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WATER VAPOUR ADSORPTION ON ORGANIC AND INORGANIC POLYMERS

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Abstract

Water vapour adsorption on polymers affects their processing behaviour and useful properties. Water vapour adsorption on organic polymers, silk, Nylon 6 fibres in undrawn and permanent set forms, polyester micro fibres, plasticised PVC films with 60 phr dioctylphthalate (DOP) and inorganic polymer sepiolite particles were investigated in this study. The materials were examined using the BET equation. The surface areas of silk, cast Nylon 6 and muss Nylon 6 were determined as 108, 46 and 23 $m^2 g^{-1}$, respectively. Sepiolite did not fit BET equation. Polyester and PVC adsorbed very small amounts of moisture.

Keywords: Nylon 6, polyester, PVC, silk, vacuum microbalance, water vapour adsorption

Introduction

Water molecules have strong specific interaction with polar surface groups and weak interaction with non-polar adsorbent surfaces. Its adsorption occurs through hydrogen bonding in the specific adsorption region. Thus water is used especially to characterise microporous adsorbents such as microporous carbons [1] and natural zeolite [2].

The adsorption of water vapour is of great importance in the context of gas separation or air purification. The presence of water vapour in gas treatment processes causes detrimental effects on the performance of adsorbents. The use of water vapour sensitive adsorbents such as carbon molecular sieve, natural or synthetic zeolite and its modified forms makes adsorption feasible for gas separation [3] and air purification [4, 5] applications. Zeolites and sepiolites are inorganic polymers which have very interesting water sorption properties. Water vapour adsorption on organic polymers affect their mechanical behaviour acting as plasticisers and lowering their glass transition temperatures.

Water sorption on solids can be studied in controlled atmospheres in equilibrium with sulphuric acid and water solutions [6], using automated gravimetric [7, 8] or volumetric [9] systems or a quartz crystal oscillating microbalance [10]. Lim *et al.* [11] studied sorption of water vapour in Nylon 6 films by controlling the atmosphere of

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the sealed glass chamber enclosing a Cahn 2000 recording microbalance and by using saturated salt solutions. Sorption isotherms for fibres with high hygroscopicity [12] and hydrophilic polymers [13] and for peptides, proteins and their formulations [14] were studied in recent years using automatic gravimetric systems.

Vacuum microbalance technique that can be operated under static or dynamic vapour dosing methods is another alternative in water vapour adsorption isotherm determination. While a close approach to equilibrium can be obtained in the static dosing method, a fast data acquisition is possible on the dynamic method.

Adsorption of water vapour is an exothermic process. In a vacuum microbalance the surface temperature of the sample rises during adsorption of water vapour due to this heat of adsorption. Since heat transfer by convection was not possible in vacuum, the only way of heat transfer is by conduction through the hangdown nichrome wire; this takes a very long time. The pressure in the chamber changes due to adsorption of water vapour by the microbalance and glass components. Thus, the temperature of the sample would never be the same as the temperature of the water bath outside the adsorption tube. The suppliers recommended lowering of the weighing pan down to the metal bottom of the hangdown tube and dissipation of adsorption heat by conduction to the metal part. In practice this process was difficult and most of the time it was unsuccessful. The pan either stuck to the wall or it ruptured from the hangdown wire.

Development of a fast method to obtain adsorption isotherms of water vapour on solids is the aim of this study. Thus a compromise was made from true sample temperature by obtaining isotherms under dynamic conditions.

Experimental

Waste silk, undrawn Nylon 6 and permanent set (Muss) Nylon 6 fibres (that were characterised in previous studies [15, 16]), polyester microfibres, plasiticised PVC film and sepiolite samples were the materials studied in this investigation. PVC films were obtained by mixing 100 parts PVC with 60 parts dioctylphthalate and 5 parts liquid organo-tin stabiliser on weight basis and heating for 10 min at 160°C. Sepiolite, which is a fibrous magnesium silicate polymer from Sivrihisar, Turkey, was characterised by Balci [17]. The summary of the properties of the samples are as given in Table 1.

A gravimetric adsorption system shown in Fig. 1 based on a Cahn 2000 recording vacuum microbalance was used. Water vapour was fed through a needle valve at a controlled rate to the vacuum chamber evacuated down to 10^{-4} mbar pressure; the pressure and sample mass were recorded *vs.* time on a strip chart recorder. The feed rate had been changed to minimise fluctuations of the weight due to heat of adsorption. At very low flow rates, mass fluctuations were low, but there was a pressure increase due to an unavoidable small leak to the vacuum chamber. Thus an optimisation of feed rate was done. The samples were first outgassed at temperatures that will not cause thermal degradation at 10^{-4} mbar pressure. The outgassing was done at 25, 50, 100 and 200°C for silk, Nylon 6, polyester and sepiolite samples, respectively. In all adsorption experiments there were complications due to electrostatic attractions between sample pan and glass wall of the Kowar hangdown sample tube. Even if anti-

Table 1 Sample properties and heat of desorption of water from polymers and approximate temperature rise for 5% moisture adsorption

Sample type	Geometry	Radius	Crystallinity/%	Heat of desorption/J g^{-1} H_2O	Adiabatic temperature rise for 5% moisture adsorption/°C
Silk	Fibre	5 μm	46	1608	48
Undrawn Nylon 6	Fibre	19 μm	75	736	22
Muss Nylon 6	Fibre	12 μm	85	1141	34
Polyester	Microfibre	1 μm	high	–	–
Sepiolite	Spherical particle	2 mm	Crystalline	1723	52
PVC-DOP	Film	200 μm thick	0	–	

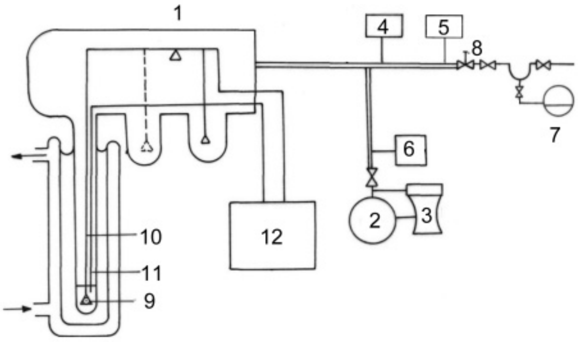

Fig. 1 Cahn Gravimetric Adsorption System: 1 – Cahn 2000, 2 – Rotary oil pump, 3 – oil diffusion pump, 4, 5 – pressure transducers, 6 – penning gauge, 7 – water reservoir, 8 – fine control needle valve, 9 – sample, 10 – Nicrom hangdown wire, 11 – thermocouple, 12 – two-channel recorder

static sprays were used it could not be completely eliminated. The temperature control was done only at the adsorption hangdown tube, but the water reservoir and the vacuum chamber were at room temperature during measurements.

Differential scanning calorimetric (DSC) analysis of the samples was done by heating the samples from 25 to 250°C at 10°C min^{-1} rate using a Setaram DSC 90 calorimeter. From the area of the endothermic peak and the mass lost during heating, the heat of desorption of water vapour from the samples was found.

Results and discussion

Even if there were inaccuracies involved using dynamic flow technique, adsorption isotherms were obtained in shorter times than using equilibrium methods. There were no problems in adsorption isotherm determination for all samples except sepiolite sample. Due to electrostatic charges concentrated in sepiolite it was attracted to the wall of the adsorption tube at low relative humidities. Thus, the adsorption isotherm data obtained for sepiolite might not represent the actual behaviour of sepiolite. In Figs 2 and 3 the water vapour adsorption isotherms of the samples are shown. The adsorption capacity was decreased in the following order: silk, undrawn Nylon 6, permanent set Nylon 6, sepiolite, polyester, plasticized PVC. Adsorption isotherms of undrawn Nylon 6, muss Nylon 6 and silk were easily determined by continuous flow method and they fitted the BET equation

$$\frac{P}{n(P_0-P)}=\frac{1}{n_\mathrm{m}C}+\left(\frac{C-1}{n_\mathrm{m}C}\right)\frac{P}{P_0} \qquad (1)$$

where C is BET constant, n_m is the monolayer coverage, P is vapour pressure and P_0 is saturation vapour pressure at the temperature of the isotherm determination. The BET constant, C, and n_m were determined by using the BET plot ($P/n(P_0–P)$ *vs.* P/P_0) and reported in Table 2. Adsorption isotherm determination of sepiolite was difficult

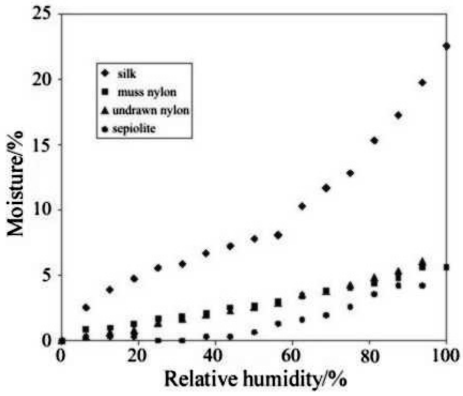

Fig. 2 Adsorption isotherms of silk, Nylon 6, sepiolite

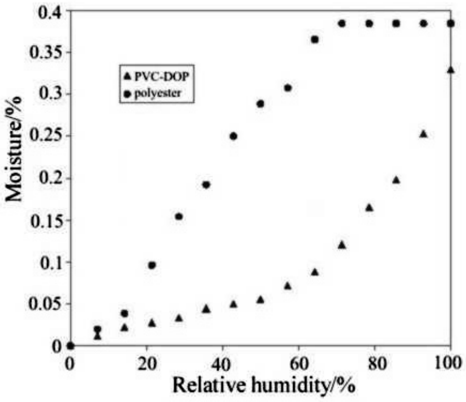

Fig. 3 Adsorption isotherm of PVC-DOP film and polyester microfibre

due to its large particle size, static electricity and high heat of adsorption. The isotherm did not fit the BET equation, since negative *C* value was obtained. Polyester and PVC-DOP adsorbed very small amounts of moisture.

Table 2 BET constants and adsorption properties of polymers

Constants	Polyester	PVC-DOP	Cast Nylon 6	Muss Nylon 6	Silk	Sepiolite
Correlation coefficient	–0.86	0.97	0.21	0.99	0.99	0.99
n_m/%	–0.32	0.033	2	1	4.6	0.2
C	–0.63	6.25	2.001	12.0	18.84	–74.7
Surface area/m^2 g^{-1}	–	0.7	46.4	23.4	107.6	4.7
Adsorption capacity/% at 100% RH	0.38	0.3	6.0	5.6	22	4.1

Water can enter only amorphous parts of the polymers and bind to functional groups by hydrogen bonding. When the structure and water vapour binding capacity at 95% relative humidity of the samples are compared, the following observations were made. Silk has low crystallinity, has –OH, $–NH_2$ and –COOH functional groups due to side chains, and binds the highest amount of moisture, 22%. Nylon 6 has high crystallinity, lower number of functional groups, and adsorbed lower amount of moisture. The cast Nylon 6 and muss Nylon 6 adsorbed 6.0 and 5.6% moisture, indicating that a small reduction in adsorption capacity occurred due to increased crystallinity by heat setting. The convex upper part of the adsorption isotherms for silk and Nylon 6 is due to relaxation of pre-existing gaps that results in swelling of matrix for hydrophilic polymers [18]. Sepiolite, which is a mesoporous solid, adsorbed considerable amounts of moisture only at high relative humidities indicating capillary condensation. The adsorbed amount of moisture was 4.1 at 95% relative humidity and this was lower than the quantities adsorbed by other sepiolite samples studied by Caturla *et al.* [19]. Polyester has high crystallinity, –OH and –COOH end groups and adsorbed very small amounts of moisture. PVC-DOP film is a flexible amorphous and hydrophobic film and adsorbed very small amounts of moisture. The upper convex part of the isotherm could be explained in terms of water cluster formation for PVC-DOP film [18].

The surface areas of the samples, assuming simple cubic packing of water molecules at the surface and using n_m values of BET equation, were found to characterise the samples [1, 2]. The surface areas of silk, cast Nylon 6 and muss Nylon 6 were 108, 46 and 23 $m^2\ g^{-1}$, respectively.

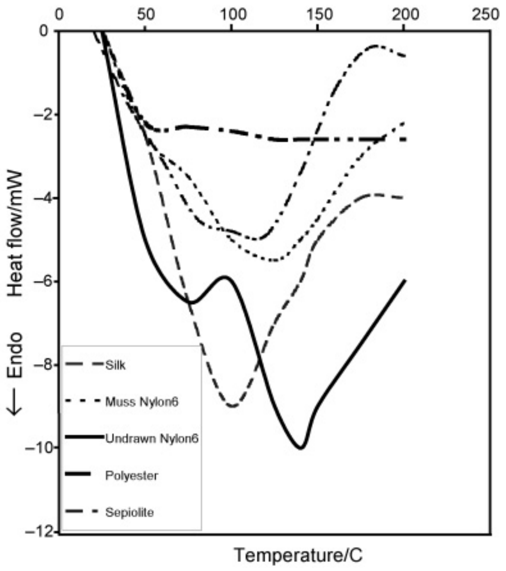

Fig. 4 Differential scanning calorimetric curves of the samples

DSC curves of the samples in Fig. 4 indicated that 736–1723 J g^{-1} H_2O energy were required for water vapour desorption as reported in Table 1. On water vapour adsorption that much of energy will be released to surroundings. On adiabatic basis, the temperature rise (ΔT) of the samples on water vapour adsorption was found from Eq. (2) using integral heat of adsorption (ΔH_a)

$$m' c_p \Delta T = m \Delta H_a \tag{2}$$

where m and m' are mass of water adsorbed and sample mass respectively. Heat capacity, c_p was taken as 1.67 J g^{-1} °C^{-1} for all samples as an approximation. If 5% water were adsorbed on the samples, temperature of the sample would increase around 22 to 52°C as seen in Table 1. Thus adsorption isotherm determination by dynamic technique has experimental errors due to temperature rise of the samples upon water vapour adsorption.

Conclusions

Continuous feeding of water vapour to vacuum chamber for adsorption isotherm determination would be successful if the heat and mass transfer area is high allowing fast equilibrium to be attained and heat of desorption is efficiently removed. For sepiolite sample, which had a very high heat of adsorption and high electrostatic charge, it could be concluded that the isotherm determination by dynamic technique would be feasible after conducting heat and static electricity from the sample.

The surface areas of silk, cast Nylon 6 and muss Nylon 6 were found as 108, 46 and 23 m^2 g^{-1} respectively since their isotherm by dynamic technique approached to their equilibrium isotherm. Polyester and PVC adsorbed very small amounts of moisture. While swelling occurred for silk and Nylon 6 samples, water clusters formed in elasticised PVC at high relative humidities.

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