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FUNCTIONAL PACKAGING MATERIALS: FACTORS AFFECTING THE
CAPACITY AND RATE OF WATER ADSORPTION IN DESICCANT COMPOSITES

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ABSTRACT

Ten different polymers were selected as possible matrix for zeolite containing desiccant composites in order to prepare functional packaging material. Water uptake was determined at 100 % RH and the results were analyzed to identify factors influencing the capacity and rate of water adsorption. The results showed that the desiccant can adsorb considerable water in its free pores. The adsorption capacity of the composites depends linearly on the amount of desiccant present, but it is independent of the type of polymer used. The diffusion of water into the composites is fast initially, but slows down with time and also with increasing desiccant content. This latter effect can be explained with the increase of the diffusion path as zeolite content increases. The initial rate of diffusion depends solely on the specific free volume of the matrix and this factor influences strongly also the overall rate of water adsorption. However, this latter characteristic depends also on other factors like the dispersion of the desiccant in the matrix. Matrix type and zeolite content must be selected according to the task to be fulfilled; fast adsorption can be achieved only with polymers having large free volume.

Keywords: zeolite, desiccant composites, capacity, rate of adsorption, free volume

1. INTRODUCTION

Plastic packaging materials form an important part of the economy and our everyday life. They have numerous functions like making possible the safe distribution of products, protecting them from the environment, informing the customer, etc [1,2]. However, the ever increasing demand of the public resulted in new solutions including functional and smart packaging materials [3-6]. The latter respond to changes in the environment, while the former fulfills some function improving the performance of the packaging. The number of such materials increases rapidly and they are used already in everyday practice. The main functions targeted for various products are oxygen scavenging [7-9], humidity control [10-14], regulating ethylene content [15], antimicrobial effect [16-19], adsorption of odorous materials, or the opposite, the release of desirable aromas [20,21]. Intensive research and development work is carried out on these materials all over the world, but mostly in industry.

Controlling the humidity of packaged wares is extremely important in several areas. The quality of food have been preserved by drying for several hundred years, but recently moisture control became very important in the pharmaceutical and electronic industries as well. Controlled and given moisture content is important in food packaging [10-12], while maintaining dry conditions mostly in pharma [13,14,22] and electronics [23]. Water being present in the atmosphere must be captured in the latter case which is done either by the adsorption or absorption of water [24]. Often used absorbents are calcium sulfate (CaSO_4) [25], calcium chloride (CaCl_2) [26] or calcium oxide (CaO) [27]. These materials absorb water either to bind it as crystal water or to react with it chemically to form a new compound. Adsorbents are able to bind considerable amount of water on their very large, high energy surface. Active carbon [28] silica gel [29], clays [30], and zeolites

[31] are often used for this purpose, the most frequently silica gel [32] and zeolite [33]. The desiccant can be added to the packaged ware in a semipermeable satchet or incorporated into the packaging material [4]. Intensive research is carried out to develop new desiccants including hybrid (adsorbent/absorbent) materials [26,34,35], natural polymers (starch, cellulose derivatives)[36,37] or superabsorbent gels (acrylates, cellulose compounds) [38-41].

In spite of the social and economical importance of active packaging materials controlling humidity, very little systematic work has been reported in the literature, at least according to our knowledge. Pehlivan et al. [33] studied the water adsorption of polypropylene (PP)/zeolite composites. They prepared their samples by compression molding from powders and before composite preparation surface modified the desiccant with polyethylene glycol (PEG). Their results were rather controversial, they measured significantly different adsorption capacities by water immersion as in an atmosphere of 100 % RH (13.5 and 24.5 %, respectively), and similar differences were observed in the rate of adsorption as well. Mathiowitz et al. [32] also studied PP composites containing zeolite treated with PEG and compared this latter to silica gel. Although the ideology of the study emphasizes the synergetic effect of PEG and zeolite on water uptake, they paid much more attention to the preparation of the composites than to the analysis of their results. The few results reported are controversial here too; the main conclusions of the authors are that desiccant composites bind water and that composites prepared with zeolite are more efficient than those containing silica gel. The parameters most important for these functional packaging materials, i.e. adsorption rate and capacity, are difficult to extract from these papers and the reliability of the results is questionable. Moreover, we do not learn much about factors determining these parameters and ways to control them.

As a consequence, the goal of our study was to carry out systematic experiments with desiccant composites prepared with a selected zeolite and to determine the effect of desiccant content and the properties of the matrix polymer on the rate and capacity of water adsorption. Ten different polymers were selected for the study and desiccant content was varied in a wide range from 0 to 50 vol%.

2. EXPERIMENTAL

Polymers with various chemical compositions, mechanical and rheological properties were selected for the study to cover a wide range of properties important in fulfilling their function. A low (LDPE, Tipelin[®] FA 24451, TVK, Hungary) and a high density (HDPE, Tipelin[®] BA 55013, TVK, Hungary) polyethylene, a polypropylene (PP, Tipolen[®] H 649 F, TVK, Hungary), a polystyrene homopolymer (PS, Sytron[®] 686 E, Dow, USA), two high impact polystyrenes (HIPS1, Styron[®] 485, HIPS2, Styron[®] 1175, Dow, USA), a styrene-acrylonitrile copolymer (SAN, Tyril[®] 880, Dow, USA), a polycarbonate (PC, Macrolon[®] 2658, Bayer, Germany), a poly(methyl methacrylate) (PMMA, Ortoglas[®] HFI 7, Arkema, France) and a PVC compound based on the Ongrovil[®] S 5258 suspension grade powder of BorsodChem, Hungary was used as matrix polymers. A 5A type zeolite was selected as desiccant (Luoyang Jianlong Chem. Ind. Co., China); we characterized several synthetic zeolites in the study and found that this grade has the largest water adsorption capacity. The average particle size of the desiccant is 4.5 μm , its density 1.66 g/cm^3 and specific surface area 533 g/m^2 as determined by nitrogen adsorption (BET). The theoretical pore diameter of this zeolite is 4.3 \AA .

Before composite preparation the zeolite was dried at 300 °C for 16 h in vacuum. The components were homogenized in a Brabender W 50 EH internal mixer attached to a

Haake Rehocord EU 10 V driving unit at 190 °C for 10 min except PC, the mixing of which was done at 240 °C. 1 mm thick plates and 100 µm thick films were compression molded from the homogenized material at 190 or 240 °C using a Fontijne SRA 100 laboratory machine for further studies. The zeolite content of the composites changed between 0 and 50 vol%.

The molecular weight of the polymers was determined by gel permeation chromatography in THF or TCB, respectively, using polystyrene standards. Density was measured using a pycnometer at room temperature. The water vapor transmission rate (WVTR) of the polymers was determined on the 100 µm thick films using a Mocon Permatran W1A equipment. Results were calculated for 20 µm thickness according to industrial practice. The water adsorption of the zeolite and the composites were determined by the measurement of weight in an atmosphere of 100 % RH on 20 x 20 x 1 mm specimens as a function of time. The zeolite content of the composites was checked by thermal gravimetry (TGA). 15 mg samples were heated to 650 °C with 80 °C/min rate in oxygen and kept there for 5 min to burn off the polymer.

3. RESULTS AND DISCUSSION

The results are presented in several sections. First the water adsorption of the zeolite and that of the composites is shown together with the approaches used for the quantitative determination of adsorption characteristics. Factors influencing these latter are discussed subsequently, and finally the diffusion process is analyzed and general correlations are established between matrix properties and adsorption rate. Brief reference is made to consequences for practice at the end of the section.

3.1. Water adsorption

The rate and amount of water adsorbed by a desiccant composite are determined by the characteristics of the components. Previous studies in the area showed that the capacity of the composites is much larger than that of the matrix polymers and increases with desiccant content [32,33]. Much less reliable information is available for adsorption rate and the contribution of the components has not been clearly defined yet [33]. The water adsorption isotherm of the 5A grade zeolite used in the study is shown in **Fig. 1**. Adsorption is relatively fast and the desiccant adsorbs 23.8 wt% water of its weight. We regard this value as the theoretical capacity of the zeolite under our conditions. The claim that water adsorption is fast is difficult to judge from the isotherm presented in **Fig. 1**. However, as results will show later equilibrium adsorption is reached after much longer times in composites than in the zeolite.

The water uptake of polycarbonate composites is presented in **Fig. 2** as a function of time and zeolite content. We can see the much slower rate of adsorption mentioned above and also that maximum adsorption is more or less proportional to the zeolite content of the composite. Similar adsorption isotherms were recorded in composites prepared from the other polymers as well. During quantitative evaluation we assumed Fickian adsorption and the equation derived from Fick's second law [42]

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

was solved for $m = 2$ to obtain the following correlation

$$M_t = M_\infty \left(1 - \frac{8}{\pi^2} \left(\exp(-a t) + \frac{1}{9} \exp(-9 a t) + \frac{1}{25} \exp(-25 a t) \right) \right) \quad (2)$$

which was fitted to the experimental data. In the equations M_t is time dependent weight in-

crease, M_∞ the final water uptake reached after infinite time, L the thickness of the sample, t the time of adsorption and a (1/s) a constant characterizing the overall rate of water adsorption. The solid lines in **Figs. 1 and 2** are the fitted correlations. It is obvious from the agreement of measured and calculated values that water adsorption can be described by Fickian diffusion reasonably well.

In order to compare the effect of the type of the polymer used as matrix material, adsorption isotherms are plotted as a function of time in **Fig. 3** for three polymers at two different zeolite contents. Fitted correlations are presented in this figure as well. The comparison of the results obtained for the three polymers shows that the adsorption capacity of the composites depends mainly on the amount of desiccant present and only slightly on the type of the polymer used as matrix. On the other hand, the rate of adsorption, indicated by the initial slope of the adsorption isotherms, depends on the properties of the polymer and in a much lesser extent on the amount of desiccant added. Since both adsorption capacity and the rate of adsorption are important for practice, quantitative analysis must be carried out in order to analyze the factors influencing them. One way to do this is the fitting of **Eq. (2)** to the experimental results. Adsorption capacity can be estimated quite accurately by extrapolated water uptake, i.e. M_∞ , while the overall rate of adsorption can be characterized by parameter a .

However, the initial rate of adsorption differs considerably from the overall rate and none of the current theories can describe equally accurately both. A common practice to characterize the initial rate of adsorption is to fit another form of Fick's law [42] to the experimental results

$$\frac{M_t}{M_\infty} = 4 \left(\frac{D t}{L^2} \right)^{1/2} \left(\pi^{-1/2} + 2 \sum_{m=0}^{\infty} (-1)^m \operatorname{ierfc} \frac{m L}{2 (D t)^{1/2}} \right) \quad (3)$$

where D is diffusion coefficient. If we plot the water uptake as a function of the square

root of time, we should obtain a straight line the slope of which, b ($s^{-1/2}$), is proportional to the initial rate of water adsorption. **Eq. (3)** was fitted to the water adsorption of all composites; an example is shown in **Fig. 4** for three PP composites. Reasonable fit is obtained again, thus the initial rate of adsorption can be determined in this way. **Fig. 4** also shows that the initial rate of water adsorption increases with zeolite content.

3.2. Factors

The results shown in the previous section indicated qualitatively that the water adsorption capacity of desiccant composites depends mainly on their zeolite content, while the type and characteristics of the polymer influences the rate of adsorption much more. In order to see the correlations and the effect of these factors much better we plotted maximum water uptake against zeolite content for three polymers in **Fig. 5**. According to the figure adsorption increases with zeolite content linearly for all three polymers indeed and it is completely independent of the type of polymer used as matrix. Very similar correlations were obtained for all the polymers used as matrix material in this study.

Much more complicated is the effect of polymer characteristics on the rate of water adsorption. The initial rate of adsorption is plotted against zeolite content in **Fig. 6** for the same three polymers as in **Fig. 5**. Adsorption rate is the fastest in the PC composites, while much slower in PVC and especially in HDPE. These relationships were more or less visible already in **Fig. 3**, but the calculation and plotting of parameter b against zeolite content reveals them much more clearly. We must also note that the increase in the rate of adsorption slows down with increasing desiccant content in PC, while it accelerates slightly in PE. The inherent properties of the polymer obviously influence water adsorption strongly, but the dominating one cannot be identified from the results presented up to now.

We must call the attention also to the fact here here, that the rate of water adsorption is at least one or two order of magnitudes faster for the neat zeolite ($b = 0.16 \text{ s}^{-1/2}$) than for the composites.

Even more surprising is the effect of these parameters, or more exactly that of zeolite content, on the overall rate of water adsorption (a) as shown by **Fig. 7**. Overall rates are in the same magnitude than initial rates and the relative order of the composites is also the same, i.e. adsorption is the fastest in PC and the slowest in HDPE, but the rate of water uptake decreases with increasing zeolite content instead of increasing. The difference among the polymers is also larger; water adsorption is very slow in PVC and HDPE and much faster in PC. The rate of water adsorption is between the values presented in **Figs. 6 and 7** for the other polymers as well. Although the comparison of **Figs. 6 and 7** calls the attention to the importance of determining both the initial and the overall rate of water adsorption, it does not explain the difference; further analysis is needed to explain the phenomenon.

3.3. Discussion

Permeation of substances through polymers is an important phenomenon in many application areas including packaging. In studies related to gas, and first of all to oxygen, diffusion the free volume of the polymer turned out to be the most important characteristics determining permeation. The fractional free volume (v_{ff}) is the ratio of the free volume to the specific molar volume (v) of the polymer, i.e.

$$v_{ff} = \frac{v - v_0}{v} \quad (4)$$

where v_0 is the occupied volume. The occupied volume can be determined by the method

of Bondi [43] from the van der Waals volume (v_W) of the polymer, $v_0 = 1.3v_W$. Both the specific molar volume and the van der Waals volume are listed by van Krevelen and te Nijenhuis [44] in their book. Often not the fractional free volume, but the specific free volume, v_{sf} , is used for the characterization of the polymers which is the fractional free volume related to the molecular weight of the repeat unit (M), i.e. $v_{sf} = v_{ff}/M$. Cohen and Turnbull [45] applied the free volume theory of Doolittle [46] to describe diffusion in polymers

$$D = C \exp\left(-\frac{\gamma v^*}{v_f}\right) \quad (5)$$

where C and γ are constants and v^* is the free volume needed for diffusion. Fujita [47] expressed the mobility of the diffusing gas (M_p) with the approach

$$M_p = A \exp\left(-\frac{B}{v_{sf}}\right) \quad (6)$$

where A and B are constants independent of the concentration of the diffusing gas. Mobility is related to permeability (P)

$$P = D S = S R T \exp\left(-\frac{B}{v_{sf}}\right) \quad (7)$$

where S is the solubility of the diffusing matter in the matrix. We can see from [Eq. 7](#) that if we plot permeability against the natural logarithm of v_{sf} , we should obtain a linear correlation with a negative slope. Lee [48] determined the permeability of oxygen through various polymers and obtained a very good correlation between permeation and v_{sf} indeed. Free volume can be calculated as indicated above or can be determined by positron annihilation spectroscopy [49]. However, this latter approach is difficult or even impossible to use for certain polymers, since, for example, chlorine or nitrile groups hinder the formation of ortho-positrons.

We used the above presented approach to analyze the effect of polymer characteristics on the water adsorption of desiccant composites. First we calculated the specific free volume of our polymers from data listed by van Krevelen and te Nijenhuis [44]. In the case of copolymers (HIPS, SAN) we calculated average values taking into account their composition. Weight averages were used in the calculation. Crystallinity was also taken into account, since diffusion occurs only in the amorphous phase in such polymers. Calculated specific free volumes are listed in the last column of [Table 1](#).

In order to check the approach, first we plotted the logarithm of water vapor transmission rate (WVTR) against the reciprocal value of v_{sf} of the neat polymers ([Fig. 8](#)). The correlation is surprisingly good, a straight line with a negative slope is obtained as predicted by theory and the deviations of the individual points from the line are very small. We can safely conclude that the approach can be applied also in our case, and the permeation of water through all of the polymers used as matrix in desiccant composites is determined by their free volume. Subsequently we plotted the rate of adsorption values (a and b) of the composites against v_{sf} in the same way. [Fig. 9](#) shows initial rates plotted in this way for composites containing 30 vol% zeolite. A very good linear correlation is obtained again with somewhat larger, but not very large deviations. We can conclude that the initial rate of adsorption is determined mainly by the free volume of the polymer. Similar correlations were obtained at other zeolite contents as well, but also for overall values of adsorption rate, although the deviations from the straight line were larger in this latter case. Nevertheless, the tendency was always the same proving that diffusion in the matrix determines both the initial and the overall rate of water adsorption in desiccant composites.

Only one question remains that we have to explain, the different composition dependence of the initial and the overall rate of water adsorption. The adsorption of all composites is much slower than that of the neat zeolite and one would expect that diffusion is

determined by the diffusion rate of the polymer. The expectation is fulfilled for the initial, but not for the overall rate of adsorption. Obviously, diffusion slows down with increasing desiccant content at longer times in the latter case. Although water adsorption is claimed to proceed in three steps and slow down with time for the neat zeolite [50], this stepwise diffusion cannot cause the effect observed in the composites, since overall rate for the zeolite is at least one order of magnitude larger than for the composites. The only reasonable explanation is the increase of diffusion path with increasing desiccant content. Fillers were shown to slow down diffusion through composites because of increasing tortuosity of the path [51]. Diffusion occurs from the edges thus particles located there are filled with water fast. Diffusion proceeds through the polymer as a consequence and water molecules must go around particles saturated with water. The effect is obviously much larger for polymers in which diffusion is fast (PC) than in polyolefins, in which it is very slow.

4. CONCLUSIONS

The study of polymer/zeolite desiccant composites prepared with ten different matrices showed that the desiccant can adsorb considerable water in its free pores. The adsorption capacity of the composites depends linearly on the amount of desiccant present, but it is independent of the type of the polymer used. The diffusion of water into the composites is fast initially, but slows down with time and also with increasing desiccant content. This latter effect can be explained with the increase of the diffusion path as zeolite content increases. The initial rate of diffusion depends only on the specific free volume of the matrix and this factor influences strongly also the overall rate of water adsorption. However, this latter characteristic depends also on other factors like the dispersion of the desiccant in the matrix. Matrix type and zeolite content must be selected according to the

task to be fulfilled; fast adsorption can be achieved only with polymers having large free volume.

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Table 1 Characteristics of the polymers used in the study

Polymer	MFR (g/10 min) at		M _n (g/mol)	M _w /M _n	Density (g/cm ³)	WVTR (g 20 μm/m ² /24 h)	Free volume v _{sf} (cm ³)
	Value	Conditions					
LDPE	0.28	190 °C, 2.16 kg	17160	6.89	0.92	15.2	0.110
HDPE	0.35	190 °C, 2.16 kg	18620	6.57	0.96	3.6	0.088
PP	2.50	230 °C, 2.16 kg	92620	4.84	0.90	6.4	0.092
PS	2.50	200 °C, 5 kg	127970	2.44	1.04	138.3	0.166
HIPS1	12.00	200 °C, 5 kg	77525	2.68	1.02	111.7	0.167
HIPS2	2.80	200 °C, 5 kg	95840	2.54	1.04	100.8	0.168
SAN	3.50	230 °C, 3.8 kg	75510	2.39	1.07	169.3	0.161
PC	13.00	300 °C, 1.2 kg	24730	2.07	1.20	105.7	0.149
PMMA	11.00	230 °C, 3.8 kg	43470	1.88	1.16	140.7	0.135
PVC	–	–	55270	2.41	1.44	25.7	0.128

7. CAPTIONS

- Fig. 1** Water adsorption isotherm of the zeolite 5A used in the study
- Fig. 2** Water adsorption of polycarbonate composites at various zeolite contents
Symbols: (○) 10, (△) 20, (▽) 30, (◇) 40, (◁) 50 vol%
- Fig. 3** Effect of polymer type and zeolite content on the water adsorption of various desiccant composites
Symbols: (□) HDPE, (○) PVC, (△) PC
- Fig. 4** Determination the initial rate of water adsorption in PP/zeolite composites with various desiccant contents
Symbols: (○) 10, (△) 30, (▽) 50 vol%
- Fig. 5** Effect of matrix type and zeolite content on the water adsorption capacity of desiccant composites
Symbols: (□) HDPE, (○) PVC, (△) PC
- Fig. 6** Influence of the type of the polymer used as matrix and zeolite content on the initial rate of water adsorption (*b*) in desiccant composites
Symbols: (□) HDPE, (○) PVC, (△) PC
- Fig. 7** Overall rate of water adsorption (*a*) plotted against zeolite content for desiccant composites prepared with different matrices
Symbols: (□) HDPE, (○) PVC, (△) PC
- Fig. 8** Correlation between the water vapor transmission rate of the polymers used as matrices for desiccant composites and their specific free volume
Symbols: (□) HDPE, (○) PP, (△) LDPE, (▽) PVC, (◇) PS, (◁) HIPS2, (▷) PC, (●) HIPS1, (★) PMMA, (◆) SAN
- Fig. 9** Effect of the free volume of the matrix polymer on the initial rate of water adsorption of desiccant composites containing 30 vol% zeolite
Symbols are the same as in Fig. 8

FIGURES

Fig. 1

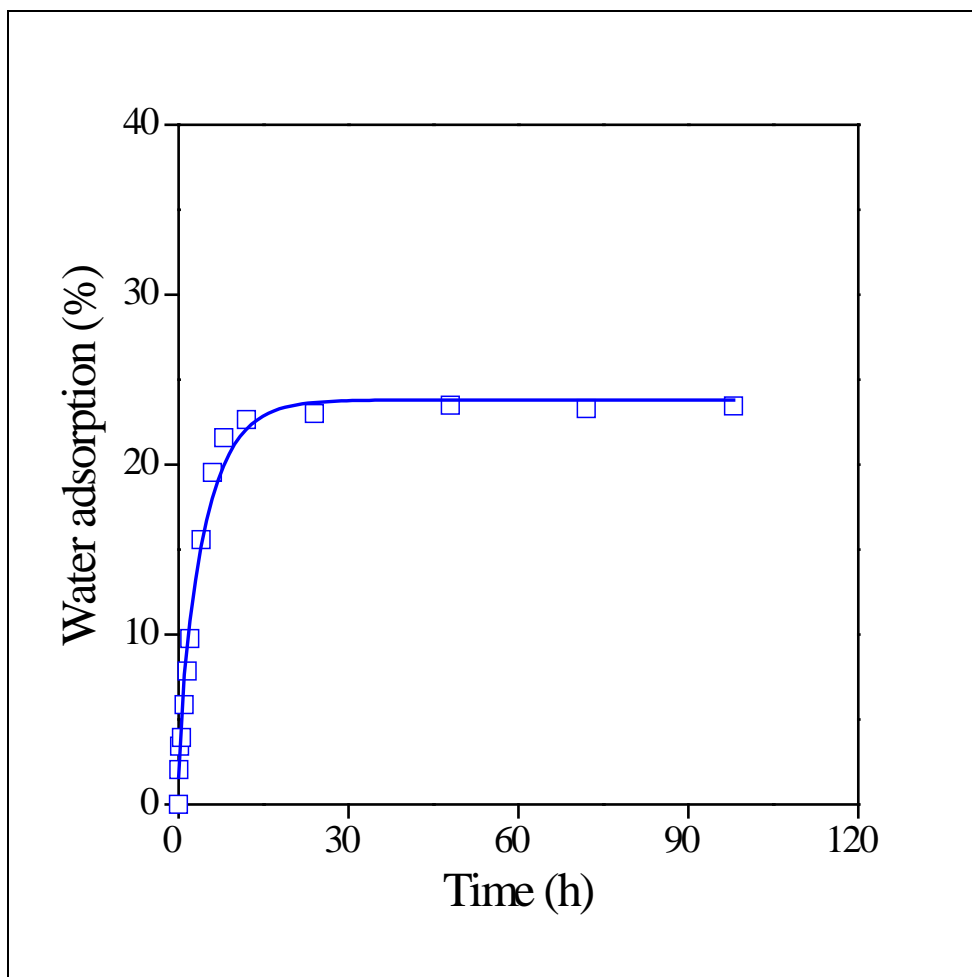


Fig. 2

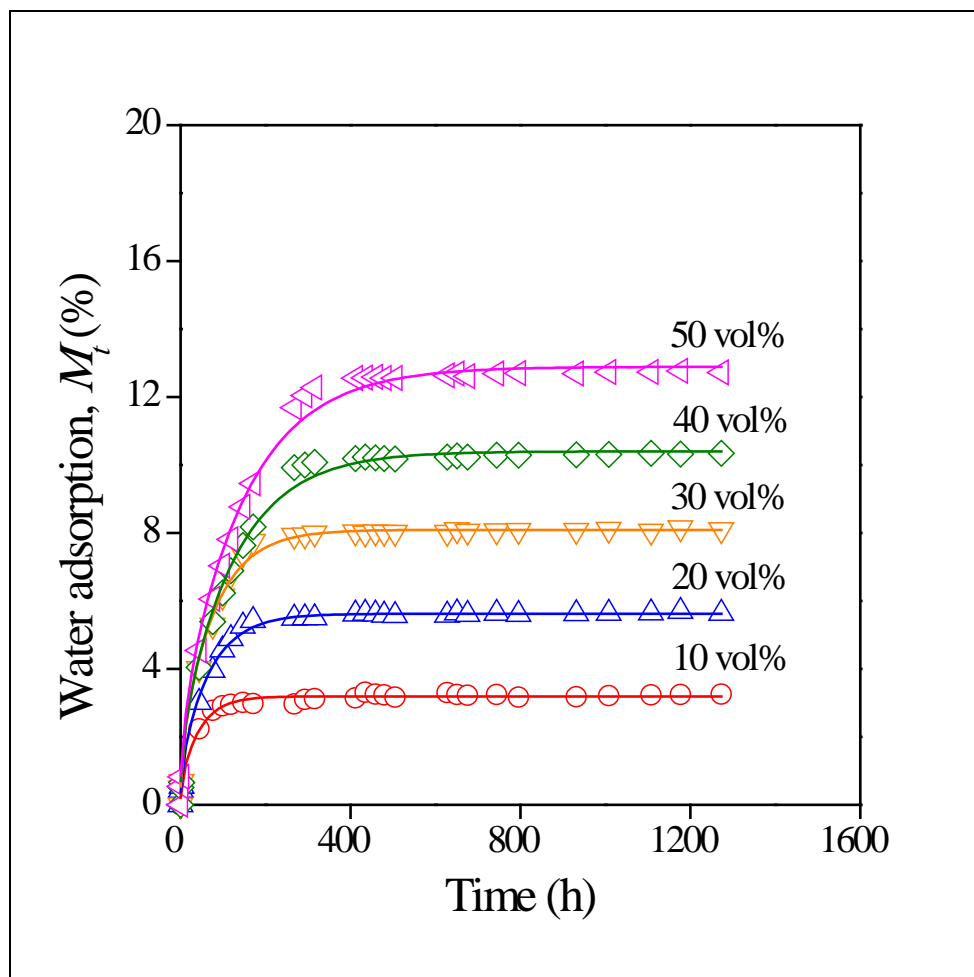


Fig. 3

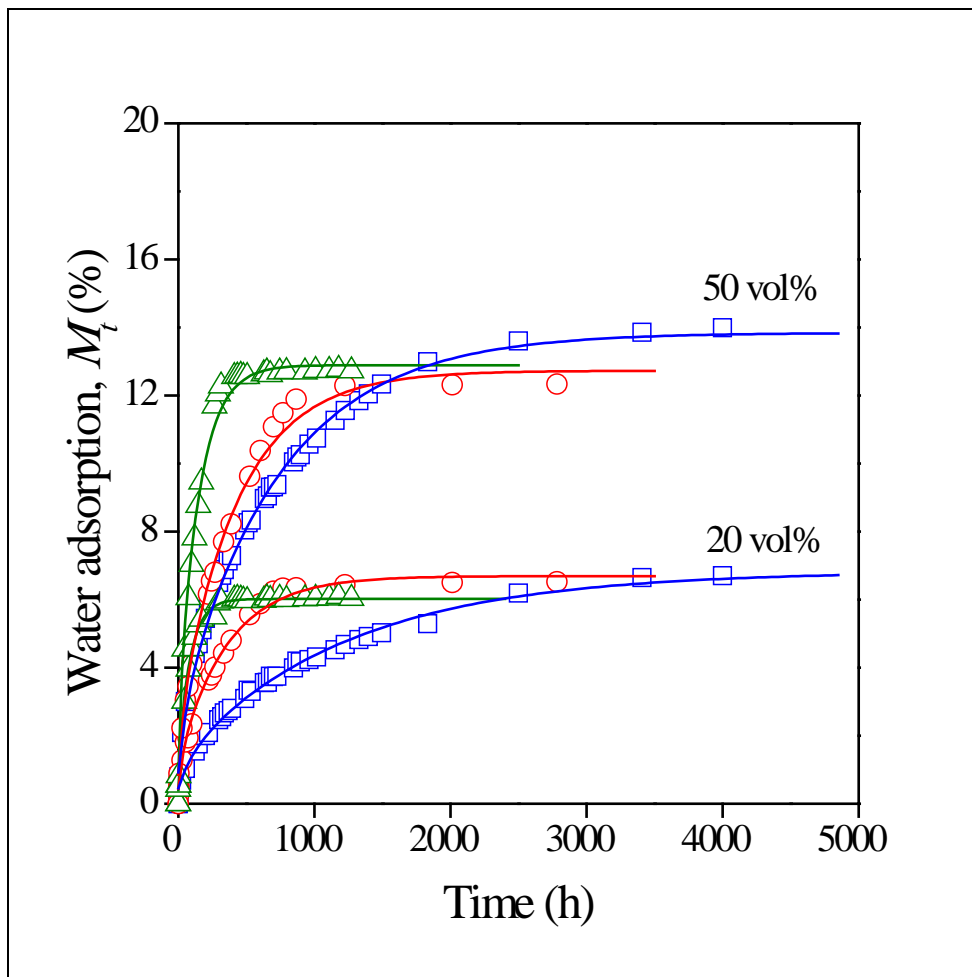


Fig. 4

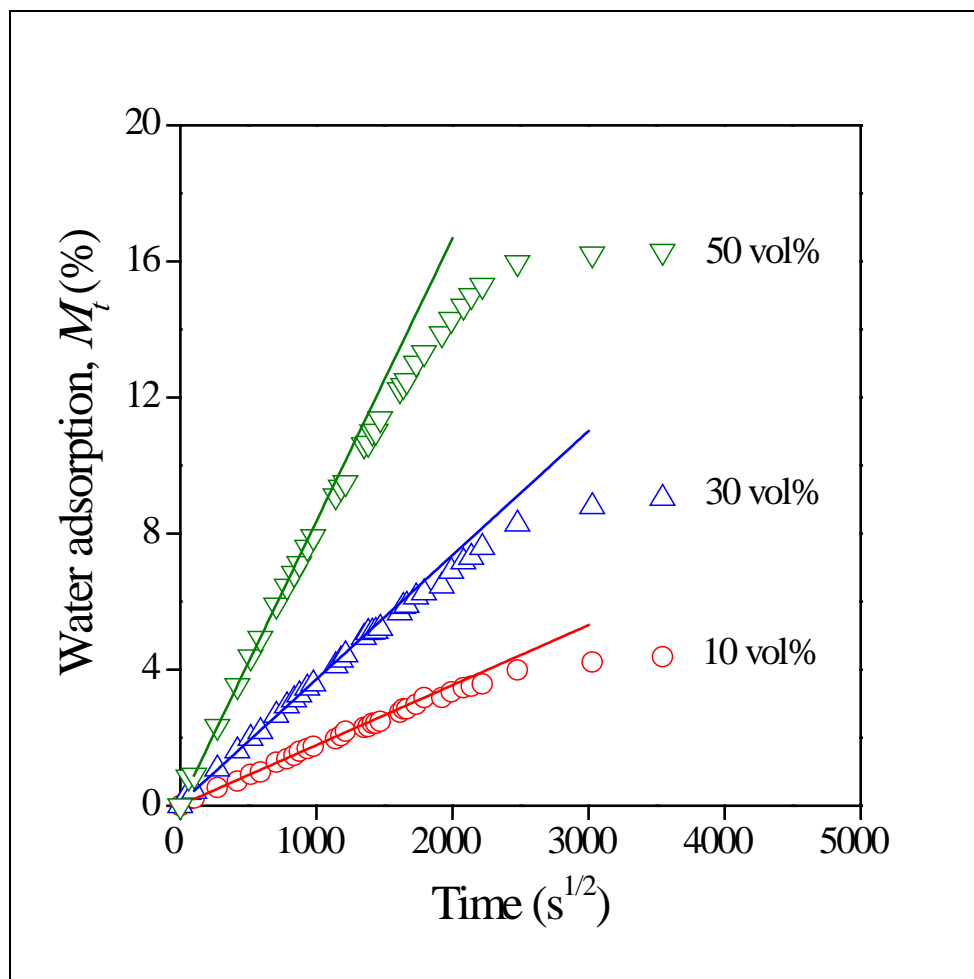


Fig. 5

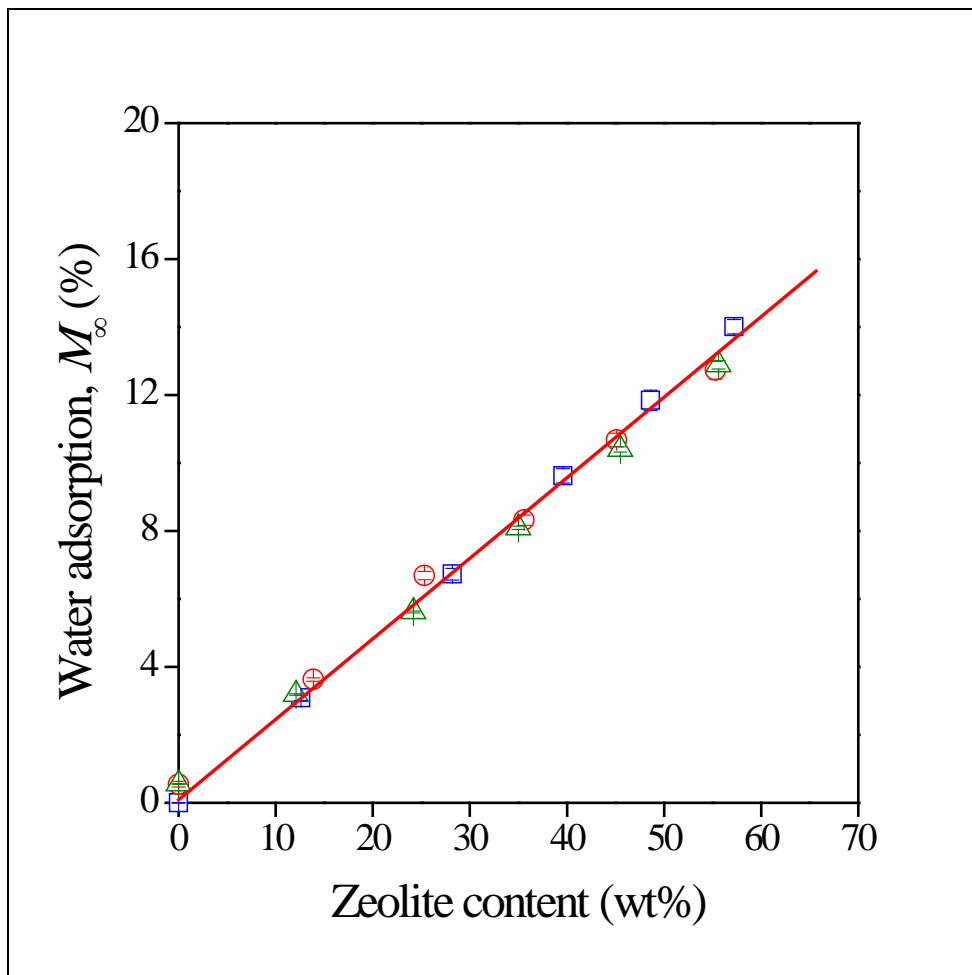


Fig. 6

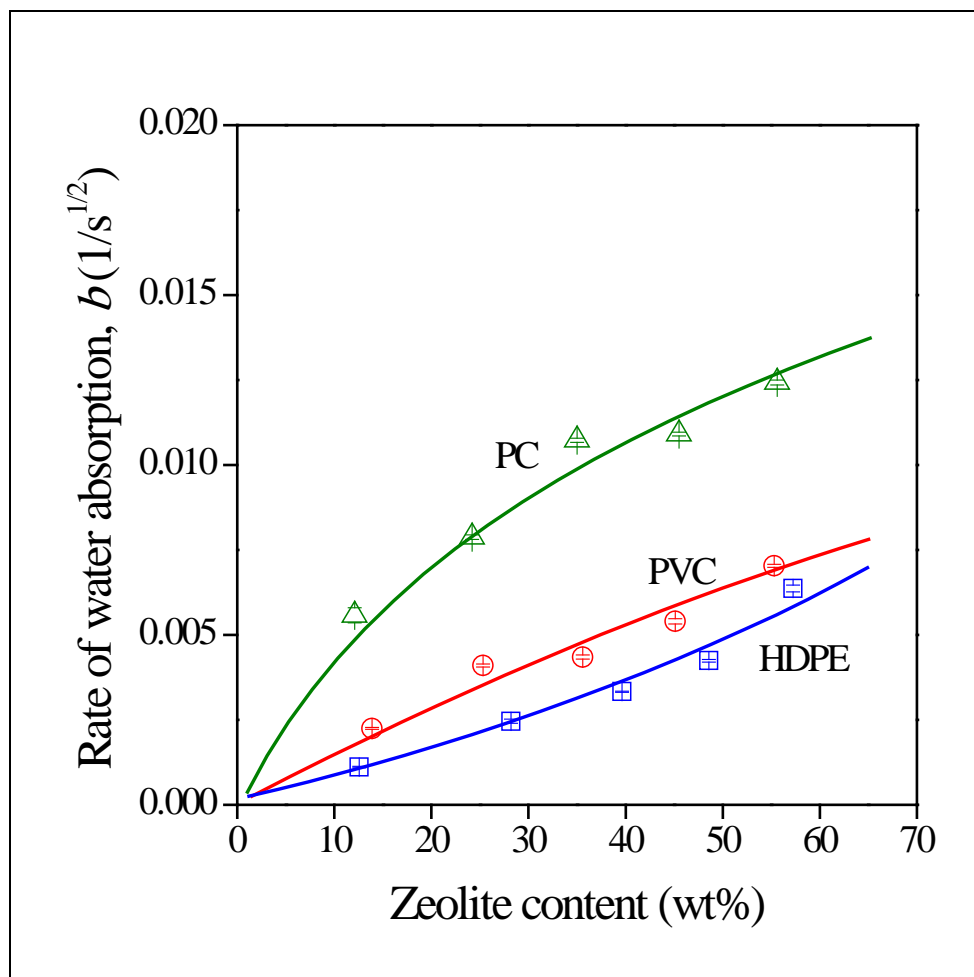


Fig. 7

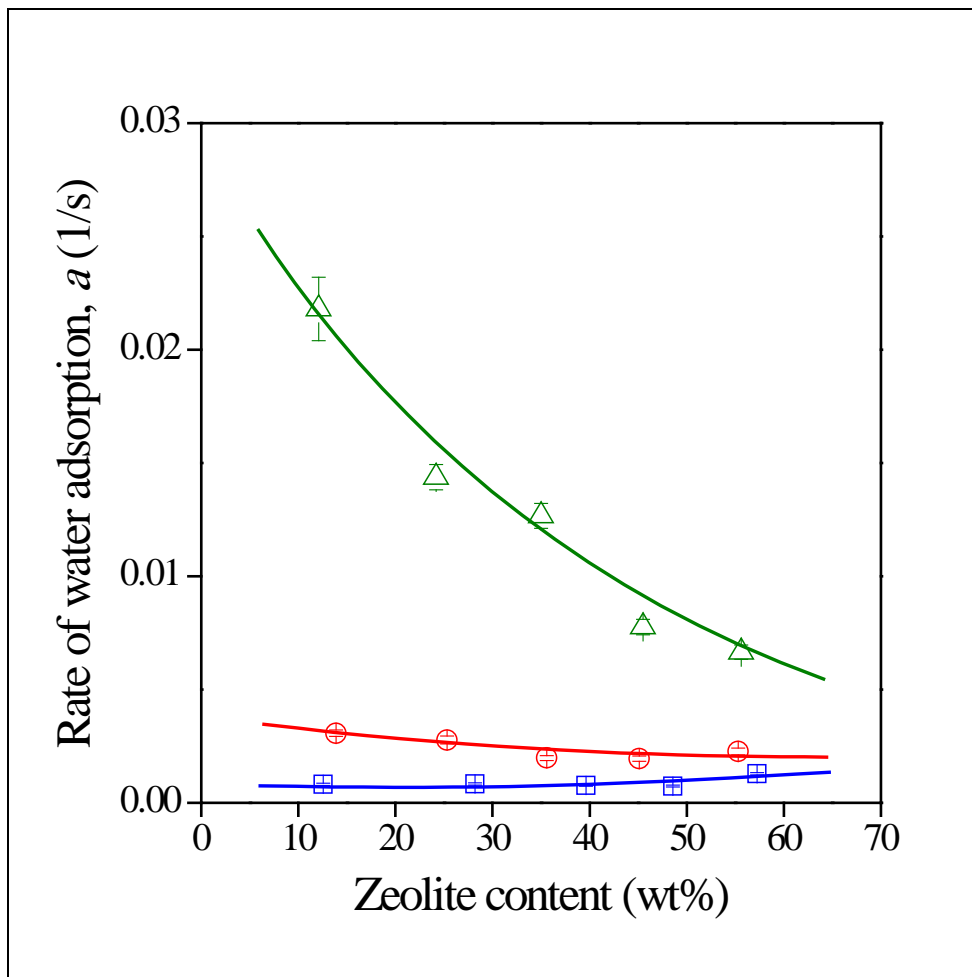


Fig. 8

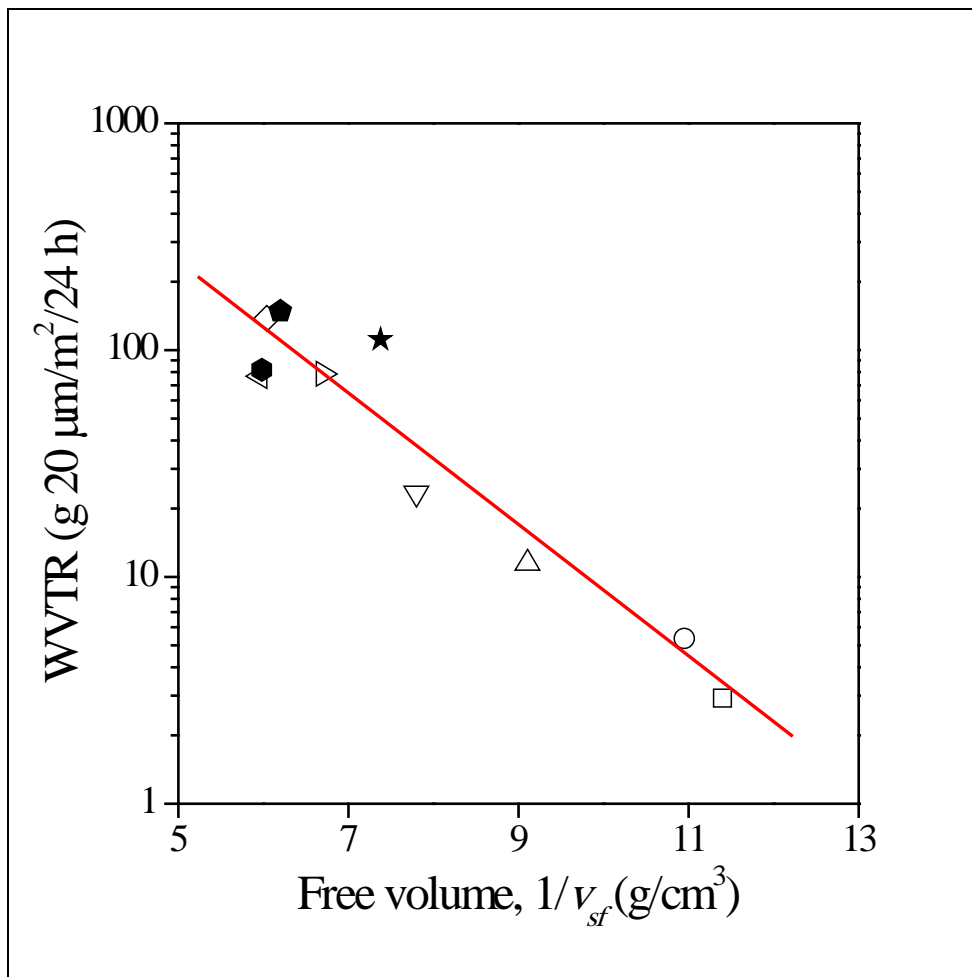


Fig. 9

