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EFFECT OF DESICCANT CHARACTERISTICS ON THE PROPERTIES OF
PS/ZEOLITE FUNCTIONAL PACKAGING MATERIALS

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ABSTRACT

Desiccant composites were prepared from a polystyrene homopolymer (PS) and a high impact copolymer (HIPS). Five zeolites were used as adsorbents which included the A and X types frequently used in industrial practice. Composites containing zeolites up to 50 vol% were homogenized in an internal mixer and then compression molded to 1 mm thick plates. The results proved that the water adsorption capacity of zeolites depends on the total volume of the pores, while the rate of adsorption on thermodynamics, on the equilibrium constant of adsorption. On the other hand, zeolite characteristics influence the moisture adsorption of the composites only marginally; adsorption capacity is determined by zeolite content, while the rate of adsorption by the properties of the polymer. Composites prepared with X type zeolites have somewhat smaller water adsorption capacity than those containing their A type counterparts. The dispersion of the zeolite is very good both in PS and in HIPS composites. Mechanical properties are excellent mainly because of the good interfacial adhesion between the components. Because of their larger surface energy, composites containing X type zeolites have larger viscosity and they reinforce the polymer more than A type desiccants. Matrix properties influence mainly application related properties, reinforcement and ductility is better in HIPS than in PS composites.

KEYWORDS: zeolite, desiccant composites, capacity, rate of adsorption, composite properties

1. INTRODUCTION

The number of functional and smart packaging materials increases rapidly and they are used already in everyday practice [1-4]. The main functions targeted for various products are oxygen scavenging [5-7], humidity control [8-12], regulating ethylene content [13], antimicrobial effect [14-17], adsorption of odorous materials, or the opposite, the release of desirable aromas [18,19]. 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. Controlled and given moisture content must be maintained in food packaging [8-10], while dry conditions must be achieved in pharma [11,12,20] and electronics [21]. Water being present in the atmosphere must be captured in the latter case which is done either by the adsorption or absorption of water [22]. Absorbents bind moisture either as crystal water or they 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 [23], silica gel [24], clays [25], and zeolites [26] are often used for this purpose, but silica gels [27] or zeolites [28] are applied the most frequently for this purpose. The desiccant can be added to the packaged ware in a semi permeable satchel or incorporated into the packaging material [3].

In spite of the social and economical importance of active packaging materials controlling humidity, very little systematic work has been reported in the literature on this question, at least according to our knowledge. Pehlivan et al. [28] studied the water adsorption of polypropylene (PP)/zeolite composites. They prepared their samples by compression molding from powders and surface modified the desiccant with polyethylene glycol (PEG) before composite preparation. They measured significantly different adsorption capacities by water immersion and in an atmosphere of 100 % RH (13.5 and 24.5 %, re-

spectively), and similar differences were observed in the rate of adsorption as well without unambiguous reason or explanation. Mathiowitz et al. [27] also studied PP composites containing zeolite treated with PEG and compared it to silica gel. Their main conclusions were that desiccant composites bind water and that composites prepared with the zeolite are more efficient than those containing the 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 important factors, like the characteristics of the desiccant or the polymer matrix have not been investigated systematically.

The papers cited above and other information indicate that zeolites are very efficient adsorbents of moisture. However, a single, specific zeolite is used in most studies [27,28], which is selected on availability or for some other reason. Zeolites may differ widely in characteristics. They can come from natural resources or can be produced synthetically [22,29]. Many of their characteristics including pore size and volume, particle size, specific surface area, surface energy, the ratio of silica and aluminum atoms, etc. may change in a wide range and some of them must influence the rate and capacity of water adsorption [30-32]. According to our knowledge, a systematic study of the effect of these parameters on the desiccant properties of functional composites has never been done before. Moreover, beside functional properties the composites must meet the requirements of the intended application and zeolite characteristics may influence the corresponding properties as well. Usually commodity polymers, e.g. polypropylene [33-36], polyethylene [26,37-40] or polystyrene [41], are used as matrices in such desiccant composites. In a previous study we showed that the free volume of the polymer plays an important role in the determination of the rate of moisture adsorption and polystyrene has large free volume leading to fast adsorption. Both glassy PS and high impact polymers (HIPS) are used as matrices for desiccant composites, but no attempt has been done yet to compare the performance of the

two types of polymers and to study the effect of the elastomer phase on desiccant and other characteristics.

As a consequence, the goal of our study was to carry out systematic experiments on desiccant composites prepared with a series of zeolites and to determine the effect of their characteristics on the rate and capacity of water adsorption, but also on other composite properties. Two different polymers were selected for the study, a PS and a HIPS, to investigate the effect of the elastomer phase on composite properties.

2. EXPERIMENTAL

A polystyrene homopolymer (PS, Styron 686 E, Dow, USA), and a high impact copolymer (HIPS, Styron 485, Dow, USA), were selected as matrix polymers in the study. Their most important characteristics are listed in [Table 1](#). The series of zeolites used as desiccants were obtained from the Luoyang Jianlong Chem. Ind. Co., China, and they included the most often used synthetic zeolites, i.e. 3A, 4A, 5A, 10X and 13X. The desiccants were thoroughly characterized with a wide range of techniques; the results are collected in [Table 2](#). Their water adsorption characteristics were determined in an atmosphere of 100 % relative humidity by the measurement of the weight of samples as a function of time. Their chemical composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). To characterize pore size and volume samples were vacuumed at 300 °C for 24 hours down to 10^{-5} Hgmm, and water and nitrogen adsorption was measured using a Hydrosorb (Quantachrome, USA) apparatus at 20 and -195 °C, respectively. The particle size and size distribution of the zeolites were determined using a Malvern Mastersizer 2000 equipped with a Sirocco powder analyzer. The dispersion component of surface energy (γ_{sd}) was determined by inverse gas chromatography (IGC)

at various temperatures by the injection of n-alkanes onto the column containing the zeolites and measuring their retention times. The density of the zeolites was measured by helium pycnometry.

Before composite preparation the zeolites were 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 Rheocord EU 10 V driving unit at 190 °C for 10 min. Torque and temperature of mixing were recorded during homogenization and used for evaluation. 1 mm thick plates and 100 µm thick films were compression molded from the homogenized material for further study at 190 °C using a Fontijne SRA 100 laboratory machine. 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 using polystyrene standards. Their density was measured using a pycnometer at room temperature. The water vapor transmission rate (WVTR) of the polymers was determined on 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 composites was 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. Mechanical properties were characterized by tensile testing using an Instron 5566 machine at 115 mm gauge length and 5 mm/min cross-head speed on specimens with 1 x 10 mm dimensions. The distribution of the zeolites in the composites and failure mechanism were studied by scanning electron microscopy using a Jeol JSM 6380 LA apparatus. Micrographs were recorded on fracture surfaces created during tensile testing.

3. RESULTS AND DISCUSSION

The results are presented in several sections. First the characteristics of the zeolites including water adsorption are compared and evaluated according to their possible influence on composite properties. Desiccant characteristics of the composites are discussed subsequently, and finally the effect of the zeolites on properties important for applications in packaging is discussed in the last section. Brief reference is made to consequences for practice at the end of the section.

3.1. Desiccant characteristics

The capacity and rate of water adsorption are the most important functional properties of desiccant composites. The characteristics of zeolites may change in a wide range and it is safe to assume that some of them influence composite properties as well. The synthetic zeolites used in this study include the A and X types used most frequently in industrial practice. The characteristics of the desiccants are collected in **Table 2** and they include the type of compensating cations, Si/Al rate, pore size and volume and characteristics related to adsorption. The type of the compensating ions and Si/Al ratio have been proved to influence the adsorption characteristics of zeolites quite strongly [30-32]. However, the diameter of the ions do not differ significantly in our case and although Si/Al ratio changes from 1.0 to 1.4 this change is very small compared to the possible range from 1 to infinite. Accordingly, we do not expect these parameters to influence the water adsorption capacity of our zeolites. However, considerable difference can be seen in capacity for A and X types, respectively, caused by some other factor. Both pore size and total pore volume differ for the two types of zeolites and the surface energy of X types is also somewhat larger than that of A type zeolites. The particle size of the desiccants is very similar;

we did not expect and did not find any effect of this parameter on desiccant and other properties.

The water adsorption isotherm of two different types of zeolite is presented in **Fig. 1**. As the figure shows, water adsorption is very fast and more than 30 % water is adsorbed at least by the X type zeolites. The capacity of the two zeolites differs considerably. As explained above the difference may result from dissimilar pore size, volume or surface energy. A detailed analysis of the results proved that the dominating factor in the determination of the water adsorption capacity of the zeolites used in this study is the total volume of the pores (V_t). We did not find any correlation between adsorption capacity and pore diameter or surface tension, or in fact any other characteristics of the desiccant, but total pore volume. The relatively close correlation between the two quantities is presented in **Fig. 2**. The zeolites used form two groups according to their type and the difference in adsorption capacity is about 10 %.

Besides capacity, the rate of water adsorption is another important attribute of desiccant composites. Similarly to capacity, this characteristic might be influenced by the type of the desiccant as well. In the determination of the rate of water adsorption we assumed Fickian type adsorption and fitted the following equation to our experimental adsorption isotherms

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

where M_t is time dependent weight increase, M_∞ the final water uptake reached after infinite time (adsorption capacity), L the thickness of the sample, t the time of adsorption and a (1/s) a constant characterizing the overall rate of water adsorption. We determined the initial rate of adsorption from a different form of Fick's law

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

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 ($\text{s}^{-1/2}$), is proportional to the initial rate of water adsorption. Comparing all the characteristics determined for the zeolites to the initial rate of water adsorption we found that it is independent of most characteristics and correlates mainly with the equilibrium constant of water adsorption (K) defined as

$$\Delta G = - R T \ln K \quad (3)$$

where ΔG is the free enthalpy of adsorption, R the universal gas constant and T absolute temperature. The correlation is shown in [Fig. 3](#). It is interesting to note that the zeolites cannot be divided into two groups and the points belonging to A and X types are located randomly along the correlation (see also [Table 2](#)). We can also conclude that the rate of adsorption changes much less with desiccant characteristics than adsorption capacity, the determined values are very similar to each other. The examination of the factors determining the water adsorption characteristics of zeolites showed that capacity depends quite significantly on the type of the zeolite, but adsorption rate does not. Accordingly, we can expect also the adsorption capacity of desiccant composites to depend on the type of the zeolite and X types are expected to perform better than the more common A types.

3.2. Water adsorption of composites

The water adsorption isotherms of a series of composites are presented in [Fig. 4](#). The comparison of the isotherms to those presented in [Fig. 1](#) may lead to several conclusions. Water adsorption in HIPS/zeolite desiccant composites can be described quite well

by the equation based on Fick's law. The rate of adsorption is considerably slower in the composites, than for neat zeolites. In accordance with earlier results, adsorption capacity is determined mainly by the amount of zeolite present, the amount of adsorbed water seems to be proportional to zeolite content. Naturally, **Fig. 4** alone does not allow the determination of the effect of the matrix polymer or that of the type of zeolite, but it shows quite well the effect of desiccant content.

Water adsorption capacity determined by the fitting of Eq. 1 to the adsorption isotherms is plotted against zeolite content in **Fig. 5** in order to compare the effect of the two parameters, i.e. zeolite and matrix type, mentioned above. The determining role of desiccant content is very clear from the figure, linear correlation exists between water adsorption capacity and zeolite content. Some differences can be seen in the slope of the line depending on the type of zeolite used. However, quite surprisingly, composites containing X type adsorb less water than those prepared with A type zeolites and the effect depends also on the type of polymer used. The adsorption capacity of the 13X type zeolite ($\nabla, \blacktriangledown$) is much smaller than that of the rest and the effect is more pronounced in neat PS than in the impact polymer. Slight differences can be seen in the other cases as well, but the influence of polymer and zeolite type is much weaker than in the case of zeolite 13X; in fact composites prepared from HIPS and the 10X zeolite have the same adsorption capacity as those containing A type zeolites.

Fig. 2 showed a very clear correlation between the adsorption capacity of zeolites and their total pore volume. The capacity of desiccant composites is plotted against the pore volume of the zeolite in **Fig. 6** at two different desiccant contents. Contrary to the neat zeolites, the water adsorption capacity of the composites decreases with increasing total pore volume of the zeolite. Although the correlation is not very strong, it is unambiguous. It is quite difficult to find a plausible explanation or even a tentative one for the phe-

nomenon; it definitely needs further study and considerations. Nevertheless, we can conclude that the water adsorption capacity of desiccant composites prepared from various zeolites depends practically only on the amount of zeolite present and only slightly on the type of desiccant used. The rate of moisture adsorption seemed to be somewhat larger in HIPS than in neat PS composites, but the differences fall within the standard deviation of the measurement thus the correlations are not shown here. In order to come to a definite conclusion about the effect of elastomer content on desiccant properties, further, more systematic experiments must be carried out as a function of elastomer content.

3.3. Application properties

The rate and capacity of water adsorption are the most important functional properties of desiccant composites. However, if we want to use these composites in packaging for any purpose, they should meet the requirements of the specific application. These requirements usually include characteristics related to processing, but also stiffness, strength and toughness. Mechanical properties of such composites depend very much on the interfacial adhesion of the components, thus interactions must be analyzed as well, especially since several contradictory statements have been published in the literature on this issue [42].

Torque measured during the homogenization of the composites, which is proportional to viscosity, is plotted against zeolite content in **Fig. 7** for the composites prepared from neat PS. The correlation is the same and even the values are similar for the HIPS composites, in spite of the considerable difference in the molecular weight of the two polymers. The viscosity of the composites prepared with the X type zeolite is considerably larger than that of the materials containing the A type. Since particle sizes are very similar

(see [Table 2](#)) irrespectively of type, the main reason must be the surface energy of the zeolite being substantially larger for the X than for the A type. Larger viscosity, especially at the large zeolite content necessary for efficient desiccation, might result in difficulties in processing and the steep increase of torque at 50 vol% silicate content indicates some homogenization problem, the slight aggregation of the desiccant.

The modulus of the polymer increases with increasing zeolite content and its composition dependence is independent of the type of zeolite (not shown). The stiffness of composites prepared with the two polymers, i.e. PS and HIPS, obviously differs from each other because of inherent differences in matrix properties. However, modulus is not very sensitive to slight differences in dispersion and/or interfacial adhesion thus the result is expected. On the other, hand the strength of composites prepared with the two matrices differs significantly as shown by [Fig. 8](#) for two desiccants (4A and 10X). The strength of composites prepared from neat PS decreases slightly with increasing zeolite content (●,▲). On the other hand, the tensile strength of composites based on HIPS increases with increasing desiccant content (○,△), i.e. true reinforcement can be achieved in this matrix polymer. The effect of A and X type zeolites also differs from each other, the reinforcing of the second being stronger than that of the first. The observed differences can be explained by the inherent property of the matrix, on the one hand, and by dissimilar interfacial adhesion on the other. Always larger reinforcement is achieved in soft matrices, than in stiff polymers, while the larger surface energy of the X type zeolite results in stronger interfacial interactions, leading to larger reinforcement.

The extent of reinforcement and the influence of adhesion can be expressed quantitatively by the model developed earlier to describe the composition dependence of tensile strength in particulate filled composites [43]

$$\sigma_T = \sigma_{T0} \lambda^n \frac{1 - \varphi}{1 + 2.5 \varphi} \exp(B \varphi) \quad (4)$$

where σ_T and σ_{T0} are the true tensile strength ($\sigma_T = \sigma \lambda$ and $\lambda = L/L_0$) of the composite and the matrix, respectively, n is a parameter expressing the strain hardening tendency of the matrix, φ is the volume fraction of the fiber and B is related to its relative load-bearing capacity, i.e. to the extent of reinforcement, which depends among other factors, also on interfacial interaction. We can write **Eq. 4** in linear form

$$\ln \sigma_{Tred} = \ln \frac{\sigma_T (1 + 2.5 \varphi)}{\lambda^n (1 - \varphi)} = \ln \sigma_{T0} + B \varphi \quad (5)$$

and the plot of the natural logarithm of reduced tensile strength against fiber content should result in a straight line, the slope of which is proportional to the load-bearing capacity of the filler and under certain conditions to the strength of interaction.

The strength of the four series of composites of **Fig. 8** is plotted in the form indicated by **Eq. 5** in **Fig. 9**. We obtain straight lines indeed with slight deviations at the largest desiccant content, because of slight homogenization problems mentioned earlier. The calculation was executed for all composites and the results are collected in **Table 3**. We can see that reinforcement is much larger in the softer matrix, as expected and predicted by the model used.

The mode of deformation and failure is also important aspects of most applications. In particulate filled composites the dominating deformation mode is debonding, the separation of the matrix and the filler at the interface under the effect of external load. The critical stress initiating debonding can be predicted by the correlation

$$\sigma^D = -C_1 \sigma^T + C_2 \left(\frac{E W_{AB}}{R} \right)^{1/2} \quad (6)$$

where σ^D and σ^T are debonding and thermal stresses, respectively, E the Young's modulus

of the matrix, W_{AB} the reversible work of adhesion, R the radius of the particles, while C_1 and C_2 are geometric constants related to the debonding process. Using the Eq. 6 we predicted debonding stress for our composites and listed the results in **Table 3**. If we compare debonding stress to the strength of the matrix, we can see that the former is larger in all cases thus debonding does not occur, but the composites fail either by the yielding or fracture of the matrix. These conclusions are further confirmed by SEM micrographs recorded on the fracture surface of composites created during tensile testing (**Fig. 10**). All the filler particles are covered by the matrix indicating good interfacial adhesion irrespectively of the presence or absence of an elastomer phase. Easy debonding may lead to premature failure, thus good adhesion and the mechanism mentioned above can be very advantageous if the composites do not become brittle as a result of filling.

Although the 1 mm thick plates prepared and used in these experiments do not allow the reliable determination of impact or fracture resistance, we can estimate the ductility of our materials from the stress vs. strain traces. Relative toughness (related to the corresponding matrix property) is compared for all composites in **Fig. 11** for two desiccants, 4A and 10X. We can see that HIPS composites perform much better than those produced with the neat PS, as expected. Accordingly, if fracture resistance is an important requirement for the intended application, impact modified PS should be selected as matrix, since it performs better than the unmodified material.

4. CONCLUSIONS

The systematic study of five zeolites and their desiccant PS composites proved that the water adsorption capacity of zeolites depends on the total volume of the pores, while the rate of adsorption on thermodynamics, on the equilibrium constant of adsorption. On

the other hand, zeolite characteristics influence the moisture adsorption of the polymer only marginally; adsorption capacity is determined by zeolite content, while the rate of adsorption by the properties of the polymer. Composites prepared with X type zeolites have somewhat smaller water adsorption capacity than those containing their A type counterparts. The dispersion of the zeolite is very good both in PS and in HIPS composites. Mechanical properties are excellent mainly because of the good interfacial adhesion between the components. Because of their larger surface energy, composites containing X type zeolites have larger viscosity and they reinforce the polymer more than the A type desiccants. Matrix properties influence mainly application related properties, reinforcement and ductility is better in HIPS than in PS composites.

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Table 1 Characteristics of the polymers used as matrix in the experiments

Polymer	MFR ^a (g/10 min)	M _n (g/mol)	M _w /M _n	Density (g/cm ³)	WVTR (g 20 μm/m ² /24 h)	v _{sf} ^b (cm ³)
PS	2.5	127,970	2.44	1.04	130 ± 8	0.166
HIPS	12.0	77,525	2.68	1.02	139 ± 2	0.167

^a at 200 °C, 5 kg

^b specific free volume

Table 2 Characteristics of the zeolites used as desiccant in the study

Type	Cation	Ion radius (Å)	Si/Al ratio	Particle size (µm)	Pore diameter (Å)	Pore volume (cm ³ /g)	M_{∞} (%)	K	γ_{sd}^a (mJ/m ²)
3A	K ⁺ , Na ⁺	0.117	1.00	4.5	3.0	0.27	26.2	42.2	219
4A	Na ⁺	0.097	1.23	4.0	3.8	0.28	27.5	47.6	216
5A	Ca ²⁺ , Na ⁺	0.099	1.25	4.5	4.3	0.29	27.8	29.4	217
10X	Ca ²⁺ , Na ⁺	0.098	1.39	4.7	7.4	0.36	34.3	57.2	235
13X	Na ⁺	0.097	1.43	4.3	8.1	0.33	33.3	33.5	240

^a dispersion component of surface tension determined by IGC

Table 3 Reinforcement and debonding stress depending on interfacial adhesion for PS and HIPS/zeolite composites

Polymer	Zeolite	Tensile strength (MPa)	Debonding stress (MPa)	Parameter <i>B</i>
PS	3A	38.3	51.0	1.97
	4A		50.9	2.09
	5A		50.8	2.95
	10X		51.8	3.19
	13X		51.9	2.99
HIPS	3A	11.8	36.7	4.30
	4A		36.6	4.14
	5A		36.6	4.35
	10X		37.3	5.76
	13X		37.4	5.65

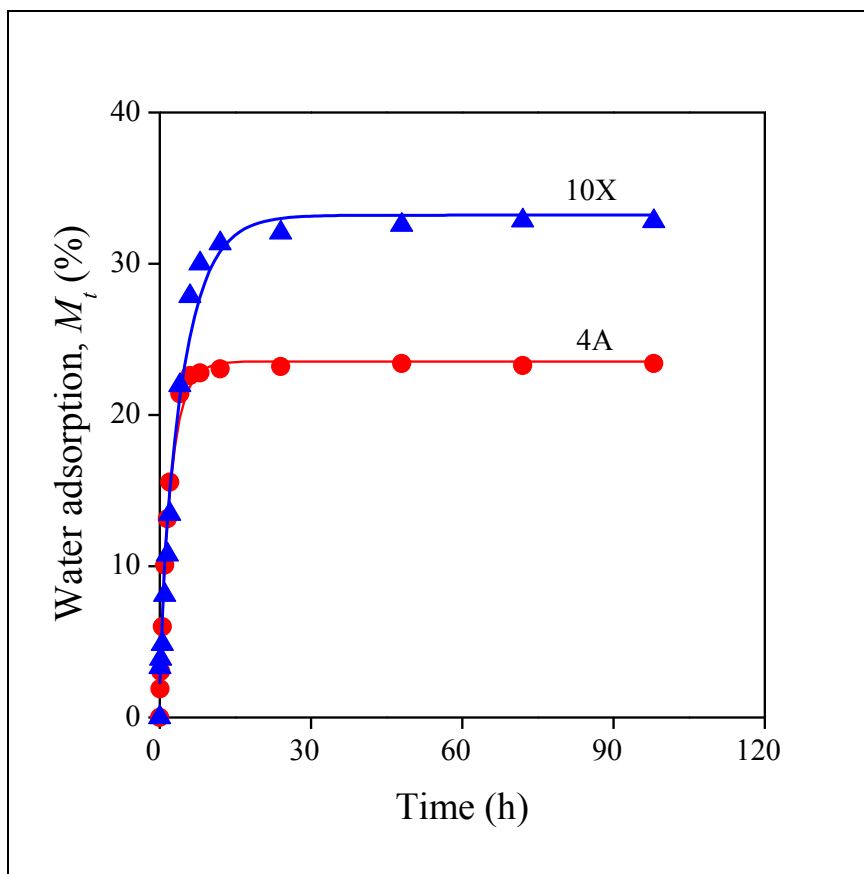
CAPTIONS

- Fig. 1 Comparison of the water adsorption isotherm of two different types of zeolites used as desiccants in the study. Symbols: (○) 4A, (△) 10 X.
- Fig. 2 Effect of the total pore volume of the zeolite on its water adsorption capacity.
- Fig. 3 Correlation between the equilibrium constant (K) and the initial rate (b) of moisture adsorption.
- Fig. 4 Water adsorption isotherms of HIPS/4A desiccant composites.
- Fig. 5 Effect of zeolite content on the water adsorption capacity (M_{∞}) of polystyrene desiccant composites. Full symbols PS, empty symbols HIPS; (□) 3A, (○) 4A, (◇) 5A, (△) 10X, (▽) 13X.
- Fig. 6 Correlation between the total pore volume of the zeolite and the water adsorption capacity of its composites. Zeolite content: (○) 10, (□) 30 vol%.
- Fig. 7 Influence of the type of zeolite on equilibrium torque measured during the homogenization of desiccant composites in neat PS matrix. Symbols: (○) 4A, (△) 10X.
- Fig. 8 Composite strength plotted against zeolite content for polystyrene/zeolite composites. Effect of matrix and zeolite type. Full symbols PS, empty symbols HIPS; (○,●) 4A, (△,▲) 10X.
- Fig. 9 Reduced tensile strength plotted against zeolite content in the representation of [Eq. 2](#) for the composites of [Fig. 7](#). Full symbols PS, empty symbols HIPS; (○,●) 4A, (△,▲) 10X.

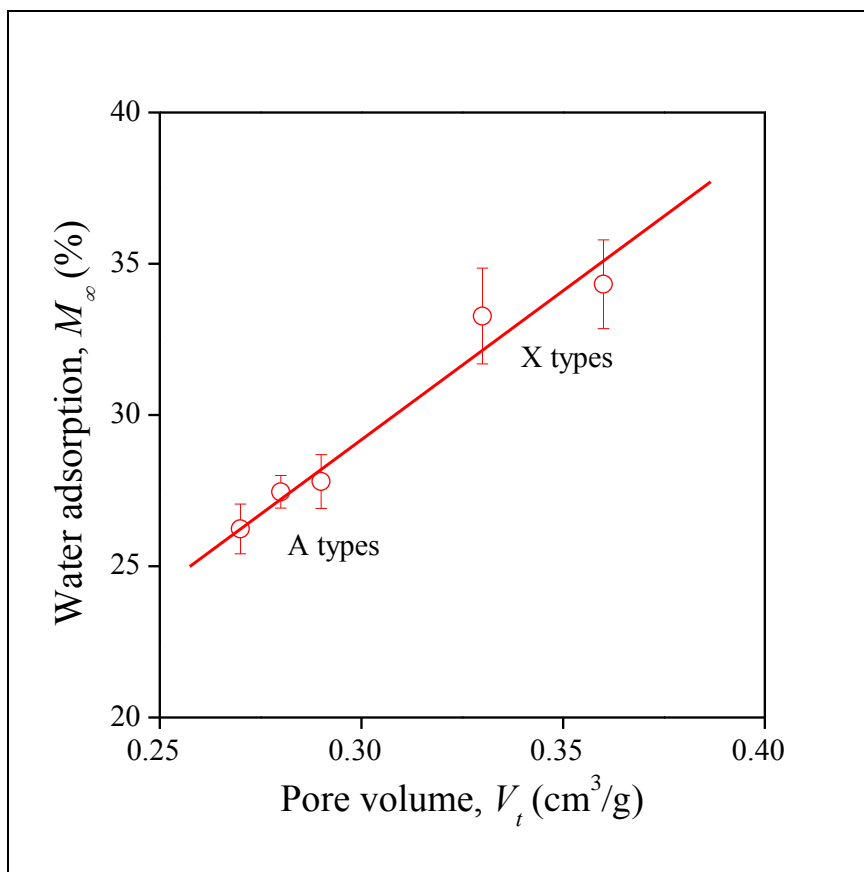
Fig. 10 SEM micrographs recorded on the fracture surface of polystyrene/zeolite composites containing 30 vol% desiccant. The surfaces were created in tensile testing. a) PS/4A, b) HIPS/4A.

Fig. 11 Composition dependence of the ductility of polystyrene/zeolite composites. Effect of matrix and zeolite type. Full symbols PS, empty symbols HIPS; (○,●) 4A, (△,▲) 10X.

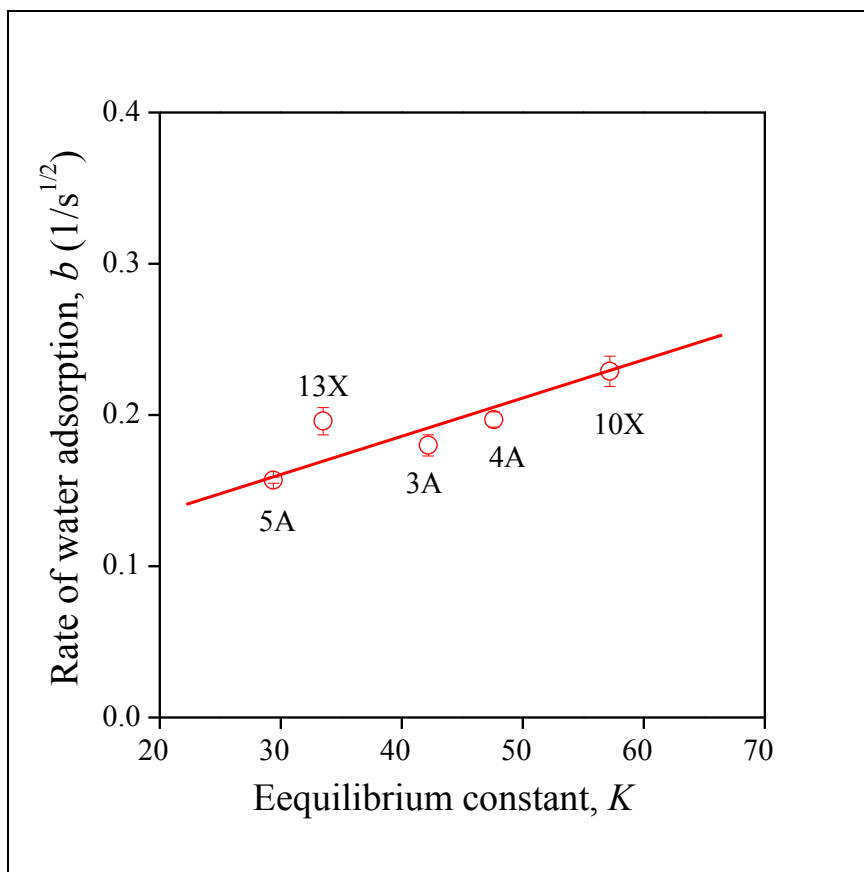
Kenyó Fig. 1



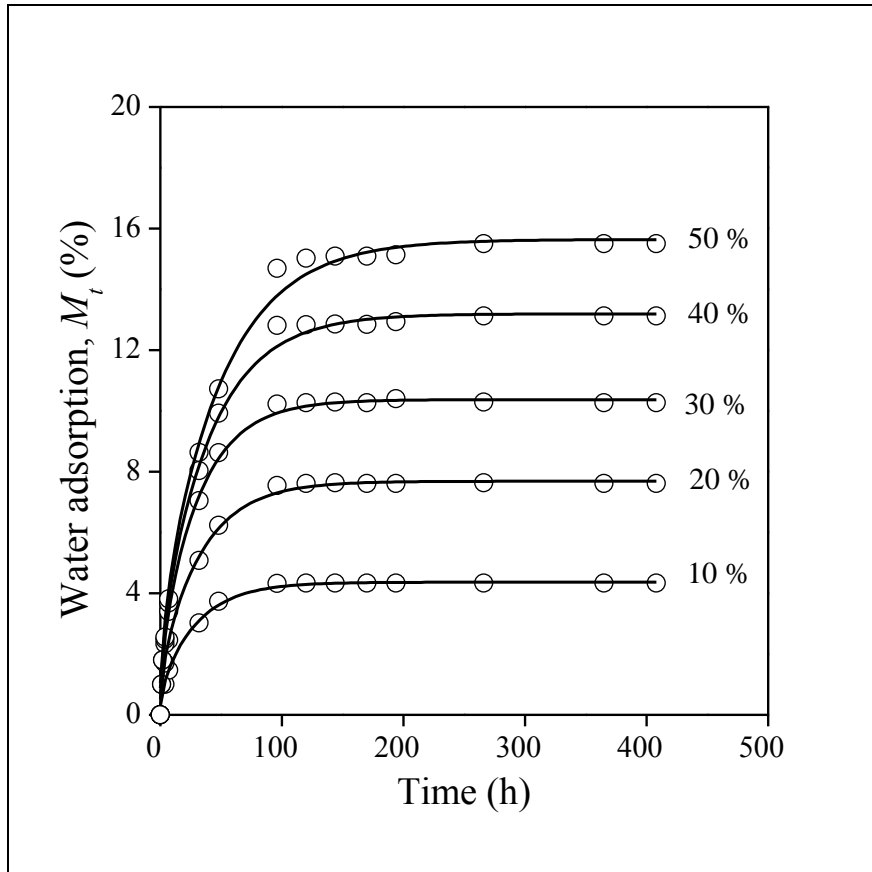
Kenyó Fig. 2



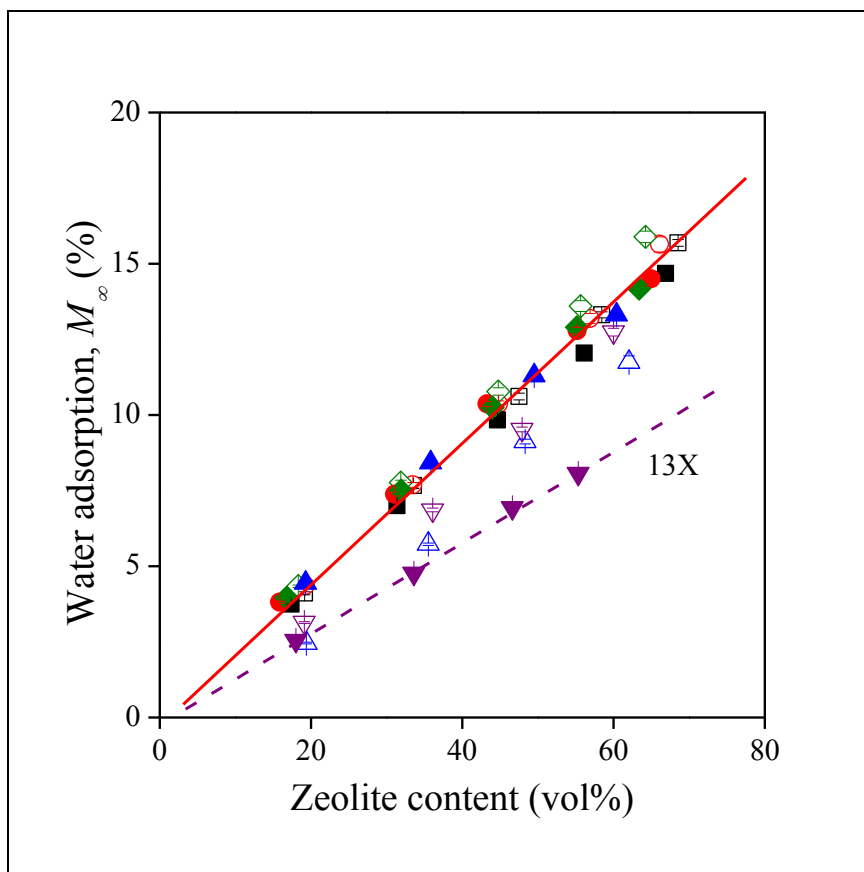
Kenyó Fig. 3



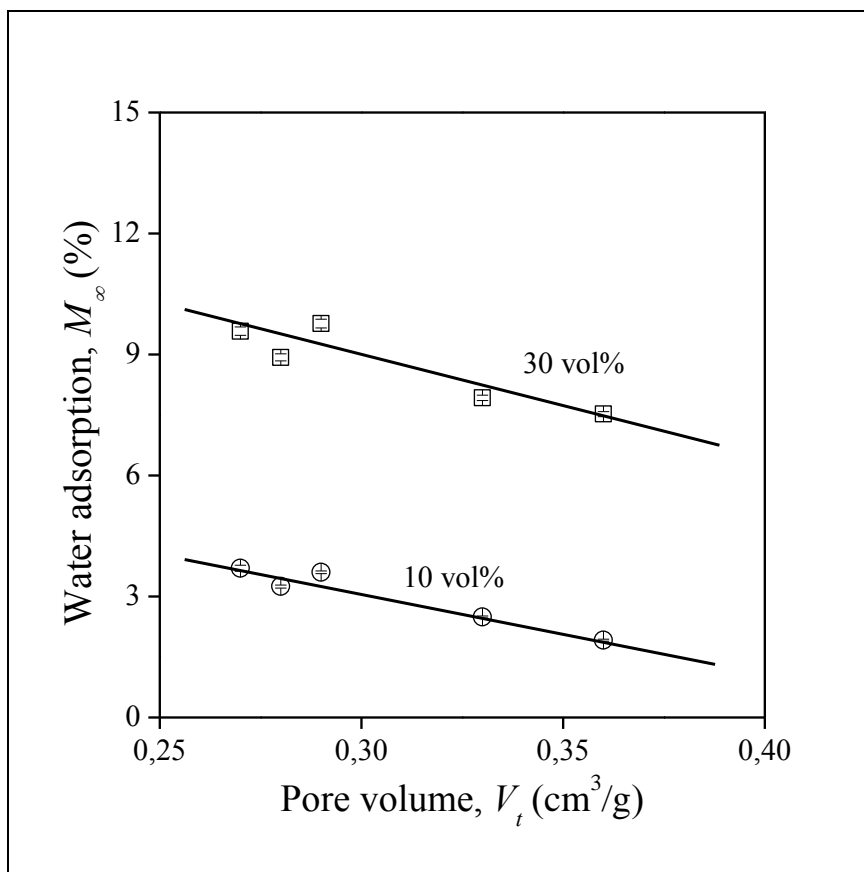
Kenyó Fig. 4



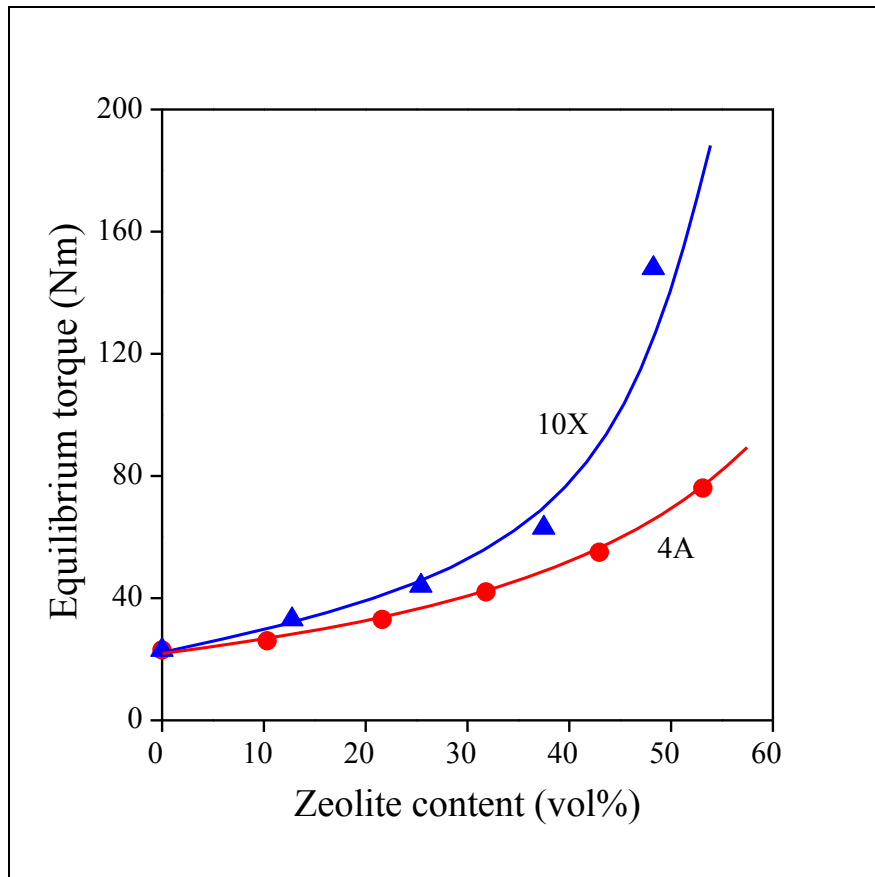
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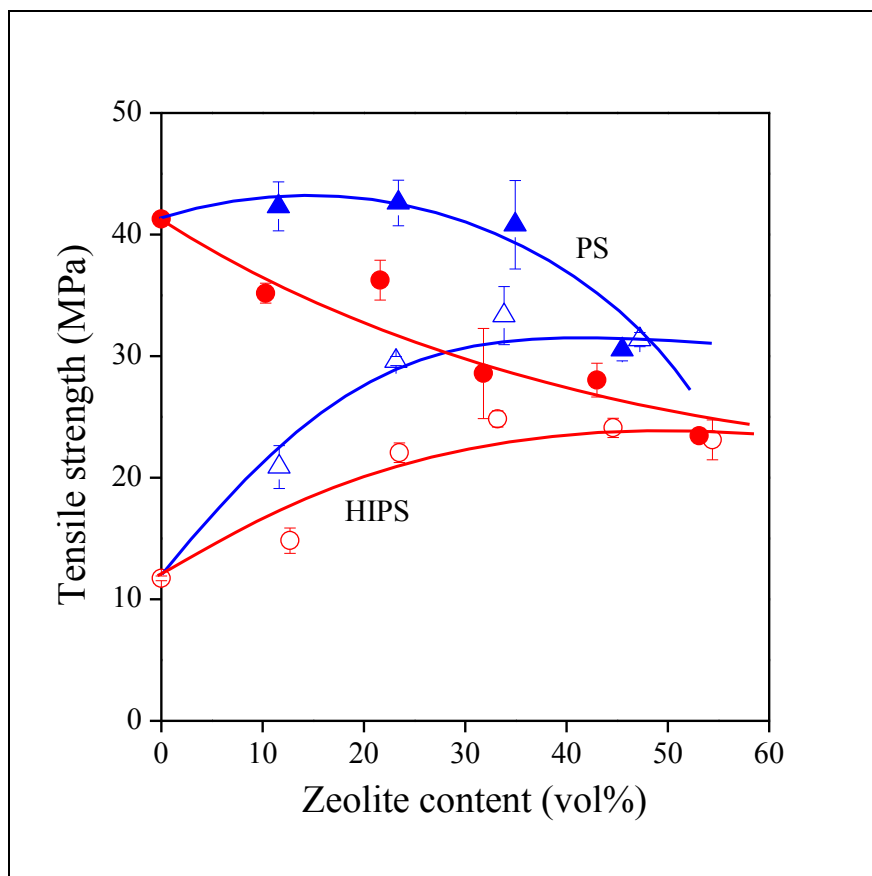
Kenyó Fig. 6



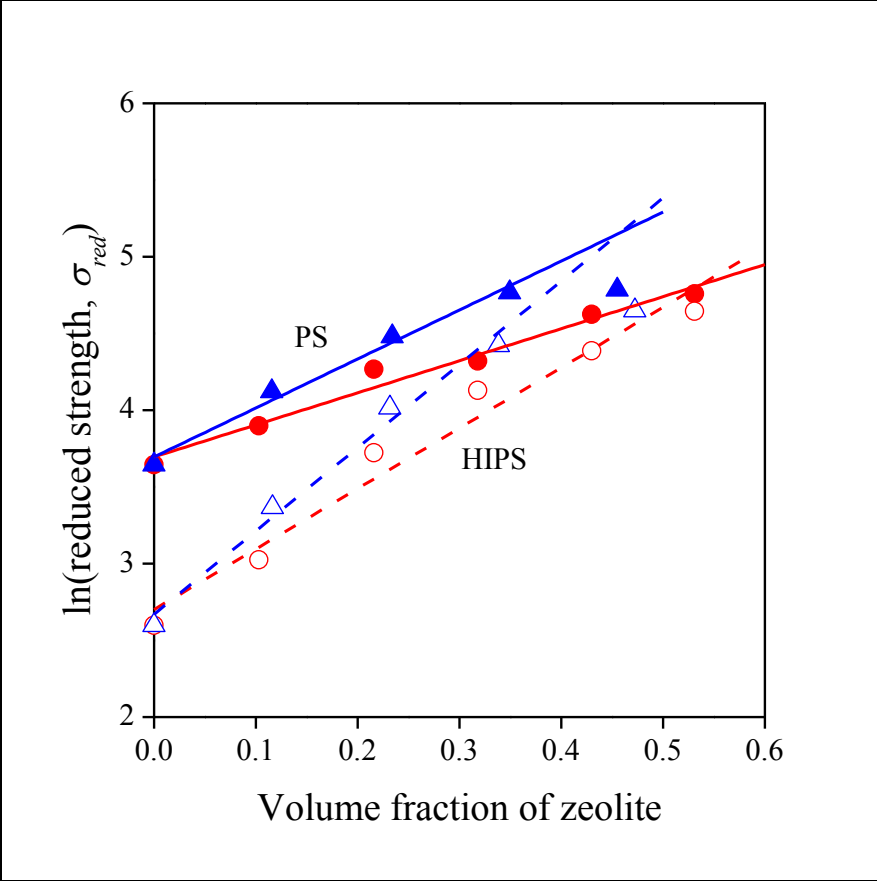
Kenyó Fig. 7



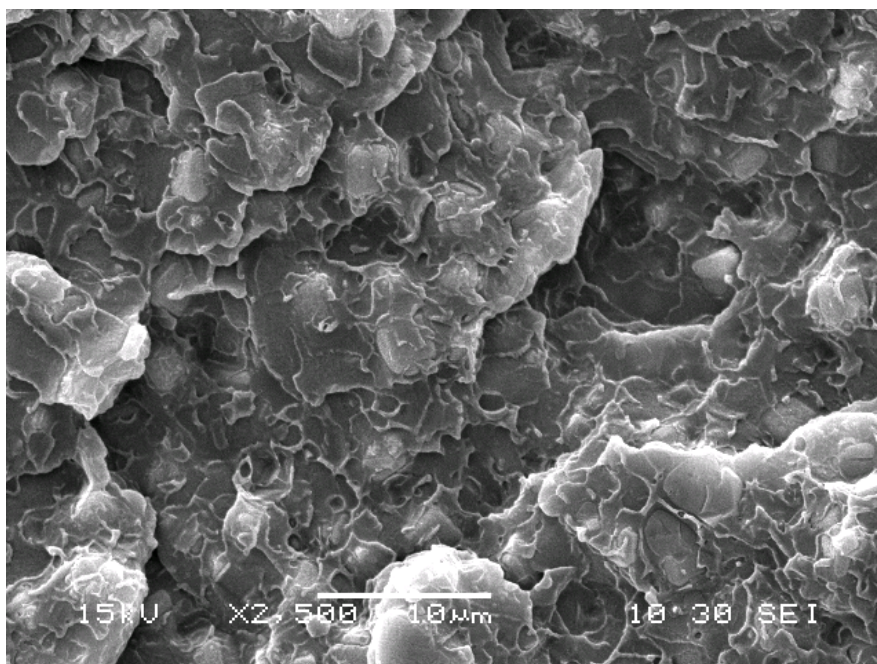
Kenyó Fig. 8



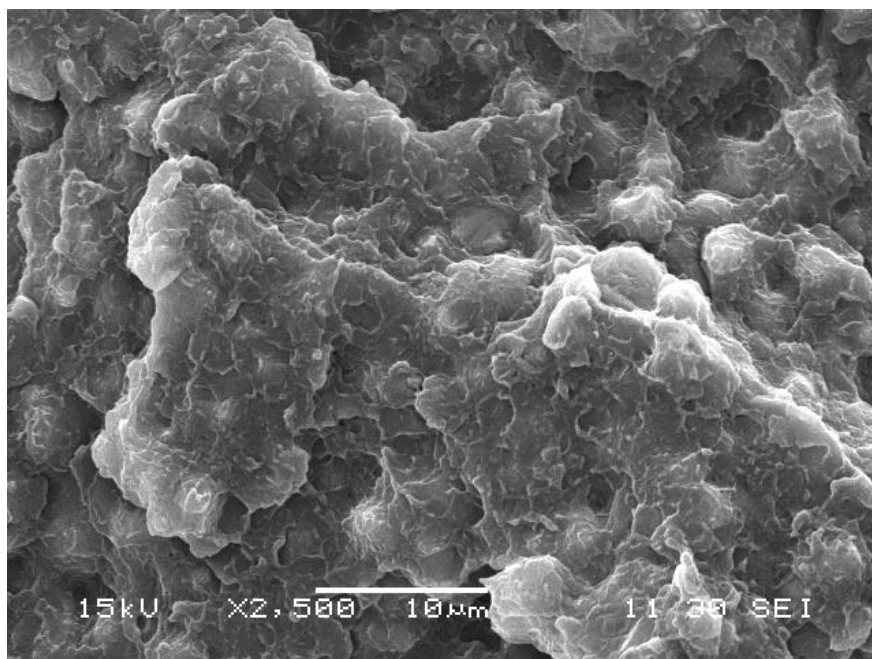
Kenyó Fig. 9



Kenyó Fig. 10



a)



b)

Kenyó Fig. 11

