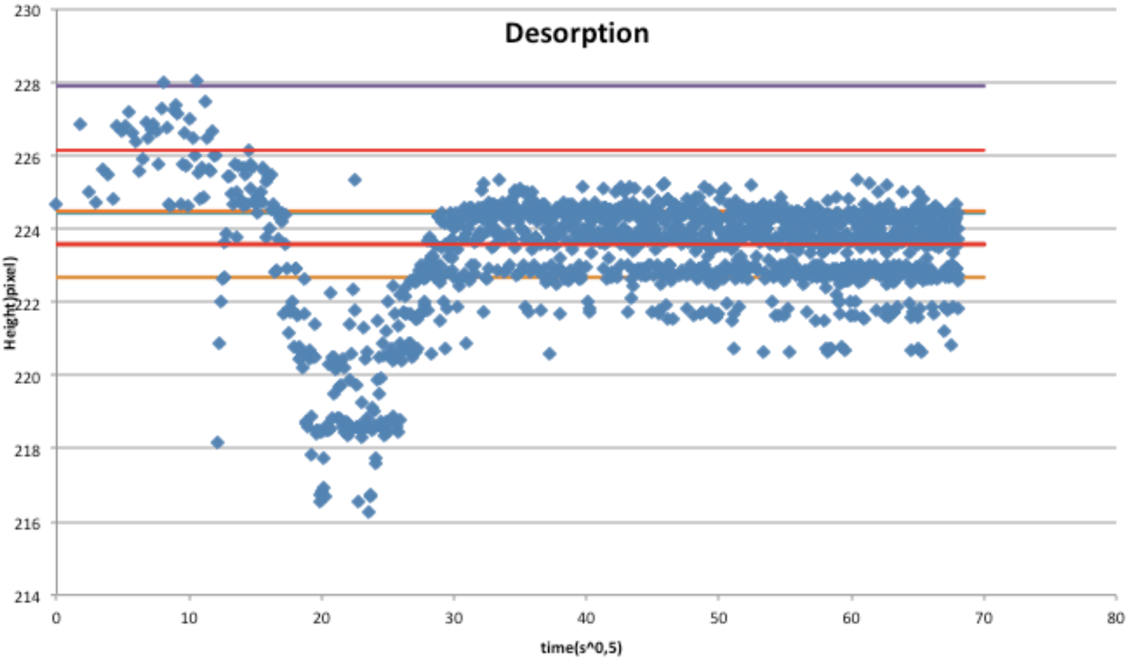
Graph 25. Saturation pressed LDPE

The variation in this experiment is again the same magnitude as the experiment with Neat LDPE. In other words, they absorb the same amount of water. Error lines remain distinct.

It experienced a variation of 5,9249pixel, 2,615E-5gH2O, 326,9298ppm.

As the experiment with Neat LDPE.

Desorption



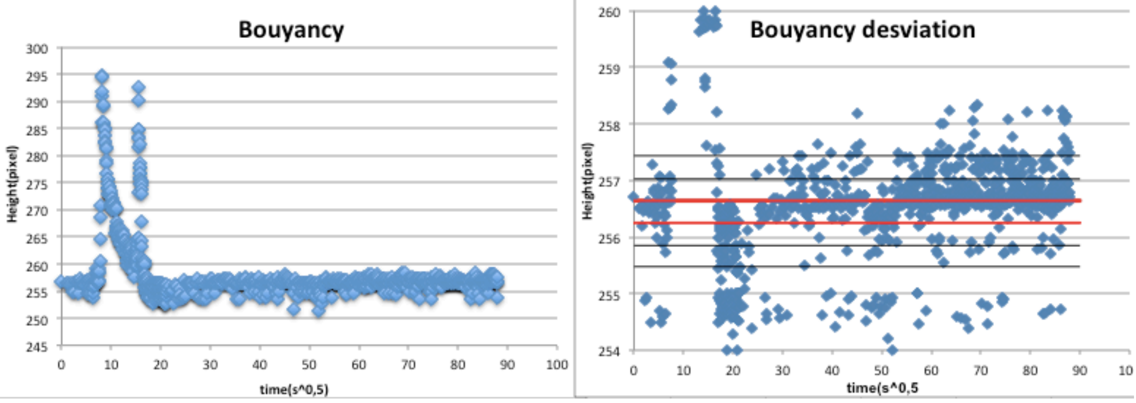
Graph 26. Desorption pressed LDPE

Again the variation in the desorption should equal in saturation. Since all the absorbed water is desorbed. Error lines overlap minimally.

The variation was 2,5776pixel, 1,13E-05gH2O, 142,4118ppm. The variation was considerably smaller, may be due to experimental errors but the results are not so different as to think that there is a greater absorption that saturation desorption.

LDPE + Heptane

Buoyancy

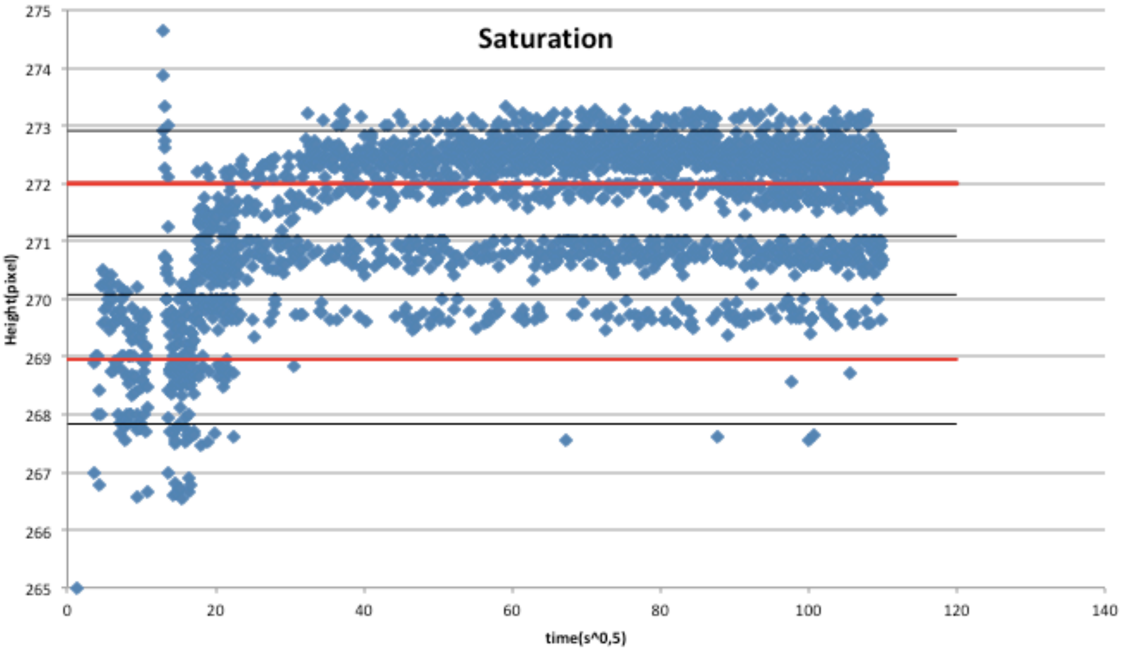


Graph 27. Buoyancy graphic LDPE + Heptane

The variation between the start and end in the experiment is minimal, little influence of the buoyancy force of the membrane.

Variation 0,3926pixel, 1,826E-6gH2O, 22,8348ppm.

Saturation



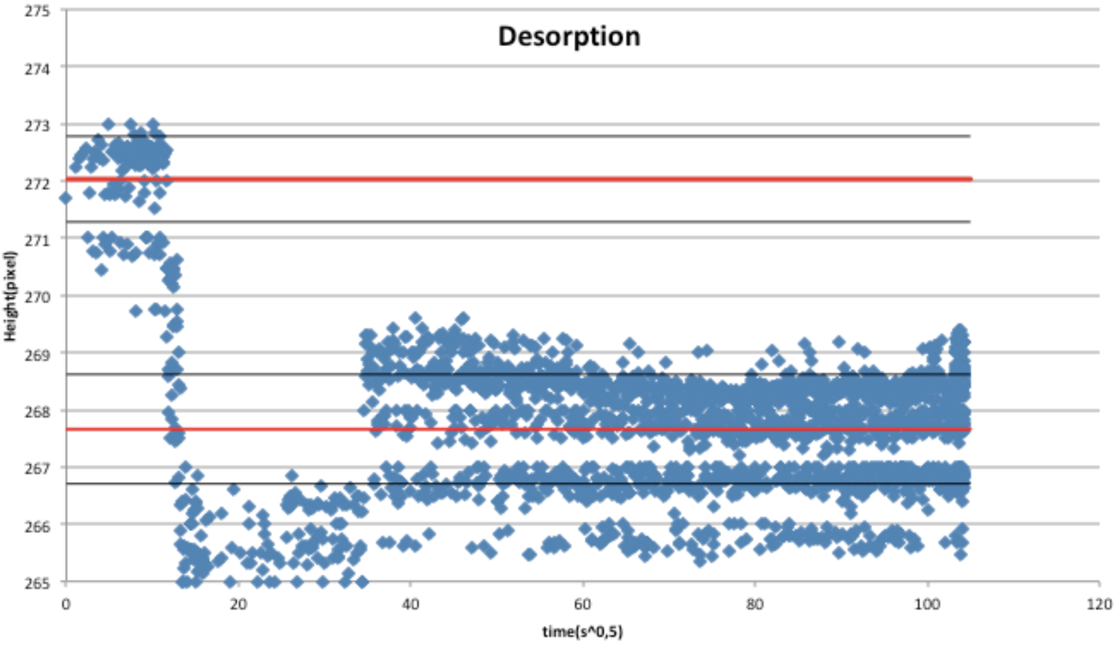
Graphic 28. Saturation LDPE + Heptane

The variation in this experiment is again the same magnitude as the experiment with LDPE and LDPE pressed Neat. There is no difference in the amount of water absorbed.

It experienced a variation of 3,0458pixel, 1,419E-5gH2O, 177,4848ppm.

Water absorption remains the same magnitude.

Desorption



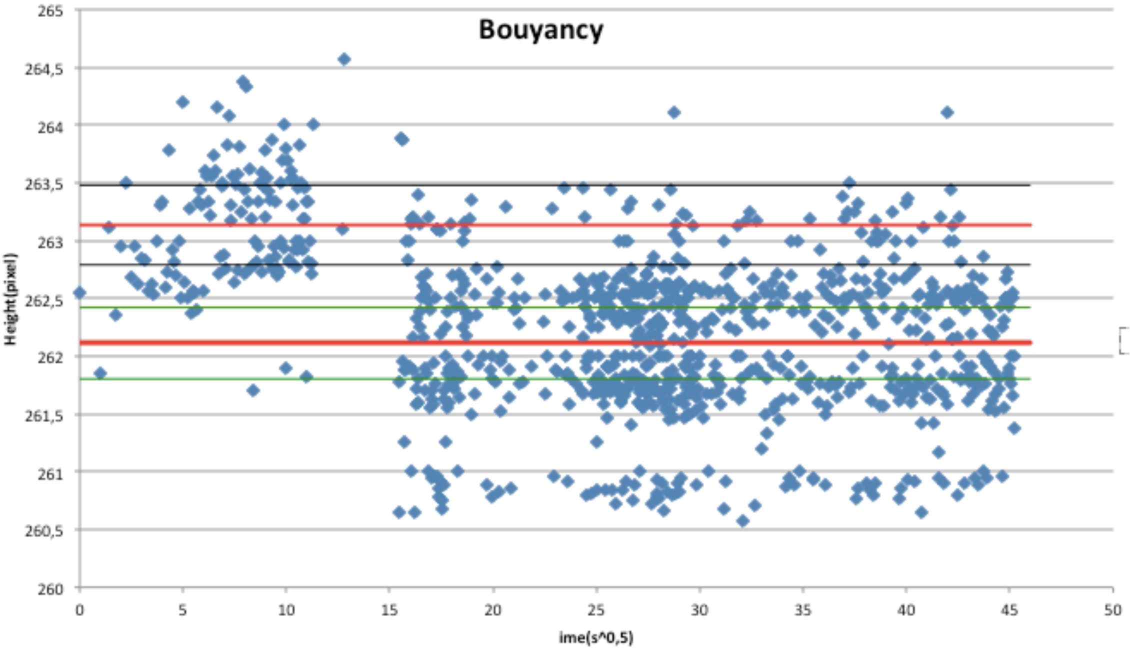
Graph 29. Desorption LDPE+Heptane

The variation in the desorption was slightly higher than the absorption. But within normal values. The error continues without overlapping.

The variation in height was 4,371pixel, 2,0371E-5gH2O, 254,6386ppm.

LDPE + w + 0.02 and AO

Buoyancy



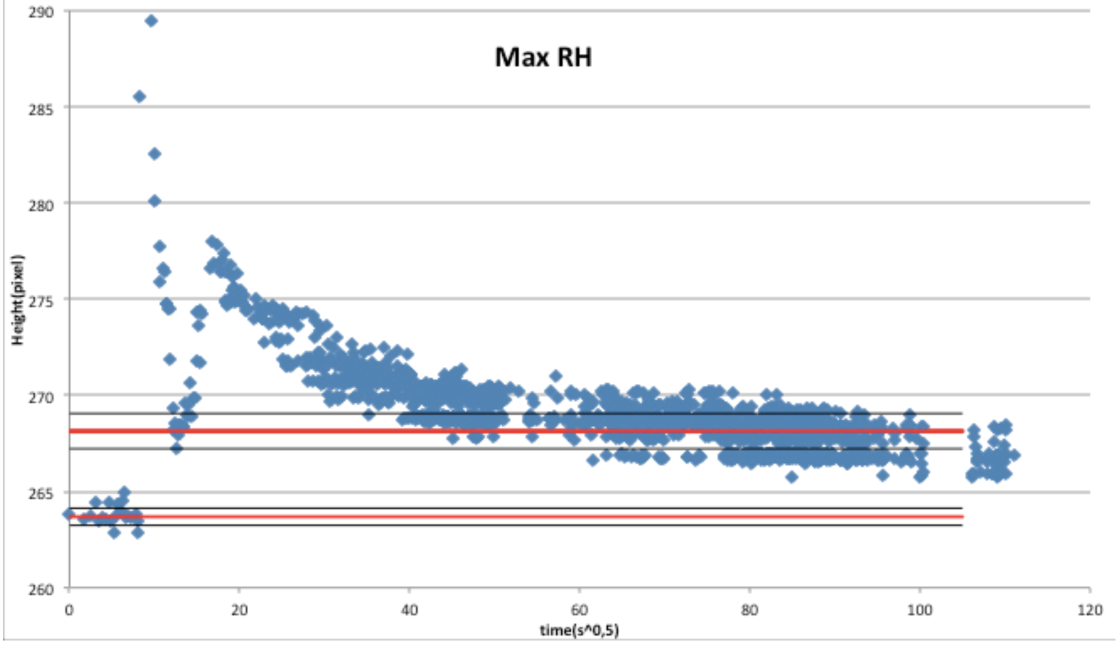
Graph 30. Buoyancy LDPE +0,02 w+y AO

Again the variation between the start and end in the experiment buoyancy is almost negligible.

He experienced a variation of 1,0225pixel, 4,917E-6gH2O, 61,465ppm.

Very small compared with other experiments.

Saturation



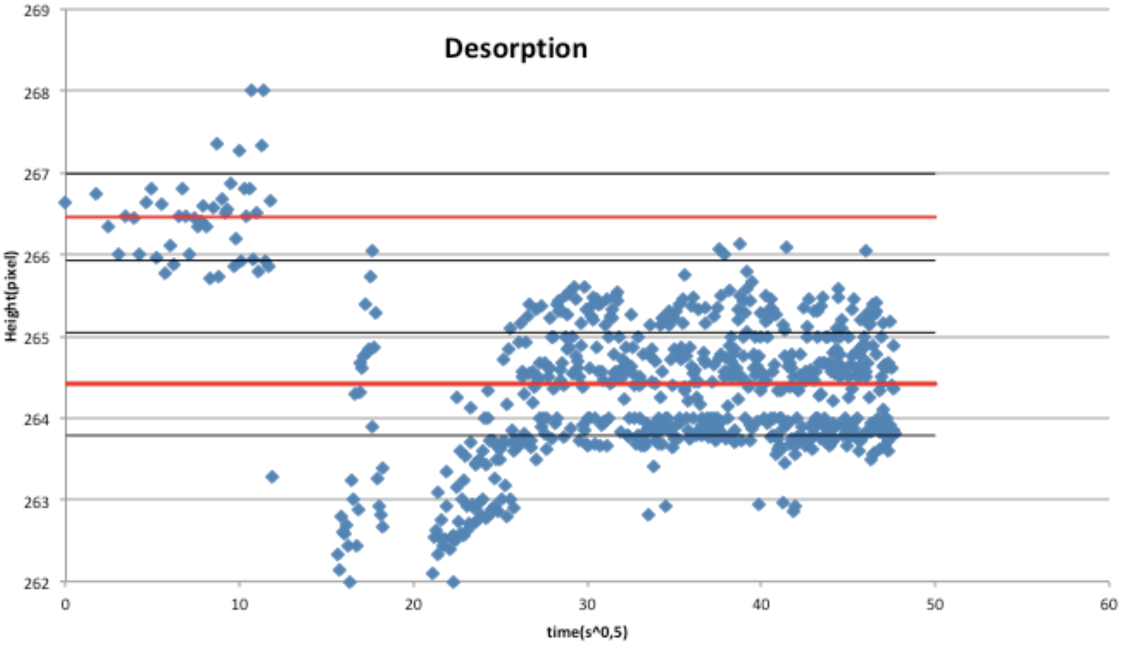
Graph 31. Saturation of LDPE +0,02 w+y AO

The variation in this experiment is again equal in magnitude to that of other experiments. There is no difference in the amount of water absorbed.

It experienced a variation of 4,455pixel, 2,141E-5gH2O, 263,6059ppm.

No major changes are seen in the amount of absorbed water.

Desorption



Graph 32. Desorption LDPE +0,02 w+y AO

In the desorption also significant variations were observed with respect to other experiments. The error continues without overlapping.

The variation in height was 2.04169pixel, 9,8999E-6gH2O, 123,749ppm.

6.Conclusions

In view of the results we can draw a number of conclusions.

The initial procedure was not good enough to give the first results as valid. After attaching another lens to the camera and duplicating the size of the sample, the results obtained were much better

The error (standard deviation) was one of the most important factors for the change in procedure. Since it could not be justified that there was a clear difference between the results at the beginning and at the end of the experiments.

Regarding the results obtained:

Bouyancy

Neat LDPE	LDPE + Heptane	LDPE pressed	LDPE + 0,02w + YAO	
	0.3927	0.6629	1.0225	pixels
	1.83E-06	2,93E-06	4,92E-06	g
	22,83487	36,607077	61,46589	ppm

Saturation

Neat LDPE	LDPE+ Heptane	LDPE pressed	LDPE + 0,02w + YAO	
5,455	3,046	5,925	4,455	pixels
2,65E-05	1,42E-05	2,62E-05	2,14E-05	g
331,3498	177,4848	326,9298	263,6059	ppm

Desorption

Neat LDPE	LDPE+ Heptane	LDPE pressed	LDPE + 0,02w + YAO	
4.5157	4.3715	2.5777	2.0417	pixels
2,19E-05	2,04E-05	1,14E-05	9,90E-06	g
273,97813	254,6386	142,4118	123,74929	ppm

It can conclude that there is a difference in the amount of absorbed water. The saturation experiments are greater in terms of the amount of water. As for the desorption, there is a clear decrease..

Recalling already seen in the introductory section. The thesis is based on an article published in "McCall 1983 Solubility and diffusivity of water in LDPE"[12] where the absorption of liquid water in Low-Density Polyethylene (LDPE) was studied. Finalizing the study explaining that the LDPE absorbed 50 ppm.

In the present thesis absorption it is calculated 200 ppm but having been performed the experiment with water gas.

However it is trying to find the time of the process in which the amount of water absorbed increases as in the article "2017Influence of water uptake on the electrical conductivity of insulating DC-LDPE / MgO nanocomposites "[4] amounts of water absorbed much higher than those of the experiment was analyzed McCall.

Therefore we can conclude that we have optimized the process so that we have reduced the error and have approached the values foreseen by McCall. However, there is still a big difference. We know that our process can be affected by impurities, temperature variations, etc. The future optimization of the process should bring ideals closer to values.

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