

# Evaluation of the Water Sorption Capacity of Some Polymeric Materials by Dynamic Vapour Sorption

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*Water sorption/desorption behaviour of the materials is very relevant for their application in pharmaceutical, food, sensor, electronics, fuel cell and biomedical fields. The sorption/desorption equilibrium, which is related with the plasticity and mechanical properties of the materials, as well as the kinetics of water sorption/desorption, which is related to the transport properties, are interesting research areas. The fully automated gravimetric analyzer is an equipment for rapid evaluation of the moisture sorption capacity in dynamic regime. The ultrasensitive microbalance measures the weight modification as the humidity is changed in the sample chamber at constant regulated temperature. Water vapour sorption behaviour of some materials belonging to different polymeric classes with various structures and morphologies were investigated.*

*Keywords: water sorption, dynamic vapor sorption, isotherm*

## The importance of moisture sorption capacity

Many of the useful properties of different materials are related to their water sorption and swelling capacity. These are relevant for their application in various fields, like pharmaceutical, food, sensors, electronics, fuel cell and biomedical. The water sorption/desorption behaviour of the materials is really important in order to assess the stability of the products, to understand how water migrates within them and to find out how they gain or lose water.

The influence of moisture on solid-state stability has been intensively studied for understanding and anticipating the behaviour of a product exposed to a variety of environmental conditions. This is necessary for recommending appropriate storage conditions for maintaining the quality of a drug [1]. The interaction of pharmaceutical products, especially the solid ones, with water can affect their chemical stability and their physical and mechanical properties. The understanding of water sorption isotherms of foods or food ingredients is also very important in food science and technology. This permits the design and optimization of processing or shelf life stability predictions that will guarantee food safety, quality and stability [2,3].

Studies dealing with the sorption isotherms have also been done in the field of building materials. One of the most comprehensive information on the sorption and desorption isotherms of building materials is given by [4].

Sorption of water vapor by some polymeric materials has been studied by several techniques. Systematic studies on water sorption capacity of synthetic linear polymers have been reported by [5]. Some chemists studied the mechanism of water sorption in polyamides and proposed a model, that suggests that amide and carbonyl groups in the regions accessible to water are the sorption centers [6]. McLaren et al. investigated the water sorption capacity of proteins and polymers [7]. In many applications, some modifications of polymers by swelling, hydrolysis or plastification can result from the sorption of water, which is facilitated, due to presence of polar and hydrophilic groups. Water sorption/desorption properties are also important for the characterization of polymeric films and membranes. The vapor sorption properties of some

materials, like polyurethanes and poly(urethane-urea)s, were well studied because of their applications in packaging, biomaterials, and membrane separations [8].

The development of an experimental technique, which would allow evaluation of the surface properties, is of great practical importance. In order to estimate the specific surface area and porous structure of a sample, the adsorption isotherms are measured and analyzed using the well-known BET theory. These two elements of the surface properties are very strongly correlated and are important parameters for characterizing solid materials that are used as sorbents in separation science, environmental protection, and column packing in chromatography, catalysts [9]. The equilibrium water sorption properties are also related to the oxygen or other gas permeability of polymers, for example, contact lenses [10]. The kinetics of water sorption/desorption are also important for the development and design of drug delivery vehicles.

## Experimental part

### Equipment

In this paper we used the fully automated gravimetric analyzer IGAsorp supplied by Hiden Analytical, Warrington (UK). An ultrasensitive microbalance measures the weight change as the humidity is modified in the sample chamber at a constant regulated temperature. The ultra-sensitive microbalance has a 0,1µg resolution for 100mg range and a 200mg capacity. A sensor placed in the sample chamber close to the sample measures the humidity. By relative mixing of wet and dry gas (N<sub>2</sub>) streams, humidity is changed and controlled to desired RH set-point. During this stage the weight signal is analyzed to determine when the uptake has reached the new equilibrium value. Once equilibrium has been attained, the next desired humidity level is set. This process is automatically performed for desorption isotherm measurement in a similar manner. A general scheme of the device is shown in figure 1.

The measurement range of relative humidity is between 1%RH and 95%RH with an accuracy of +/-1% (0-90%RH) and +/-2% (90-95%RH). The measurement range of temperature is between 5 and 80°C with an accuracy of

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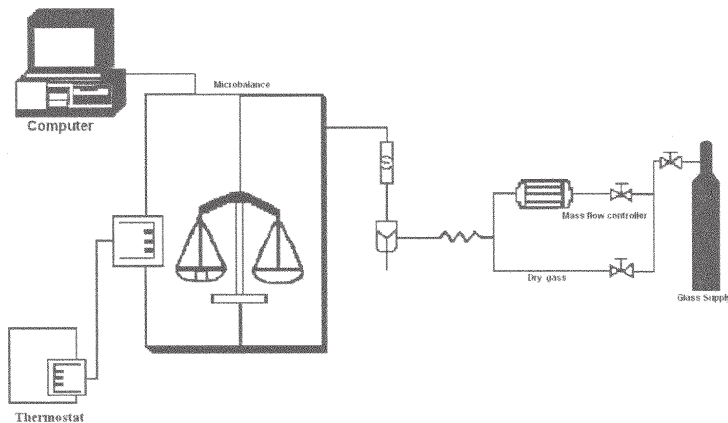


Fig. 1. Schematic flow diagram of DVS equipment

+/-0.05°C. The sample container is a gas permeable micromesh stainless pan for solids or a Pyrex bulb for liquids and fine powders.

#### Investigated samples

In order to demonstrate the applicability of the procedure a few samples of very different materials were approached.

- A commercial porous silica, Aerosil 380 (Degussa), 100% purity, specific surface 380 m<sup>2</sup>/g, particle diameter 0.003 - 0,015(μm) (Silica);

-A high temperature curable silicone, which is a crosslinked polydimethylsiloxane/silica composite, was prepared in our laboratory, according to the procedure described in [11] (Silicone);

-Cellulose acetate – a linear, hydrophilic polymer with M<sub>n</sub> =29000 and 40% degree of substitution was purchased from Fluka and processed as film (CA).

#### Sample preparation

The polymeric materials (Silicone and CA) were processed as thick films and small fragments of these films were cut and placed in the stainless steel sample bucket of fine mesh.

For the polymeric samples, silicone and CA, in film form; the stainless steel sample bucket of fine mesh was used. The amount of sample is dictated by: the capacity of the microbalance and the vapor adsorption capacity of the sample. For the investigation of the silica powder sample, the Pyrex glass container was used. The initial amounts of samples used are shown in table 1.

Table 1  
THE CHARACTERISTICS OF THE ANALYZED SAMPLES

Sample	Weight (mg)		Weight (%)
	Initial	Final	
Silicone	3.6406	3.6661	0.7641
Silica	3.0513	3.6422	19.3890
CA	2.5860	2.8592	10.5860

#### Determination of the water sorption/desorption isotherms

The samples placed in the appropriate container were positioned on the microbalance, and then the chamber was closed and tightened. The sample were dried at 25°C in flowing nitrogen until the weight of the sample is in equilibrium at RH<1%. This value is considered the dry mass. After drying, the measurements began with the absorption curve. After the maximum level for RH has been reached, desorption steps can begin.

#### Results and discussions

##### Theory- Sorption Isotherms Types

The understanding of adsorption isotherms is relevant in a large range of fields of current research interest. Almost all analysis of adsorption equilibria begins by matching the obtained isotherm with the classical one. The first attempt to interpret adsorption isotherms for gas/solid equilibrium was made by (BDDT) in 1940 [12], which classified the sorption isotherms in five types (fig. 2 A).

The BDDT classification became the starting point for the modern IUPAC classification of adsorption isotherms that included also a sixth steps isotherm [13-15]. In the case of adsorption where capillary condensation occurs,

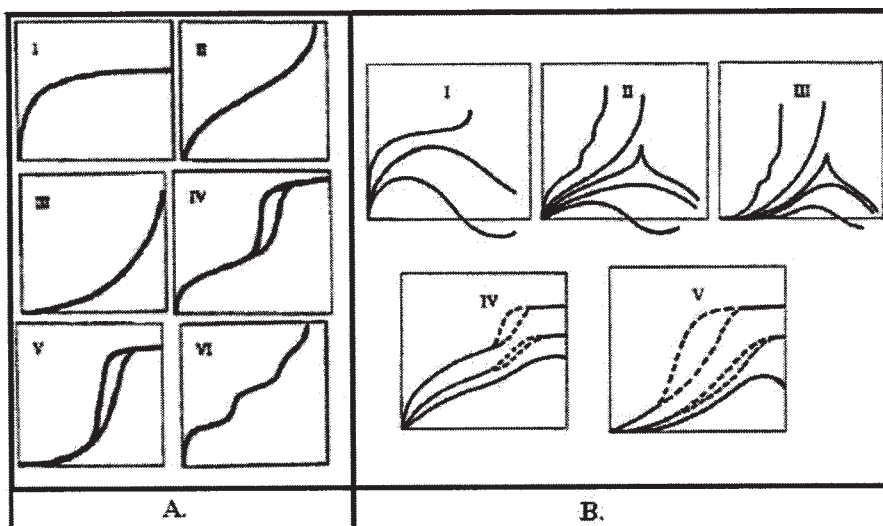


Fig. 2. Five sorption isotherm types according to BDDT classification and stepwise isotherm (type VI) -2A and another classification for adsorption isotherms 2B [12]

hysteresis appears. Generally, it is accepted that the isotherms of type I are characteristic for microporous solids, type II for nonporous, type III for macroporous, and type IV for mesoporous solids [16]. Type V also suggests the presence of the pores [13]. The types III and V are characteristic for systems with a very weak adsorbent-adsorbate interaction and the isotherms of type II are shaped when strong adsorbate-adsorbent interactions occur. Types IV and V represent adsorption isotherms with hysteresis. The type VI isotherm represents stepwise multiplayer adsorption on a uniform nonporous surface. The step height represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or more adsorbed layers [17].

However, the IUPAC classification presents the idealized isotherms as monotonic functions of pressure [14]. In reality, the isotherms are not always monotonic ones showing more diverse range of shapes. Recent studies classified the hysteresis loops in a similar way to IUPAC adsorption isotherm scheme. The explanation for hysteresis is based on a change of geometry during the adsorption and desorption process [16].

In figure 2B there is a new classification of adsorption isotherms, which is meant to be qualitative [16]. In this classification, type I shows adsorption isotherms on microporous adsorbents for subcritical, near critical, and supercritical conditions. Types II and III give adsorption isotherms on macroporous adsorbents with strong and weak affinities. Types IV and V characterize mesoporous adsorbents with strong and weak affinities. For lower temperature they show hysteresis [16].

Determination of moisture sorption isotherms is the general approach for characterizing the relationship between water and solid. The characterization of different types of adsorption isotherms provides guidance to the most appropriate mathematical model, which correlates the experimental data and gives us a link between the macroscopic behaviour and the physical structure and molecular characteristics of the adsorbent and adsorbate.

#### *Methods of measurement*

Two "classical" methods were used over the years for determining the sorption curves describing the hygroscopic properties of the materials.

Desiccator method (gravimetric technique), where the relative humidity in desiccator is maintained by the saturated salt solutions and the weight is monitored discontinuously. The salts (lithium chloride, magnesium nitrate, sodium chloride, potassium sulfate and distilled water) are generally chosen to provide an equilibrium relative humidity ranging from 10 to 100% for adsorption and desorption [17].

Climatic chamber method, where both temperature and relative humidity of the air in the chamber are controlled [18]. If the temperature is maintained constant during the measurements, the resulting curves are called the sorption isotherms.

The Dynamic Vapours Sorption (DVS) is a more up-to-date and rapid method for characterization of sorption/desorption behaviour of various materials.

Almost all of them interact with moisture from atmosphere. In all areas of industry from manufacturing to processing or packaging it is vital that this behaviour is understood. The interaction is most commonly characterized by the percentage weight content of moisture retained in the material at a given relative humidity (% RH) and temperature. Measurements of such isotherms over a range of temperature characterize the material for

defined environmental conditions. The DVS equipment performs precisely this function in an accurate reproducible manner, which allows a rapid consistent comparison of materials. In addition the DVS method determines the kinetics of the sorption/desorption process, which is useful in the determination of rate constants for such studies as shelf-life determination and drying. In essence, the DVS is a vital tool in understanding the moisture sorption properties of materials [19].

The main advantage of this rapid method is the reduction of the time used for experiments. If we compare with the other method, desiccator method and climatic chamber method, DVS needs only few days towards several months in the case of the others. Among the advantages of this method are: the ability for fast equilibration of the sample; it uses the same sample for the whole isotherm; easy measurements of adsorption and desorption isotherms; it can use very small samples; it is not necessary to move the sample during the complete isotherm measurement; it is possible to measure at any increasing or decreasing water activity steps and oscillation mode.

The main disadvantage is the fact that in the majority of the DVS equipment existing on the market, only one sample can be measured. Another issue is the proper choice of the equilibration time. By using reduced times for the tests there is an increased risk that the equilibrium moisture content not to be reached. Therefore, it is necessary to find a good compromise between the accuracy and the time saving.

This dynamic method can be used for studying micro-level drying characteristics, water activity, for simulating modified atmosphere drying, and for identifying other structural characteristics, such as glass-rubber transition, and surface cracking.

#### *Applications of DVS method for different materials comparative results*

In this paper, the DVS method was applied for a set of materials having different composition and water affinity. In order to obtain a reproducible isotherm, the time pre-established for equilibration at each RH step should be long enough. In the case of adsorption, water equilibrium content increased with the increase of RH, and opposite trend was observed in the case of desorption.

It is known that the results of such a study: sorption isotherms and kinetics are complex functions on the material type, size, shape and electronic structure. In figure 3 are shown the water vapor sorption isotherms recorded for Silica, CA and Silicone samples.

In figures 4 and 5, the kinetics curves of the two processes are presented for all the samples. These graphs describe the evolution of the sample weight as a function of time and RH.

Analyzing the figure 3 we can presume that the shapes of the sorption isotherms registered for all samples can be associated to the isotherm of type IV according to IUPAC classification. This is an isotherm with hysteresis which characterizes mesoporous adsorbents with strong affinities for water or containing OH-groups [8, 9].

In the case of our samples, the presence of uncondensed -OH groups in silica may be responsible for such behaviour. A better comparison between sorption behaviours of the silicone and silica samples can be done based on the figure 5. As expected, the porous silica has the higher water vapour sorption capacity (19.39%) as compared with silicone (0.8%). This is a normal result since it is known that polydimethylsiloxane is a hydrophobic

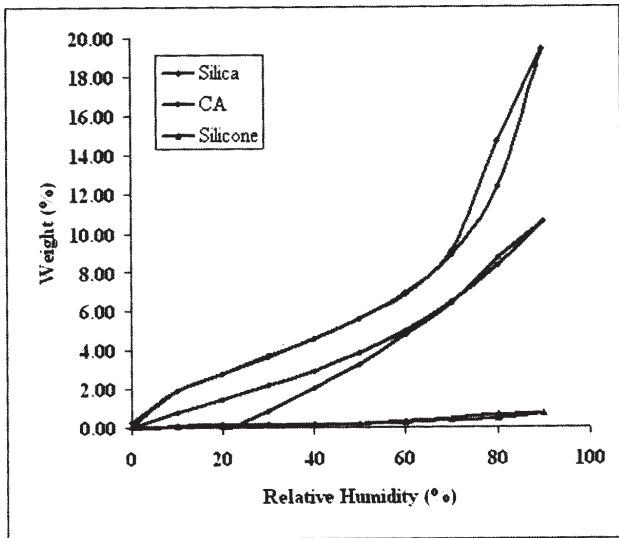


Fig. 3. Sorption isotherms for water vapour on Silica, CA and Silicone

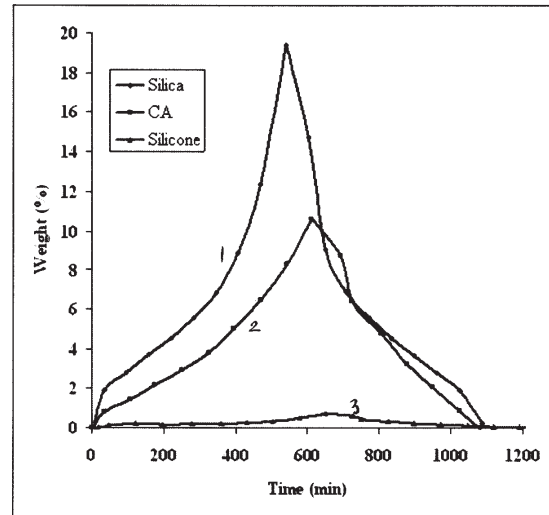


Fig. 4. Comparison between the kinetics of Silica, CA and Silicone

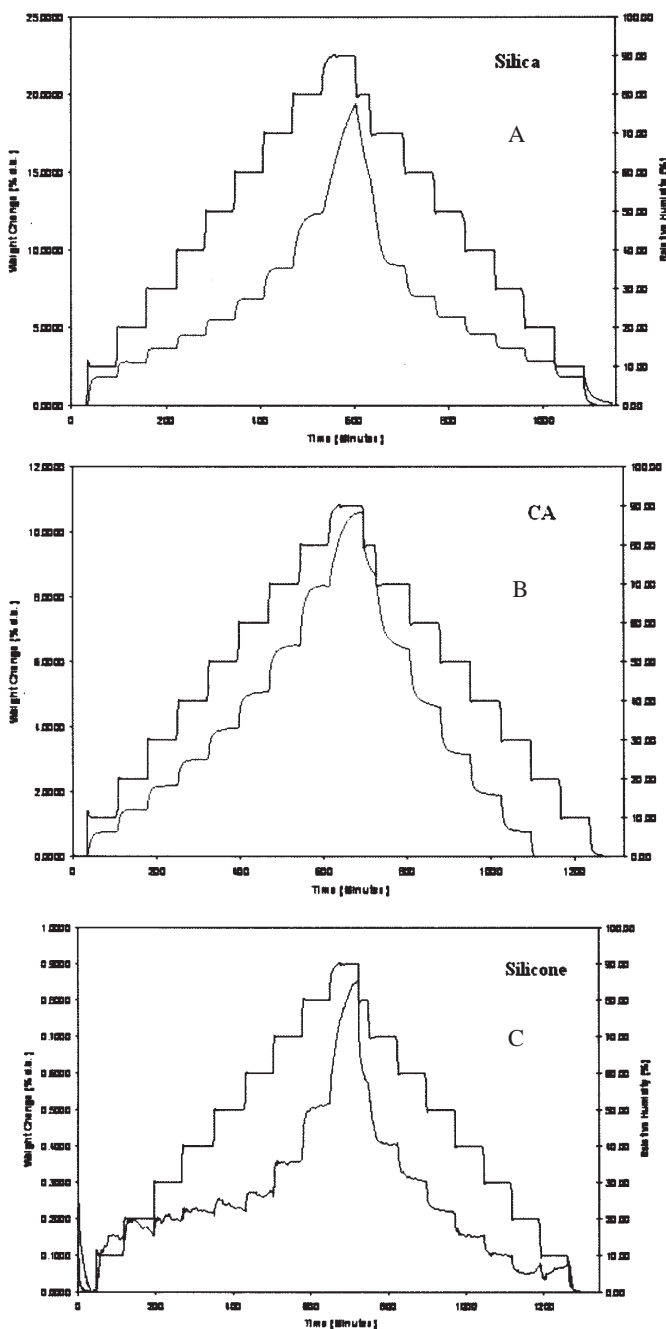


Fig. 5. The kinetics of Silica (A), CA (B) and silicone (C)

material, and on the other hand the amount of silica present in the composite is very small.

The difference between the sorption capacities of these two materials can also be explained by the difference in their structure and morphology. Silica is a porous material with high specific surface area having hydroxyl groups on the surface. Contrary, silicone is more compact and highly hydrophobic material. It is presumed that its sorption is determined by the silica presence in its composition and probably to a certain porosity formed as a result of the catalyst decomposition during vulcanization. The DVS method exploits the relaxation behavior of the material after pressure changes to simultaneously evaluate kinetic parameters and the asymptotic uptake [20].

The CA sample also contains  $-OH$  groups (un-protected), with high affinity for water. Nevertheless, its maximum water uptake is lower than for silica, which is probably due to the different state of the two samples (film and powder, respectively). The water sorption capacity of Silica has the highest value (20.00%) comparative with the value of moisture sorption capacity for CA which is (12.82%). The rate of water vapours desorption was found to be slower than the sorption rate.

The difference of the equilibrium properties between water sorption and desorption is not unusual for polymer systems or other materials and has been reflected in hysteresis [21-23]. There may be different causes for the hysteresis, like shrinkage of the materials, sorption sites that may resist to water vapor when they are filled with gas after drying.

The kinetics of adsorption and desorption isotherms could be used to explore the structural characteristics [24], like glass transition. Also the mass transfer rate constant or diffusivity could be estimated from these data.

Another capacity of the DVS equipment existent nowadays on the market is the calculation of BET and GAB surface areas of the porous materials based on the moisture sorption isotherms [25-28].

### Conclusions

DVS is a valuable technique for the study of the materials behaviour in controlled humidity and temperature media. The nature of the sample determines the shape of water vapor sorption isotherms and the amount of sorbed water.

Three different kinds of materials have been investigated and the applicability of this method has been verified. The

results confirm the fact that accurate comparisons are possible only for samples with similar state and granulation.

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