# MEASUREMENT AND MODELLING OF SORPTION EQUILIBRIUM CURVE OF WATER ON PA6, PP, HDPE AND PVC BY USING FLORY-HUGGINS MODEL

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## Abstract

*The sorption of water on granular polyamide-6 (PA6), granular polypropylene (PP), and powdery high density polyethylene (HDPE) and powdery polyvinyl chloride (PVC) were measured using a gravimetric method in a magnetic suspension balance (MSB). The Flory-Huggins model was successfully applied on the sorption equilibrium curve of all investigated polymers. The influence of temperature is low. The value of Flory-Huggins parameters($\chi$) of PA6, PVC, PP and HDPE were 1.8, 5.8, 6.3, and 8.1, respectively. The water in PA6 is mainly bound moisture, while in PP, HDPE and PVC it is mainly surface moisture.*

**Keywords***: Flory-Huggins, polymer, sorption*

## Abstrak

*Kurva kesetimbangan penyerapan air pada granul polyamide-6 (PA6), granul polypropylene (PP), dan bubuk high density polyethylene (HDPE) dan bubuk polyvinyl chloride (PVC) telah diukur menggunakan metode gravimetri dalam suatu alat magnetic suspension balance (MSB). Semua kurva kesetimbangan ini mengikuti model Flory-Huggins. Pengaruh suhu kecil. Nilai parameter Flory-Huggins ($\chi$) untuk PA6, PVC, PP dan HDPE adalah 1,8; 5,8; 6,3; dan 8,1. Air di PA6 sebagian besar merupakan uap terikat, sedangkan di PP, HDPE dan PVC sebagian besar merupakan uap permukaan.*

**Kata kunci:** *Flory-Huggins, polimer, penyerapan.*

## INTRODUCTION

In the production of polymers, drying is one of the major recovery operations employed to obtain a final saleable product from a reaction process. Since it consumes large amounts of energy, the drying process deserves attention towards both energy savings and improvement of the quality of dried polymer. Furthermore, a study of drying kinetics could be helpful in the selection of adequate drying systems (Mujumdar and Hasan, 2006). One important part in study of the drying kinetics is the equilibrium sorption curves of materials. The equilibrium moisture content in the solid particles would determine how much residual moisture content in a drying process. In the process of simulation, the equilibrium moisture content value was used as the value of moisture on the surface of solid. The value of equilibrium moisture content is usually presented by the sorption isotherm

curve. The sorption isotherm is a curve which displays the relationship between solid water content and air humidity at equilibrium. At a given constant temperature, a sorption isotherm indicates corresponding water content value for each humidity value. Because of the complexity of sorption process, the sorption isotherms can hardly be determined by calculation, but must be recorded experimentally for each product. Generally, the results of these measurements would be fited with the model of sorption curve.

Furthermore, in this paper granular polyamide-6 (PA6) and granular polypropylene (PP), powdery high density polyethylene (HDPE) and powdery polyvinyl chloride (PVC) is studied. The previous results showed that PA6 is a hygroscopic polymer that can absorb moisture of about 3% in normal condition (50% RH and 23°C) (Kohan, 1995). PP is a non-

hygroscopic polymer, which has very low tendency to absorb moisture (Maier and Calafut, 1998). The Flory-Huggins model gives a good agreement with sorption isotherm for water in PA66 and PA610, where the F-H interaction parameter $\chi$ is 1.46 and 2.18, respectively (Starkweather, 1959). The water in PA6 is immobile at low water content, and considerably mobile at higher water contents (Kawasaki, K. and Y. Sekita, 1964; Auerbach and Carnicom, 1991). The mechanism of water sorption in nylon is firmly bounded water, loosely bound water, and sites for capillary condensed water (Lim *et al.*, 1999). However, for PP, HDPE and PVC is hard to find the publications about the modelling of sorption curve of water.

The ultimate goal of this study was to collect experimental data necessary to elucidate the water vapour sorption mechanism on PA6, PP, HDPE and PVC. In addition, the Flory-Huggins model was applied on the sorption isotherm curve of the studied polymers.

## METHODOLOGY
### Modeling

A typical sorption isotherm curve has three stages (van der Wel and Adan, 1999). For low vapour pressure, a linear rise of moisture is observed (Henry law). For increasing vapour pressure, X seems to approach a limiting value as it can be derived for monomolecular adsorption to the inner surfaces of the material (Langmuir). Usually, the asymptote is not reached due to the building up of multimolecular layers of water molecules (Brunauer, Emmett, Teller). At high vapour pressure, a continuous liquid film exists in the pores, vapour pressure is reduced in small pores due to the curved water surface (Kelvin, Thomson) and capillary condensation takes place: the higher the vapour pressure, the bigger are pores that are filled with liquid by this mechanism.

For polymer products, there are two possibilities regarding the modelling of sorption equilibrium, namely localized sorption theories and dissolution theory (van der Wel and Adan, 1999). However, in this paper only dissolution theory will be discussed and applied. A number of models have been proposed assuming homogeneous dissolution of penetrant in polymers. Flory (1942) discussed the entropy of mixing small molecules and large polymers. He assumes that polymer-water systems do not display strong interactions and, thus, do not have strong deviations from ideal behaviour (van der Wel and Adan, 1999). Flory and Huggins assumed that the liquid phase behaves like a lattice of balls (see Figure 1). White circles are solvent, while polymer units are black circles, that behave like a pearl neck when forming the polymer chain.
The F-H model is given by :

$$\ln(\phi) = \ln \varphi_1 + (1 - \varphi_1) + \chi(1 - \varphi_1)^2 \qquad (1)$$

where $\varphi$ is the water activity, $\phi_1$ is the volume fraction of dissolved water and $\chi$ is the F-H interaction

parameter. The parameter $\chi$ has to be fitted to sorption equilibrium data.
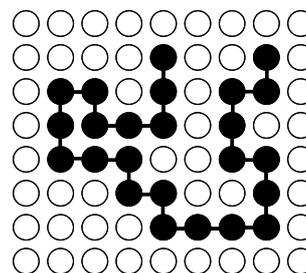


Figure 1. Model of the quasi-crystalline liquid lattice for macromolecules (black circles) in a solution (white circles) (Sauare, 1997)

### Experimental Set-up

A magnetic suspension balance (MSB) produced by Rubotherm (Bochum, Germany) has been used for determination of sorption equilibrium curve. The MSB is equipped with a periphery capable of establishing different atmospheres of conditioned air, as schematically depicted in Figure 2.
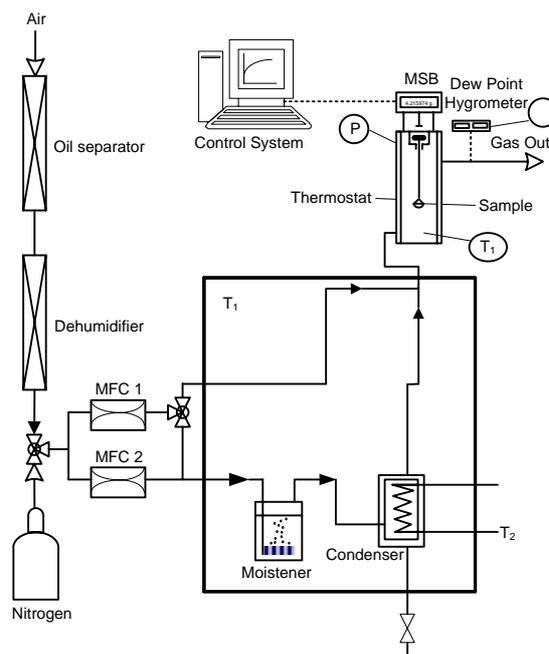


Figure 2. Apparatus set-up

This feature can be used for determination of sorption equilibrium curve on different temperatures. Nitrogen gas from the flask has been used in the determination of the dry mass of the sample. The mass flow rate of either air or nitrogen is adjusted by mass flow controllers MFC 1 and MFC 2 (EL-Flow, Bronkhorst). The mass flow controllers have been calibrated by means of a Film Flow Meter. The sorption cell is a vessel made of stainless steel with an inner diameter of 25 mm and a height of 280 mm. The temperature in the vessel is set by means of a thermostat with an accuracy of 0.1 K. The pressure in the vessel is measured by a pressure transducer (in

mbar) and adjusted by means of an outlet valve. A very low gas velocity in the vessel of about 0.01 m/s has been used in all experiments in order to increase accuracy and reproducibility of weighing. Moreover, the humidity of outlet gas is measured by means of a dew point mirror hygrometer (i.e. Michell Instruments).

The humidity of air is prepared by means of an air conditioning cabinet. This consists of a moistener, condenser and heater. First, the temperature (here $T_1$) and the relative humidity ($\varphi$) in the drying vessel, which are going to be used in the measurement, are chosen. Then, the temperature of condenser ($T_2$) that is necessary in order to obtain the desired relative humidity is calculated from the relationship

$$\phi = \frac{P^*(T_2)}{P^*(T_1)} \qquad (2)$$

where the saturation pressures P* are calculated by the Antoine equation, $T_1$ is the temperature in the vessel that is also equal to the temperature in the air condition cabinet, and $T_2$ is the temperature of condenser. This set-up is checked via measurement of the dew point of air by means of dew point hygrometer.

For material properties, Table 1 shows the particle and density of materials.

Table 1. The physical properties of materials

| Properties | PA6 | PP | PVC | HDPE |
|---|---|---|---|---|
| $d_p$ x $10^3$, m | 2.9 | 2.5 | 0.147 | 0.135 |
| $\rho_p$, kg/m$^3$ | 1075 | 820 | 1114 | 810 |

## RESULTS AND DISCUSSION
### Sorption Equilibrium of Granular Polymers (PA6 and PP)

Figure 3 shows that the measured sorption equilibrium of water on PA6 gives a good agreement with literature data and also with the Flory-Huggins model. The F-H interaction parameter, $\chi$, was fitted to measured data, obtaining a value of 1.75. As a comparison, Rudobashta et al. (1979) developed a model for the desorption isotherm at 70-90°C:

$$X_e = a_e \phi + b \qquad (3)$$

where for $\varphi < 0.5$, $a_e$ and b are $5.8 \cdot 10^{-2}$ and 0, and for $\varphi > 0.5$, $a_e$ and b are $14.2 \cdot 10^{-2}$ and $4.5 \cdot 10^{-2}$, respectively. Meanwhile, Kawasaki and Y. Sekita (1964) conclude that there are two characteristic sorption types of water in nylon 6, that is, water molecules are comparatively immobile at low water content, and considerably mobile at higher water contents above 4 wt.-%. The influence of temperature is low, which is typical for polymeric materials (Sauare, 1997).
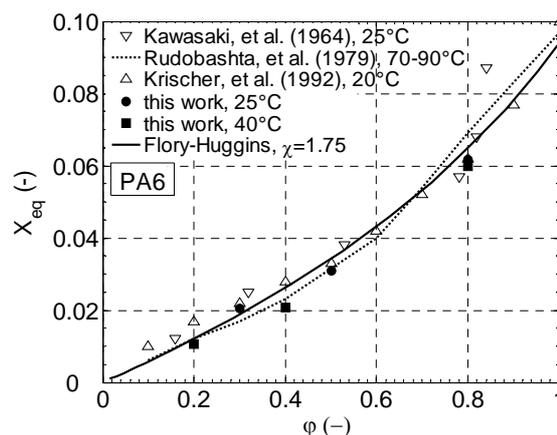


Figure 3. Sorption equilibrium of water on PA6

Some additional information is included in an infrared study of sorption equilibrium of water on PA 6,6 by Lim et al. (1999). The study indicated that the average hydrogen-bond strength to the N-H group was weaker in the presence of moisture content than in its absence. This is in agreement with the model proposed by Puffr and Sebenda in Lim et al. (1999) (see Figure 4).
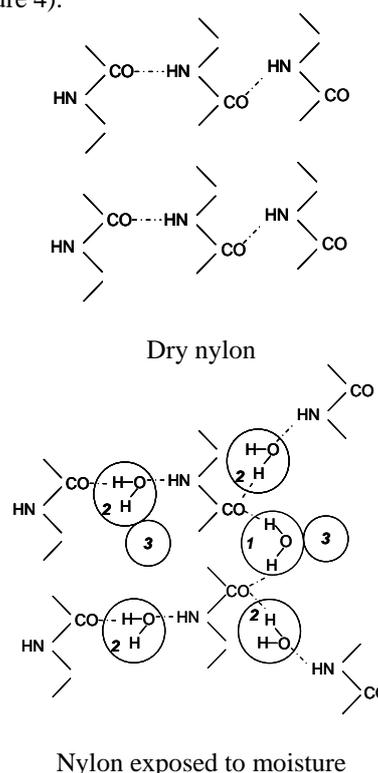


Figure 4. Mechanism of water sorption in nylon as proposed by Puffr and Sebenda in Lim et al. (1999): (1) firmly bound water; (2) loosely bound water; (3) sites for capillary condensed water

In their model, a water molecule will first form double hydrogen bonds with two C=O groups at low air humidity and is considered to be firmly bound water. The other two molecules of water will then

form bridges between the already hydrogen-bonded C=O groups and the hydrogen atoms of N-H groups, and they may be classified as less tightly bound water.

Furthermore, Figure 5 shows that the measured sorption equilibrium of water in PP agrees well with the Flory-Huggins model, where the value of fitted $\chi$ is 6.34. The measured data can not be compared, due to lack of literature data for sorption equilibrium of water on PP. The amount of water sorption is low. This means that PP is a nearly non-hygroscopic polymer, which is in agreement with literature (Maier and Calafut, 1998).
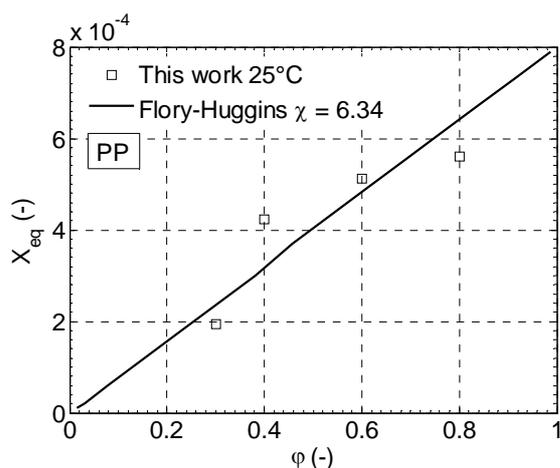


Figure 5. Sorption equilibrium of water on PP

**Sorption Equilibrium of Powdery Polymers (PVC and HDPE)**
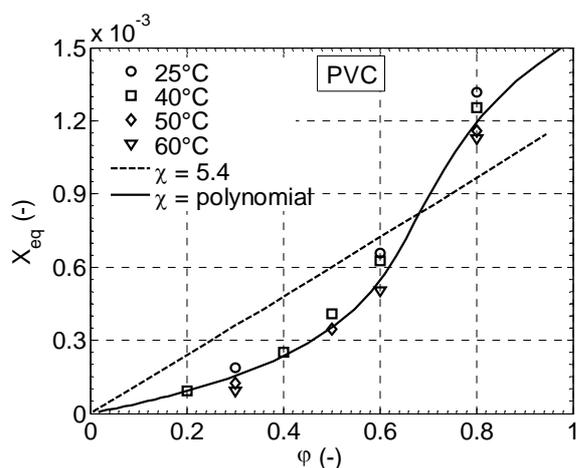


Figure 6. Sorption equilibrium of water on PVC

Figure 6 shows the experimental results on sorption equilibrium for PVC in comparison with calculations using the Flory-Huggins model.

The influence of temperature is low, which is typical for polymeric materials. For PVC and a constant $\chi = 5.4$ the calculated function does not give a good agreement with the experiments. However, if $\chi$ is treated as a function of water concentration in

polynomial order 2 (see eq. 4), a good agreement with the measured data can be achieved for :

$$\chi = 3.517 \cdot 10^6 \varphi^2 - 1388.5\varphi + 6.5 \qquad (4)$$

Figure 7 shows the experimental results on sorption equilibrium for HDPE in comparison with calculations using the Flory-Huggins model. For HDPE and a constant $\chi = 8.1$ the calculated function gives a good agreement with the experiments.
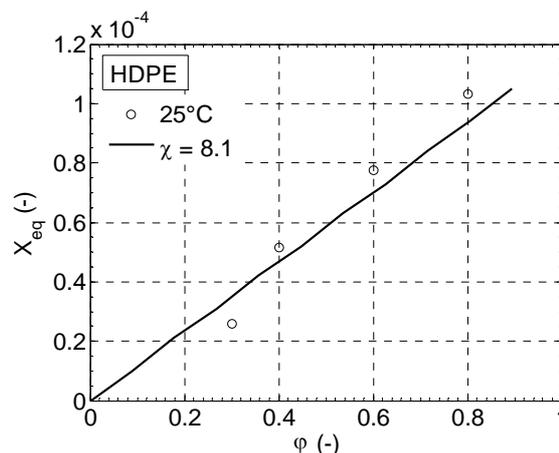


Figure 7. Sorption equilibrium of water on HDPE

From these experimental results it can be concluded that both PVC and HDPE are non hygroscopic polymers. It also can be seen that both PVC and HDPE have a high value of $\chi$. This means that the polymer does not like to dissolve in water (= small deviation from Henry's law). The measured data both for PVC and HDPE can not be compared to literature data, due to lack of literature data.

**Comparison of sorption equilibrium curve for all investigated materials**

Table 2 shows that only PA6 is hygroscopic, while the other polymers are non-hygroscopic.

Table 2. Some parameters of sorption equilibrium for all investigated materials

| Parameter | PA6 | PP | PVC | HDPE |
|---|---|---|---|---|
| $X_{sat}$ (kg/kg) | 0.1 | 0.0008 | 0.0015 | 0.00012 |
| Flory-Huggins parameter, $\chi$ (-) | 1.8 | 6.3 | 5.8 | 8.1 |

All the moisture in PA6 is essentially bound moisture, while in the other materials it is mainly surface moisture. It can also be seen that the F-H interaction parameter of PA6 is the lowest one. In dissolution theory a low interaction parameter is caused by a small difference of solubility parameters between solvent (i.e. water) and polymer (Miller and

Koenig, 2003). The smallest interaction parameter leads to the easiest dissolution of polymer in water.

Furthermore, Figure 8 shows that the sorption isotherm of PA6 is concave upwards, while the other curves are almost linear. Linear isotherms imply that Henry's law is valid over the entire range of water (= penetrant) activities, since Henry's law expresses ideality of dissolution. It implies insignificance of penetrant-polymer interactions and is plausible for water sorption in hydrophobic or non-hygroscopic polymers. Non-linear isotherms consequently indicate that the sorption process deviates from ideality and reflect interactions between water molecules and polymer structure (van der Wel and Adan, 1999).



Figure 8. Compariosn of sorption equilibrium for all investigated materials

**CONCLUSION**

Gravimetric method (i.e. Magnetic Suspension Balance) was successfully for measurement sorption equilibrium curve on different temperature and humidity. PA6 is an hygroscopic polymer, while PP, HDPE and PVC are non-hygroscopic. The water in PA6 is mainly bound moisture, while in PP, HDPE and PVC it is mainly surface moisture. The Flory-Huggins model was successfully applied on the sorption equilibrium curve of all investigated polymers. The value of Flory-Huggins parameters of PA6 is the lowest compared to other polymer.

**NOMENCLATURE**

$\varphi$      water activity, (-)
$\phi_1$      volume fraction of dissolved water , (-)
$\chi$      Flory-Huggins parameter, (-)
$P^*$      saturation pressure, (Pa)
$T_1$      temperature in the vessel, (°C)
$T_2$      temperature of condenser, (°C)
$X$      solid moisture content, (-)

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